

**Singlet Exciton Delocalization and Localization in
Oligosilanes**

by

Matthew Kellar MacLeod

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Josef Michl

Prof. David Jonas

Date _____

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

MacLeod, Matthew Kellar (Ph.D., Chemistry and Biochemistry)

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Thesis directed by Professor Josef Michl

The aim of this thesis is to reproduce and interpret the trends in electronic absorption and emission spectra of permethylated oligosilanes by theoretical means. Longstanding questions concerning the structures responsible for various emissions from electronically excited singlet states that have been observed are addressed. New deactivation mechanisms that allow oligosilanes to return to ground state equilibrium geometries are also presented. The question of how saturated systems accommodate $\sigma\sigma^*$ excitation is addressed computationally. Finally, new bonding patterns in excited states of oligosilanes have been identified. These include large geometry distortions from the ground state equilibrium structures, rehybridization, and in some cases the involvement of 4s, 4p and 3d Si atomic orbitals results in pentavalent Si for special cases where electronic excitation becomes highly localized.

Dedication

This thesis is dedicated to my mother, Cynthia MacLeod-Soppe.

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Chapter 1

Introduction

1.1 Motivation

The work in this thesis is focused on investigating electronic delocalization in permethylated oligosilanes. The goal of the thesis is to provide physical insight into molecular phenomena. More specifically, the aim is to reproduce experimental data with accurate methods, make simple models to understand the experimental trends and finally to push experiment by predicting new unobserved results.

This chapter aims to provide a general background of localization and delocalization in saturated systems. A broad introduction to previous work on oligosilanes will be presented and the presentation of the current work in this thesis will be outlined.

1.2 Theoretical Considerations

In order to discuss and interpret results of the calculations and models presented in this work, some background is necessary. Theoretical chemistry has two major goals: to develop methods that can accurately and consistently reproduce experimental results, and to create simple models that can be easily used to understand and predict experiments. Theoretical chemistry often deals with large systems and understanding the assumptions and approximations used to allow calculations of large systems is of the utmost importance if meaningful interpretations of the results is desired. Methodologies and models in quantum chemistry often both begin at the same starting point, the time-independent Schrödinger equation,¹ and differ only in approximations to this equation:

$$\hat{H}\Psi(r, R) = E\Psi(r, R) \quad (1.1)$$

where $\hat{H}$ is the Hamiltonian, which operates on Ψ , the total wave function, which is a function of the positions of the electrons (r) and the nuclei (R), to give E , the energy. The Hamiltonian is made up of the following terms,

$$\hat{H}_{tot} = \hat{T}(R) + \hat{T}(r) + \hat{V}_{el} + \hat{V}_{el-nuc} + \hat{V}_{nuc} \quad (1.2)$$

where $\hat{T}$ represents kinetic energy operators and $\hat{V}$ potential energy operators of electrons (el) and nuclei (nuc), the $el - nuc$ index describes interactions between electrons and nuclei. An exact solution to eq. (1.1) is only possible for the smallest systems, although some progress towards larger systems has recently been made: by inverting eq. (1.1) and using scaling properties, solutions to eq. (1.1) to larger systems, such as the boron atom (5 electrons) are now possible.² However, for practical systems of interest, many approximations need to be made to solve eq. (1.1). These approximations usually involve reducing the complexity of $\hat{H}$ or Ψ , or both.

The usual first approximation is to simplify both $\hat{H}$ and Ψ through the Born-Oppenheimer (BO) approximation,³ which separates the motion of the nuclei, ψ_{nuc} , and the electrons, ψ_{el} .

$$\Psi(r, R) = \psi_{el}(r; R)\psi_{nuc}(R) \quad (1.3)$$

In this approximation, the nuclei are taken to be frozen in configuration space and the electronic energy is evaluated explicitly by solving the Schrödinger equation to find the eigenvalues and eigenvectors of the electronic coordinates (r). It should be noted that the electronic energy still depends parametrically on the coordinates of the nuclei (R). In the Born-Oppenheimer approximation, the electronic energy (E_{el}) is the eigenvalue of the electronic Hamiltonian operating on the electronic wave function.

$$\hat{H}_{el}\psi_{el}(r; R) = E_{el}(R)\psi_{el}(r; R) \quad (1.4)$$

$$\hat{H}_{el} = \hat{T}_{el}(r) + \hat{V}_{el} + \hat{V}_{el-nuc} \quad (1.5)$$

The total energy (eq. (1.6)) is then given by the sum of the electronic energy and the repulsion of the nuclei, which is a constant at the geometrical configuration for which eq. (1.4) was evaluated.

$$E_{tot}(R) = E_{el}(R) + V_{nuc}(R) \quad (1.6)$$

The Born-Oppenheimer approximation is usually accompanied by the adiabatic approximation which assumes that electronic states do not interact. This approximation is usually valid if the electronic state of interest is energetically separated from other electronic states.⁴⁻⁷ Problems can arise with light atoms (fast nuclei)^{8,9} and slow electrons (in Rydberg or anionic states).¹⁰⁻¹² Near degeneracies of electronic states can also cause a breakdown in the BO approximation.^{13,14} From this point on, Ψ will be taken to mean ψ_{el} , unless otherwise denoted.

The wave function, Ψ , needs to be antisymmetric with respect to exchange of electrons. This requirement is most simply fulfilled by expressing the wave function as a single Slater determinant composed of n spinorbitals (χ), for a total of n electrons. A spinorbital for electron i is given by

$$\chi(i, \omega) = \begin{cases} \psi(i)\alpha(\eta) \\ \psi(i)\beta(\eta) \end{cases} \quad (1.7)$$

and corresponds to the description of the electron by three spatial coordinates and one spin coordinate, η . The spatial part of the spinorbital is usually the same for spin functions describing opposite spin eigenvalues and the spinorbitals with opposite spins are grouped together. Therefore one spatial orbital can be occupied by two electrons without violating the Pauli principle which reflects the fact that electrons are fermions. The spinorbitals are functions that describe the spatial (ψ) and spin (η) coordinates of a single electron and are given by either the α or β spin functions, the eigenvalues of which correspond to 1/2 or -1/2 respectively. These eigenvalues represent the z component of the electron spin. When the spinorbitals are combined into a normalized Slater determinant, both possibilities of spin are included for each electron.

The columns of the Slater determinant describe the spinorbitals and the rows describe the labels of the n electrons,

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \dots & \chi_n(1) \\ \chi_1(2) & \chi_2(2) & \dots & \chi_n(2) \\ \vdots & \vdots & & \vdots \\ \chi_1(n) & \chi_2(n) & \dots & \chi_n(n) \end{vmatrix} \quad (1.8)$$

The Slater determinant is often abbreviated and only the diagonal elements are shown between double bars, or simply as a bra or ket vector.

$$\Psi = \left\| \chi_1(1) \quad \dots \quad \chi_n(n) \right\| = |\chi_1(1) \dots \chi_n(n)\rangle \quad (1.9)$$

The use of a Slater determinant ensures that the Pauli principle is obeyed, due to the antisymmetry of the determinant with respect to row interchange. Thus some limited electron correlation (section 1.2.1) between electrons of the same spin, the Fermi correlation, is already introduced into the wave function. The correlation between electrons with opposite spins, the Coulomb correlation, is however not included in a Slater determinant of one-electron spinorbitals.

In order to solve eq. (1.4) with a traditional Ψ , *i.e.*, consisting of a single Slater determinant of spinorbitals, more approximations to $\hat{H}$ still need to be made for many electron systems where the inter-electron correlation needs to be described. Using atomic units, as will be the case throughout this work, the explicit electron repulsion operator $\hat{V}_{el}$, which is defined as

$$\hat{V}_{el} = \sum_i^n \sum_{j>i}^n \frac{1}{|r_i - r_j|} \quad (1.10)$$

and describes the instantaneous repulsion of each electron with every other individual electron. The inclusion of eq. (1.10) in eq. (1.1) leads to intractable equations. Electron replusion is therefore approximated. In the most basic ab initio method, the Hartree-Fock (HF) procedure, the Hamiltonian is approximated to be a sum of one-electron operators. For closed shell systems they are

defined as follows:

$$\hat{H}_{HF}(1) = \hat{H}_{core}(1) + \hat{G}(1) \quad (1.11)$$

$$(1.12)$$

$$\hat{H}_{core}(1) = -\frac{1}{2}\nabla^2(1) - \sum_A \frac{Z_A}{|R_A - r(1)|} \quad (1.13)$$

$$(1.14)$$

$$\hat{G}(1) = 2\hat{J}(1) - \hat{K}(1) \quad (1.15)$$

where $\hat{H}_{core}$ describes the electronic kinetic energy operator and the attractive electron-nuclear potential energy operator and where now the electron repulsions are approximated by the Roothaan total electron interaction operator, $\hat{G}$. The Roothaan operator consists of the Coulomb, $\hat{J}$, and exchange, $\hat{K}$ operators. These one-electron operators act on the spatial component of the spinorbital in the following manner,

$$\hat{J}_j(1)\psi_i(1) = \left(\int \psi_j^*(2) \frac{1}{r_{12}} \psi_j(2) d\nu_2 \right) \psi_i(1) \quad (1.16)$$

$$\hat{K}_j(1)\psi_i(1) = \left(\int \psi_j^*(2) \frac{1}{r_{12}} \psi_i(2) d\nu_2 \right) \psi_j(1) \quad (1.17)$$

The HF $\hat{J}$ and $\hat{K}$ operators involve the wave function that is being solved in eq. (1.18) and so eq. (1.18) needs to be solved for in a self-consistent iterative manner. The value of the exchange operator's action on ψ_i , $\hat{K}\psi_i$, depends on the value of ψ_i throughout space and thus the exchange operator is a nonlocal operator as opposed to $\hat{J}$ which represents the average local potential at r_i and is a local operator. By eliminating the spin component of the spinorbitals and by a constrained minimization of the energy and orbital transformations, the pseudo eigenvalue HF equation is obtained,

$$[\hat{H}_{core}(1) + G(1)]\psi_i(1) = \varepsilon_i\psi_i(1) \quad (1.18)$$

Solving eq. (1.18) in a self-consistent manner means that the starting orbitals have to be guessed before the energy is minimized by orbital optimization. There are several approaches to guessing

starting orbitals.^{15–17} The variational theorem ensures that by optimizing the orbitals, we are able to lower the energy and approach that of the real system. One needs to be aware that stationary points can obscure real minima if second derivatives are not evaluated and are not positive.¹⁸

Left multiplication of eq. (1.18) by ψ^* and integration lead to the equations for the total closed shell HF energy, which is not a simple sum of orbital energies, but includes the effects of averaged electron repulsions.

$$E_{HF}^{tot} = 2 \sum_i^{n/2} \varepsilon_i - \sum_i^{n/2} \sum_j^{n/2} (2J_{ij} - K_{ij}) \quad (1.19)$$

where ε_i represents the closed-shell ($n/2$) HF orbital energy and the Coulomb (J_{ij}) and exchange (K_{ij}) energies are sums of two-electron repulsion integrals. These integrals are given below, followed by the Dirac bracket or physicists' notation and finally by the Coulomb notation, also known as Mulliken or the chemists' notation:¹⁹

$$J_{ij} = \iint \psi_i^*(1)\psi_j^*(2) \frac{1}{|r_1 - r_2|} \psi_i(1)\psi_j(2) d\tau_1 d\tau_2 = \langle ij|ij \rangle = (ii|jj) \quad (1.20)$$

$$K_{ij} = \iint \psi_i^*(1)\psi_j^*(2) \frac{1}{|r_1 - r_2|} \psi_j(1)\psi_i(2) d\tau_1 d\tau_2 = \langle ij|ji \rangle = (ij|ji) \quad (1.21)$$

The electron repulsion in the HF scheme is thus a time averaged repulsion which is not simply the average classical electron repulsion J , but less $(J - K)$, as electrons of the same spin avoid each other (Fermi correlation). The total energy also depends only on occupied orbitals, which are optimized in the HF procedure. This has consequences for excited states and will be mentioned later.

To efficiently solve the HF equations they are transformed into algebraic equations, in which the eigenvectors and eigenvalues can be obtained by simple diagonalization. To do this the wave

functions, ψ_i , are expanded into a finite basis set, which is usually done using a linear combinations of atomic orbitals (LCAO).²⁰ Now Latin subscripts will refer to the molecular orbitals and Greek subscripts to the atomic orbitals:

$$\psi_i = \sum_{\nu} c_{\nu i} \phi_{\nu} \quad (1.22)$$

Substitution of eq. (1.22) into eq. (1.18) leads to the algebraic Roothaan-Hall equations.^{20,21} The resulting equation can be multiplied by ϕ_{μ} and integrated to yield the equations for the energy. The wave functions in the $\hat{J}$ and $\hat{K}$ operators also are expanded terms of atomic basis functions to yield the following equations:

$$\sum_{\nu} c_{\nu i} \left\{ H_{\mu\nu}^{core} + \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} [2(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] \right\} = \sum_{\nu} c_{\nu i} \varepsilon_i(\mu|\nu) \quad (1.23)$$

where $H_{\mu\nu}$ is the energy expectation value for orbital ψ_{μ} and ψ_{ν} . The density matrix or so called charge-density bond-order matrix $P_{\lambda\sigma}$ is defined by

$$P_{\lambda\sigma} = 2 \sum_i^{n/2} c_{\lambda i}^* c_{\sigma i} \quad (1.24)$$

and thus named as twice the diagonal elements give the orbital occupation numbers (charges) and the off diagonal elements the overlap densities (bond orders). The orbitals that diagonalize the density matrix are called natural orbitals (NOs). The occupied natural orbitals represent a well defined compact set.¹⁹ They are useful for describing biradicals, and also in post-HF methods.²²

The four (atomic) center two-electron integrals have the form

$$(\mu\sigma|\lambda\nu) = \iint \phi_{\mu}^*(1) \phi_{\sigma}(1) \frac{1}{r_{12}} \phi_{\lambda}^*(2) \phi_{\nu}(2) d\tau_1 d\tau_2 \quad (1.25)$$

and are numerous, but this computational hardship can be reduced in many ways. The first route taken is to approximate the basis functions in terms of Gaussian functions. Some additional ways

of reducing the computational cost are the density fitting approach,²³ Cholesky decomposition,^{24,25} pseudospectral,²⁶ and dual basis approaches.^{27,28} A common method is that of the resolution of the identity (RI).²⁹ In the RI approach, one 4-index integral can be transformed into a sum involving 3-index integrals, by insertion of an auxiliary basis set and summing over the auxiliary indices, PQ ,

$$(\mu\nu|\lambda\sigma) \approx \sum_{PQ} (\mu\nu|P)[J^{-1}]_{PQ}(Q|\lambda\sigma) \quad (1.26)$$

where $[J]_{PQ}^{-1}$ is the inverse Coulomb metric in the auxiliary basis set, where the Coulomb metric is defined as

$$[J]_{PQ} = \int P(1) \frac{1}{r_{12}} Q(2) d\tau \quad (1.27)$$

and the new 3-index integrals from eq. (1.26) are $(\mu\sigma|P)$ and $(Q|\lambda\nu)$.

By defining the Fock operator in terms of atomic orbitals:

$$\hat{F}_{\mu\nu}(1) = \hat{H}_{\mu\nu}^{core}(1) + \hat{G}_{\mu\nu}(1) \quad (1.28)$$

the final equation resulting from the energy minimization or partial differentiation of the energy with respect to a particular coefficient, say c_μ on the expanded HF equation is given by the secular equation,

$$\sum_{\nu} c_{\nu} [F_{\mu\nu} - \varepsilon_i S_{\mu\nu}] = 0 \quad (1.29)$$

which can be written in the matrix form

$$\mathbf{FC} = \mathbf{SC}\varepsilon \quad (1.30)$$

which is also known as the Roothaan equation, and can be solved using techniques from linear algebra.¹⁹ The final energy can also be neatly decomposed.

$$E = \frac{1}{2} \sum_{\mu,\nu} P_{\mu\nu} (H_{\mu\nu}^{core} + F_{\mu\nu}) \quad (1.31)$$

The HF method provides a starting point for more exact (post-HF) methods as well as for less exact (semiempirical) methods. The HF method also provides a practical starting point for the discussion and the calculation of excited states (cf. section 1.2.2).

1.2.1 Electron Correlation

In order to produce more accurate results than those of the Hartee-Fock method, *i.e.*, results which can be directly compared to experiment or used to parameterize models, dynamic electron correlation needs to be introduced. Dynamic correlation is the energy lowering due to correlating the motion of the electrons, opposed to the energy lowering due to adding flexibility to the wave function, ie the static correlation. Unfortunately, the effects of static and dynamic correlation can not be rigorously separated.³⁰ The electron correlation energy is defined as the difference between the zero-order HF energy and that of the exact non-relativistic solution to the Schrödinger equation. Explicit electron correlation is not included in the HF method as there is no spatial correlation between electrons with different spins in the wave function. This can be illustrated by noting that the probability to find electrons in volume elements dr_1 and dr_2 of two electrons with different spins in two orbitals is nonzero in general:

$$P(1, 2) dr_1 dr_2 = \frac{1}{2} [|\psi_1(1)|^2 |\psi_2(2)|^2 + |\psi_1(2)|^2 |\psi_2(1)|^2] dr_1 dr_2 \quad (1.32)$$

whereas the probability to find two electrons of the same spin in the same location is zero, *i.e.*, they avoid each other and the HF method does not account for this but only includes electron repulsion by a mean field approximation.

For small systems, a simple way to include electron correlation is to use an explicitly correlated wave function. The wave functions that explicitly include the distance between two electrons, r_{12} , are known as geminal wave functions, usually in the form of multiple gaussians, and are termed R12 methods.³¹ For He, the geminal wave function can be expressed as

$$g(r_{12}) = N e^{-a_1 r_1^2} e^{-a_2 r_2^2} [1 - e^{-b r_{12}^2}] \quad (1.33)$$

where N is a normalization constant and a and b are exponents for the gaussian functions of electrons 1 and 2, and where r_{12} is the distance of the two electrons. This method was first introduced by Hylleras for He.³² Ten-ho has recently shown that the use of Slater-type geminal functions can reduce the cost of the R12 approach.³³ R12 methods which use a single short range correlation factor, usually based on Slater-type geminal functions, are known as F12 methods.³⁴ If the nuclear wave functions are also included, the description of the total wave function close to the nuclei, known as the cusp, can also be greatly improved.³⁵

In the standard HF scheme, the electron-electron repulsions have been approximated via $\hat{J}$ and $\hat{K}$. One route to include electron correlation is to include electron repulsions in a perturbative manner according to Rayleigh-Schrödinger perturbation theory. Starting from the HF equations, this is given by the Møller-Plesset (MP) formulation where the second order correction for the ground state energy is given by

$$E^{(2)} = \sum_K \frac{-|\langle \Psi_K | H | \Psi_0 \rangle|^2}{E_K - E_0} = \sum_{i < j} \sum_{a < b}^{n/2 \text{ virt}} \frac{-|(ab||ij)|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \quad (1.34)$$

where

$$(ab||ij) = \iint \chi_a^*(1) \chi_b(1) \frac{1}{r_{12}} \chi_i^*(2) \chi_j(2) d\tau_1 d\tau_2 - \iint \chi_a^*(1) \chi_b(1) \frac{1}{r_{12}} \chi_j^*(2) \chi_i(2) d\tau_1 d\tau_2 \quad (1.35)$$

and the χ represents the spinorbitals (further integration over spin needs to be done before suitable equations for calculations are obtained). The total second order (MP2) energy is given by the sum

$$E_{MP2} = E^0 + E^1 + E^2 \quad (1.36)$$

Where $E^0 + E^1$ is the zero order Hartree-Fock energy. The E_{MP2} energy can be computed without corrections to the HF wave function, but if gradients or properties are needed, additional corrections to the wave function are required. MP theory is size extensive, *i.e.*, the method scales properly with the number of particles and the accuracy does not deteriorate as the system size is increased. Some methods are not size extensive, so this is an important consideration, especially for calculations on chemical reactions or simply for calculations involving more than one molecule.

MP2 calculations can be viewed as adding certain excitations to the wave function and thus represent a form of truncated configuration interaction (CI). The CI wave function is a linear combination of determinants with the expansion coefficients determined by the variational principle, *i.e.*, requiring the energy to be a minimum. Double excitations and higher are needed to describe electron correlation. In full CI, the wave function includes all possible excitations and the full Hamiltonian includes all possible matrix elements.

Another method that adds selected excitations in a size-consistent manner is termed coupled cluster (CC) theory. CC theory is based on the wave operator, e^T which usually acts on the HF reference wave function, Ψ_0 ,

$$\Psi_{CC} = e^{\hat{T}} \Psi_0 \quad (1.37)$$

where T is the excitation or cluster operator,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \dots \quad (1.38)$$

The singles excitation operator gives excitations according to

$$\hat{T}_1 = \sum_i t_i^a \Psi_0 \quad (1.39)$$

where the t_i^a are the amplitudes for single excitations of electrons from occupied orbitals i to virtual orbitals a . The T_2 excitation operator induces double excitations

$$\hat{T}_2 = \sum_i t_{ij}^{ab} \Psi_0 \quad (1.40)$$

where t_{ij}^{ab} are the amplitudes for the double excitations. The CC plus single and double excitations (CCSD) energy is given by

$$E_{CCSD} = \langle \Psi_0 | H e^{\hat{T}_1 + \hat{T}_2} | \Psi_0 \rangle \quad (1.41)$$

To obtain the CCSD energy the amplitudes are needed and can be solved for with the following equation

$$\langle \mu_i | e^{-\hat{T}_1 - \hat{T}_2} H e^{\hat{T}_1 + \hat{T}_2} | \Psi_0 \rangle = 0 \quad i = 1, 2 \quad (1.42)$$

It should be noted that eq. (1.42) can be rewritten as

$$\langle \mu_1 | \hat{H} + [\hat{H}, \hat{T}_2] | \Psi_0 \rangle = 0 \quad (1.43)$$

where $[\hat{H}, \hat{T}_2]$ is the commutator notation for the following operation on the wave function:

$$[\hat{H}, \hat{T}_2] \Psi_0 = \hat{H} \Psi_0 - \hat{T}_2 \Psi_0 \quad (1.44)$$

and where μ_1 in eq. (1.43) is the single excitation manifold (the expansion of Slater determinant which includes all possible single excitations). Another equation is also used in the coupled cluster method,

$$\langle \mu_2 | \hat{H} + [\hat{H}, \hat{T}_2] + \frac{1}{2} [[\hat{H}, \hat{T}_2], \hat{T}_2] | \Psi_0 \rangle = 0 \quad (1.45)$$

where μ_2 is the double excitation manifold.

The CC equations are automatically size consistent due to the CC ansatz. To determine if the correlation due to the limited amount of excitations is able to accurately describe the energy of the molecule, the D_1 and D_2 diagnostics have been used.^{36,37} The D_1 diagnostic is defined as,

$$D_1 = \sqrt{\max\left(\lambda_{\max}\left[\sum_i t_i^a t_i^b\right], \lambda_{\max}\left[\sum_a t_i^a t_j^a\right]\right)} \quad (1.46)$$

where $\lambda_{\max}$ is the largest eigenvalue of the positive definite matrix of the single-substitution amplitudes. D_1 reflects the largest eigenvalue of the single excitations. Large D_1 values (greater than 0.05) indicate a multireference character of the ground state introduced by strong orbital relaxation effects. Similarly, D_2 reflects the largest eigenvalues of the double-substitution amplitudes:

$$D_2 = \sqrt{\max\left(\lambda_{\max}\left[\sum_{ijc} t_{ij}^{ac} t_{ij}^{bc}\right], \lambda_{\max}\left[\sum_{kab} t_{ik}^{ab} t_{jk}^{ab}\right]\right)} \quad (1.47)$$

If D_2 values are greater than 0.18, they should be carefully checked. The D_2 diagnostic checks the inadequacy of the HF reference, caused by low-lying doubly excited states.

The dispersion forces which rely on electron correlation are thus included in the MP2 method, but have been shown to be overestimated when compared to CCSD(T) level calculations.³⁸ While the MP2 method does include dynamic electron correlation, it does not include static electron correlation, which can be included by expanding the wave function as a linear combination of Slater determinants. Without static electron correlation covalent bond breaking and transition states are not properly described.³⁹

Another way of including electron correlation into a calculation is not to use the HF method, but a method which has been parametrized and includes the effects of electron correlation. One method that is heavily used in this thesis is that of density functional theory (DFT). Pure DFT does not use a wave function but only the electron density, simplifying the calculation of the electronic

energy. In the HF method the electronic energy depends on $3N$ spatial variables, where N is the total number of electrons, whereas in pure DFT, the energy is a functional of the total electron density, which only depends on three spatial variables, independent of the number of electrons. In practice, however, the expression for the kinetic contribution to the energy based on the density is not accurate and orbitals are reintroduced in the Kohn-Sham (KS) procedure.⁴⁰ DFT is still often preferred to the HF method as more correlation is included in the DFT calculation. This is done through the exchange and correlation terms which usually both have empirical parameters. The energy in DFT can be partitioned into terms which all depend on the density,

$$E[\rho] = T[\rho] + V_{ext}(R) + J_H[\rho] + E_{XC}[\rho] \quad (1.48)$$

where T is the kinetic energy of the electrons, V_{ext} is the energy due to the repulsions of the nuclei, and J_H the energy due to classical Hartree repulsion:

$$J_H = \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' \quad (1.49)$$

and E_{XC} is the remaining exchange and correlation energy difference between a system of non-interacting electrons and the exact value. By introducing Kohn-Sham orbitals, ϕ^{ks} , the kinetic energy is calculated as:

$$T[\rho] = \sum_i^n \langle \phi_i^{ks}(r) | -\frac{1}{2} \nabla^2 | \phi_i^{ks}(r) \rangle \quad (1.50)$$

The kinetic energy still depends on the density as the KS orbitals must also define the true density of the system through the following equation

$$\rho(r) = \sum_i^n |\phi_i^{ks}(r)|^2 \quad (1.51)$$

The potential is the sum of the repulsions of the nuclei, ν_{ext} , the classical electron Hartree potential, ν_H :

$$\nu_H = \int \frac{\rho(r')}{|r - r'|} dr' \quad (1.52)$$

and, the exchange correlation potential, ν_{XC} , which incorporates the remaining many-body effects into a one-body potential. All of these can still be expressed as functionals of the density,

$$\nu_s[\rho](r) = \nu_{ext}(r) + \nu_H[\rho](r) + \nu_{XC}[\rho](r) \quad (1.53)$$

Thus the pseudo eigenvalue Kohn-Sham equation is,

$$\left[-\frac{1}{2}\nabla^2 + \nu_s[\rho](r)\right]\phi_i^{ks}(r) = \epsilon_i\phi_i^{ks}(r) \quad (1.54)$$

and can be solved in a self-consistent manner. The Kohn-Sham molecular orbitals, ϕ^{ks} , minimize the energy eq. (1.54). While they are physically meaningful,⁴¹ there are important differences between the Kohn-Sham molecular orbitals and those obtained in the HF procedure. These differences will be seen in discussion of ionization potentials (IPs) and electron affinities (EAs).

If the exchange correlation potential were known exactly, DFT would give exact results. Unfortunately the exact exchange correlation functional is not known and is thus the source for all the errors in DFT. The major shortcomings of DFT include the delocalization error and the static correlation error.⁴² The delocalization error includes the effects of the self-interaction error (*vide infra*), the lack of derivative discontinuity (upon removal or addition of electrons to the system) of the exchange correlation potential, and the lack of proper dispersion interactions, leading to underestimated transition state energies as well as poor charge-transfer binding energies.⁴³ The static correlation error gives rise to poor descriptions of bond breaking and degenerate states.⁴⁴ Finally, while DFT might be viewed as one of the best semi-empirical methods (as parameters are

determined for atoms, not molecules), it is usually still empirical and suffers from the same major weakness as all empirical methods viz., lack of systematic improvement.

Perhaps the largest problem that results from the empirical exchange correlation terms is an artificial repulsion or self-interaction of the electron with itself. In HF theory the energy for a single occupied spinorbital is,

$$\varepsilon_i = h_i + \sum_{ij}^n (J_{ij} - K_{ij}) = h_i \quad (1.55)$$

where the sum runs over all occupied spinorbitals. Here the index $i = j$ is allowed and as seen from eqs. (1.16) and (1.17), thus for a single electron

$$J_{ii} - K_{ii} = 0 \quad (1.56)$$

i.e., the electron does not interact with itself according to HF theory. In DFT this cancellation is not present by default, as the exchange energy is given not as the nonlocal contribution from the charge density overlap and thus this error can cause problems in many applications. Self-interaction error is important to consider in calculations involving reactions (bond breaking), in the location of transition states, and as will be discussed later, in excited states. Self-interaction is also cited as a cause for the inaccurate first ionization potentials when these are estimated by the HOMO energy of the molecule according to the DFT equivalent of Koopmans’ theorem—which is only valid for exact functionals.⁴⁵

Bond stretching is problematic with *ab initio* methods which use a single determinant-based description of the wave function, as a single determinant does not allow proper homolytic dissociation.⁴⁶ For DFT however, this is not necessarily a problem, because, if the exact exchange correlation potential was known, bonds could dissociate correctly. Indeed, for simple molecules this has been shown to be true when an accurate density obtained from use of the adiabatic connection formula was used to obtain the correct dissociation curve for H₂ and Be₂ within 0.1 eV.⁴⁷ Since for most

cases the exact exchange potential is not known, dissociation and bond stretching remain a major challenge to DFT. One new method that can overcome this shortcoming is spin-flip DFT.⁴⁸

The absence of derivative discontinuities in the energy upon an integer change of electrons leads to poor orbital energy values and also gives rise to an exchange-correlation potential that decays exponentially, instead of as $1/r$.⁴⁹ The fact that the potential is not stabilized at longer distances can lead to poor results for loosely bound systems, such as anions and excited states.

Another major problem arising from not knowing the exact correlation exchange potential is that there is no systematic improvement of the results, or even a method to predict the accuracy of the next calculation. One way to provide better results in DFT is to use more complicated exchange correlation, or meta-functionals,⁵⁰ however more accurate results are still not guaranteed.

Despite these limitations, DFT provides a way to include electron correlation effects (semi-empirically) in larger molecules, the energies and gradients of which cannot be calculated with post HF methods due to size limitations. DFT also provides a practical starting point for calculations of excited state properties (TDDFT, *vide infra*).

1.2.2 Excited States

In order to understand data obtained from electronic spectroscopy, transitions to excited state transitions need to be calculated. Spectroscopy is a good tool for identifying excited states and monitoring photochemical reactions. Results are often interpreted by the Franck-Condon principle, which can be stated semiclassically as the assumption that the electronic photoexcitation occurs without significant nuclear motion. This is due to the large difference in the mass of the electrons and the nuclei which gives rise to different natural oscillation periods for the electrons and the nuclei. However, there are many shortcomings when experimental spectroscopy is used to explain photochemical results. One reason can be the existence of dark states that are not observed with various spectroscopic techniques. Also, the structural details of the molecule as it relaxes after excitation are not easily known. Sometimes conditions of the experiment such as temperature or the properties of the system under study such as excited lifetime, exclude some molecular

conformations from being measured. If accurate theory and experiment are used together, more reliable results and interpretations can be obtained.

A first order picture for a simple electronic transition involving excitation of one electron from the ground to excited singlet states can be modeled as follows,

$${}^1\Delta E_{i\rightarrow a} = IP - EA - J_{ia} + 2K_{ia} \quad (1.57)$$

where J_{ia} and K_{ia} are the electron repulsion integrals between relevant orbitals in the transition from occupied orbital i to unoccupied orbital a and where IP is the ionization potential, or the energy required to remove an electron, and EA is the electron affinity, or the energy gained when an electron is added to the molecule. The repulsion integrals, which are orbital specific, are an important contribution to the excitation energy as can be seen in eq. (1.57). The exchange integral, K_{ia} , also determines the singlet-triplet gap (2K) and if this integral is small, transition dipole moments (as well as oscillator strengths) will also be small. Equation (1.57) can be derived from the HF equations upon consideration of the removal and addition of electrons.²²

Orbital energies are related to the IP via Koopmans' theorem:

$$IP = -\epsilon_{HOMO} \quad (1.58)$$

and thus are important as they are the zero order contribution to the excitation energy. Orbital energies can vary depending on the method used in the calculation. While HF methods give better IPs and EAs, as the equations relate directly to taking away or adding an electron, this is not so for DFT, which uses the same potential for occupied and virtual orbitals. In DFT the HOMO energy can be so bad as to more closely relate to the average of the IP and EA energies, than the (negative of the) energy of the HOMO.⁴⁹

Excitation energies as well as transition intensities can be compared to experiment. The

experimental oscillator strength is given by

$$f = \frac{4.319 \times 10^{-9}}{n} \int \epsilon(\tilde{\nu}) d\tilde{\nu} \quad (1.59)$$

where n is the solvent refractive index and integration is done over the absorption band frequencies (ϵ) given in cm^{-1} . The theoretical oscillator strength for transition is proportional to the square of the transition dipole moment,

$$f \propto |M|^2 \quad (1.60)$$

where the transition dipole moment, M , is given by

$$M = \langle \Psi_f | \hat{M} | \Psi_i \rangle \quad (1.61)$$

The transition dipole moment models the interaction of the wave function of the final and initial states with light given in the length representation,⁵¹ by the following description of the transition dipole moment operator, $\hat{M}$,

$$\hat{M} = \sum_j r_j \quad (1.62)$$

where r_j is the position of the j^{th} electron. The transition dipole moment can be thought of as the dipole moment of the transition density between two states. For simple transitions consisting of a single excitation the transition dipole moment can be thought of as the dipole moment of the overlap density of the two orbitals. For this type of transition, this is not an approximation, as the Slater determinant describing the wave function for the initial and final states can be reduced (via the Slater Condon rules) to only the molecular orbitals involved in the excitation,

$$M = \langle \psi_f | \hat{M} | \psi_i \rangle \quad (1.63)$$

From calculated values of transition dipole moments, the radiative lifetime can be estimated⁵² from the Einstein coefficient (A_{21}) and the Strickler-Berg equation,⁵³

$$A_{21} = \frac{1}{\tau_{rad}} = 2.142005 \times 10^{10} M^2 E_{max}^3 \quad (1.64)$$

where the radiative lifetime (τ_{rad}) is in seconds, E_{max} is the calculated emission energy, and all other magnitudes are in atomic units.

Experimental oscillator strengths can also provide a first order description of the fluorescence rate constant (k_f) via the Strickler-Berg equation,⁵³

$$k_f = 2.88 \times 10^{-9} n^2 (\tilde{\nu}_{max})^2 \int \epsilon d\tilde{\nu} \quad (1.65)$$

where n is the refractive index of the solvent, $\tilde{\nu}_{max}$ is the wave number of the peak maximum, and the intensity of the absorption band is integrated. This equation assumes there is little or no difference in the transition dipole moment of the absorptive and emissive species and works better for strong transitions. If these conditions are met and the fluorescence quantum yield is unity, the radiative lifetimes can be compared $1/\tau_{rad}$.

Experimental absorption and fluorescence bands are well described theoretically by the cross section,⁵⁴ derived from first order time dependent perturbation theory as, σ_s ,

$$\sigma_s(\omega) = \frac{4\pi^2\omega}{\hbar cn} \sum_{i,f} (\rho_i - \rho_f) |M|^2 \delta(\omega_{fi} - \omega) \quad (1.66)$$

where c is the speed of light, ω is the light frequency, $\hbar$ is Planck's constant divided by 2π , ρ_i and ρ_f are the probabilities of certain configurations in the ensemble of the initial and final states (i and f are their respective wave functions), M is the transition dipole moment operator (defined in

eq. (1.61)), and δ is the Dirac δ function in terms of the frequency (energy) difference between the final and initial states (ω_{fi}).

The cross-section includes the effects of electronic absorption at different geometries on the absorption spectrum, and is the basis for the semi-classical approach to spectrum simulation.⁵⁵ As a molecule distorts from its equilibrium geometry, transition strength may grow or decrease; the cross section accounts for this with the probability factor, which implies all geometries are sampled and their contribution to the spectrum is weighted by the probability. The weighting can be modeled by a Boltzmann distribution,

$$\rho_i - \rho_f = \rho_i(1 - e^{-\beta\hbar\omega}) \quad (1.67)$$

where $\beta = (k_B T)^{-1}$, and k_B is Boltzmann's constant and T , the temperature. A Wigner distribution,⁵⁶ which gives a quantum correction to the Boltzmann distribution by expanding the probability of certain configurations in a power series of $\hbar$,

$$P(x; p) = e^{-\beta\hbar\omega} + \hbar f_1 + \hbar^2 f_2 + \dots \quad (1.68)$$

can also be used to model the conformational distribution. In eq. (1.68) f_n is a function of the potential energy.⁵⁶

The Franck-Condon overlap of the electronic $S_0 \rightarrow S_1$ transition is given by the overlap of the ground, $\psi_{nuc,0}^0(R)$, and excited state, $\psi_{nuc,n}^1(R)$, vibrational wave functions,

$$S_{(FC),0,n} = \langle \psi_{nuc,n}^1 | \psi_{nuc,0}^0 \rangle \quad (1.69)$$

The change in absorption intensity upon molecular distortion for weak transitions can not be modeled by the simple inclusion of the Franck-Condon factors, which are the square of the Franck-Condon overlap. The Franck-Condon factors are useful however to describe the shape of the vibrational envelope of allowed electronic transitions. They cannot be used to simulate weak transitions

as the experimental spectra of these transitions can involve intensity borrowing from nearby allowed transitions, and a post Condon approach, such as the semi-classical method based on using multiple configurations of the nuclei, is necessary.⁵⁴ Experimentally, forbidden transitions can often be seen with 2-photon spectroscopy or by electron energy loss spectroscopy (EELS). The electron-induced transition selection rules differ from the selection rules of light-induced spectroscopy. At times even these methods are not helpful and experimentalists must rely on theoretical estimates.

Other experimental methods,⁵¹ such as linear dichroism, (LD), can give the polarization of the electronic transitions. Fluorescence anisotropy measurements can give relative polarizations of transition dipole moments for different excited states. Magnetic circular dichroism (MCD) can be used to identify electronic transitions based on excited state symmetry. More sophisticated methods which utilize pulsed laser (pump-probe) techniques are useful experimental tools to monitor molecular dynamics, such as excited state relaxation. Multidimensional spectroscopies can probe the coupling between various excited states and monitor vibrational relaxation after excitation via alterations to duration, sequence, frequency, polarization, and shape of the laser pulses.⁵⁷

1.2.3 Excited State Methods

Many methods that are currently used to calculate molecular valence excited states are based on the response of molecular properties to a time-dependent perturbation and are described by response theory. The time-dependent perturbation is given by uniform electric field (light),

$$E(r, t) = r \cos(\omega t) \quad (1.70)$$

and the time dependent Schrodinger equation,

$$i\hbar \frac{\partial}{\partial t} \Psi(r, t) = \hat{H} \Psi(r, t) \quad (1.71)$$

which is a partial differential equation in spatial coordinates and time and governs the evolution of Ψ . The most basic of the response theory equations is that of time-dependent Hartree Fock, TDHF

theory.⁵⁸ This method is based on eq. (1.71) or the Heisenberg equation of motion,

$$i\frac{\partial}{\partial t}\mathbf{P}(t) = [\mathbf{P}(t), \hat{H}] \quad (1.72)$$

in propagator methods which follow the time dependent evolution of the property, $\mathbf{P}(t)$. In the polarization propagator method this property is the dipole moment,

$$\mathbf{P} = \langle \Psi_0 | r | \Psi_0 \rangle \quad (1.73)$$

and its response due to a time-dependent perturbation, $\mathbf{Q}$, in the case of the polarization propagator, represented by the electric field (eq. (1.70)). In the time domain the polarization propagator can be described with commutator notation as

$$\ll \mathbf{P}; \mathbf{Q} \gg = -i\theta(t - t') \langle \Psi_0 | [\mathbf{P}, \mathbf{Q}] | \Psi_0 \rangle \quad (1.74)$$

where θ is a Heaviside step function,

$$\theta(x) = \begin{cases} 0 & \text{if } x < 0, \\ 1 & \text{if } x > 0. \end{cases} \quad (1.75)$$

This equation can be Fourier transformed into the frequency domain and when written with excitation and de-excitation operators it can be expressed via the following non-Hermitian coupled equations,

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} \quad (1.76)$$

where the $\mathbf{A}$ matrix is given by

$$\mathbf{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia||jb) \quad (1.77)$$

and the B matrix is given by

$$\mathbf{B}_{ia,jb} = (ia|bj) + (ia||bj) \quad (1.78)$$

The X and Y matrices are the solution eigenvectors which correspond to the transition amplitudes. Equation (1.76) is the basis for the time-dependent Hartree-Fock (TDHF) method if the HF reference function is used. The TDHF energies can be improved by adding electron correlation via perturbative treatments. The algebraic diagrammatic construction through second order, ADC(2), is based on perturbative (diagrammatic construction) corrections to the polarization propagator.⁵⁹ These equations can be written in matrix form similar to eq. (1.76),

$$(\mathbf{K} + \mathbf{C})\mathbf{Y} = \Omega\mathbf{Y} \quad (1.79)$$

where $\mathbf{K}$ is the TDHF (polarization propagator eq. (1.76)) excitation energy operator, $\mathbf{C}$ a corrective term, Ω the excitation energies and the eigenvectors are given by $\mathbf{Y}$. This method includes second order correction (2) and single and double excitations.

The equation of motion coupled cluster methods are also based on response theory.⁶⁰ In this case, the coupled cluster equations are inserted into response theory and propagator machinery to get excitation energies.

The CC2 model⁶¹ uses approximate values for the cluster amplitudes. Compared to the full value of μ_2 in eq. (1.45), the CC2 doubles amplitudes are truncated to

$$\langle \mu_2 | [\hat{F}, \hat{T}_2] + \hat{H} | \Psi_0 \rangle = 0 \quad (1.80)$$

where the Hamiltonian, $\hat{H}$, in eq. (1.80) is the sum of the $\hat{F}$ operator and the fluctuation, $\hat{U}$, operator. The fluctuation operator describes the difference between the electron repulsion and the Fock potential.⁶¹

A commonly used theoretical excited state method is time-dependent density functional theory (TDDFT).⁴⁵ Formally the KS-DFT equation (eq. (1.54)) is inserted along with a time dependence into the time-dependent Schrödinger equation to give

$$i \frac{\partial}{\partial t} \phi_i^{ks}(r, t) = \left(-\frac{1}{2} \nabla_i^2 + \nu_{ext}[\rho](r, t) + \nu_H[\rho](r, t) + \frac{\delta A_{XC}[\rho]}{\delta \rho(r, t)} \right) \phi_i^{ks}(r, t) \quad (1.81)$$

where the exchange correlation action functional, $(\frac{\delta A_{XC}[\rho]}{\delta \rho(r, t)})$, is usually approximated via the adiabatic local density approximation (ALDA),

$$\frac{\delta A_{XC}[\rho]}{\delta \rho(r, t)} = \frac{\delta \nu_{XC}[\rho]}{\delta \rho(r)} \delta(t) \quad (1.82)$$

in order to allow the TDDFT to be solved with the exchange correlation potential obtained from a static ground state DFT calculation. ALDA approximates the nonlocal (in time) exchange correlation potential to be that from the ground state potential of a uniform gas, which is local in time, making the exchange kernel, when Fourier-transformed, frequency independent.⁶² This can lead to problems (*e.g.*, with transitions involving double excitations, charge transfer), but it usually is a good approximation.⁴⁵

Equation (1.81) can be reformulated in a matrix formulation using the linear time dependent response of the ground state (time independent) density to a time dependent perturbation due to an external field. By using linear response techniques (see eq. (1.76)), reformulation into Casida's equation,⁶³ (eq. (1.83)) is possible, and excitation energies and oscillator strengths are obtained with techniques from linear algebra, *i.e.*, the wave function does not have to be propagated in time. Casida's equation,

$$\mathbf{R}\mathbf{F} = \omega^2 \mathbf{F} \quad (1.83)$$

in which $\mathbf{R}$ is $(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{1/2}$ and writing eq. (1.83) in an expanded form,

$$(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{1/2} \mathbf{F} = \omega^2 \mathbf{F} \quad (1.84)$$

and where ω is the excitation frequency and $\mathbf{F}$ is the following

$$\mathbf{F} = (\mathbf{A} + \mathbf{B})^{-1/2}(\mathbf{X} + \mathbf{Y}) \quad (1.85)$$

The $\mathbf{X}$ and $\mathbf{Y}$ matrices are the solution matrices which correspond to the transition amplitudes. In order to write eq. (1.83), the difference matrix, $(\mathbf{A}-\mathbf{B})$, must be positive definite, otherwise instabilities (where imaginary frequencies are obtained) occur. In the TDDFT formulation, the $\mathbf{A}$ matrix includes the orbital energy gap, which is based on the ground state DFT calculation, as well as the following integrals,

$$\mathbf{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia|jb) + (ia|f_{xc}|jb) \quad (1.86)$$

where the xc kernel in the last equation is defined as

$$(ia|f_{xc}|jb) = \int dr dr' \phi_i^*(r) \phi_a(r) \frac{\delta^2 E_{xc}}{\delta \rho(r) \delta \rho(r')} \phi_b^*(r') \phi_j(r') \quad (1.87)$$

The $\mathbf{B}$ matrix in the TDDFT formulation is,

$$\mathbf{B}_{ia,jb} = (ia|bj) + (ia|f_{xc}|bj) \quad (1.88)$$

and includes the effects of double excitations, but it should be noted that for excited states described significantly with double excitations, the inclusion of the $\mathbf{B}$ matrix is usually not sufficient.⁴⁵ Both the $\mathbf{A}$ and $\mathbf{B}$ matrices are included in the random phase approximation (RPA) version of TDDFT. The $\mathbf{B}$ matrix is neglected in the Tamm-Dancoff approximation (TDA) of the TDDFT equations. The TDA approximation corresponds to singly excited CI. The TDDFT/RPA formulation gives

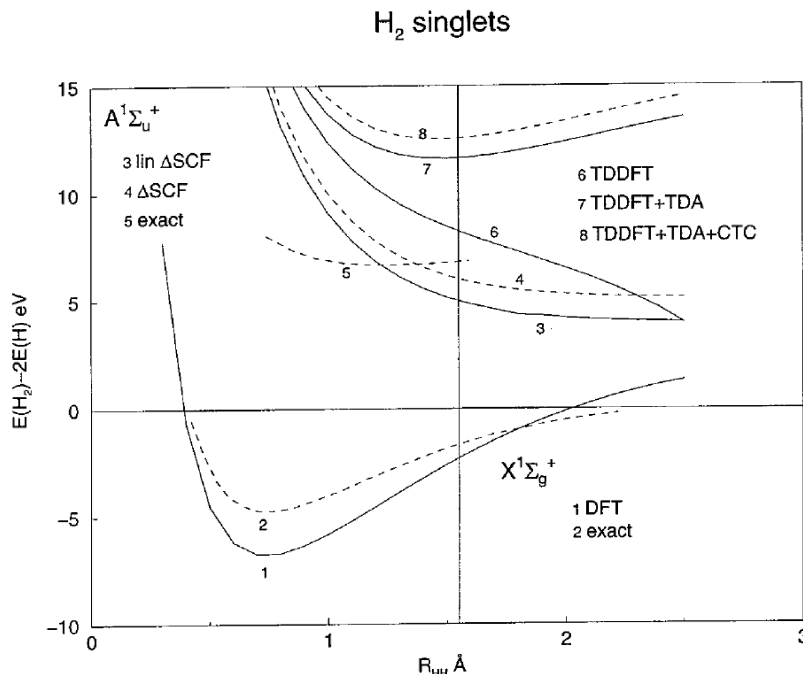


Figure 1.1: Application of TDDFT to electronic excited states of H_2 , from Casida. This figure shows that TDDFT with the RPA approximation leads to artificial excited state dissociation, (path 6).⁶⁴

more accurate oscillator strengths, while the TDDFT/TDA formulation is useful for geometry optimizations of molecules that have singlet or triplet instabilities.⁶⁴

There are many deficiencies of TDDFT, and charge transfer, multireference states, complicated excitations, *e.g.*, those involving double excitations, are some of the instances when TDDFT can give spurious results.⁴⁵

TDDFT usually works quite well for valence excited states. This is because the orbital energy difference corresponding to the first term of excitation energy is underestimated and the **A** and **B** matrices raise the excitation energies by an amount which typically agrees with experiment.⁴⁵ However for charge transfer (CT) or Rydberg states (*i.e.*, where excitation is to an orbital of higher principal quantum number than that of the valence orbitals), the excitation energies are low as the effective exchange integrals diminish due to no overlap of the active orbitals and imperfect kernels (where derivative discontinuities of the energy variation with density are not obeyed).⁴⁵ One way

to fix this is to add HF exchange. Now orbital energy differences more closely correspond to IP and EA energies and the $1/R$ dependence is added through an effective Coulomb integral which originates from the ground state HF exchange (*vide infra*). The new TDDFT integrals for hybrid functionals are

$$\mathbf{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia|jb) - c_{HF}(ij|ab) + (1 - c_{HF})(ia|f_{xc}|jb) \quad (1.89)$$

and

$$\mathbf{B}_{ia,jb} = (ia|bj) - c_{HF}(ib|aj) + (1 - c_{HF})(ia|f_{xc}|bj) \quad (1.90)$$

where the amount of HF exchange enters via the coefficient c_{HF} . These equations (eq. (1.89) and eq. (1.90)) show that adding HF exchange to the ground state functional has the effect of adding a Coulomb-like term, $(ij|ab)$, to the response equations. Likewise, the response of the Coulomb operator corresponds to an exchange-like term, $(ia|bj)$. This is important as the additional Coulomb like term $(ij|ab)$ from the added ground state HF exchange counteracts the importance of the exchange like term $(ia|bj)$ in Casida's equations. Including added HF exchange is found in later chapters to be important for structure optimization. Adding HF exchange can be done with a hybrid functional, or to a more extreme correction, the range corrected functionals. Here the exchange energy, E_x , is modified via the electron repulsion operator which is split into short and long range components given by the following,

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}}, \quad (1.91)$$

where r_{12} is the interelectronic distance between electrons at coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ and erf represents the standard error function,

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad (1.92)$$

The first term of eq. (1.91) represents the short range repulsion and the second term the long range part. As μ approaches zero, the pure DFT functional is obtained; as μ increases, more nonlocal HF exchange is included.

The Λ diagnostic⁶⁵ is helpful in determining CT character of an excitation and is given by

$$\Lambda = \frac{\sum_{i,a} k_{ia}^2 O_{ia}}{\sum_{i,a} k_{ia}^2} \quad (1.93)$$

where O_{ia} is the inner product of the moduli of two orbitals,

$$O_{ia} = \langle |\phi_i| | \phi_a| \rangle \quad (1.94)$$

Not all CT excitation energies are underestimated with traditional TDDFT, only those with low Λ values (0.3 and less).⁶⁵ These excitation energies as well as those of Rydberg states can be improved with long range corrected functionals. This will be demonstrated in Chapter 2. The Λ parameter value is known to not always be capable of identifying CT, as was shown for the L_a state in polycyclic aromatic molecules.⁶⁶ For cases where charge transfer contamination may play a role, a comparison of the standard TDDFT excitation energies to those of the LC-TDDFT method is suggested.⁶⁶

1.2.4 Qualitative Models

Once accurate methods or experimental data are available, simple models can be constructed that can reproduce the results from sophisticated methods. These models should be simple enough that the underlying reasons for the resulting trends can be recognized. Hückel molecular orbital (HMO) theory is a model that is invaluable for interpreting many chemical trends. In this model the electron repulsions of the Roothaan operator $G_{\mu\nu}$ are set to zero and their effects are accounted for in a semiempirical manner by fitting $H_{\mu\nu}$ to experimental or calculated values. The overlap matrix, $S_{\mu\nu}$, is also assumed to be an identity matrix. The total energy is now given by

$$E_{tot} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} = \sum_{\mu=\nu} P_{\mu\nu} \alpha_{\mu} + \sum_{\mu,\nu}^{neighbors} P_{\mu\nu} \beta_{\mu\nu} \quad (1.95)$$

where $H_{\mu\nu}^{core}$ is given as $H_{\mu\nu}$, according to the convention of HMO theory. In HMO theory, the resonance integral, $\beta_{\mu\nu}$ is defined between p orbitals that are nearest neighbor atoms, but in different models additional interactions *i.e.*, resonance integrals are defined. In the Ladder C model, the resonance integrals between orbitals located on nearest neighbor atoms are still only defined, but here, more valence hybrid orbital interactions on neighboring atoms are taken into account. These interactions will be defined later. The formal neglect of the repulsions means that the total energy is a sum of the occupied orbital energies. The orbital energies can be decomposed:

$$\varepsilon_i = \sum_{\mu=\nu} c_{\mu i} c_{\nu i} \alpha_{\mu} + 2 \sum_{\mu\nu} c_{\mu i} c_{\nu i} \beta_{\mu\nu} \quad (1.96)$$

Understanding the energetic contributions to an orbital energy can sometimes be helpful for excited state analysis via eq. (1.57), where the orbital energies play a major role in the excitation energy.

Hückel theory is a model that allows for the understanding of many molecular trends. These include the rationalization and prediction of aromaticity, and prediction of excitation energies.⁶⁷ Hückel theory predicts that excitation energies of linear polyene chains with even numbers of carbon atoms (n), will decrease (as $1/n$) as the chain length increases; this is indeed experimentally observed.⁶⁸ The energy for the HOMO-LUMO excitation in polyenes (and to the first order, also for polymethines) is,⁶⁷

$$h\nu = 4\beta \sin \frac{\pi}{(2n+1)} \quad (1.97)$$

Perturbation theory can also be used simply to predict excitation energies in larger π systems, which works very well if the structure can be broken into two alternating systems with an odd number of electrons.⁶⁹ Hückel theory can also be used to rationalize the effects of delocalization, as will be mentioned in section 1.3.1.

Sometimes localized models are useful to understand bonding and reactivity in molecular systems. One such qualitative model is that of natural bond orbitals (NBOs).⁷⁰ NBOs are built from natural atomic orbitals (NAOs). These are special atomic orbitals that are defined from diagonalization of a density matrix that has been constructed to be blocked on the atomic centers. This density matrix is then orthogonalized in a special manner and atomic populations can be analyzed.

$$\mathbf{P} = \begin{pmatrix} \mathbf{P}^{AA} & \mathbf{P}^{AB} & \mathbf{P}^{AC} & \dots \\ \mathbf{P}^{BA} & \mathbf{P}^{BB} & \mathbf{P}^{BC} & \dots \\ \mathbf{P}^{CA} & \mathbf{P}^{CB} & \mathbf{P}^{CC} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \quad (1.98)$$

NBOs are defined as the orbitals which have high occupations when two atomic center blocks of the density matrix are diagonalized. The coefficients of the NAOs which make up the NBOs give the effective hybridization and natural hybrid orbitals (NHOs) can be defined.

The NBO method is based on the first order density matrix. The relaxed density is used in the NBO procedure to analyze interactions from different resonance structures. Another related method is that of block localized wave functions (BLW), which separately optimizes wave functions for different structures, and provides superior hyperconjugative energetics.^{71,72} While MO theory is useful for spectroscopy and its trends, a model that is useful for understanding chemical reactivity and structure (*e.g.*, excited state relaxation) is that of valence bond (VB) theory.⁷³

1.3 σ Delocalization Review

1.3.1 Delocalization

Delocalization and its effects in molecules were first investigated by Erich Hückel,⁷⁴ who provided the Hückel Molecular orbital (HMO) model for understanding molecular properties based on a simplified version of molecular orbital (MO) theory. The simplicity of this model is crucial for

understanding trends and developing chemical theories, not just for reducing the difficulty of calculation. Thus Hückel theory today is more of a qualitative model than an accurate theoretical framework.

Electronic delocalization in polyatomic molecules has been defined as the deviations from the localized Lewis (2-center 2-electron bond) structure.⁷⁵ Delocalization is the product of combined interactions in the molecule that are not related to those of the primary bond. Examples of these interactions will be given in section 1.4.1.

Aromaticity is not directly measurable experimentally, but can be evaluated indirectly on the basis of structural, magnetic, energetic or spectroscopic criteria.⁷⁶ The phenomenon known as σ aromaticity, the increased stabilization of cyclic $4n+2$ skeletal electron systems due to delocalization, is now believed to not be the main stabilizing force in cyclopropane by Wu et al.⁷⁶ The concept of σ aromaticity is still believed to be valid however in other systems such as H_3^+ and boron based clusters.⁷⁷ Wu et al. find cyclopropane to be stabilized by only 3.5 kcal mol⁻¹ with respect to propane (they find the cyclotrisilane, Si_3H_8 , to be stabilized by 6.2 kcal mol⁻¹ in an analogous comparison) and no extra stabilization with respect to *n*-butane (which has similar number of C-C bonds as cyclopropane).⁷⁶ It is argued that flat cyclopropane is stabilized by bond bending, re-hybridization and strengthened C-H bonds. The C-H bonds have greater s character ($sp^{2.6}$) than those of cyclobutane ($sp^{3.3}$) and this leads to stronger bonding.⁷⁶ In the case of H_3^+ , σ conjugation and delocalization reduce the Coulombic repulsions among the nuclei.⁷⁸

The effects of σ delocalization of oligosilanes will be examined in this work. σ Delocalization effects are manifested in changes to the UV absorption and emission spectra of oligosilanes and will be addressed in this thesis.

1.4 Oligosilanes

1.4.1 Models for σ Conjugation

As σ bonds compose the framework of all molecules, it is of interest to understand the basic interactions in saturated systems and their effects on molecules. Sandorfy pioneered an interest in the theoretical description of the interactions of the σ framework in molecules. The Sandorfy C model⁷⁹ is shown in Figure 1.2. Even more simplified models such as the linear combination of bonding orbitals (LCBO), Figure 1.2, have been used for rationalizing photoelectron spectra with limited success.⁸⁰ This model is not sufficient to describe excited states, however, and more complicated models such as the Ladder C and H descriptions of σ conjugation have been developed.⁸¹

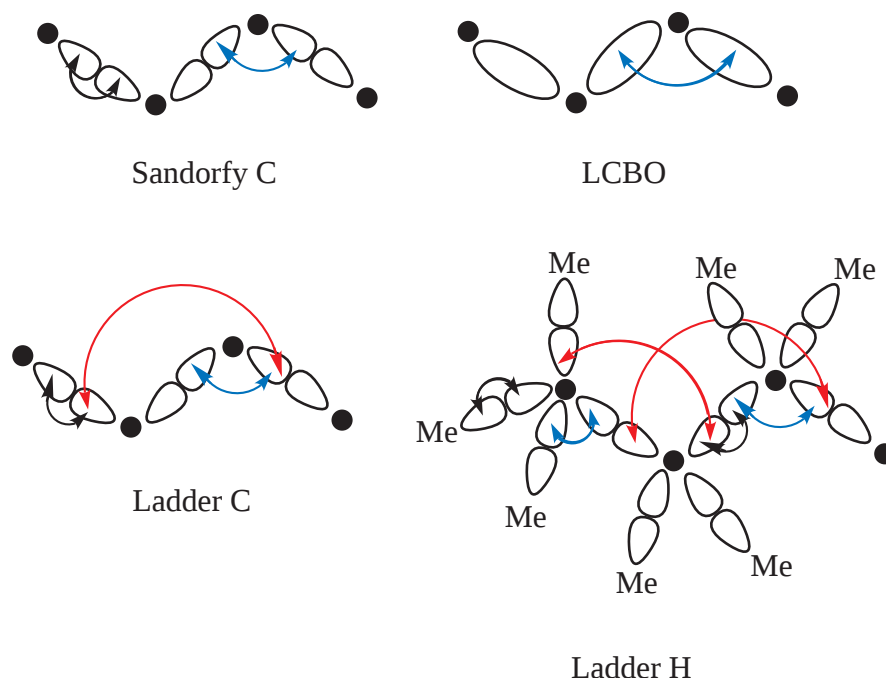


Figure 1.2: Models developed to describe σ interactions: Sandorfy C, LCBO, Ladder C and Ladder H models. Primary, geminal, and vicinal interactions are indicated with black, blue and red double-headed arrows, respectively.

σ Conjugation is due to the interaction between hybrid orbitals located on the same atom, σ hyperconjugation is due to vicinal interactions *i.e.*, secondary interactions between hybrid orbitals

located on neighboring atoms, neither of which are involved in primary bond formation (red arrows in Figure 1.2).⁷⁵ σ Hyperconjugation is also referred to as delocalization by through-bond coupling.⁸² Mulliken, Hoffmann and Dewar were the first to introduce these ideas into chemistry.⁸²⁻⁸⁴ Together, these interactions cause σ delocalization.

It is extremely important to note, that even though sp hybrid orbitals are orthogonal, they interact strongly and have nonzero resonance integrals. This was pointed out by Dewar⁶⁹ and can be seen from the following equation, which shows the interaction energy for sp hybrid orbitals,

$$\langle sp_1 | H | sp_2 \rangle = \frac{1}{2} \langle s + p | H | s - p \rangle = \frac{1}{2} [\langle s | H | s \rangle - \langle p | H | p \rangle] = \frac{1}{2} [\epsilon_s - \epsilon_p] \quad (1.99)$$

where the hybrid orbitals have been expanded in the atomic orbital contributions. Equation (1.99) shows the interaction energy of the neighboring sp hybrid orbitals, *i.e.*, the σ conjugation, to be dictated by the atomic s and p orbital energy difference. More p hybridization (*e.g.*, sp³) leads to less interaction and weaker conjugation between hybrid orbitals.

The effects of σ conjugation can be seen in the preferred geometries of certain radicals. While the methyl radical prefers a planar geometry, the effects of σ conjugation take over and pyramidalize other radicals, such as *t*-butyl radical and the trimethylsilyl (TMS) radical, shown in Figure 1.3.

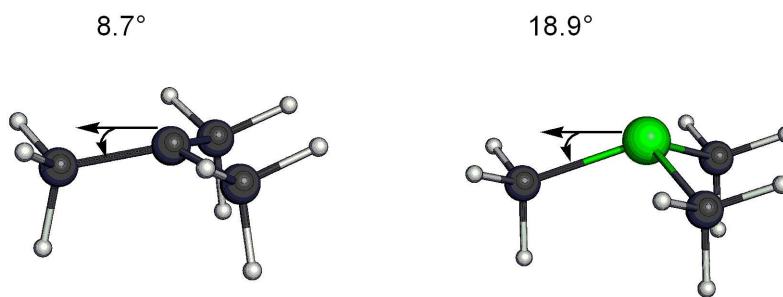


Figure 1.3: Pyramidalization of *t*-butyl and TMS radicals. Structures from RIUMP2/aug-cc-pVTZ optimizations, but similarly pyramidalized structures have long been known in the literature.^{69,84-86}

Pyramidalization allows the radical p orbital to hybridize with the s atomic orbital and

mix with vicinal sp^3 hybrids. The deviation from planarity for the *t*-butyl radical and TMS radical are 8.7° and 18.9° , respectively (RIUMP2/aug-cc-pVTZ). This deviation from planarity is attributed by Dewar to σ conjugation (sp radical orbital with that of the vicinal sp^3 hybrids) as he argued that steric and hyperconjugative effects would favor planar geometries.⁶⁹ Most likely, the minimum energy structures for radicals result from a combination of steric, hyperconjugative and σ -conjugative interactions.^{86,87} The anions of *t*-butyl and trimethylsilyl are pyramidalized more (19.3° and 30.1° , RIUMP2/aug-cc-pVTZ), but the preferred geometries of the anions are attributed to factors other than σ conjugation.⁶⁹

Another example of pyramidalization due to σ conjugation is in permethylated silene.⁸⁸ Here the silene adopts a trans bent C_{2h} structure which includes slight pyramidalization of the methyl groups.

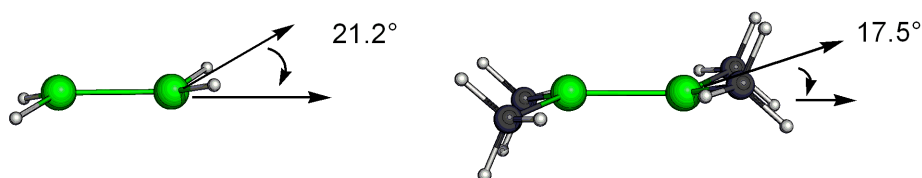


Figure 1.4: Pyramidalization of silenes, Si_2H_4 and Si_2Me_4 into trans bent structures of C_{2h} symmetry. Structures from RIMP2/aug-cc-pVTZ optimizations. Similar structures have long been known in the literature.⁸⁸

There are other explanations for the pyramidalization of silenes, namely those of Carter and Goddard⁸⁹ and Malrieu and Trinquier⁹⁰. These explanations are based on interacting silylene fragments.⁹¹ The σ conjugation based argument^{92,93} is based on a battle between π and σ conjugation, the latter of which is more important for olefins and the former in heavier (group XIV) analogs. By bending the groups attached to the Si atoms, the formally 3p Si orbitals hybridize and are able to interact with neighboring orbitals through σ conjugation.

A final example of the effects of σ conjugation on structure concerns the CXC valence angle of the triplet state of carbene and analogs, shown in Figure 1.5. An extensive amount of calculations

have been carried out on the structures of these low coordination molecules.^{94–98}

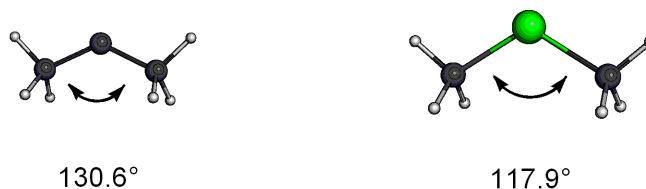


Figure 1.5: Triplet 3B_1 state of CMe_2 and $SiMe_2$, structures from RIUMP2/aug-cc-pVTZ optimizations.

A larger valence angle for the triplet state of CMe_2 indicates less σ conjugation than in the silicon analog, $SiMe_2$. Similar valence angles (to dimethylsilylene) are obtained for the dimethylgermylene (Table 1.1).

Table 1.1: Geometries of the RIMP2/aug-cc-pVTZ and RIUMP2/aug-cc-pVTZ optimized singlet (1A_1) and triplet (3B_1) respective structures of XMe_2 systems. Hybridization for in plane (CXC) nonbonding orbital (NBO analysis at the HF and UHF/6-311G(d,p) level of theory) of singlet and triplet structures is also given.

XMe_2	$^1\angle MeXMe$	$^3\angle MeXMe$	1A_1 sp^x	3B_1 sp^x
C	111.1	130.6	2.10	2.15
Si	97.0	117.9	0.36	0.55
Ge	95.0	117.9	0.28	0.44

In linear chains, delocalization can be shown to be cyclic or 2-dimensional.⁹⁹ σ Delocalization can be described as the combined effects of the relative strengths of the geminal and vicinal interactions. These interactions are illustrated in Figure 1.6. The interplay and various magnitudes of these interactions are responsible for the differences in structure and properties of different group XIV saturated systems (*e.g.*, alkanes, silanes, germanes, stannanes, plumbanes).

The resonance integrals in oligosilanes are similar to those in other group XIV saturated systems but differ in relative magnitude, from system to system (*e.g.*, silanes versus alkanes), as illustrated in ???. Relative differences in σ conjugation between different saturated group XIV structures have their origin in the energy gap between atomic s and p orbitals, as shown by Dewar, eq. (1.99). The focus of this work is on σ delocalization in oligosilanes. While alkanes are more

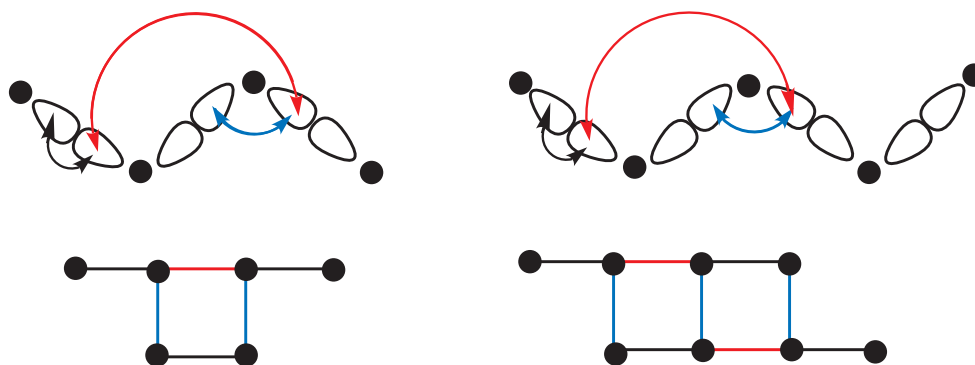


Figure 1.6: Interactions between sp^3 hybrid orbitals in the ladder C model: red represents the vicinal interaction, blue the geminal interaction and black the primary interaction between hybrid orbitals. These interactions can be mapped to a 2-dimensional space (ladder) and show that σ delocalization can be thought of as having a cyclic nature, even in linear chains.⁸¹

Table 1.2: NHO Resonance integrals for Group XIV saturated systems, structures from RIMP2/Def2-TZVP and NBO analysis with the HF/6-311G(d,p) method. The NHO primary resonance integral given first, corresponds to the terminal bond and the second to the central bond in each C_{2h} symmetric A_4H_{10} molecule.

Compound	β_{prim} (terminal) / eV	β_{prim} (internal) / eV	β_{gem} / eV	β_{vic} / eV
C_4H_{10}	-13.6	-13.6	-0.9	1.9
Si_4H_{10}	-7.3	-7.3	-1.8	1.1
Ge_4H_{10}	-7.3	-7.4	-2.2	1.1

ubiquitous, oligosilanes are easier to study experimentally and theoretically (*vide infra*). Table 1.3 gives the experimental values, fitted to the ladder C model, of the resonance integrals of the ground state minima and anti conformation of Si_4Me_{10} .⁸¹ Schepers and Michl⁸¹ used the following formula to describe the conformational dependence of the β_{vic} resonance integral,

$$\beta_{vic} = c_1 + c_2 \cos \omega \quad (1.100)$$

where in the ladder C model the first coefficient, c_1 , was found to be 0.02 eV, and the second, c_2 , to be -0.3 eV. For these parameters the β_{vic} resonance integral passes through zero at an all Si dihedral angle of 86° , Figure 1.7.

The equilibrium bond strength is roughly proportional to the overlap of the two sp^3 hybrid

Table 1.3: Experimental resonance integrals for $\text{Si}_4\text{Me}_{10}$ ground state conformations (SiSiSiSi dihedral angles of 180, 165, 90, 55° correspond to anti, trans, ortho and gauche conformers, respectively). Experimental values are fitted to the ladder C model according to the Schepers and Michl⁸¹

Compound	Conformation	β_{prim} / eV	β_{gem} / eV	β_{vic} / eV
$\text{Si}_4\text{Me}_{10}$	C_{2h} anti	-3.4	-0.8	0.32
$\text{Si}_4\text{Me}_{10}$	C_2 trans	-3.4	-0.8	0.31
$\text{Si}_4\text{Me}_{10}$	C_2 ortho	-3.4	-0.8	0.02
$\text{Si}_4\text{Me}_{10}$	C_2 gauche	-3.4	-0.8	-0.15

orbitals the Si atoms. The vicinal resonance integral (β_{vic}) varies with dihedral angle, as seen in Figure 1.7. The sign change of β_{vic} is consistent with the overlap of sp^3 hybrid orbitals. As the dihedral angle passes through approximately 90°, when starting from 0°, the overlap changes sign and so does β_{vic} .

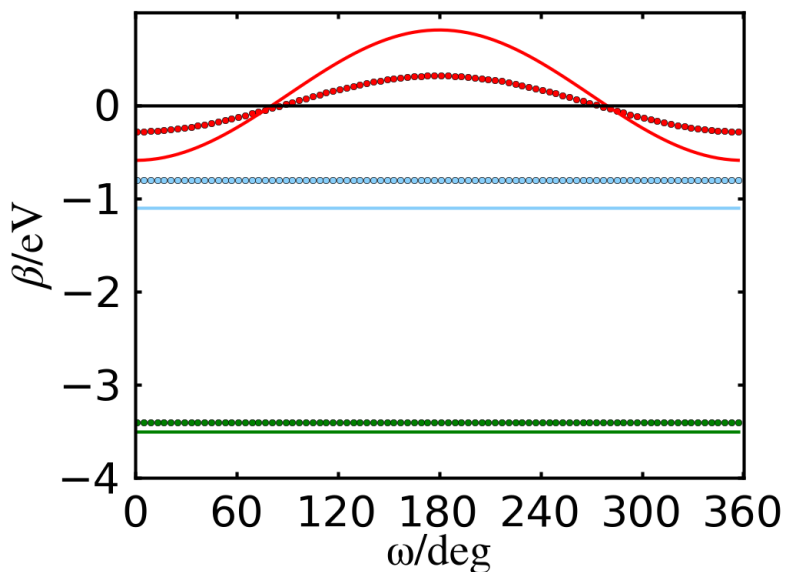


Figure 1.7: SiSiSiSi Dihedral angle dependence (red dots represent values fitted from experiment to the Ladder C model, and red lines are from fitted values based on ab initio calculations fitted to the Ladder C model according to Schepers and Michl)⁸¹ of vicinal interaction between sp^3 hybrid orbitals in oligosilanes. Blue and green lines represent similar values for the geminal (blue) and primary (green) interactions.

The geminal resonance integral, β_{gem} , has a valence angle as well as hybridization dependence. As pointed out by Dewar, sp hybrid orbitals, which are pointed in opposite directions, have the largest interaction;⁶⁹ thus wide angles are expected to give large hybrid interaction energies and these hybrids are expected to have smaller p character. These expectations are realized in calculation of the geminal interaction dependence on the SiSiSi Valence angle, as shown in Figure 1.8.

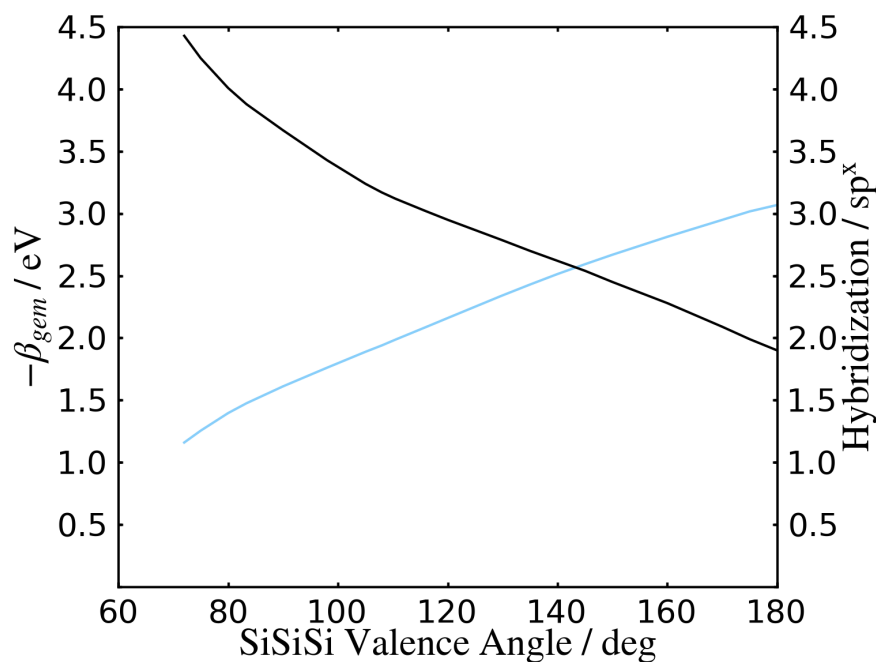


Figure 1.8: SiSiSi valence angle dependence of the geminal interaction (black line), calculated from RIMP2/Def2-TZVP geometries and NBO analysis (HF/6-311G(d,p)), and of hybridization, sp^x (blue line), of the internal Si hybrids which are directed towards Si neighbors.

1.4.2 Excited States in Oligosilanes

To understand excited states in oligosilanes, a large amount of effort has been invested in linear systems,^{99,100} as they are arguably the simplest and therefore a good starting point.

Delocalized molecular orbitals of oligosilanes chains are of two types.¹⁰⁰ The first type is of

σ nature and is symmetric with respect to reflection across a local plane defined by the local Si backbone (local refers to the plane made by three Si atoms) and the second type, the π orbitals, are antisymmetric to this plane. The overall character of a molecular orbital must then be averaged over all Si atoms. The σ^* orbitals are composed of Si-Si antibonds and the π^* orbital is composed of Si-C antibonds. The least stable σ orbital of an infinite Si chain has a node at each atom and is a combination of $3p_z$ Si atomic orbitals (axes parallel to the chain direction, z). The most stable σ^* orbital has nodes between Si atoms and consists mainly of $3s$ and $3p_y$ contributions. The π^* orbital interacts with alkyl substituents through the Si atomic $3p_x$ orbitals, the axes of which are perpendicular to the local SiSiSi plane. These orbitals are shown in Figure 1.9.

Excitation from the σ orbitals leads to two basic types of low lying electronically excited states in oligosilanes: $\sigma\sigma^*$ and $\sigma\pi^*$. The σ , σ^* , and π^* orbitals can be seen for octamethyltrisilane in Figure 1.10. The transition from the ground to $\sigma\sigma^*$ state in oligosilanes is strongly allowed (Figure 1.11) and the transition from the ground to $\sigma\pi^*$ state is usually very weak, except in disilanes, where it is strong due to the nodal properties of its molecular orbitals.¹⁰¹ As the chain length increases, the overall transition dipole moment to the $\sigma\pi^*$ state is largely cancelled out (especially in chains with odd numbers of silicon atoms) due to opposing contributions along the chain, as can be seen in the figure of the $\sigma\pi^*$ transition density of in the smallest members of the permethylated n -oligosilane series, Figure 1.12. To analyze the nodal structure of a MO, the NHO basis is ideal, while for extended linear chains, the AO basis is better suited for analysis of the density.

Methylation has many effects on silanes. Permethylation allows hyperconjugative interactions which raise the HOMO energy level and stabilize the π^* orbital. Rydberg excited states are also higher in energy than the valence states for permethylated silanes, which is helpful for calculation of the valence excited states as there will be less artificial mixing between these two types of states.

In octamethyltrisilane, the $\sigma\pi^*$ state is slightly lower in energy than the $\sigma\sigma^*$ state when calculated with TDDFT methods and experimentally.^{102,103} The π^* orbital however is higher in energy than the σ^* orbital, re-emphasizing the fact that the orbital energy difference is only a zero order

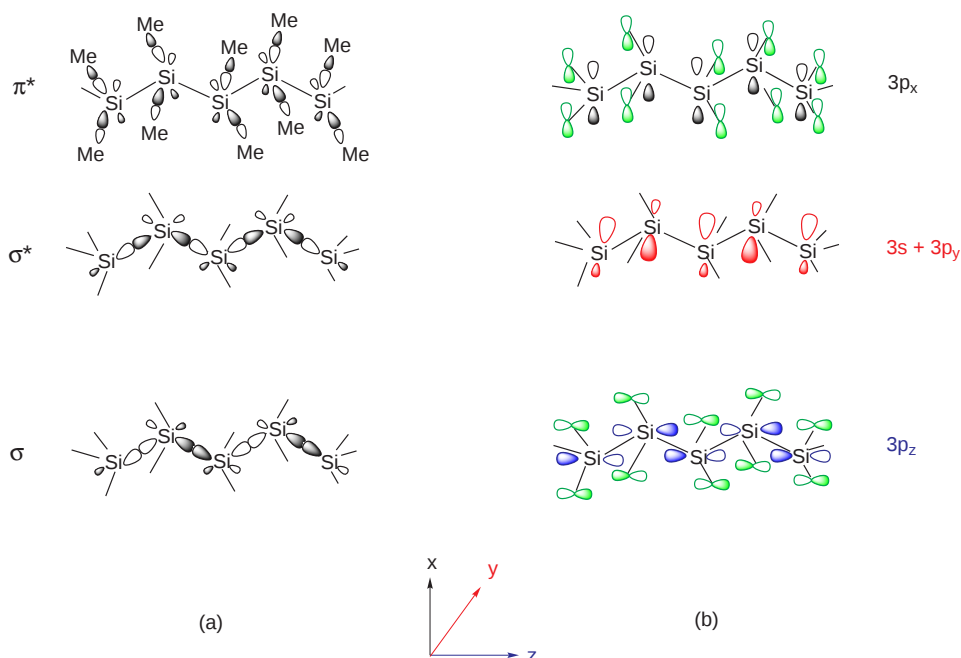


Figure 1.9: Equivalent representations based on hybrid orbitals, (a), and atomic contributions, (b), to the frontier molecular orbitals, σ , σ^* , and π^* in dodecamethylpentasilane. Strong Si-C orbital interactions which destabilize the HOMO and stabilize the LUMO (relative to hydrogenated silane), are shown in green in the atomic orbital basis for the σ and π^* orbitals.

approximation to the excitation energy. A similar situation occurs in decamethyltetrasilane.¹⁰⁴

The $\sigma\sigma^*$ state drops in energy relative to the $\sigma\pi^*$ as chain length increases. The intensity of the ground to $\sigma\sigma^*$ transitions can become quite large for long oligosilane chains and the experimental oscillator strength for $\text{Si}_{10}\text{Me}_{22}$ is around 0.53.¹⁰² The intensity of the ground to $\sigma\sigma^*$ state grows with chain length because the transition dipole moment is a sum of individual bond contributions for the transition. This is shown in Figure 1.11.

Longer chains increase the complexity of these systems. The number of conformations increases rapidly as oligosilanes are extremely floppy and, depending on the length, can access many different dihedral angles.^{105–107} Many properties show a strong conformational, *i.e.*, Si backbone dihedral angle dependence; a couple of examples include electron transfer and UV absorption. According to theoretical work using density functional theory combined with a nonequilibrium Green's

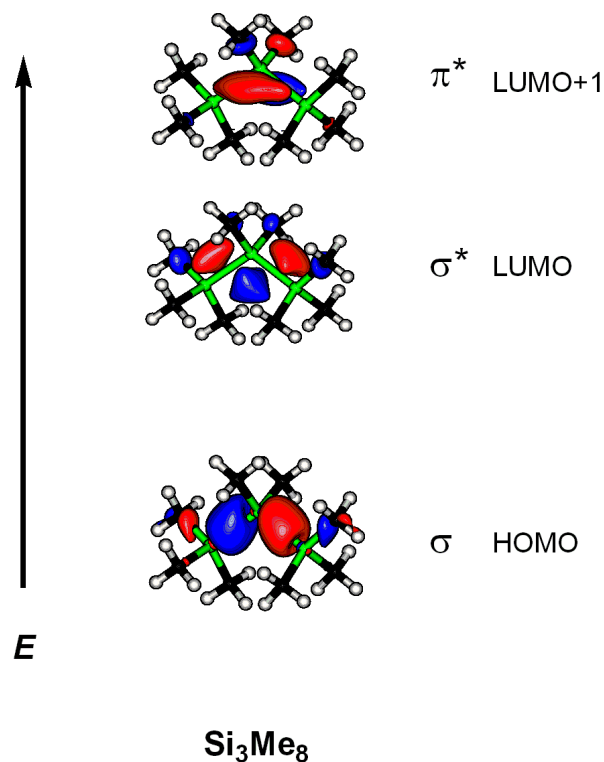


Figure 1.10: The S_1 (2^1A) state in octamethyltrisilane is described by the $\sigma\pi^*$ transition. The S_2 (1^1B) state in octamethyltrisilane is predominantly described by the $\sigma\sigma^*$ transition.¹⁰³

function approach, changing the backbone conformation can increase the conductance by up to 3 orders of magnitude.¹⁰⁸ The conformational effect on electronic absorption can be so strong that it can suppress the effects of delocalization in constrained oligosilanes, as there is no longer a chain length absorption energy dependence in compounds with alternating cisoid and anti dihedral angles (Figure 1.13).¹⁰⁹

At lower temperatures all transoid ($\pm 165^\circ$) Si dihedrals are favored, as σ delocalization is maximized. According to σ delocalization, all anti dihedral angles would be even more favorable, but methylation introduces steric repulsions (due to substituents in 1 and 3 positions) which results in the transoid dihedral angle structures. The splitting of the alkane-preferred dihedral angle of 60° into two minima, a 90° (ortho) dihedral and a gauche dihedral less than 60° , is due to repulsions of substituents in the 1 and 4 positions.¹¹⁰ The ortho($\pm 90^\circ$) dihedral angle minimum was first reported by Welsh et al.¹¹¹ This behavior is also observed for perfluoro-*n*-butane¹¹² and other analogs.¹¹³

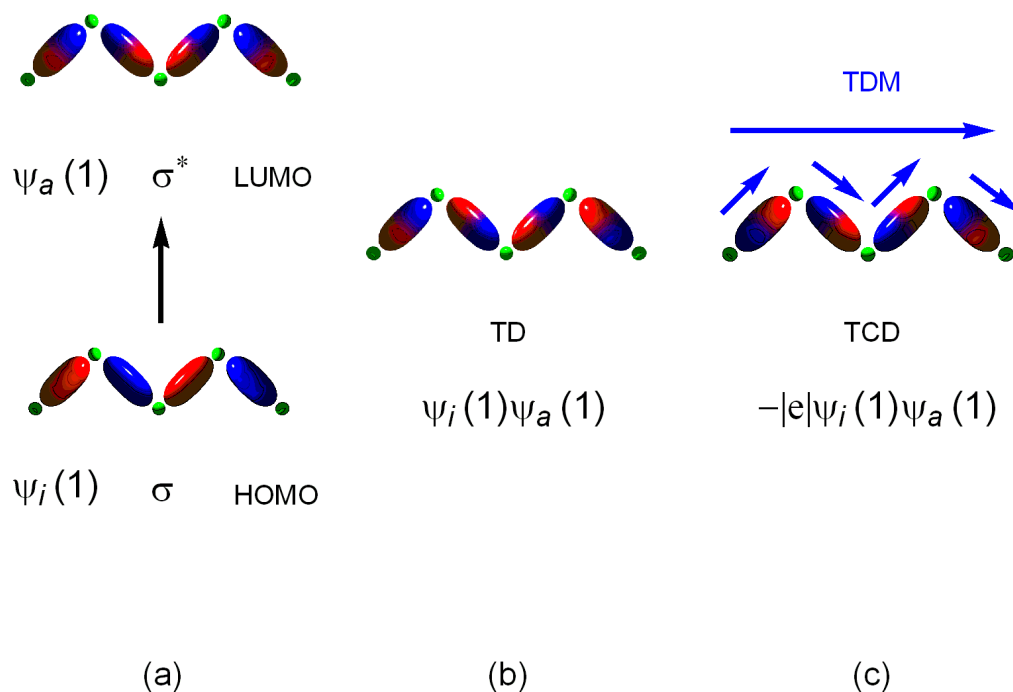


Figure 1.11: Schematic derivation of the transition dipole moment for the ground to $\sigma\sigma^*$ state. The S_1 (1^1B) state in longer oligosilane chains is described by the HOMO-LUMO ($\sigma\sigma^*$) transition (a). The transition density (TD) for the $\sigma\sigma^*$ transition is given in (b). The transition dipole moment (TDM), indicated by the blue arrows, is the sum of the bond contributions from the bond transition charge densities (TCD), shown in (c).

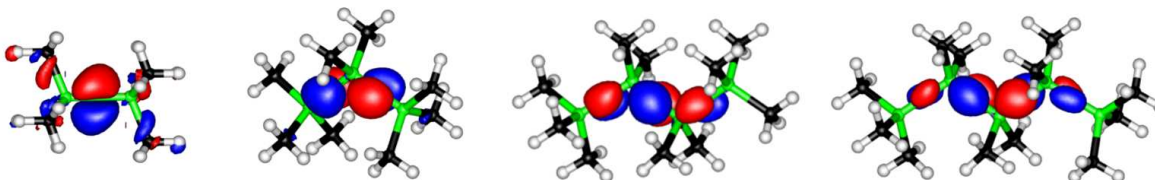


Figure 1.12: The $\sigma\pi^*$ transition density (CIS/6-31G(d)) in the n -oligosilanes series ($2 \leq n \leq 5$). All transition densities are plotted on the ± 0.006 isosurfaces.

Table 1.4 lists proposed nomenclature for structural conformations based on Si backbone dihedral angle put forth by Michl and West.¹¹⁴

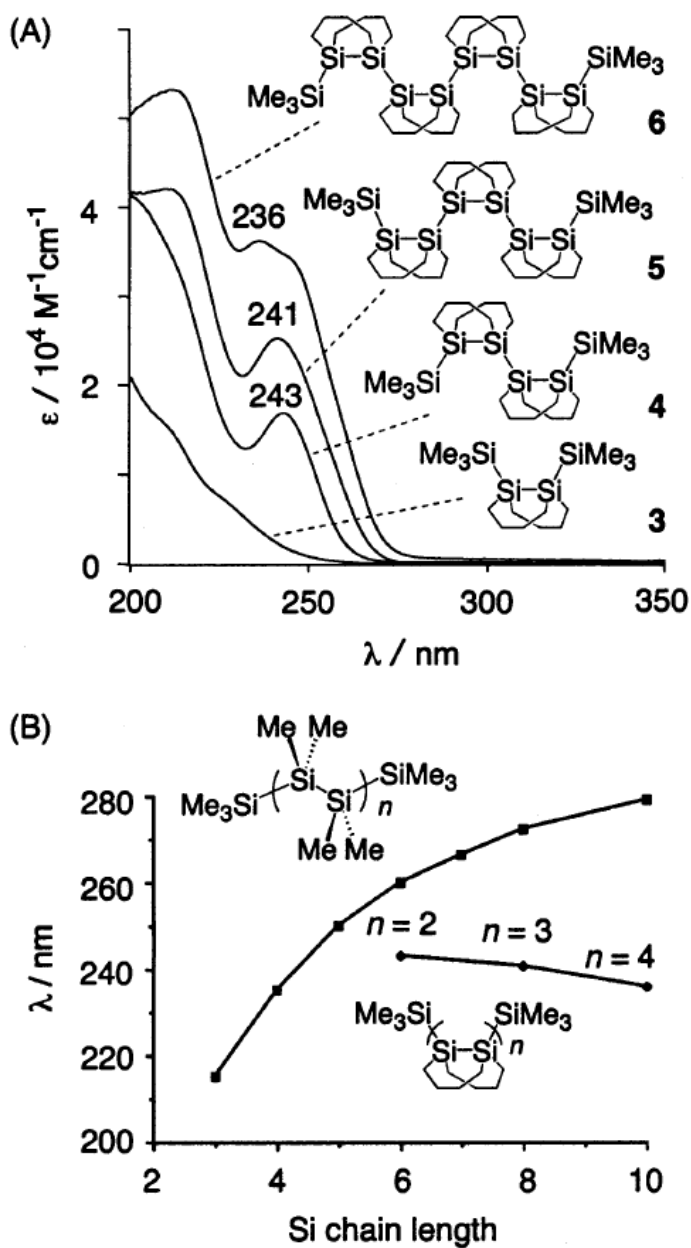
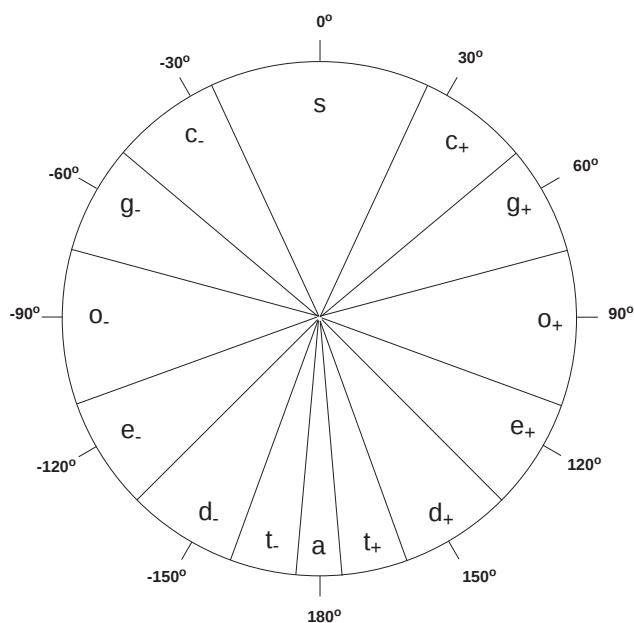


Figure 1.13: Constrained (alternating cisoid and anti Si dihedral angles) oligosilane absorption. Figure adapted from Tamao and coworkers.¹⁰⁹

Mixing of the σ and π character of the MO occurs as the SiSiSiSi dihedral angle is distorted from 0 or 180 degrees.⁷⁵ Orbitals which have large mixing are labeled as μ or μ^* depending on whether they are a bonding or antibonding orbital, respectively. Historically, strongly mixed antibonding orbitals, such as those of the gauche and ortho decamethyltetrasilane conformers (Figure

Table 1.4: Nomenclature for conformation and corresponding Si backbone dihedral angle.¹¹⁴

Conformation	ω / deg
syn, $s_{\pm}$	$\pm 0-25$
cisoid, $c_{\pm}$	$\pm 25-50$
gauche, $g_{\pm}$	$\pm 50-74$
ortho, $o_{\pm}$	$\pm 75-110$
eclipsed, $e_{\pm}$	$\pm 110-135$
deviant, $d_{\pm}$	$\pm 135-160$
transoid, $t_{\pm}$	$\pm 160-175$
anti, $a_{\pm}$	$\pm 175-180$

**Figure 1.14:** A graphical representation of the Si backbone dihedral angle nomenclature from Michl and West.¹¹⁴

1.15) were labeled as being of σ^* nature.¹⁰⁴

1.4.3 Excitation Localization

The theory that describes nuclear (or lattice) rearrangement upon electronic excitation was first described in physics by Landau as pointed out by Matsui.¹¹⁵ The theory involves the description of the phonon-exciton coupling constant, g , which describes the interaction between the lattice (nuclei) and the exciton (electrons). A large-radius exciton describes delocalized excitation, and as

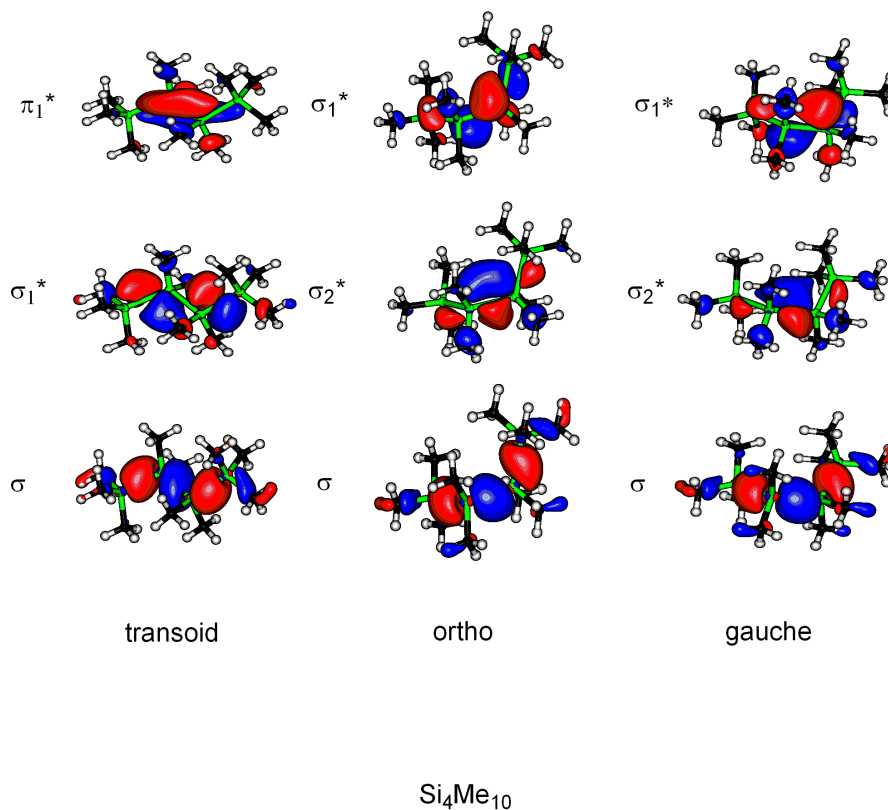


Figure 1.15: The ± 0.04 isodensity contours for the σ , σ^* and π^* orbitals of the different rotational isomers of decamethyltetrasilane. As the SiSiSiSi dihedral angle deviates from the transoid structure the σ^* and π^* orbitals mix, and labels (for the σ^* orbitals) for gauche and ortho conformations are shown here for historical context.¹⁰⁴

the critical value of g is reached, the excitation becomes localized, resulting in a self-trapped small radius exciton. The phonon exciton coupling constant is given as

$$g = S/B \quad (1.101)$$

where S is the site distortion energy and B is the half width of the delocalized exciton band. The site distortion represents the energy gained by localization, whereas B represents the energy gained by delocalization. In very long transoid polysilanes, the exciton is delocalized over 20-30 Si-Si bonds.¹¹⁶ In the carbon analog (polyethylene) this length is drastically reduced.¹¹⁷ As a large system is reduced in size, quantum confinement reduces the band width (as well as the amount of

σ conjugation) and B decreases, while S stays fairly constant, as it represents the localized limit. Once the critical value of g is reached the exciton becomes self-trapped or localized. In practice, S can be represented by half of the Stokes shift energy value of the localized system and B can be estimated by the difference in absorption band maxima between the localized limit (*e.g.*, smallest member of the series) and of the system being measured. For oligosilanes, (σ -bonded systems), this value is estimated to be $g_{critical} = 0.85$ and represents the small radius self-trapped exciton, imposed by quantum confinement.¹¹⁶ As we will see in Chapter 2, half of the Stokes shift energy is a poor approximation to the site distortion energy as ground states are usually more strongly destabilized than the excited states are stabilized. This thesis will show that oligosilanes, molecular systems solely bound by σ bonds, have many localization methods at their disposal as the effects of quantum confinement and structural relaxation mechanisms will be investigated.

In chemistry, less abstract models are sought. One way to understand geometrical rearrangements is through orbital and state correlation diagrams which relate products to reactants based on symmetry arguments.⁶⁸ These diagrams can be misleading however as orthogonal or unconsidered relaxation pathways and products are possible due to many degrees of freedom available to polyatomic molecules. Actual potential energy surfaces, kinetic energy and couplings between different states are ignored. These diagrams are nevertheless useful starting models for understanding photochemical reactivity.

The tetrahedral ground state equilibrium structure of saturated molecules has been known for a long time, in the latter half of the 19th century.¹¹⁸ Relaxed excited state structures are more ephemeral and represent a contemporary challenge. How and why excitation becomes localized in actual molecules or molecular systems (classes of molecules) is a major component of theoretical photochemistry.²² Progress towards understanding the relaxation of unsaturated π systems has developed and these systems are relatively well understood. Unsaturated π bonded systems can twist, and C-H and C-C bonds can develop a pyramidalized structure on one carbon (the negatively polarized) site on the femtosecond (fs) time scale according to *ab initio* molecular dynamics calculations, Figure 1.17.¹¹⁹

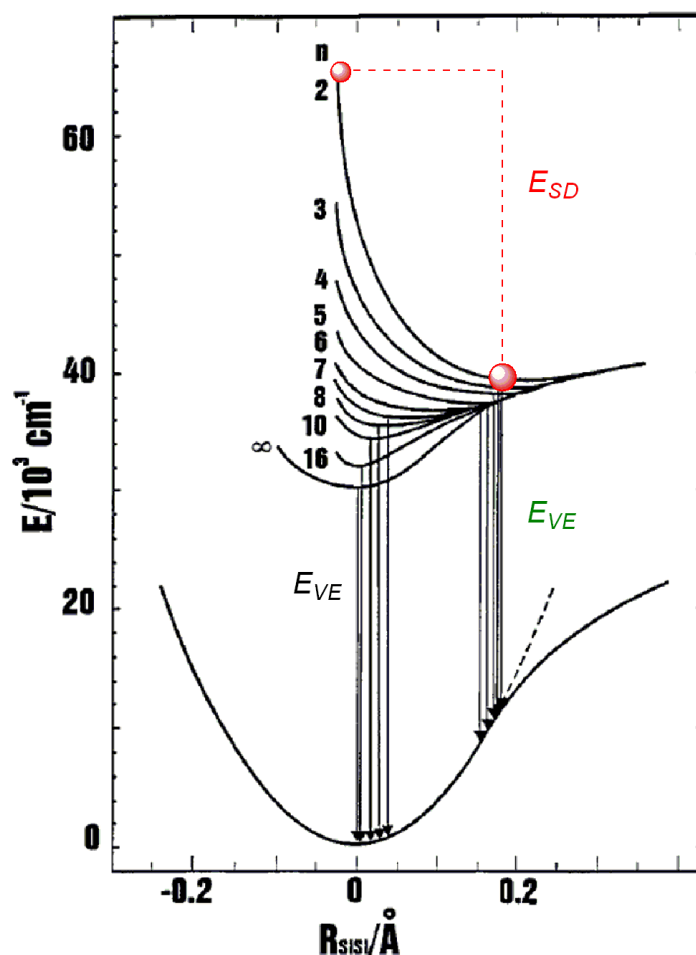


Figure 1.16: Schematic from Raymond and Michl¹¹⁶ of the change in energy of a single Si-Si bond in oligosilanes of varying length ($\text{Si}_n\text{Me}_{2n+2}$) for ground and S_1 state. E_{SD} is defined as the difference in S_1 energy at the vertical and relaxed geometries (red). The vertical emission energy, E_{VE} , is also labeled in black for delocalized emission and in green for localized emission.

At first sight, a localized $\sigma\sigma^*$ state might appear to be dissociative, since an electron in a σ orbital is less strongly bonding than an electron in a σ^* orbital is antibonding, however this is only valid for the triplet excited state. If a $^1\sigma\sigma^*$ state is tritopic (or higher), or if nuclei have very different electronegativities, only then is dissociation predicted. If the electronegativities are equal or similar (as in the simplest case of H_2), the singlet excited state is described as having the character

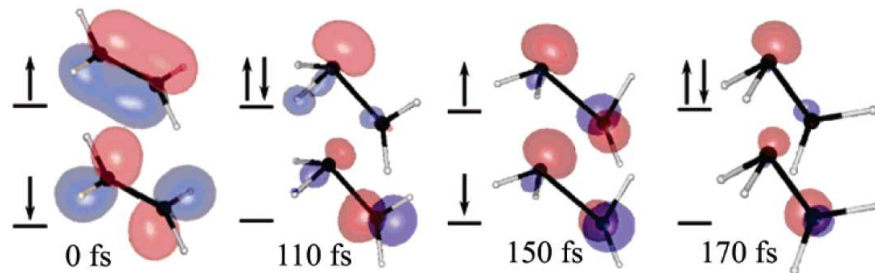


Figure 1.17: Schematic from Martínez.¹¹⁹ This figure shows the relaxation of ethylene after electronic excitation into the S_1 state.

of a zwitterionic tight ion pair. This state is stabilized by electrostatic forces in the combination of zwitterionic resonance structures which describe the state. Dissociation does not happen as this charge separation would cost energy. For polyatomic molecules, large structural changes are expected based on the experimentally observed large Stokes shifts and broad emission peaks.¹²⁰ Instead of simple bond stretching the molecule can find other ways to stabilize the simultaneous presence of positive and negative charges arranged in a zwitterionic excited singlet state. Along the way to minima various conical intersections are expected to be found for polyatomic molecules. These are points where the gradient difference vector, $\mathbf{x}_1$,

$$\mathbf{x}_1 = \frac{\partial(E_1 - E_2)}{\partial \mathbf{q}} \quad (1.102)$$

which is largest in the direction which maximizes the difference of the upper and lower states, and the nonadiabatic coupling vector (nuclear displacement wave function mixing vector), $\mathbf{x}_2$,

$$\mathbf{x}_2 = \langle \Psi_1 | \frac{\partial \Psi_2}{\partial \mathbf{q}} \rangle \quad (1.103)$$

define the only coordinates that lift the degeneracy of the two electronic states. The nonadiabatic coupling vector describes the direction in which two adiabatic wave functions strongly mix. Often it is not necessary to pinpoint the exact location of the conical intersection as the nonadiabatic

coupling between states becomes strong in the general vicinity of a conical intersection and will lead to excited state quenching and reduction of the emission quantum yield. The emission is expected to be characterized as fluorescence since the triplet surface is dissociative.

One of the most basic questions this thesis attempts to answer concerns the nature of bonding in σ -bonded structures which have reorganized due to electronic excitation into a particular excited state—in the case of this work, the lowest electronic singlet state.

In order to study structural rearrangement in saturated systems, a suitable choice must be made. Fluorescence from saturated alkanes has been known for decades¹²⁰ and still has yet to be assigned. Alkanes have their electronic transitions at energies higher than 48 000 cm^{-1} , requiring work in the vacuum UV.¹¹⁷ Oligosilanes have much lower excitation energies due to the fact that Si has a lower IP and EA than C. The explanation of why the EA of Si is greater than that of C, opposite to the general trend of group XIV, is related to the increased inner shell repulsions in C.¹²¹ Computationally, permethylated oligosilanes are much less vulnerable to Rydberg contamination of the valence excited states of the Si backbone.¹⁰⁴

Multiple types of fluorescence from permethylated (linear) oligosilanes ($\text{Si}_n\text{Me}_{2n+2}$) have been observed. For longer oligosilanes ($n \geq 7$) emission is only slightly Stokes-shifted, and is a mirror image of the absorption band; this emission has been termed normal emission and the exciton is of strongly delocalized nature.¹¹⁶ For shorter oligosilanes, ($n \leq 7$) more strongly Stokes-shifted emission is observed (“blue emission”). Permethylated heptasilane has been found to show dual emission, both the normal and blue type, from different conformers.¹²² The blue emission has a slight chain length dependence and varies from 26 000 to 30 000 cm^{-1} . For certain conformations, green emission (centered around 20 000 cm^{-1}) has also been observed.⁹⁹

Fluorescence indicates the presence of stable excited state minima which are accessed as the molecule relaxes. Strongly Stokes-shifted fluorescence values indicate strong exciton-phonon coupling. Convincing structures for the actual geometry rearrangement responsible for the blue and green emission in n -oligosilanes have been sought in this work.

1.5 Presentation of Current Work

The objective of this work is to understand the effects of σ -delocalization in oligosilanes.

Chapter 2 describes excited state relaxation in small oligosilanes. These small silanes include hexamethyldisilane and octamethyltrisilane. While longer oligosilane chains ($n \geq 4$) emit light, the hexamethyldisilane and octamethyltrisilane compounds do not show any emission even at low temperatures.¹¹⁶ This is attributed to efficient decay mechanisms, which have been identified. The existence of several minima has also been identified by computational means. These minima are located close to funnel regions of near S_0 - S_1 degeneracy which can deactivate the excited molecules and explain the lack of fluorescence. Barriers from the minima to these funnels are either nonexistent, or very low in energy, much more so than the site distortion energies, which are calculated to be extremely large ($10\,000\text{ cm}^{-1}$). Analogs of the S_1 minima found for permethylated disilane and trisilane are possible in longer oligosilanes as well. For these compounds emission has been detected and described in subsequent chapters.

Chapter 3 describes structures responsible for strongly Stokes-shifted blue emission as well as the Franck-Condon allowed emission in longer oligosilane chains ($n \geq 8$). This emission, in the middle UV spectral region, is slightly Stokes-shifted and is referred to as the normal emission. The normal emission is easily reproduced with calculational techniques. The blue emission in permethylated oligosilanes has been known since the early 1990s.¹²³ While it has long been postulated that bond stretch minima were responsible for this emission,¹²⁴ reliable relaxed excited state structures have not been found until this work. Understanding the nature of this exciton explains why $\text{Si}_7\text{Me}_{14}$ shows dual emission (blue and normal). Additional calculations on longer oligosilanes which include changes in the conformational backbone show that the blue exciton should exist in longer oligosilanes as well, even though this has not been experimentally verified. The low quantum yield of fluorescence in the blue spectral region is rationalized.

Chapter 4 describes structures believed to be responsible for the recently discovered, most highly Stokes-shifted emission in the green spectral region.¹²⁵ Previous emission energy estimates

from TDDFT ($12\,000\text{ cm}^{-1}$)¹²⁵ did not match experimental emission energies ($20\,000\text{ cm}^{-1}$) and thus considerable doubt was cast on the validity of the excited state structures responsible for this emission. Reasons for the discrepancy between theory and experiment are given in this chapter. Additional structures have been found through excited state stochastic search techniques that could also be responsible for the green emission. These minima have a trigonal bipyramidal (TBP) coordination pattern on one Si atom. The structure found by Teramae and Michl¹²⁶ originally thought to be responsible for blue emission, is found in this work to emit at much lower energies. Another isomer of this structure has been found where the LUMO is localized on the terminal Si-Si bond (as opposed to the central Si-Si bond). Finally a highly localized minimum, originally found in shorter chains, has been found for dodecamethyltetrasilane and longer chains. These various minima have geometrical rearrangements of the molecular framework localized on one or two Si atoms. These structures yield a small emission energy dependence on chain length, which is expected for structures which have large structural rearrangements in one localized region of the molecule.

A summary of the results, their interpretations, practical considerations, and suggestions for further work is provided in Chapter 5.

Chapter 2

Short Oligosilanes and Their Photoproducts

2.1 Introduction

This chapter examines excited state relaxation on the S_1 surface of a common oligosilane photoproduct, dimethylsilylene (**1**), and the shortest members of the permethylated n -oligosilane ($\text{Si}_n\text{Me}_{2n+2}$) series, where $2 \leq n \leq 16$ (**2-16**): hexamethyldisilane (**2**) and octamethyltrisilane (**3**). These oligosilanes are, contrary to longer members of the series, known to not show fluorescence even upon irradiation at very low temperatures.¹¹⁶ These experiments were carried out with (argon) matrix isolation techniques; fluorescence was not observed at ~ 30 K for hexamethyldisilane.¹²⁴ For octamethyltrisilane, fluorescence was not observed at even lower temperatures (10 K).¹²⁷

Longer members ($n \geq 4$) of the linear oligosilane series do show fluorescence; a normal emission (slightly Stokes-shifted) in the UV spectral region which is chain length dependent¹¹⁶ and a more Stokes-shifted emission in the blue (centered around $26 - 30\,000\text{ cm}^{-1}$)^{116,122,128} and green ($20\,000\text{ cm}^{-1}$) spectral regions, which depends much less on chain length.⁹⁹ The blue emission of decamethyltetrasilane, **4**, dodecamethylpentasilane, **5**, tetradecamethylhexasilane, **6**, and longer oligosilanes is the main subject of Chapter 3. The green emission of longer oligosilanes ($n > 3$) is addressed in Chapter 4. As the oligosilane chain (chromophore) is shortened, excitation becomes localized and eventually a self-trapped exciton is encountered.¹¹⁶ The disilane chromophore represents the limit of exciton localization in oligosilane chains and therefore fluorescence is highly desired as the site distortion energies and the limit of quantum confinement and exciton localization would then be known for these systems. While emission is not observed as previously mentioned,

calculations can provide us with clues for the absence of emission and also theoretical emission energy values if minima exist. Indeed, several excited state minima and S_0 - S_1 funnels have been located and will be described in this chapter. As localization increases, site distortion energies increase as well. For small systems, these energies are extremely large. This is to be expected as the Si-Si σ bonds rearrange, since the geometry distortion does not represent a small perturbation, but a large modification to the framework that holds the molecule together. For a comparison, see the calculated and experimental Stokes shift energies for the so-called normal emission (Chapter 3).

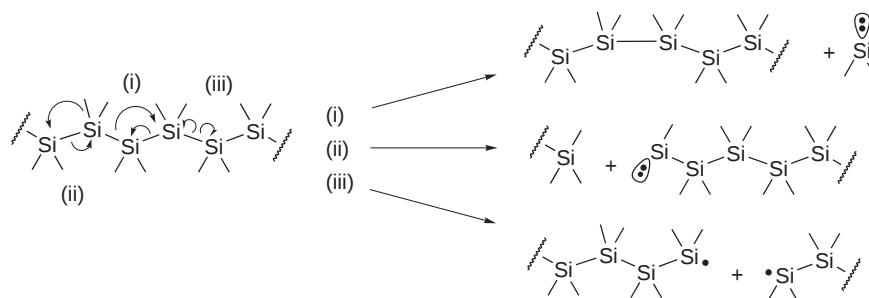


Figure 2.1: Photochemical excited state deactivation pathways in polysilanes.⁶⁸

There are three well-known photochemical degradation pathways (Figure 2.1) for oligosilane chains.¹⁰⁰ These include (i) chain abridgement via dialkylsilylene extrusion: this is the dominant process for longer ($n \geq 3$) chains.¹⁰⁰ The silylene has been trapped with Et_2MeSiH ,¹²⁹ triethylsilane (Et_3SiH), and various alcohols.¹⁰⁰ Dimethylsilylene has also been observed directly.^{130,131} The conical intersection which gives rise to the extrusion process has been identified with computational methods.^{132,133} This extrusion has been modeled with 2-methyltrisilane ($\text{SiH}_3\text{-SiH-(CH}_3\text{)-SiH}_3$) by Robb and coworkers,¹³³ and is shown in Figure 2.2. The omission of (most of the) methyl groups is a significant approximation to modeling permethylated oligosilanes, as will become clear in this chapter.

The calculations by Robb and coworkers involved the CASSCF(6,6)/6-31G(d) method for geometry optimization. One fragmented structure, representing a conical intersection, was found and structures along the linearly interpolated path (fragmentation parameter) were subsequently opti-

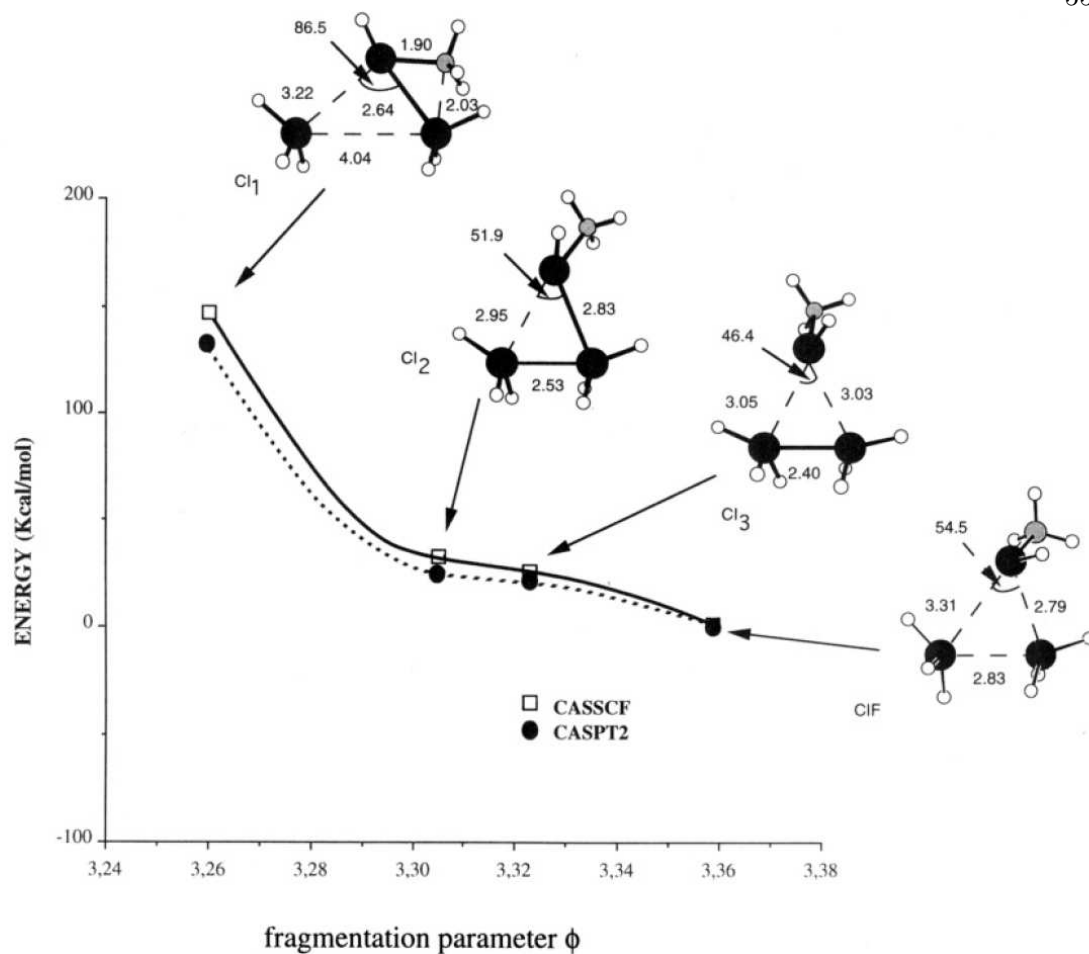


Figure 2.2: The hyperline along the S_0 - S_1 conical intersection seam energies was computed for the CASSCF/6-31G(d) optimized structures (full line) and additional energies were calculated with the CASPT2/6-31G(d) method (dashed line). Structural parameters are given in Å and degrees. Figure adapted from Robb and coworkers.¹³³

mized and signify points along the hyperline, or seam of the S_0 - S_1 conical intersection. Remarkably, only one type of conical intersection and no minima were located for 2-methyltrisilane.

There is another reductive elimination process, (ii), in which silylsilylene is extruded, the chain is broken and a new C-Si bond is formed. Silylsilylene is known to rapidly convert to disilene.^{134–138} Finally, the last well established photodegradation pathway involves (iii) chain cleavage via homolytic cleavage. This process is expected to take place on the triplet surface,¹³² but has been postulated also to happen on the singlet potential energy surface — through a recoupling of valence electrons at silylene extrusion type conical intersections.¹³³ The recoupling is shown in

Figure 2.3.

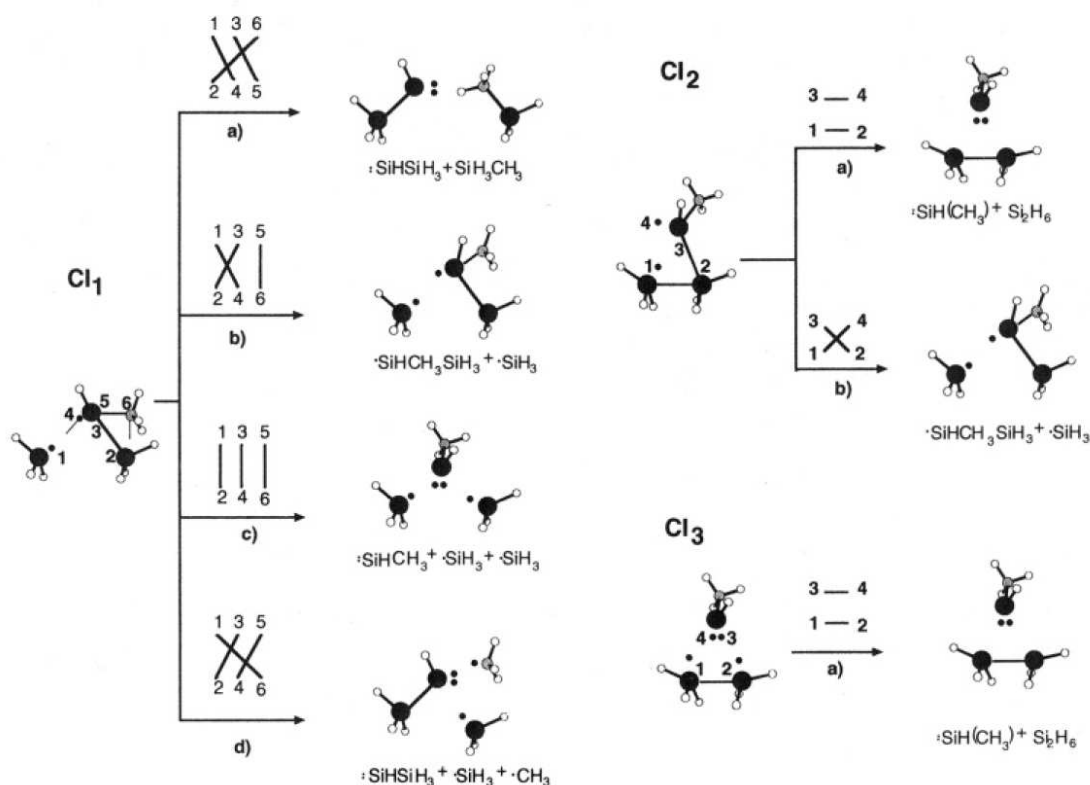


Figure 2.3: Schematic of possible photochemical excited state recoupling in polysilanes, inferred from inspection of the CASSCF/6-31G(d) wave function. Figure adapted from Robb and coworkers.¹³³

Robb and coworkers analyzed the electronic wave function of 2-methylsilane along the seam and found S_0 and S_1 to be represented by covalent states. The various products were therefore postulated to be formed from a covalent recoupling of the electrons 1-4 in Figure 2.3. Based on the various bond distances between Si atoms, the probability of various photoproducts was predicted. The authors noted that Cl_1 has a large Si-Si separation, suggested a pair of radicals could be generated (routes b and c in Figure 2.3), and predicted the internal silylene extrusion to be the most probable ground state return product from Cl_3 due to the shorter distance between SiH_3 centers. Work presented in this chapter will show that process (iii) can happen on the singlet potential energy manifold through various mechanisms, not necessarily only from conical intersections of

dimethylsilylene extrusion character.

The lack of fluorescence in the trisilane and lower than unity fluorescence quantum yields of longer oligosilanes have been attributed mainly to (i), but this mechanism is not possible for hexamethyldisilane. Therefore the lack of fluorescence in hexamethyldisilane is troubling, and more calculations are warranted. The expected photoproducts from hexamethyldisilane are shown in Figure 2.4.

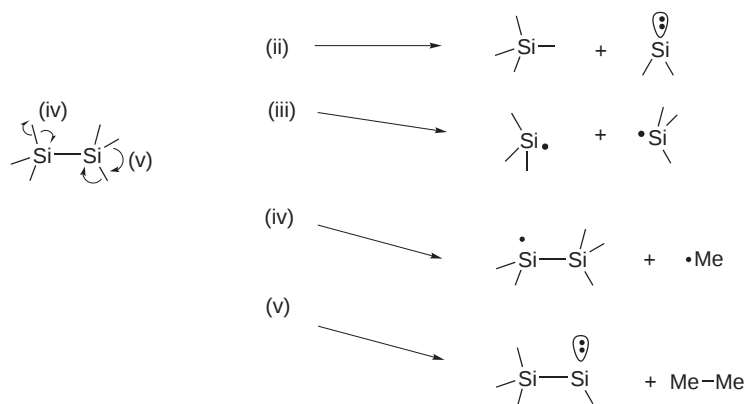


Figure 2.4: Photochemical excited state deactivation pathways in permethylated disilanes.

New S_0 - S_1 funnels and rearrangement products, which yield Me radicals (iv) and ethane side products (v), have been located for the permethylated disilane (Figure 2.4) and trisilane as well. These funnels often include large rearrangements of the Me substituents. The lack of fluorescence in small silanes is attributed to large site distortion energies and to small barriers which connect minima to S_0 - S_1 funnel regions.

A considerable amount of calculations have been done on the vertical absorption spectrum of hexamethyldisilane.^{99,101,139} The first strongly allowed transition has been attributed to the $\sigma\pi^*$ state. The $\sigma\pi^*$ and $\sigma\sigma^*$ state notation is explained in Chapter 1. For **2**, according to recent TD-DFT/B3LYP calculations using asymptotic correction and cc-pVTZ/cc-pVTZ/6-311G basis sets (for Si, C, and H atoms, respectively), this is an allowed transition ($f=0.145$) which is much lower in energy ($52\,100\text{ cm}^{-1}$) than the $\sigma_1\sigma_1^*$ state ($57\,100\text{ cm}^{-1}$).¹³⁹ The calculated S_0 - S_1 oscillator strength agrees very well with the experimental oscillator strength for this transition at 298 K (0.151).¹⁰¹

The hexamethyldisilane molecular orbitals are shown in Figure 2.5. In longer silanes, however, the ground to $\sigma\pi^*$ state transition is much weaker, as discussed in Chapter 1.

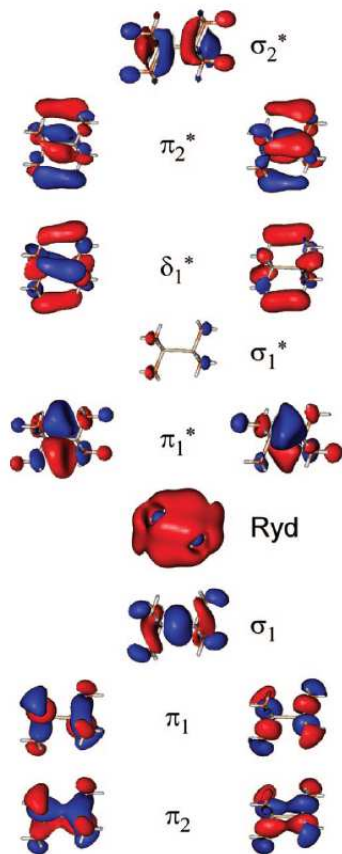


Figure 2.5: Hexamethyldisilane DFT orbitals (for the ground state equilibrium structure) plotted on the ± 0.03 isodensity surface value, except for the Rydberg orbital, for which it is 0.012. Figure from Michl and coworkers.¹³⁹

Dimethylsilylene, the major photoproduct of the irradiation of the permethylated n -oligosilane series, does fluoresce (band maximum is centered at $15\,270\text{ cm}^{-1}$).¹³⁰ Furthermore, it is important to examine this species as longer green emitters have pre-dimethylsilylene extrusion character (Chapter 4). The absorption band maximizes at $22\,070\text{ cm}^{-1}$ which, compared with the maximum of the slightly broader fluorescence band, gives a fairly large Stokes shift of $6\,800\text{ cm}^{-1}$. Understanding shifts in the emission energy of this simple molecule will be helpful when examining the green

emission in longer chains (Chapter 4).

This chapter aims at describing electronic relaxation for these short species. Because of their size, they are good candidates for in-depth analysis which will provide insight that will be useful for the analysis of longer silanes. Additional calculations have been carried out to strengthen the analysis of the results for the new S_1 minimum energy structures (five new minima for **2** and eight new minima for **3**) found in this chapter, which describe new bonding patterns in oligosilane excited states. New deactivation pathways have also been located: four for **2** and six for **3**. The following questions will be addressed in this chapter: Can the experimental absorption and fluorescence of **1** be reproduced? Do minima similar to those that are responsible for the blue and green emission exist in the short oligosilanes? What are the excited state deactivation mechanisms for the shortest members of the permethylated n -oligosilane series? Is there a way to hinder these deactivation mechanisms in the short oligosilanes so that fluorescence can be observed? Are there experiments that might lend support to the new deactivation mechanisms found in this chapter?

2.2 Computational Methods

Ground state geometry optimizations were carried out with Turbomole 6.2.¹⁴⁰ They were done with the B3LYP,¹⁴¹ PBE0¹⁴² and BHLYP¹⁴³ functionals with the TZVP and aug-cc-pVDZ basis sets.^{144–146} Ab initio optimizations with the approximate singles and doubles coupled-cluster (RICC2)¹⁴⁷ and the algebraic diagrammatic construction through second order (RIADC(2))¹⁴⁸ methods and TZVP basis sets were also carried out. These ground state optimizations were used to get starting structures for excited state optimization as well as structures to obtain Stokes shifts and site distortion energies. Site distortion energies were computed as the difference in S_1 energy at the relaxed ground and excited state geometries. The magnitude of the site distortion energy is related to the amount of excitation localization.¹¹⁶ The B3LYP functional used throughout this work was the version which employs the VWN 5 correlation functional.¹⁴⁹ For DFT calculations large integration grids (size 5)¹⁵⁰ were used.

Excited state (S_1) geometry optimizations were done both with time-dependent density

functional theory (TDDFT) in the Tamm-Dancoff approximation (TDA) with various functionals (B3LYP, PBE0, BHLYP),¹⁵¹ and with the ab initio methods, using the Ahlrichs TZVP basis set¹⁴⁴ (on all atoms). The TDA formulation of TDDFT often yields more reasonable structures for relaxed excited states, especially for saturated systems.⁶⁴ The ab initio based methods were the RICC2 method^{147,152} and a polarization propagator method, RIADC(2)¹⁴⁸ in Turbomole 6.2. Excited state convergence criteria were set to gradient differences of 1×10^{-6} and energy differences of 1×10^{-9} Hartree. Excited state vibrational analysis was used to identify minima.

Excitation (absorption and emission) energies were calculated with TDDFT in the random phase approximation (RPA) and the B3LYP functional and Def2-TZVP basis set¹⁵³ in Turbomole 6.2. The RPA formulation of TDDFT closely reproduces oscillator strengths and excitation energies.⁴⁵ This functional and basis set yield results which agree with the multistate formulation of second-order multireference perturbation theory (MSCASPT2) values in similar systems.¹⁰³ Oscillator strengths were obtained with the length description of the transition operator.

Due to the diffuse nature of the first excited state at some S_1 minima, the aug-cc-pVDZ basis set^{145,146} was also used with the B3LYP functional. Functionals that are not asymptotically corrected are known to underestimate excitation energies for charge-transfer and Rydberg states and this approximation was therefore checked by additional calculations involving various asymptotically corrected functionals (B3LYP-AC, the asymptotic correction approach of Casida and Salahub¹⁵⁴ with the empirical linear correlation of Zhan, Nichols, and Dixon^{155,156} in NWChem 5.11,¹⁵⁷ and the CAM-B3LYP¹⁵⁸ and LC-BLYP functionals¹⁵⁹ from GAMESS¹⁶⁰, version October 1, 2011), as well as with the RICC2 ab initio method to calculate excitation energies. The NWChem fine grid, designed to have a total energy target accuracy of 1×10^{-7} Hartree, was used for TDDFT calculations. For DFT and TDDFT calculations in GAMESS, the number of radial points in the Euler-MacLaurin quadrature was set to 96 and the number of angular points in the Lebedev grids was set to 302. These parameters were the default for ground state calculations and were higher than the default TDDFT grid size. The range correction cutoff parameter μ was optimized to a value of $0.23 a_0^{-1}$ to reproduce the disilane $\sigma\pi^*$ experimental excitation energy and when used

is denoted as the LC-BLYP method. Minimal augmentation was also added to basis sets (when the basis set is given the mD suffix) in the style of the maug-cc-pVTZ basis set of Truhlar and co-workers.¹⁶¹ The Def2-TZVP-mD basis set refers to a similarly minimally augmented basis set where an additional diffuse s function was added to the Si, C and H atoms in the Def2-TZVP basis set. The diffuse s orbital exponents, $0.48475401370 \times 10^{-1}$ and $0.37000771280 \times 10^{-1}$ for C and Si, respectively, were taken from the Def2-TZVP-D basis set,¹⁶² and the diffuse s hydrogen exponent of 0.2526000×10^{-1} from the aug-cc-pVTZ basis set was used. Basis set normalization was carried out internally in GAMESS.

Stochastic search methods¹⁶³ have been effective in searching the configurational space of molecules and locating hard-to-find minima in ground state chemistry.¹⁶⁴ With this motivation, an excited state stochastic search was run on **2** and **3** with TDDFT. To do this, a Fortran 90 program was written to apply random stochastic displacements to the nuclei, followed by excited state optimization with the PBE0/SVP method, using Turbomole 6.2. Here a set of 100 structures was generated by random kicks limited to 50 % of the ground state Si-Si bond distance for Si, 40% of the Si-C ground state bond length for C, and 30 % of the C-H ground state bond length for H. The multiple kick size strategy allows for efficient investigation of relevant excited state surfaces (larger kicks to H and Me groups result in many calculations for which the wave function does not converge as these geometries are somewhat unphysical).

To test the ground state fate of **2** deposited into various S_0 - S_1 funnel regions, stochastic kicks were applied to the funnel structures. The size of one set of displacements was limited to 20% of the ground state Si-Si bond distance for Si, 10% of the Si-C ground state bond length for C, and 5% of the C-H ground state bond length for H. In the second set, larger kicks were applied where the maximum displacement sizes were increased by a factor of three. Finally a set of displacements with increased Si-Me kicks were carried out as some excited state minima and structures in the S_0 - S_1 funnel region had large Si-C bond stretching. The displacements were limited to 50% of the ground state Si-Si bond distance for Si, 50% of the Si-C ground state bond length for C, and 25 % of the C-H ground state bond length for H. Approximately 100 optimization paths for each set

were run with the complete active space self-consistent field, CASSCF(8,8)/6-31G* method for each parent structure. In some cases (especially for the **2Fa** funnel) an active space of 10 electrons in 10 orbitals was required for wave function convergence. The CASSCF calculations were performed with the full optimized reaction space (FORS) approach in GAMESS.

S₀-S₁ transition densities were calculated at geometries of excited state minima with the QChem program,¹⁶⁵ using configuration interaction with singles (CIS) with the 6-31G* basis set. In all cases the CIS calculations gave qualitatively similar S₁ states as other methods used to calculate emission energies. Natural bond orbital (NBO) analysis was carried out with GAMESS and NBO 5.9. The NBO analysis was done for the CIS/6-311G(d,p) S₁ density unless otherwise mentioned.

2.3 Results

2.3.1 Dimethylsilylene

Various methods were used to obtain starting structures for vertical absorption and emission energies. The structure **1** was optimized with RICC2, RIADC(2), and DFT methods in the ground state (S₀) to give structure **1G**, the ground state equilibrium structure. Excited state optimizations with the RICC2, RIADC(2) and TDDFT methods gave the S₁ relaxed equilibrium structure **1a**. The **1G** and **1a** structures obtained with the RICC2/TZVP method are shown in Figure 2.6.

The ground state equilibrium structure of **1**, **1G**, which has a singlet electronic configuration, was optimized with various methods listed in Table 2.1. The ground state optimization with the RICC2/TZVP method produced a CSiC valence angle of 96.9°. This valence angle is quite close to values reported in the literature, 97.8°(B3LYP/6-311G(d,p)).¹⁶⁶ The methyl groups are twisted, reducing the C_{2v} symmetry to C₂, and Si-C bond lengths are 1.914 Å. Other optimization methods gave similar structures (Table 2.1).

Excited state optimization on the S₁ surface with the RICC2/TZVP method increased the CSiC valence angle to 119.6° and stretched the Si-C bond lengths to 1.930 Å. The relaxed structure

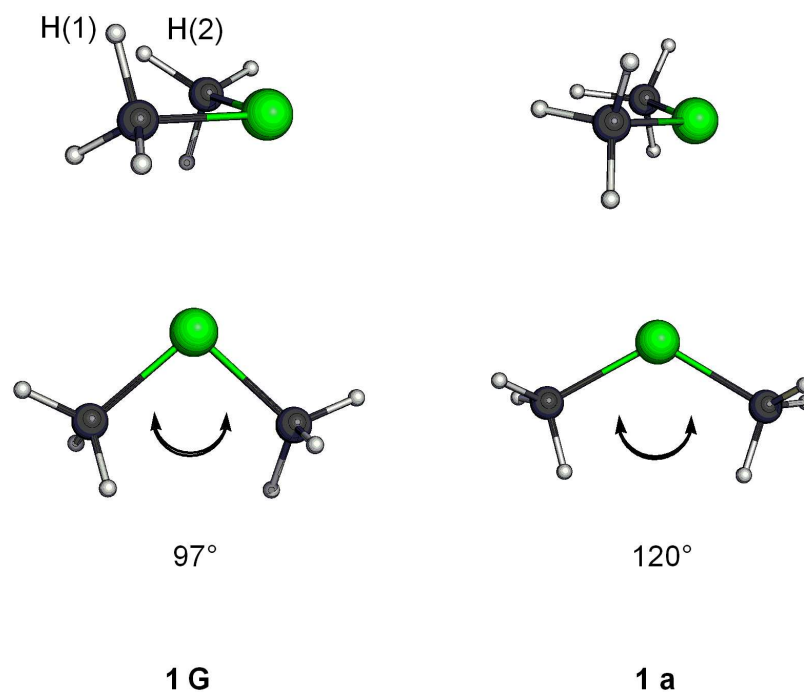


Figure 2.6: S_0 optimized (**1G** and S_1 optimized (**1a**) SiMe_2 RICC2/TZVP structures.

Table 2.1: S_0 equilibrium dimethylsilylene (**1G**) structures calculated with ab initio and DFT methods.

Method (Structure)	ω H(1)CSiC / deg	ω H(2)CSiC / deg	$\angle$ CSiC / deg	Si-C / Å
RICC2/TZVP	82.6	33.7	96.9	1.914
RIADC(2)/TZVP	82.4	34.0	97.0	1.913
BHLYP/TZVP	77.3	39.6	97.9	1.908
PBE0/TZVP	79.8	36.7	97.7	1.911
B3LYP/TZVP	78.9	37.9	98.0	1.923

also allows the methyl groups to align to give overall C_{2v} symmetry to **1a**. Other optimization methods give similar relaxed S_1 structures (Table 2.2). The **1a** structure is very similar to that found with the HF/DZ+d method by Grev and Schaefer.⁹⁶ This structure also had overall C_{2v} symmetry, a CSiC valence angle of 121.3° and Si-C bond lengths at 1.915 Å.

Table 2.2: S_1 equilibrium dimethylsilylene (**1a**) structures calculated with ab initio and TDDFT methods.

Method (Structure)	ω H(1)CSiC / deg	ω H(2)CSiC / deg	$\angle$ CSiC / deg	Si-C / Å
RICC2/TZVP	118.1	118.1	119.6	1.930
RIADC(2)/TZVP	118.0	118.0	120.0	1.926
BHLYP/TZVP	118.6	118.6	120.8	1.920
PBE0/TZVP	118.5	118.5	120.8	1.920
B3LYP/TZVP	118.5	118.5	120.4	1.938

The experimental absorption band maximum ($22\,070\text{ cm}^{-1}$) is well reproduced with TDDFT (B3LYP/Def2TZVP) calculations on the **1G** structures. The **1G** RICC2/TZVP structure gave a vertical absorption energy of $21\,400\text{ cm}^{-1}$, which is a typical vertical absorption energy for **1G** structures (Table 2.3). The calculated values compare well with previous absorption energy estimates from TDDFT calculations ($20\,440\text{ cm}^{-1}$),¹⁶⁶ and from ab initio methods ($21\,930\text{ cm}^{-1}$).⁹⁶ The 1^1A to 1^1B electronic state transition was calculated to be weak, with oscillator strengths ranging from 0.020 to 0.028. This transition corresponds to electron excitation from the silylene lone pair to the orthogonal p_x orbital on the Si atom. These orbitals are shown in Figure 2.7.

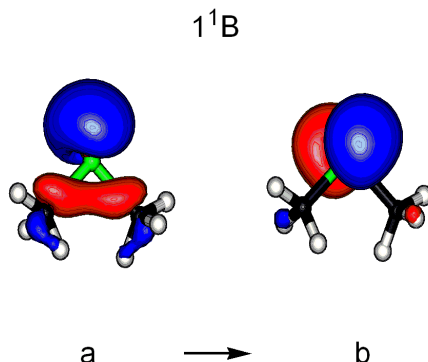


Figure 2.7: Singly occupied orbitals a (ground state HOMO) and b (ground state LUMO) of dimethylsilylene at the S_0 equilibrium geometry. Structure obtained from RICC2/TZVP optimization. The DFT orbitals are plotted using isodensity values of ± 0.06 .

Vertical emission energies for the **1a** structures were also calculated with the B3LYP/Def2TZVP method. The experimental vertical emission band maximum ($15\,270\text{ cm}^{-1}$) was reproduced less

well than the absorption energies, with calculated emission values ranging from 12 200 cm^{-1} (RICC2/TZVP and B3LYP/TZVP structures) to 12 060 cm^{-1} (PBE0/TZVP), (Table 2.3). The S_0 - S_1 oscillator strengths for the **1a** structures were much lower, approximately half the value of the oscillator strengths for the same transition in the **1G** structures. Grev and Schaefer⁹⁶ did not report the calculated vertical emission energy of **1a**, but using their reported structure with TDDFT (B3LYP/Def2-TZVP) yielded a similarly red-shifted emission energy of 12 320 cm^{-1} with an oscillator strength of 0.009.

Table 2.3: Vertical absorption (E_{VA}), emission (E_{VE}), site distortion (E_{SD}) and Stokes shift (E_{SS}) energies and oscillator strengths (f) calculated with the TDDFT B3LYP/Def2TZVP method for **1G** and **1a**.

Method (Structure)	E_{VA}^a / cm^{-1}	f	E_{VE}^a / cm^{-1}	f	E_{SD} / cm^{-1}	E_{SS}^a / cm^{-1}
RICC2/TZVP	21 400	0.021	12 200	0.009	4 200	9 200
RIADC(2)/TZVP	21 380	0.028	12 090	0.009	4 190	9 290
BHLYP/TZVP	20 910	0.021	12 160	0.009	3 710	8 750
PBE0/TZVP	21 160	0.021	12 060	0.009	3 970	9 100
B3LYP/TZVP	20 920	0.020	12 200	0.009	3 700	8 720

^a These values can be compared to experimental absorption and emission band maxima (measured in 3-methylpentane at 77 K) which are located at 22 070 and 15 270 cm^{-1} , respectively, and yield a Stokes shift of 6 800 cm^{-1} .¹³⁰

The TDDFT vertical absorption energy is in close agreement with the maximum of the absorption band (22 070 cm^{-1}). The vertical emission energy, however, is very low (12 200 cm^{-1}) when compared to the experimental band maximum (15 270 cm^{-1}). If the CSiC valence angle is contracted (keeping the rest of the geometry intact) however, both the oscillator strength of the transition and the energy for the ground state to 1^1B_1 transition increase (Figure 2.8). Likewise, ground state to 1^1B_1 transition energy decreases as the valence angle increases.

The **1G** ground state equilibrium structure is similarly affected by CSiC valence angle distortions (Table 2.1). Over an approximate 15° angle increase (with all other parameters kept constant) the S_0 - S_1 oscillator strength only decreased to 0.015, 71 % of the original value (0.021), whereas a 15° CSiC valence angle increase (with all other parameters kept constant) to the **1a** structure produced an S_0 - S_1 oscillator strength decrease to 0.004 (44 % of the original value), Table 2.4. An

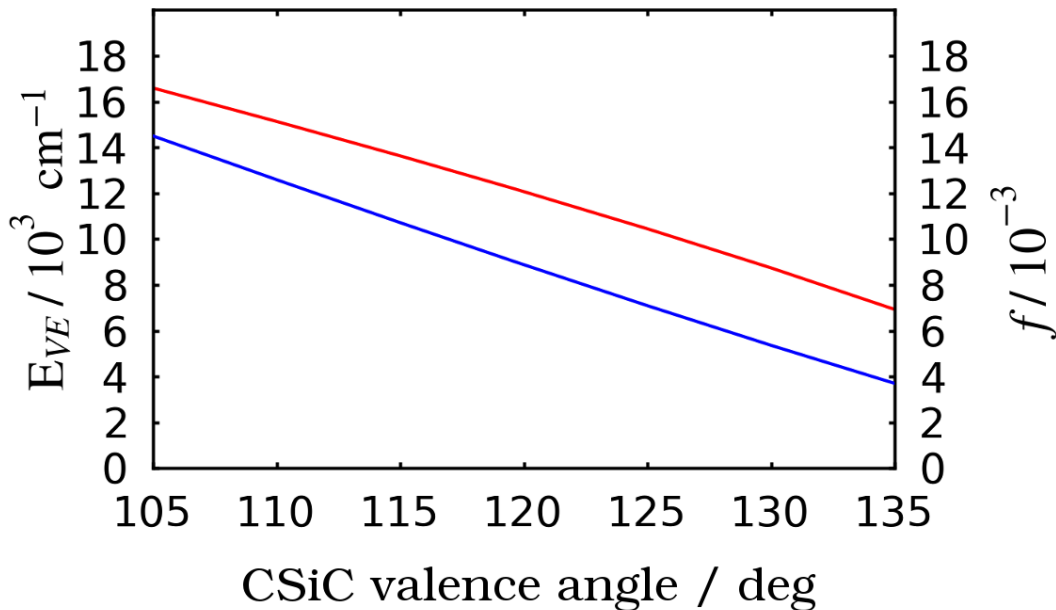


Figure 2.8: Vertical emission energy (blue) and S_0 - S_1 oscillator strength dependence on CSiC valence angle (all other parameters constant). Vertical calculations done with the TDDFT B3LYP/Def2TZVP method on structures derived from the 1^1B_1 structure obtained from RICC2/TZVP optimization .

Table 2.4: Vertical emission energy and S_0 - S_1 oscillator strength dependence on CSiC valence angle (with all other geometrical parameters held constant). Vertical calculations done with the TDDFT B3LYP/Def2-TZVP method on structures based on the S_1 relaxed minimum **1a**, which was obtained with the RICC2/TZVP method.

$\angle$ CSiC deg	E_{VE} / cm^{-1}	f
105.0	16 590	0.014
110.0	15 130	0.013
115.0	13 630	0.011
119.6	12 200	0.009
125.0	10 450	0.007
130.0	8 740	0.005
135.0	6 920	0.004

explanation of these results will be given in the Discussion.

When the CSiC valence angle in **1G** is varied from 80.0° to 115° (with all other parameters kept constant), the calculated S_0 - S_1 absorption energy ranges from $25\,470$ to $16\,680 \text{ cm}^{-1}$,

Table 2.5: Vertical emission energy dependence and S_0 - S_1 oscillator strength on the CSiC valence angle (while other parameters are held constant). Vertical calculations were done with the TDDFT B3LYP/Def2TZVP method on structures based on the S_1 relaxed minimum **1a** (RICC2/TZVP).

$\angle$ CSiC deg	E_{VE} / cm^{-1}	f
80.0	25 470	0.027
85.0	24 250	0.025
90.0	23 060	0.024
97.0	21 400	0.021
100.0	20 640	0.020
105.0	19 380	0.018
110.0	18 060	0.017
115.0	16 680	0.015

respectively. The spread of calculated absorption energies varies more slowly ($250 \text{ cm}^{-1}/\text{deg}$) than the spread of emission energies ($320 \text{ cm}^{-1}/\text{deg}$) for the **1a** structures which contained similarly distorted CSiC valence angles ($\pm 15^\circ$ with respect to the S_1 equilibrium value), varying from 105° to 135° . The CSiC angle dependence of the emission energies (while all other parameters are kept constant) can be seen in Figure 2.8.

Figure 2.10 shows the S_0 - S_1 transition density for a reduced CSiC valence angle (80°) structure derived from the RICC2/TZVP **1G** structure with all other parameters held constant (a), the RICC2/TZVP **1G** structure (b), and an increased CSiC valence angle (135°) structure derived from the RICC2/TZVP **1a** with all other parameters held constant (c). Inspection of the transition density shows decreased overlap between the Si lone pair (sp_z) and p_x orbital as well as increased overlap between the Si-C hybrids (sp_y) and the p_x orbital as the CSiC valence angle is increased.

The D_1 and D_2 diagnostics for the RICC2 **1G** and **1a** structures were computed and are collected in Table 2.6. The D_1 and D_2 values for **1G** and **1a** are relatively low.^{36,37}

Table 2.6: D_1 and D_2 diagnostics (calculated with the RICC2/TZVP method) for **1G** and **1a** structures obtained with the RICC2/TZVP method.

Structure	D_1	D_2
1G	0.018	0.21
1a	0.021	0.21

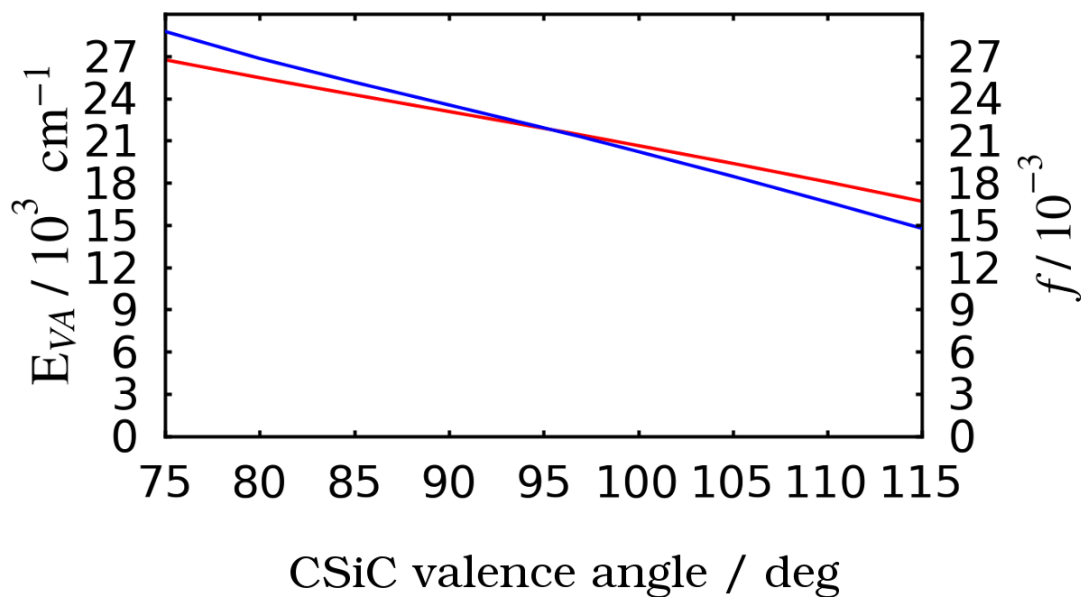


Figure 2.9: Vertical absorption energy (blue) and S_0 - S_1 oscillator strength (red) dependence on CSiC valence angle (all other parameters are kept constant). Vertical calculations done with the TDDFT B3LYP/Def2-TZVP method on structures derived from the 1^1A (**1G**) structure obtained from ground state RICC2/TZVP optimization.

2.3.2 Hexamethyldisilane

To summarize the results for hexamethyldisilane briefly, five different S_1 minima have been located. One of these structures (**2a**) resembles those found (in new work presented in Chapter 3) to be responsible for the blue emission from longer oligosilanes and corresponds to a Si-Si bond stretch minimum. The remaining minima, **2b**, **2c**, **2d** and **2e**, had not been previously identified. They include a C-Si bond stretch minimum (**2b**), a diffuse Si-Si bond stretch minimum (**2c**), a Rydberg minimum (**2d**) and a polarization minimum (**2e**). These minima have subsequently been found to exist in longer oligosilanes as well (see Chapter 4). Various structures near the S_0 - S_1 touching (funnels) and their ground state return products have also been identified. A detailed description of the results now follows.

A complete search of the S_1 surface of **2** is precluded by the number of atoms present in the molecule, and the general search for excited state minima and regions of near S_0 - S_1 touching

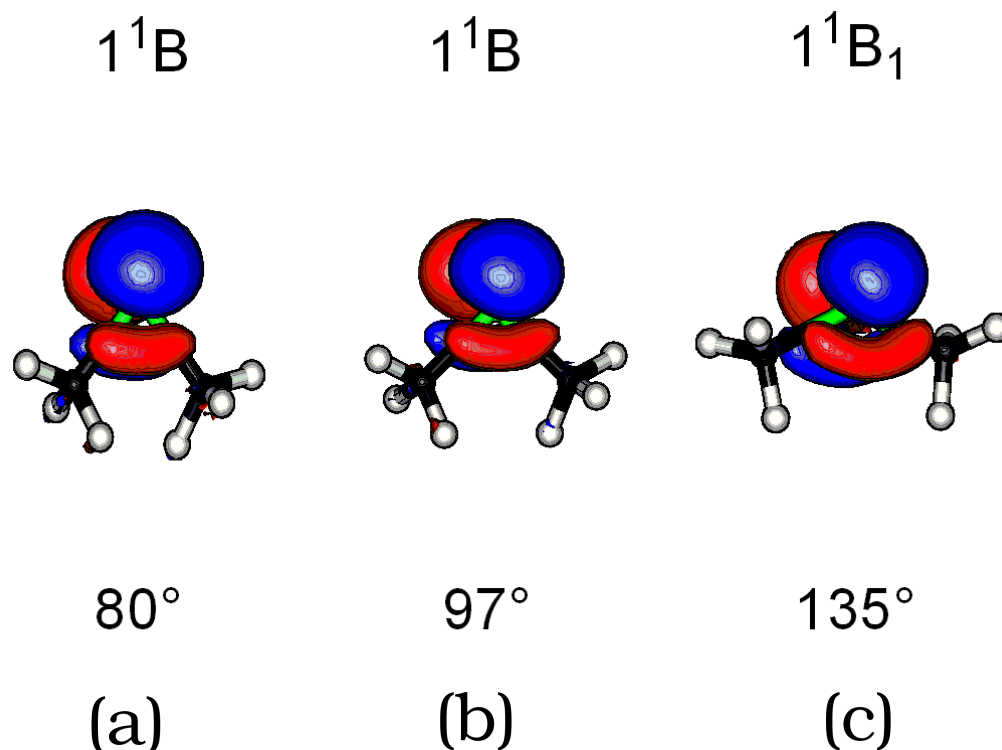


Figure 2.10: S_0 - S_1 transition density for a reduced CSiC valence angle (80°) structure (a) derived from the RICC2/TZVP **1G** structure (with all other parameters held constant), the RICC2/TZVP **1G** structure (b), and an increased CSiC valence angle (135°) structure derived from the RICC2/TZVP **1a** (with all other parameters held constant) (c) are shown (left to right). The transition density (CIS/6-31G(d)) is plotted at isodensity values of ± 0.004 .

(funnels, conical intersections) was focused to regions of geometries that are relatively close to the ground state equilibrium geometry. After an initial vertical excitation, these geometries are likely to be reached first, and if they return the molecule to the S_0 state, the presence of additional more distant funnels will be irrelevant. Stationary points have been identified and vibrational frequency analysis was used to distinguish between minima and saddle points. When the optimization led to a region of very small S_0 - S_1 energy differences, a funnel was assumed to be present. No attempts were made to determine whether the funnels corresponded to true conical intersections or to merely regions of avoided surface touching, and the exact location of the conical intersections was not determined, since the single-reference methods of calculation available for molecules of this size are not appropriate for regions of near degeneracy, and these distinctions have no practical consequences

for our purposes. Once the energy difference between S_1 and S_0 is less than a few thousand cm^{-1} , return from S_1 to S_0 becomes so fast that further travel on the S_1 surface becomes very unlikely in any event. The difference between near degeneracy and exact degeneracy between S_1 and S_0 , as well as the exact location of the minimum energy in the conical intersection subspace then become immaterial for the photophysics.

2.3.2.1 Hexamethyldisilane Excited State Geometry Relaxation

Excited state optimization for hexamethyldisilane started at various choices of geometry. (i) The ground state D_{3d} equilibrium geometry **2G**, at which the S_1 state is of $\sigma\pi^*$ nature, both experimentally¹⁰¹ and by calculation.¹³⁹ (ii) A geometry **2***, similar to that **2**, but with the Si-Si bond stretched to 2.5 Å and the Si(2)Si(1)C(1) and Si(1)Si(2)C(6) valence angles (Figure 2.11) increased to 120°. At this geometry, the S_1 state is calculated to be of $\sigma\sigma^*$ character, and there are experimental indications¹⁰¹ that this result is correct. (iii) A set of geometries, **2****, derived from structure **2** by stochastic kicks to Si, C and H. The various structures resulting from S_1 optimization of the geometries **2**, **2***, **2**** are shown in Figure 2.11, and the funnel structures are depicted in Figure 2.12. The resulting geometries will be described next.

Optimization on the S_1 surface, starting at the vertical geometry **2G**, resulted in four stationary points (**2a**, **2c**, **2d**, **2e**), and one funnel, **2Fa**, depending on the method used. Both RIADC(2) and RICC2 with the TZVP basis set produced **2a**, whereas only TDDFT B3LYP/TZVP yielded **2c**. S_1 optimization of **2c** led to the funnel **2Fa** with the BHLYP/TZVP method and to the funnel **2Fc** with both the RIADC(2)/TZVP and RICC2/TZVP methods. The B3LYP/aug-cc-pVTZ optimization of **2c** gave **2d**. The B3LYP/aug-cc-pVTZ optimization of **2G** and distortion along the imaginary frequency gave **2d**. Optimization of **2G** with TDDFT PBE0/TZVP led directly to **2e** and with TDDFT BHLYP/TZVP, to the funnel **2Fa**. Distortion (widening) of the C(1)Si(1)Si(2) valence angle in **2e** and subsequent optimization (RIADC(2)/TZVP) led to the funnel **2Fe**, this funnel is very similar to **2Fa**: they differ only by rotations of the methyl groups on Si(2) (Figure 2.12).

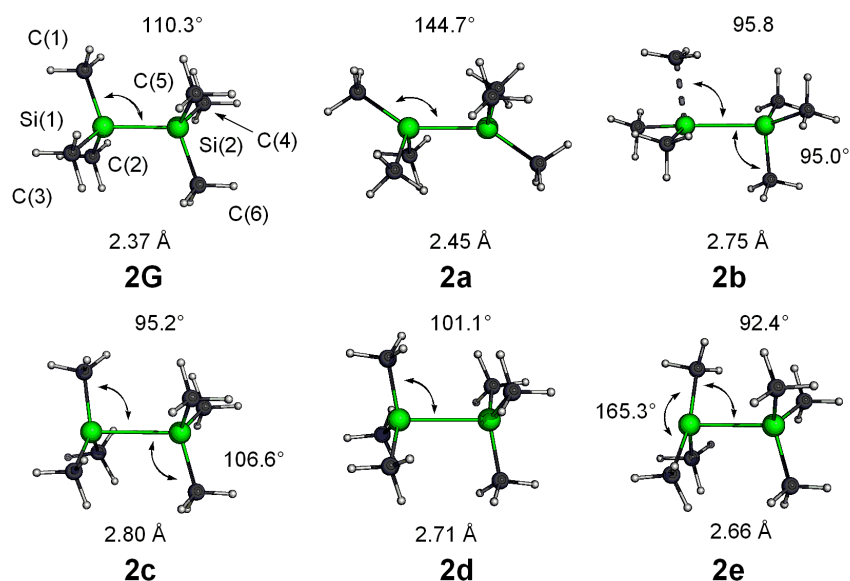


Figure 2.11: Ground state equilibrium structure **2G** (RIMP2/TZVP) and S_1 stationary points: **2a** (PBE0/TZVP), **2b** (B3LYP/TZVP), **2c** (B3LYP/TZVP), **2d** (B3LYP/aug-cc-pVDZ) and **2e** (PBE0/TZVP). Si-Si bond lengths are shown in Å and various CSiSi or CSiC angles (double-headed arrows) in deg. For atom numbering, see **2G**.

Results obtained starting at the geometry **2*** also depended strongly on the method of calculation used. While all methods led to the stationary point **2a**, only with the PBE0/TZVP method was this a minimum. Other functionals as well as RIADC(2)/TZVP and RICC2/TZVP ab initio methods produced similar stationary structures, but they were saddle points (transition states).

Starting from structures **2**** generated by stochastic search, TDDFT PBE0/TZVP yielded the structures **2a**, **2Fa**, and **2e**, as well as one new structure, **2b**. Structure **2b** proved to be a minimum on S_1 only when reoptimized with the TDDFT B3LYP/TZVP method. Optimization with the PBE0/TZVP, B3LYP/TZVP, and RICC2/TZVP methods returned the molecule to the funnel **2Fa**, and optimization of **2b** with RIADC(2)/TZVP method led to a different funnel, **2Fb**.

The structures of the stationary points on S_1 obtained by different methods are very similar. All structures obtained for the Si-Si bond stretch minimum **2a** belong to the C_i symmetry group and their important geometrical parameters are listed in Table 2.7. At these geometries the S_1

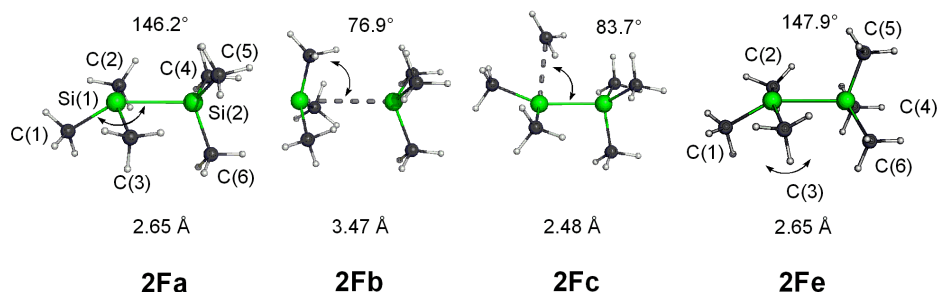


Figure 2.12: Approximate S_0 - S_1 funnel geometries obtained with the RIADC(2)/TZVP method for (**2Fa-Fc** and **2Fe**). Si-Si bond lengths in Å and various CSiSi or CSiC angles (double-headed arrows) in deg. For atom numbering, see **2G** in Figure 2.11.

state is of $\sigma\sigma^*$ nature. Figure 2.11 shows the structure **2a** obtained with the TDDFT PBE0/TZVP method. This structure is referred to as a Si-Si bond stretch minimum since its Si-Si bond is stretched relative to **2G** (2.366 Å, PBE0/TZVP) to values ranging from 2.454 Å (PBE0/TZVP) to 2.560 Å (RIADC(2)/TZVP). The 2.454 Å bond length may seem less striking as the large valence angle changes (discussed below), but this bond length is longer when calculated with different methods for analogous minima in longer oligosilanes (Chapter 3). The CSiSi valence angles are also strongly affected. The C(1)Si(1)Si(2) valence angle is increased, from 110.3° in the ground state (PBE0/TZVP) to values ranging from 142.8° (BHLYP/TZVP) to 147.0° (RIADC(2)/TZVP). The C(2)Si(1)Si(2) angle is reduced to values ranging from 88.2° (RIADC(2)/TZVP) to 91.0° (BHLYP/TZVP). The C(3)Si(1)Si(2) angle has values varying between 98.0° (RIADC(2)/TZVP) and 102.9° (PBE0/TZVP). The most Si-C bond stretching occurred between atoms Si(1) and C(2), to values ranging from 1.935 Å (BHLYP/TZVP) to 2.017 Å (B3LYP/TZVP). The least Si-C bond stretching occurred between atoms Si(1) and C(3), to values ranging from 1.903 Å (BHLYP/TZVP)

Table 2.7: Geometrical parameters for stationary points on the S_1 surface of **2a** optimized with TDDFT PBE0/TZVP (minimum), B3LYP/TZVP, RIADC(2)/TZVP and RICC2/TZVP (transition states).

Structure	$\angle$ CSiC /deg	$\angle$ CSiSi /deg	SiSi /Å	SiC /Å
Si ₂ Me ₆	110.2	89.0	2.454	1.981
PBE0/TZVP	103.2	102.9		1.904
C_i	103.6	144.7		1.934
2a	110.2	89.0		1.981
	103.2	102.9		1.934
	103.6	144.7		1.904
Si ₂ Me ₆	108.6	89.9	2.473	2.017
B3LYP/TZVP	102.9	104.2		1.913
C_i	102.4	144.7		1.950
2a	108.6	89.9		2.017
	102.9	104.2		1.913
	102.4	144.7		1.950
Si ₂ Me ₆	113.0	91.0	2.554	1.935
BHLYP/TZVP	104.3	99.1		1.903
C_i	105.6	142.8		1.920
2a	113.0	91.0		1.935
	104.3	99.1		1.903
	113.0	142.8		1.920
Si ₂ Me ₆	111.4	88.2	2.560	1.941
RIADC(2)/TZVP	104.5	98.0		1.906
C_i	105.3	147.0		1.924
2a	111.4	88.2		1.941
	104.5	98.0		1.906
	105.3	147.0		1.924
Si ₂ Me ₆	111.4	88.3	2.541	1.946
RICC2/TZVP	104.3	98.6		1.907
C_i	105.1	146.7		1.926
2a	111.4	88.3		1.946
	104.3	98.6		1.907
	105.1	146.7		1.926

to 1.907 Å (RICC2/TZVP). An intermediate Si-C bond stretch occurred between atoms Si(1) and C(1), separated by a distance ranging from 1.920 Å (BHLYP/TZVP) to 1.950 Å (B3LYP/TZVP).

Excited state vibrational analysis of **2a** (Table 2.7) revealed that only the structure obtained with the PBE0/TZVP method corresponds to an energy minimum on the S_1 surface. The other methods (B3LYP/TZVP, BHLYP/TZVP, RIADC(2)/TZVP and RICC2/TZVP) found the lowest

frequency to be imaginary and showed that the stationary point corresponds to a transition state on the S_1 surface. These frequencies are shown in Table 2.8.

Table 2.8: The lowest vibrational frequency for the stationary points **2a-e** on the S_1 surface.

Structure	Method	Lowest Frequency Vibration
2a	PBE0/TZVP	27.8
	PBE0/aug-cc-PVDZ	33.0
	PBE0/cc-PVTZ	28.8
	B3LYP/TZVP	<i>i</i> 29.8
	BHLYP/TZVP	<i>i</i> 19.2
	RIADC(2)/TZVP	<i>i</i> 31.8
	RICC2/TZVP	<i>i</i> 33.0
2b	B3LYP/TZVP	38.1
2c	B3LYP/TZVP	27.6
2d	B3LYP/aug-cc-pVDZ	37.6
2e	PBE0/TZVP	21.9
	B3LYP/TZVP	22.2
	B3LYP/aug-cc-pVDZ	26.1
	BHLYP/TZVP	18.9
	RIADC(2)/TZVP	26.7
	RIADC(2)/Def2-TZVP-mD	23.4
	RICC2/TZVP	29.8

The C-Si bond stretch minimum structure **2b** (B3LYP/TZVP) is marked by a long 2.358 Å C(1)-Si(1) bond (Figure 1 and Table 2.9). This bond is 25 % longer than the in the ground state (1.907 Å). The Si-Si bond is also considerably stretched, to 2.745 Å, which is 16% longer than the ground state Si-Si bond length. The second longest (1.943 Å) Si-C bond, C(2)Si(1), makes a wide C(2)Si(1)Si(2) valence angle of 156.3°. The point group symmetry is C_1 . The C(2), C(3), and Si(2) atoms nearly form a plane with the Si(1) atom. This can be seen by the rather small C(1)Si(1)C(2) angle 91.7°, a C(1)Si(1)C(3) angle of 93.8°, and finally by the small C(1)Si(1)Si(2) angle of 95.8°. This resembles a trigonal bipyramidal arrangement on Si(1).

The B3LYP/TZVP optimization of **2G** led to the diffuse Si-Si bond stretch minimum structure **2c** which has a three-fold rotational symmetry axis and belongs to the C_3 symmetry group. At 2.797 Å, the Si-Si bond is stretched more in this structure than in any other found. The 119.2° CSiC valence angle at Si(1) is slightly larger than those at Si(2), which are 112.3°. The CSi(1)Si(2)

Table 2.9: Geometrical parameters for S_1 minima **2b**, **2c**, and **2d**.

Structure	$\angle \text{CSiC}$ /deg	$\angle \text{CSiSi}$ /deg	SiSi /Å	SiC /Å
Si ₂ Me ₆	105.6	95.0	2.745	1.917
B3LYP/TZVP	106.2	136.7		1.935
<i>C</i> ₁	107.6	102.9		1.914
2b	100.3	156.3		1.943
	91.7	101.6		1.913
	93.8	95.8		2.358
Si ₂ Me ₆	119.2	95.2	2.797	1.884
B3LYP/TZVP	119.2	95.2		1.884
<i>C</i> ₃	119.2	95.2		1.884
2c	112.3	106.5		1.888
	112.3	106.5		1.888
	112.3	106.5		1.888
Si ₂ Me ₆	116.4	101.1	2.708	1.876
B3LYP/aug-cc-pVDZ	116.4	101.1		1.876
<i>D</i> ₃	116.4	101.1		1.876
2d	116.4	101.1		1.876
	116.4	101.1		1.876
	116.4	101.1		1.876

valence angles are smaller (95.2°) than those at the neighboring silicon (CSi(2)Si(1)), which are closer to those in the ground state. This results in a flattening of the methyl groups at Si(1). The lengths of the Si-C bonds are almost identical, with those at Si(1) being slightly shorter (1.884 Å) than those at Si(2) (1.888 Å). The Si-C bonds are slightly shorter than those in the ground state, 1.907 Å (B3LYP/TZVP).

The Rydberg minimum structure **2d**, obtained with the B3LYP/aug-cc-pVDZ method (Table 2.9), belongs to the D_3 symmetry point group. Slight methyl rotations and CSiSiC dihedral angles of 169.1° cause a deviation from D_{3d} symmetry. The Si-Si bond length (2.708 Å) is elongated compared to the ground state (2.375 Å for B3LYP/aug-cc-pVDZ). The Si-C bonds (1.876 Å) are only slightly shorter than those in the ground state (1.907 Å). The CSiSi valence angles (101.1°) are smaller than in the ground state (108.6°) and CSiC valence angles (116.4°) are larger than those in the ground state (110.3°).

The polarization minimum structure **2e**, obtained with TDDFT PBE0/TZVP optimization

of **2G**, contains a mirror plane that cuts through atoms C(2), Si(1), Si(2) and C(3) (and two additional hydrogen atoms), and is of C_s symmetry. Optimization with other functionals, B3LYP and BHLYP, as well as with RIADC(2) and RICC2 methods, led to structures with similar geometrical parameters (Table 2.11).

Table 2.10: Structural parameters for S_1 minimum **2e**, optimized with various methods as indicated below.

Structure	$\angle$ CSiC /deg	$\angle$ CSiSi /deg	SiSi /Å	SiC /Å
Si ₂ Me ₆	112.7	107.5	2.657	1.881
PBE0/TZVP	112.7	103.9		1.880
C_s	111.9	107.5		1.881
2e	165.3	92.4		1.990
	96.2	92.4		1.990
	96.2	103.2		1.910
Si ₂ Me ₆	112.3	108.1	2.734	1.891
B3LYP/TZVP	112.3	103.9		1.891
C_s	111.6	108.1		1.891
2e	164.7	92.7		2.008
	96.5	92.7		2.008
	96.5	101.6		1.919
Si ₂ Me ₆	112.5	107.4	2.690	1.877
BHLYP/TZVP	112.5	105.0		1.874
C_s	111.5	107.4		1.877
2e	167.2	90.1		1.977
	95.9	90.1		1.977
	95.9	112.6		1.908
Si ₂ Me ₆	112.2	107.7	2.704	1.886
RIADC(2)/TZVP	112.2	106.0		1.883
C_s	110.7	107.7		1.886
2e	168.0	86.4		1.958
	95.8	86.4		1.958
	95.8	112.9		1.906
Si ₂ Me ₆	112.4	107.3	2.667	1.885
RICC2/TZVP	112.4	106.1		1.882
C_s	111.0	107.3		1.885
2e	168.2	87.6		1.967
	95.9	87.6		1.967
	95.9	110.0		1.910

Vibrational analysis with the respective optimization method reveals the **2e** structures to

be minima on the S_1 surface (Table 2.8). The Si-Si bond length of **2e** varies from 2.657 Å (PBE0/TZVP) to 2.734 Å (B3LYP/TZVP). The longest Si-C bonds are from Si(1) to C(1) and C(3) (these C atoms are equivalent by symmetry). The Si(1)-C(1) bond lengths range from 1.958 Å (RIADC(2)/TZVP) to 2.008 Å (B3LYP/TZVP). The Si(1)-C(2) is the next most elongated Si-C bond, ranging from 1.906 Å (RIADC(2)/TZVP) to 1.919 Å (B3LYP/TZVP). Large geometrical rearrangements of C(1) and C(2) give rise to a very wide CSiC valence angle, ranging from 164.7° (B3LYP/TZVP) to 168.0° (RIADC(2)/TZVP) and to narrow CSiSi valence angles, ranging from 86.4° (RIADC(2)/TZVP) to 92.7° (B3LYP/TZVP). A graphical summary of the S_1 optimization results is provided in Figure 2.13.

Table 2.11: Structural parameters for the S_1 polarization minimum **2e**, optimized with various methods which include augmented basis sets.

Structure	$\angle$ CSiC /deg	$\angle$ CSiSi /deg	SiSi /Å	SiC /Å
Si ₂ Me ₆	112.7	107.3	2.719	1.890
B3LYP/aug-cc-PVDZ	112.7	104.2		1.889
C_s	112.1	107.3		1.890
2e	162.5	92.9		1.998
	97.6	92.9		1.998
	97.6	101.0		1.917
Si ₂ Me ₆	112.7	107.3	2.719	1.890
B3LYP/Def2TZVP-mD	112.7	104.2		1.889
C_s	112.1	107.3		1.890
2e	162.5	92.9		1.998
	97.6	92.9		1.998
	97.6	101.0		1.917
Si ₂ Me ₆	112.0	108.8	2.725	1.874
RIADC(2)/Def2TZVP-mD	112.0	103.9		1.871
C_s	110.9	108.8		1.874
2e	165.2	85.4		1.934
	97.2	85.4		1.934
	97.2	114.9		1.888

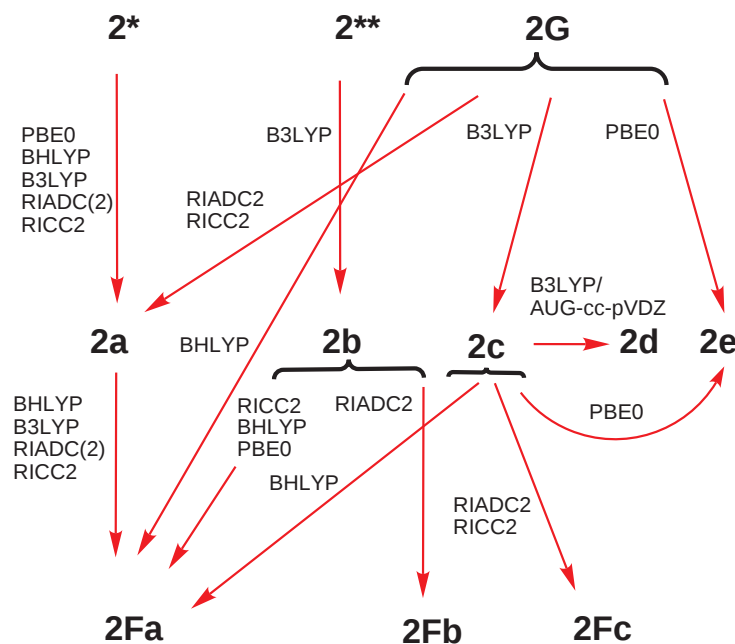


Figure 2.13: Excited state (S_1) optimization process for hexamethyldisilane. The method used is listed to the left of or above the arrow.

2.3.2.2 Hexamethyldisilane Structures Near the S_0 - S_1 Touching, Funnels

To re-emphasize, the geometries found here with single reference methods are not really those of the conical intersections, just close to them. These structures are referred to as funnels, are near the S_0 - S_1 surface touching. To obtain accurate conical intersection structures multireference methods, dynamic electron correlation, as well as the calculation of the gradient difference vector (eq. (1.102)) and the nonadiabatic coupling vector (eq. (1.103)) would be necessary. Again, the exact location of the conical intersection is not believed to be necessary to describe the basic photophysics as radiationless quenching of the electronically excited state happens in the general vicinity of the conical intersection.

Geometry distortion along the lowest imaginary mode of the transition state **2a** on the S_1 surface led to a funnel between S_1 and S_0 surfaces (structure **2Fa** in Figure 2.12). This structure is marked by an inverted C(1)Si(1)Si(2) bend of 213.8° (or new internal angle of 146.2° , Figure 2.12 and Table 2.12). There is also a large C(2)Si(1)C(3) valence angle of 155.4° . The corresponding C(2)Si(1) and C(3)Si(1) bonds are the longest at 1.965 Å and 1.982 Å, respectively. There is a

small C-Si-Si valence angle of 80.0° between atoms C(3), Si(1) and Si(2). The C(2)Si(1)C(1) and C(3)Si(1)C(1) angles are 92.9° and 91.5° , respectively.

RIADC(2)/TZVP S_1 optimization of **2b** led to the funnel **2Fb**. The optimization path from **2b** to **2Fb** follows the Si(1)-C(1) stretching coordinate. In the **2b** structure, the C(1)Si(1) bond length was extended from 2.358 Å in **2b** to 2.525 Å in **2Fb**. The Si-Si bond length is shortened to 2.477 Å in **2Fb** in comparison to **2b** (2.745 Å). In **2Fb**, both C(2)Si(1) and C(3)Si(1) bonds are equally stretched to 1.922 Å. The C(1)Si(1)Si(2) bond angle decreased from 95.8° in **2b** to 76.9° in **2Fb**. The 157.0° C(2)Si(1)Si(2) angle is similar to that in **2b**.

RIADC(2)/TZVP and RICC2/TZVP S_1 optimization of **2c** led to the funnel **2Fc**. This funnel has an extremely long Si-Si bond length (3.471 Å). Opposing SiMe₃ groups are not completely symmetrical and the Si(1)C bond lengths are slightly shortened (1.805 Å to 1.811 Å), whereas the Si(2)C bond lengths are slightly extended (1.941 Å to 1.944 Å).

The S_1 and S_0 RIADC(2)/TZVP energies of the minima and funnels are shown in Table 2.12. The C-Si bond stretch minimum **2b** has the least stable S_1 energy compared to **2G**. The **2Fb** funnel is similarly the least stable of the funnels located. The diffuse Si-Si bond stretch minimum **2c** structure has a slightly lower S_1 energy than **2b**, and has a much more stabilized S_0 energy. The polarization minimum **2e** has the lowest S_1 energy, *i.e.*, the largest site distortion energy, of the minima. Details of the calculated energy differences will be presented in section 2.3.2.6. A RIADC(2)/TZVP optimization of a structure based on **2e**, but with a wide C(1)Si(1)Si(2) valence angle (150.0°), led to the funnel **2Fe**. This funnel is very similar to **2Fa**: they differ only by rotations of the methyl groups on Si(2) (Table 2.12 and Figure 2.12). The C(1)Si(1)Si(2)C(x), $x = 4, 5, 6$, dihedral angles for **2Fa** are 99.4° , -141.7° , and -21.9° , respectively. For **2Fe**, the C(1)Si(1)Si(2)C(x), $x = 4, 5, 6$, dihedral angles are 60.0° , 180.0° , and -60.0° , respectively. Thus the Me groups on Si(2) in **2Fe** are rotated approximately 40° to those in **2Fa**. The funnel **2Fe** has C_s symmetry.

Table 2.12: S₀-S₁ funnel geometries (RIADC(2)/TZVP) for **2**.

Structure	$\angle$ CSiC / deg	$\angle$ CSiSi / deg	SiSi / Å	SiC / Å
2Fa <i>C</i> ₁	107.5	107.3	2.646	1.898
	108.3	80.0		1.895
	110.4	114.0		1.896
	155.4	109.3		1.965
	92.9	83.0		1.939
	91.5	146.2		1.982
2Fa ^a <i>C</i> ₁	91.3	154.6	2.552	1.950
	160.6	85.1		1.995
	92.4	83.5		1.983
	110.1	109.3		1.897
	110.2	108.0		1.888
	105.3	113.9		1.888
2Fb <i>C</i> ₁	96.8	157.0	2.477	1.922
	119.8	83.7		2.525
	73.7	97.8		1.922
	108.4	111.6		1.890
	107.9	99.5		1.887
	108.8	119.9		1.904
2Fc <i>C</i> ₃	115.7	76.9	3.471	1.810
	114.8	77.2		1.805
	115.7	77.0		1.811
	106.7	112.7		1.941
	106.1	112.6		1.941
	107.1	111.3		1.944
2Fe <i>C</i> _s	109.2	105.6	2.651	1.888
	111.2	109.8		1.888
	111.2	109.8		1.885
	160.4	83.4		1.976
	91.8	83.4		1.976
	91.8	147.9		1.925

^a This funnel was obtained from the BHLYP/TZVP TDA optimization of **2a**, distorted along the imaginary vibration.

2.3.2.3 Hexamethyldisilane Ground State Geometry Relaxation

Ground state optimization starting at the geometry **2Fa** with both BLYP/6-31G* and CASSCF/6-31G* methods returned the disilane to the ground state equilibrium geometry, **2G**. The set of stochastically minimally kicked structures generated from **2Fa**, followed by ground state CASSCF/6-31G* optimization, also returned the molecule to **2G**. The set of larger kicks gave

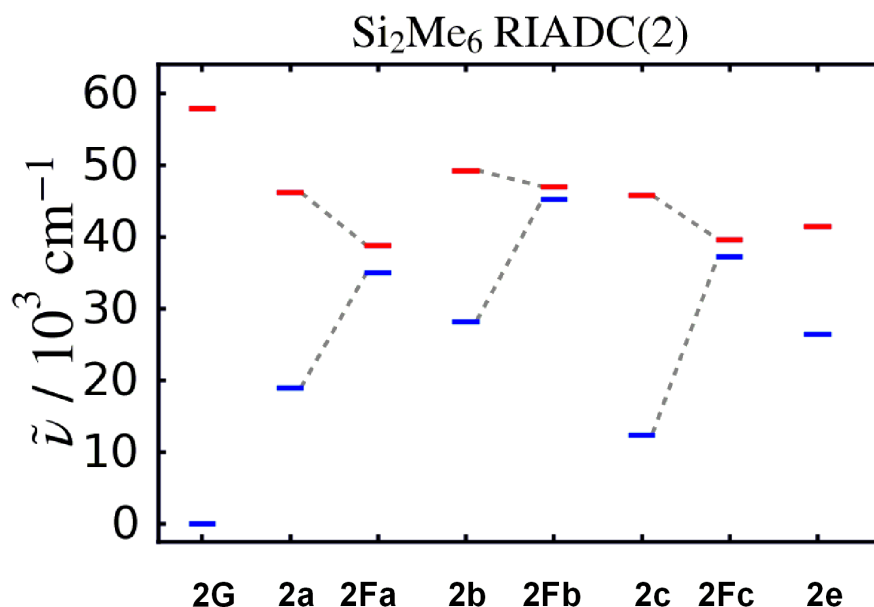


Figure 2.14: RIADC(2) plot of hexamethyldisilane ground state equilibrium structure and S₁ minima and funnels. S₀ energies are shown in blue and those of S₁ are in red.

mostly **2G**, but new products also appeared. These were the homolytic Si-Si cleavage product **17**, and the dimethylsilylene extrusion plus tetramethylsilane product **18**. When large (Si, C) kicks were given, a small portion of the optimizations returned to **17** or **18** or a new dissociation product: the methyl radical plus the pentamethyldisilyl radical Me₂Si₂Me₃ **19**.

Ground state optimization of **2Fb** with BLYP/6-31G* and CASSCF/6-31G* led back to the ground state equilibrium structure, **2G**. The set of stochastically minimally kicked structures generated from **2Fb** returned to **2G** with the CASSCF/6-31G* ground state optimizations. Upon CASSCF/6-31G* ground state optimization, the more strongly kicked structures mostly returned to **2G**, but also gave **18** or **19**. Finally, the large Si-C kicked set gave similar results with the addition of a new outcome, the ethane plus MeSiSiMe₃ product **20**.

Ground state optimization of **2Fc** with the CASSCF/6-31G* method led to **2G**. Minimally kicked structures also returned to **2G**, with the exception of one case where the dissociation product **17** was formed. The structures with larger kicks returned all the molecules to **2G**.

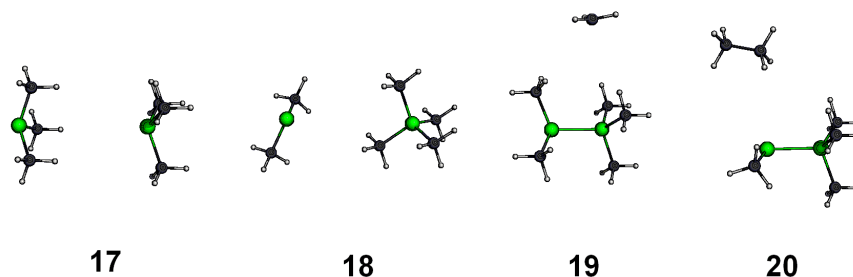


Figure 2.15: Ground state return products (**17-20**) from funnels resulting from the CASSCF ground state optimizations.

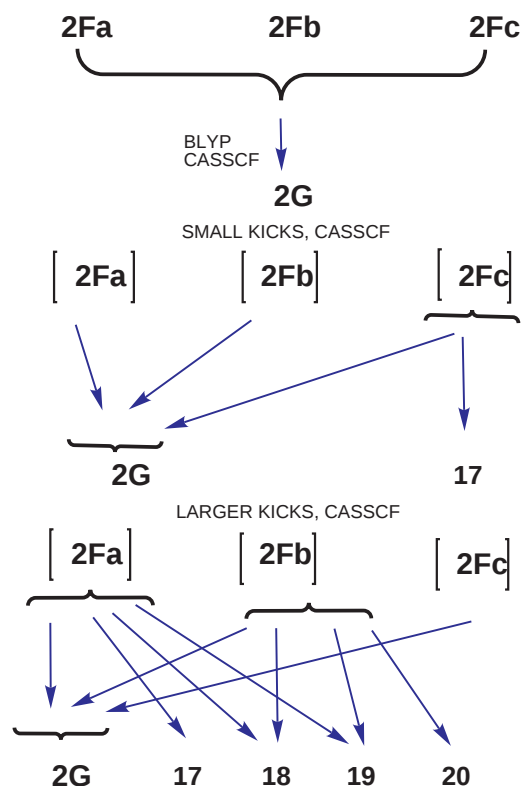


Figure 2.16: Ground state optimization results from funnel regions. Optimization method is given to the right of or above arrow.

2.3.2.4 Hexamethyldisilane Radical Anion Ground State Geometries

To further rationalize the excited state geometries obtained in section 2.3.2.1, ground state optimization of the anion was carried out with the RIUMP2/Def2-TZVP method. The structural changes that take place when the neutral species deals with an extra electron are similar to those

observed when the neutral species accommodates $\sigma\sigma^*$ excitation. Relaxed radical anion structures of **2** are shown in Figure 2.17.^a

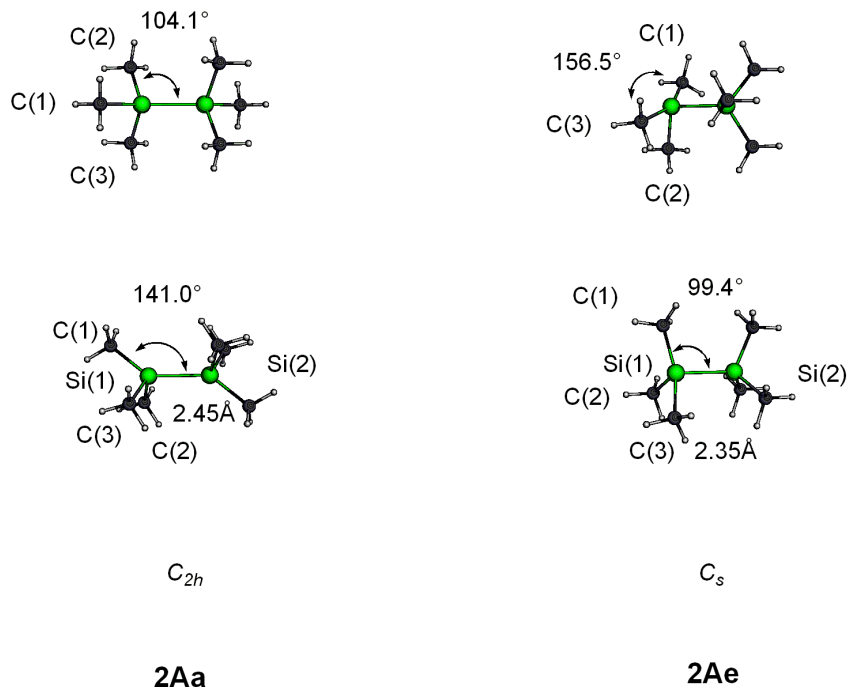


Figure 2.17: Ground state geometries obtained with the RIUMP2/Def2-TZVP method for the hexamethyldisilane radical anion, **2Aa** and **2Ae**.

Optimization of structures derived from the ground state equilibrium structure and **2a** led to a C_{2h} structure, **2Aa**. This structure was determined to be a minimum on the radical anion surface (lowest vibrational frequency 34.9 cm^{-1}). Optimization of the radical anion from the **2e** structure led to a similarly distorted minimum, **2Ae** (for which the lowest vibrational frequency was 22.5 cm^{-1}). The geometric parameters for these structures are given in Table 2.13.

Besides belonging to a higher symmetry group, the Si-Si bond of **2Aa** is less stretched (2.447 Å), than the RICC2 **2a** minimum, and has a wider $\text{C}(1)\text{Si}(1)\text{Si}(2)$ valence angle (141.0°). The **2Ae** structure has a much shorter Si-Si bond length (2.348 Å), and a slightly reduced $\text{C}(1)\text{Si}(1)\text{C}(3)$ valence angle (156.5°). At the RIUMP2/Def2-TZVP level, the **2Aa** structure is stabilized by

^a The hexamethyldisilane radical anion has a more diffuse (Rydberg) nature if diffuse basis functions are used in the open shell calculation, however, valence radical anions are found in the longer oligosilanes, even with diffuse basis functions, which are similar in character to the disilane structures found without diffuse functions.

Table 2.13: Minimum energy geometries (RIUMP2/Def2-TZVP) for ground state of the Si_2Me_6 radical anion.

Structure	Method	$\angle \text{CSiC}$ / deg	$\angle \text{CSiSi}$ / deg	SiSi / Å	SiC / Å
2Aa C_{2h}	RIUMP2/Def2-TZVP	99.3	141.0	2.447	1.957
		105.1	104.1		1.920
		99.3	104.1		1.920
		99.3	141.0		1.957
		105.1	104.1		1.920
		99.3	104.1		1.920
2Aa C_{2h}	RICC2/Def2-TZVP	99.3	141.4	2.449	1.957
		105.0	103.9		1.920
		99.3	103.9		1.920
		99.3	141.4		1.957
		105.0	103.9		1.920
		99.3	103.9		1.920
2Ae C_s	RIUMP2/Def2-TZVP	104.5	113.5	2.348	1.910
		106.2	113.6		1.902
		104.5	113.6		1.902
		156.5	99.4		1.990
		94.0	99.4		1.990
		94.0	106.5		1.947
2Ae C_s	RICC2/Def2-TZVP	106.4	113.5	2.344	1.903
		104.4	113.6		1.903
		104.4	113.6		1.911
		156.1	99.5		1.987
		94.1	99.5		1.987
		94.1	106.5		1.946

3 030 cm^{-1} , compared to **2Ae**. The RIUMP2 optimization of the radical anion starting from the **2b** structure led to the **2Aa** structure. The RIUMP2 optimization of the radical anion starting from the **2c** structure led to the **2Ae** structure.

For comparison purposes, the neutral and radical cation ground state structures were also calculated with the RIMP2/Def2-TZVP and RIUMP2/Def2-TZVP methods, Table 2.14. For the disilane radical cation, **2C**, the D_{3d} structure is a transition state and the minimum has D_3 symmetry, with a slightly lower symmetry due to methyl rotations. The lowest vibrational frequency for the minima are collected in Table 2.15. The radical cation geometry is similar to that of the Rydberg minimum **2d** (Table 2.9). The radical cation also is of D_3 symmetry and has a large

Si-Si bond at 2.666 Å (Table 2.14), slightly shorter than the Si-Si bond in **2d** (2.708 Å) but these structures were calculated with different methods, so the overall agreement is close.

Table 2.14: Neutral and radical cation ground state geometries (RIMP2/Def2-TZVP and RIUMP2/Def2-TZVP) for the Si₂Me₆.

Structure	$\angle$ CSiC / deg	$\angle$ CSiSi / deg	SiSi / Å	SiC / Å
2G <i>D</i> _{3d}	108.8	110.1	2.353	1.886
	108.8	110.1		1.886
	108.8	110.1		1.886
	108.8	110.1		1.886
	108.8	110.1		1.886
	108.8	110.1		1.886
2C <i>D</i> ₃	116.2	101.5	2.666	1.853
	116.2	101.5		1.853
	116.2	101.5		1.853
	116.2	101.5		1.853
	116.2	101.5		1.853
	116.2	101.5		1.853

Table 2.15: The lowest vibrational frequency for the stationary points **2G**, **2A**, and **2C** in Si₂Me₆.

Structure	Symmetry	Method	Lowest Frequency Vibration
2Aa	<i>C</i> _{2h}	RIUMP2/Def2-TZVP	34.9
2Aa	<i>C</i> _{2h}	RICC2/Def2-TZVP	27.3
2Ae	<i>C</i> _s	RIUMP2/Def2-TZVP	22.5
2Ae	<i>C</i> _s	RICC2/Def2-TZVP	18.5
2G	<i>D</i> _{3d}	RIMP2/Def2-TZVP	12.0
2C	<i>D</i> ₃	RIUMP2/Def2-TZVP	33.0

2.3.2.5 Hexamethyldisilane Natural Hybrid Orbital Analysis

Unless otherwise noted, the natural hybrid orbital (NHO) analysis is done for orthogonalized NHOs. These orbitals are built from orthogonal natural atomic orbitals NAOs as discussed in Chapter 1. Natural bond orbitals (NBOs) are likewise composed of natural hybrid orbitals. If the NHOs are constructed from NAOs for which the final interatomic orthogonalization step has not been taken, *i.e.*, pre-orthogonalized (pNAOs), these orbitals are referred to the pre-orthogonalized

NHOs (pNHOs). Just as the pNAOs of one atom are orthogonal to other pNAOs centered on the same atom, but not necessarily to the pNAOs of other atoms, the pNHOs centered on one atom are orthogonal, but not necessarily to the pNHOs centered on neighboring atoms. The orthogonalized NHOs have so called delocalization tails which have to be introduced in order to make them orthogonal to one another. In some ways the pre-orthogonalized orbitals are more physically meaningful as they have not been altered in order to insure orthogonality. These orbitals also have the interesting property that the size of the pNHO orbital overlap (which can also be visually inspected) is directly related to the matrix element between pNHOs.¹⁶⁷ For rigorous solutions of the approximate HF and NBO equations however, orthogonal atomic orbitals must be used.⁷⁰ The orthogonalized NHOs are default orbitals in the NBO 5.9 program.

The natural hybrid orbital (NHO) analysis of S_1 density of the Si-Si bond stretch minimum, **2a**, shows that electron density is transferred from the Si-Si bond to the Si(1)-C(1) bond upon excitation. The NHO pointing from Si(1) to Si(2) gained p character (sp^4) and the NHO pointing from Si(1) to C(1) gained s character, resulting in sp^2 hybridization (Figure 2.18). The NHOs on Si(2) are equivalent according to the C_i symmetry of the molecule. The main natural resonance structure for the S_1 density is the covalent structure, but resonance structures which involve a lone pair on Si(1) as well as a lone pair on C(1) and the symmetry equivalent resonance structure with lone pairs on Si(2) and C(6), contribute to the description of the S_1 density as well.

The NHO analysis of the **2a** transition state (structure obtained with the RICC2/TZVP method) shows almost equal occupation ($0.67 e^-$) in the hybrid pointing from Si(1) to C(2) and in the more highly p hybridized (sp^{31}) orbital ($0.69 e^-$) between the Si-Si bond (Figure 2.19). The RICC2/TZVP **2a** structure also shows a preference for the dimethylsilylene extrusion type resonance structure as a secondary contributor to the description of the S_1 density.

The C-Si bond stretch minimum, **2b**, also shows rehybridization of the valence orbitals. The NHO pointing from Si(1) to Si(2) has gained s character to give sp^2 hybridization and the NHO pointing from Si(1) to C(1) is no longer hybridized and is of pure p character, with the former orbital gaining electron occupation and the latter orbital losing electron occupation, Figure 2.20. Natural

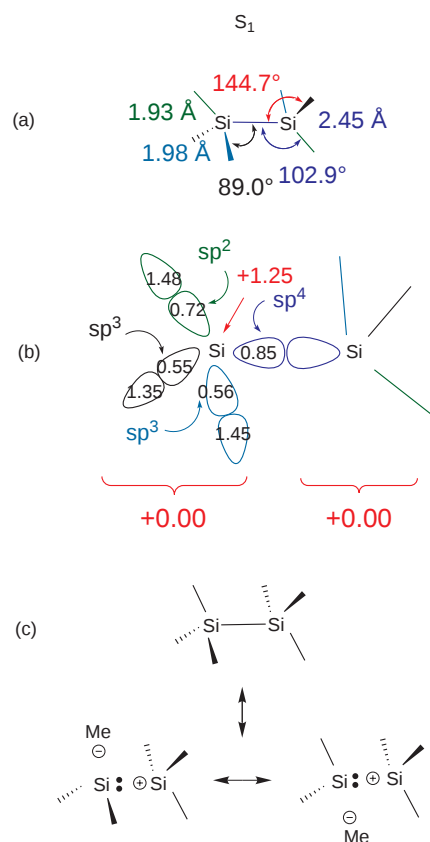


Figure 2.18: NHO analysis for **2a** (PBE0/TZVP structure) S_1 density, selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method. Symmetry equivalent densities, hybridizations and resonance structures not shown.

resonance structures that describe this density are of the covalent nature as well as structures which place a lone pair on Si(1) and C(1).

NHO analysis of the diffuse Si-Si bond stretch minimum **2c** shows that electron density is moved from the Si-Si bond to Si(1) upon excitation. Si(1) has an essentially pure p orbital pointing towards Si(2) and a diffuse sp orbital (labeled as a Rydberg in the NHO output) pointing in the opposite direction. This NHO mainly consists of the 4s Si atomic orbital and has an occupation of 0.12 e^- . Natural population analysis partitions 0.62 e^- to Rydberg orbitals with 0.20 e^- on Si(1) and 0.08 e^- on Si(2) (Figure 2.21).

The NHO analysis of the polarization minimum **2e** also shows Rydberg contributions to the excited state bonding description. In this case however, 4s and some 4p character is mixed

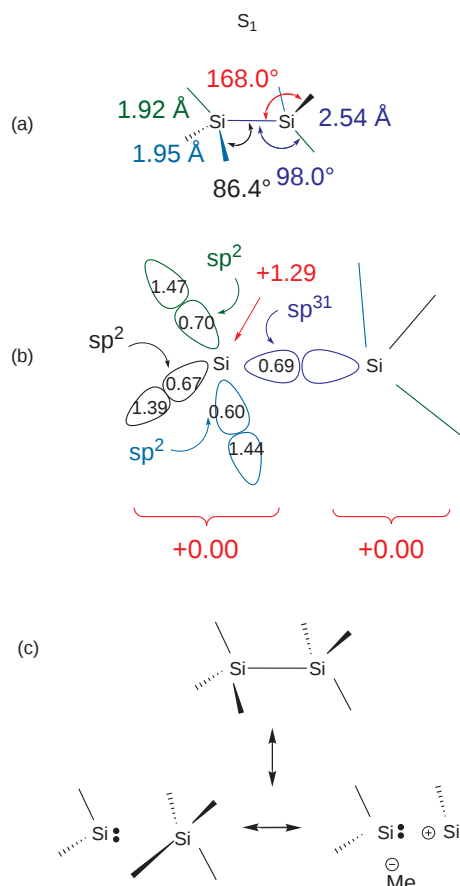


Figure 2.19: NHO analysis for **2a** S_1 density of the transition state (RICC2/TZVP) structure, selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

into all hybrid orbitals on Si(1) (Table 2.18). For the RIADC(2)/Def2TZVP-mD **2e** structure, these include a p orbital pointing towards Si(2), sp^2 hybridized orbitals pointing to C(1) and C(3), and an sp^3 hybridized orbital pointing towards C(2). There is also a diffuse sp hybridized orbital in a direction that bisects the angle formed by the Si(1)-C(1) and Si(1)-C(3) bonds. This NHO population analysis shows occupation ($0.86 e^-$) is lowered in the Si-Si bond and occupation increases in the diffuse orbital ($0.10 e^-$) and the sp^2 Si(1) hybrids ($0.60 e^-$) upon excitation, Figure 2.28. The natural resonance structures that describe **2e** are the covalent structure, a zwitterionic structure with a positive charge on Si(1) and negative charge on Si(2), a structure with a lone pair on C(3), a resonance structure with broken C(3)-Si(1) and Si(1)-Si(2) bonds and a lone pair on both C(3) and

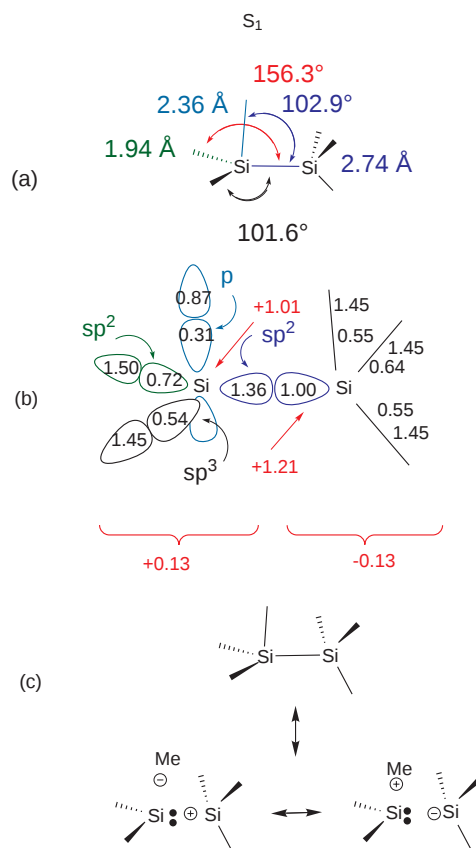


Figure 2.20: NHO analysis for **2b** S_1 density (B3LYP/TZVP structure), selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

Si(1), along with the C_s symmetry equivalent resonance structures. The polarization minimum **2e** shows the largest SiMe₃ fragment polarization (where total NAO charges have been summed over SiMe₃ fragments and total fragment charges are compared). For the polarization minimum **2e** the SiMe₃ fragment charges ranged from ± 0.32 to ± 0.22 depending on the optimization method.

As the NHO analysis for **2e** (RIADC(2)/Def2TZVP-mD structure) is unusual compared to the other **2** minima, more of the **2e** minima (optimized with different methods) were analyzed. The analysis of the RICC2/TZVP structure gave similar results compared to the RIADC(2)/Def2TZVP-mD structure and are shown in Figure 2.23. Notably, the extra nonbonding orbital on Si(1) has a higher occupation ($0.18 e^-$), the Si(1) hybrids pointing to C(1) and C(3) have lower occupations and Si(1) now has a smaller natural charge, +1.19.

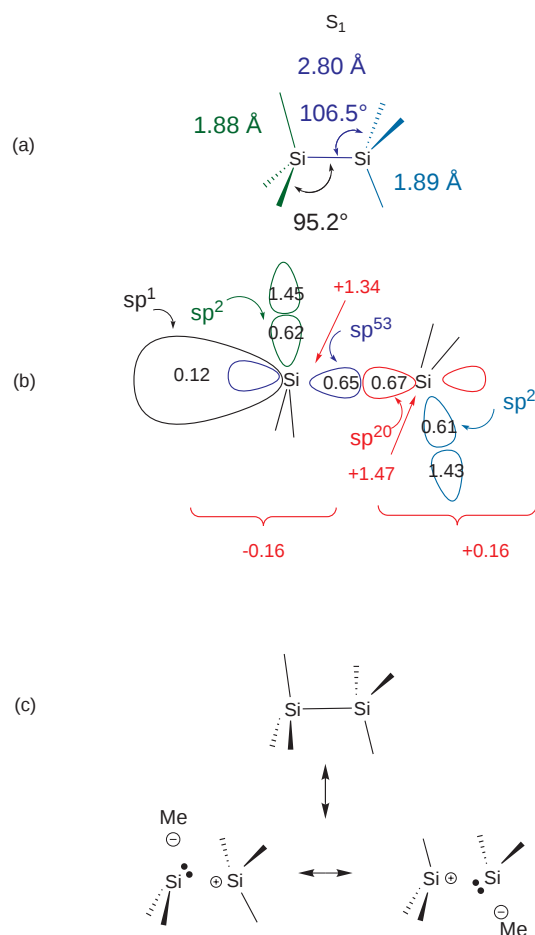


Figure 2.21: NHO analysis for **2c** S_1 density, selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

The NHO analysis for the **2e** TDDFT structures show a more pronounced shift in occupation from the Si(1) nonbonding orbital ($0.09 e^-$), Figure 2.24, to the sp^2 hybrids of Si(1) pointing to C(1) and C(3) atoms. There is still a large natural charge difference on Si atoms, Si(1) having a natural charge of +1.14 and Si(2) a natural charge of +1.60. The composition of the extra nonbonding orbital found for the **2e** minima is tabulated in Table 2.16. The actual NAO% composition of the nonbonding orbital varies between the different minima, but in general, this orbital is composed mainly of 4s, $4p_z$ and $3d_{x^2-y^2}$ and to a lesser extent $3d_{z^2}$ Si NAOs. In all cases, the total 4s and 4p character is greater than the total 3d character.

The optimized structures for the hexamethyldisilane radical anions **2Aa** and **2Ae**, were also

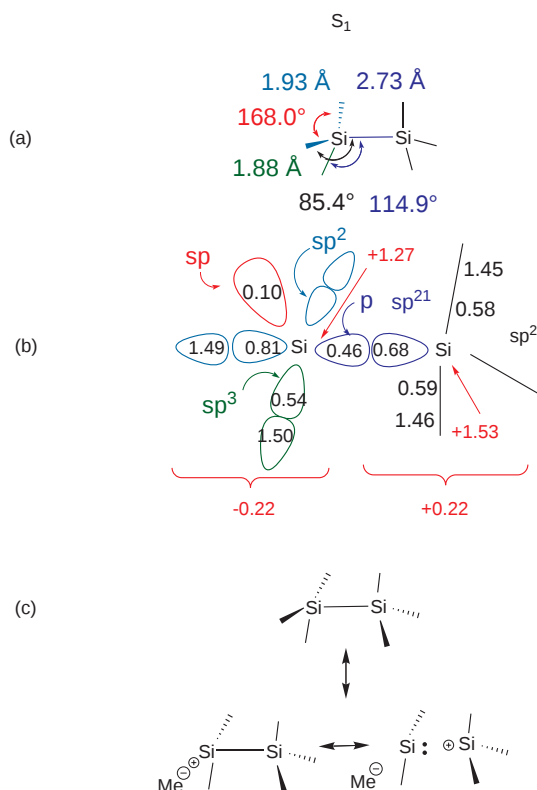


Figure 2.22: NHO analysis of the S_1 density of the **2e** structure (RIADC(2)/Def2TZVP-mD), selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

analyzed. The NHO analysis of the occupation numbers for **2Aa** shows that the anion corresponds to an having an electron in a (three-electron) double bond. The UHF/6-311G(d,p) density for the **2Aa** structure is analyzed in Figure 2.25 and the UMP2/6-311G(d,p) density is shown in Figure 2.26.

The UHF/6-311G(d,p) density analysis of **2Aa** shows that the double bond resonance structure has lower weight than from the natural resonance analysis of the ground state radical anion UMP2 density (Figure 2.26). Also, a different hybridization scheme is created for the α electron UMP2 density. This involves an extra orbital of sp^7 hybridization. This orbital is mainly made of Si 3s, 3p and 4p orbitals (Table 2.17). There is also an 11% contribution from the 3d orbitals. The nonbonding hybrid orbital has an occupation of 0.41 α electrons. By symmetry there are two sp^7



orbitals, therefore they describe a majority of the electron density which was added to the neutral molecule **2**.

The NHO UMP2 density analysis is very similar to the UHF density analysis for **2Ae**. There is a lower electron occupation in the nonbonding orbital (0.88 e⁻). This nonbonding orbital has a small (5%) contribution from 4s and 4p orbitals and no contribution from 3d orbitals. The NHO

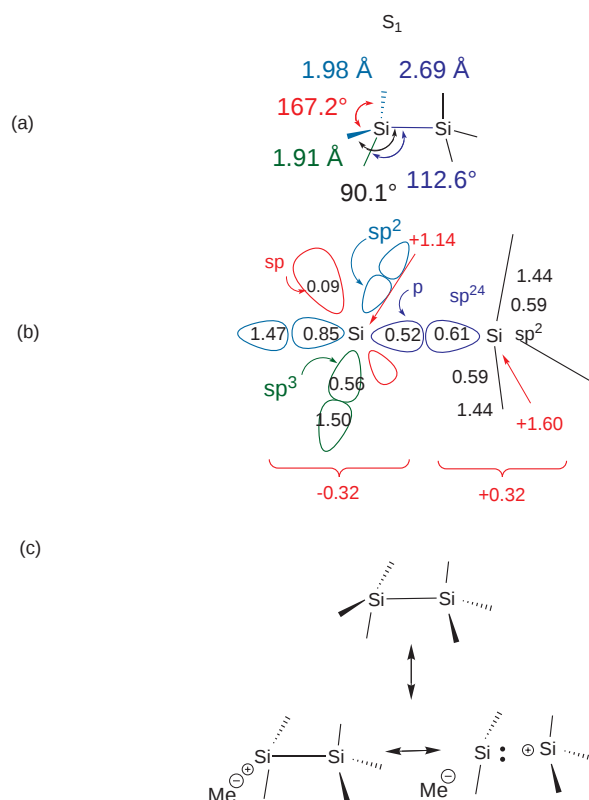


Figure 2.24: NHO analysis of the S_1 density of the **2e** structure (BHLYP/TZVP), selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

pointing from Si(1) to C(1) has larger 4s and 4p orbital contributions (10 and 18% respectively). The hybrid pointing from Si(1) to C(3) is equivalent by symmetry.

NHO analysis of the polarization minimum shows that extra Si 4s and 4p orbitals contribute to the Si(1) hybrid orbitals. This gives the Si(1) atom hypervalent character as five hybrid orbitals have significant occupation in the S_1 state. These hybrids have additional 3d character as well. Starting from hybrid orbitals made of purely 3s and 3p atomic orbital contributions, a total of 100 and 300 % s and p character is expected when the atomic orbital contributions for the hybrid orbitals on this atom are summed. For the Si(1) atom in the RIADC(2)/Def2-TZVP-mD **2e** minimum, however, there is a higher percentage of s character (139%), p character (326%) and 3d contribution (36.1%) to the overall hybridization of Si(1). These percentages exceed the normal Si hybridization values (of 100 and 300%) as five hybrid orbitals on Si(1) now need to be taken into

Table 2.16: The polarization minimum **2e** nonbonding orbital composition. NAO orbitals with a weight exceeding 1 % are included below. NAO type (valence or Rydberg orbital) is defined by the principal quantum number. NHO analysis done with the CIS/6-311G(d,p) method.

Structure	%	NAO	Type
RIADC(2)/Def2TZVP-mD	1.1	s	Val (3s)
	37.9	s	Ryd (4s)
	3.8	p_x	Val (3p)
	23.9	p_z	Ryd (4p)
	25.5	$d_{x^2-y^2}$	Ryd (3d)
	6.4	d_{z^2}	Ryd (3d)
RICC2/TZVP	5.4	s	Val (3s)
	16.1	s	Ryd (4s)
	21.3	p_x	Val (3p)
	5.2	p_z	Val (3p)
	23.4	p_z	Ryd (4p)
	1.1	d_{xz}	Ryd (3d)
	18.7	$d_{x^2-y^2}$	Ryd (3d)
	8.4	d_{z^2}	Ryd (3d)
BHLYP/TZVP	30.6	s	Ryd (4s)
	4.0	p_x	Val (3p)
	29.5	p_z	Ryd (4p)
	24.2	$d_{x^2-y^2}$	Ryd (3d)
	9.7	d_{z^2}	Ryd (3d)

account (Table 2.18).

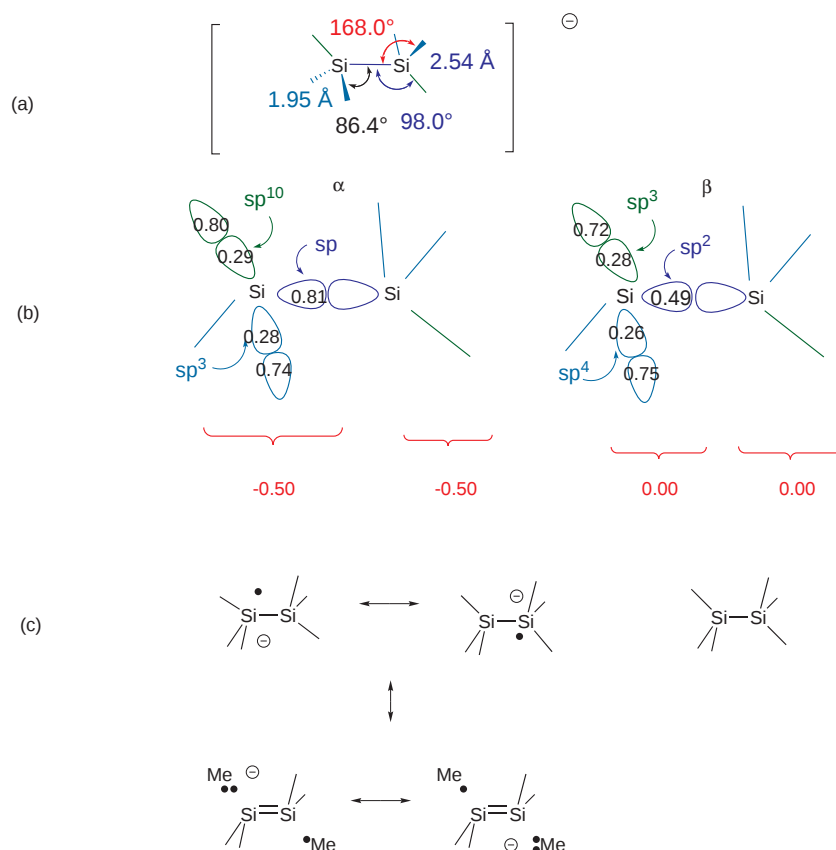


Figure 2.25: NHO analysis of the UHF density for the radical anion **2Aa** (RIUMP2/Def2-TZVP structure), selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the UHF/6-311G(d,p) method.

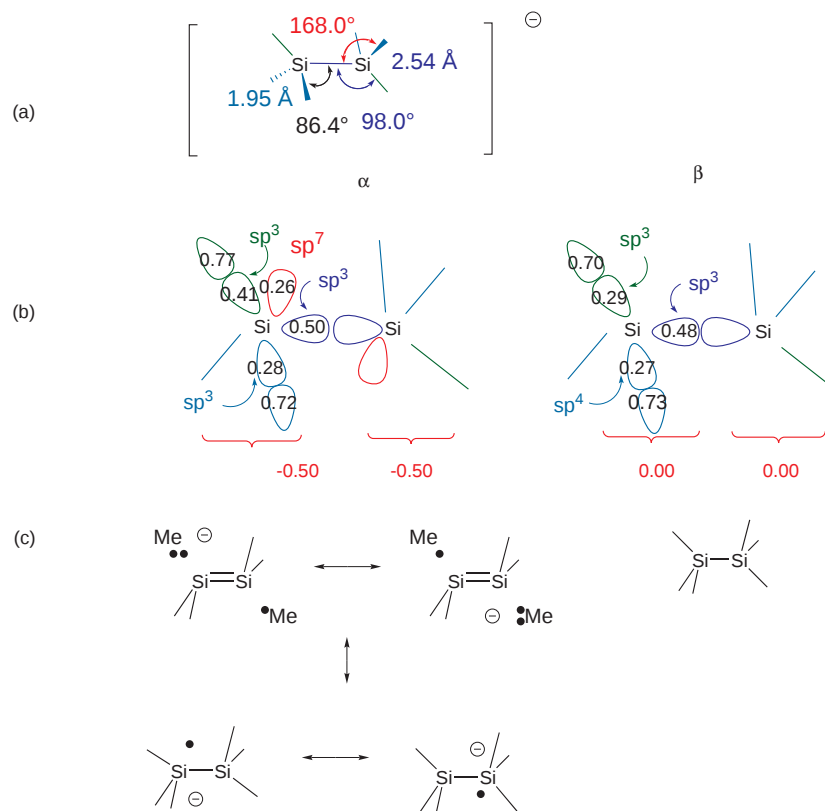


Figure 2.26: NHO analysis of the UMP2 density for the radical anion **2Aa** (RIUMP2/Def2-TZVP structure), selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the UMP2/6-311G(d,p) method.

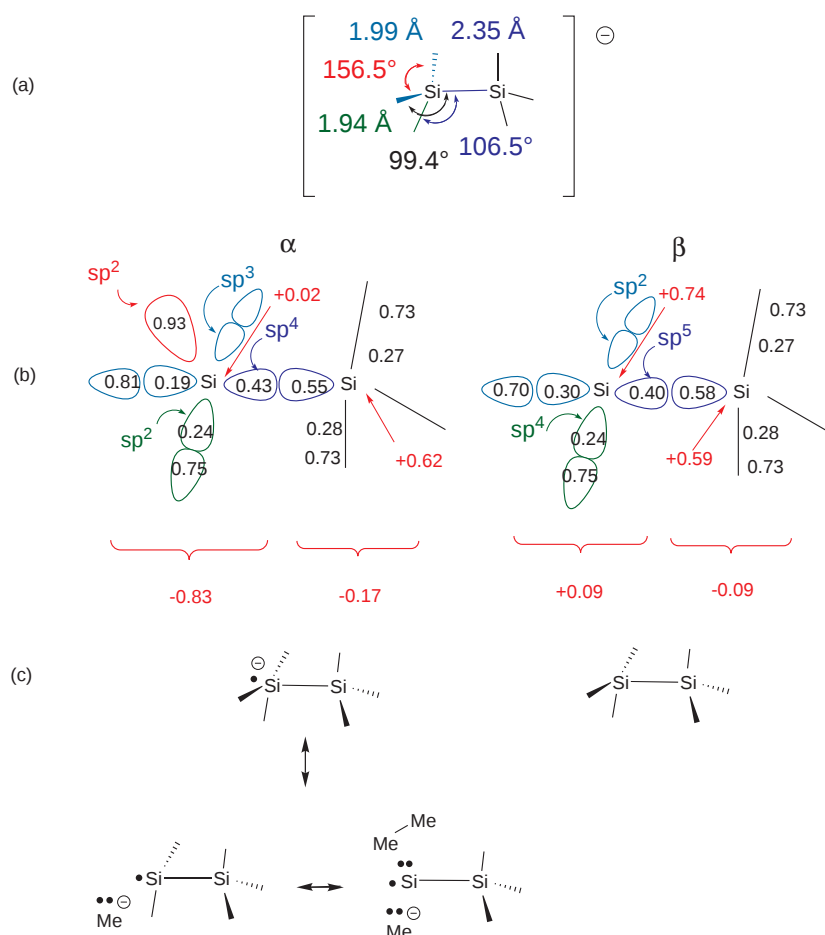


Figure 2.27: NHO analysis of the UHF density for the radical anion **2Ae**, selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the UHF/6-311G(d,p) method.

Table 2.17: The **2Aa** and **2Ae** nonbonding orbital composition (structures obtained with the RIUMP2/Def2-TZVP method). NAO orbitals with a weight exceeding 1 % are included below. NAO type (valence or Rydberg orbital) is defined by the principal quantum number. NHO analysis done with the UMP2/6-311G(d,p) method for the **2Aa** minimum and with UHF/6-311G(d,p) method and UMP2/6-311G(d,p) methods for **2Ae**.

Structure	%	NAO	Type
2Aa UMP2	8.5	s	Val (3s)
	2.2	s	Ryd (4s)
	1.0	p_x	Ryd (4p)
	39.7	p_z	Val (3p)
	36.3	p_z	Ryd (4p)
	6.6	d_{xz}	Ryd (3d)
	4.0	$d_{x^2-y^2}$	Ryd (3d)
2Ae UHF	32.3	s	Val (3s)
	1.4	s	Ryd (4s)
	5.4	p_x	Val (3p)
	56.7	p_z	Val (3p)
	3.7	p_z	Ryd (4p)
2Ae UMP2	33.2	s	Val (3s)
	1.3	s	Ryd (4s)
	5.6	p_x	Val (3p)
	55.8	p_z	Val (3p)
	3.6	p_z	Ryd (4p)

Table 2.18: Si(1) hybridization for the **2e** minimum in Si₂Me₆. NBO analysis done with the CIS/6-311G(d,p) method.

Structure	NBO analysis	%s	%p	%d
2e RIADC(2)/Def2TZVP-mD	CIS/6-311G(d,p)	139.1	326.7	36.1
2e RICC2/TZVP	CIS/6-311G(d,p)	129.2	328.1	42.7
2Ae RIMP2/Def2TZVP	MP2/6-311G(d,p)	124.8	352.0	23.4
2Ae RIMP2/Def2TZVP	HF/6-311G(d,p)	126.0	346.1	27.9

2.3.2.6 Hexamethyldisilane Vertical Emission

The vertical emission energy (E_{VE}) of each relaxed S₁ stationary point was calculated with the B3LYP/Def2-TZVP method (Table 2.19).

Table 2.19: Vertical emission energies and oscillator strengths (B3LYP/Def2-TZVP) for stationary points on S₁ surface for various TDDFT and ab initio methods for **2**. S₁ site distortion and Stokes shift energies, E_{SD} and E_{SS} , respectively, are calculated with respect to the $\sigma\pi^*$ state of the ground state structure, optimized with a similar method as indicated in the Method column.

Structure	Method ^a	State	E_{VE} / cm ⁻¹	f	E_{SD} / cm ⁻¹	E_{SS} / cm ⁻¹	S ₁ Dipole /Debye
2a	PBE0	1A _u $\sigma\sigma$	25 470	0.044	9 590	27 310	0.00
2a	B3LYP	1A _u $\sigma\sigma$	25 430	0.041	9 370	27 230	0.00
2a	BHLYP	1A _u $\sigma\sigma$	27 500	0.077	9 740	25 380	0.00
2a	RIADC(2)	1A _u $\sigma\sigma$	24 360	0.073	9 760	28 480	0.00
2a	RICC2	1A _u $\sigma\sigma$	24 600	0.068	9 780	28 250	0.00
2b	B3LYP	2A $\sigma\mu^*$	17 100	0.003	8 890	35 560	2.79
2c	B3LYP	2A $\sigma\sigma^*$	29 960	0.049	11 100	22 700	3.26
2d	B3LYP ^b	2A ₁ $\sigma 4s$	28 470	0.000	7 530	16 390	0.02
2e	PBE0	2A' $\sigma\sigma^*$	17 700	0.005	13 780	35 090	3.58
2e	B3LYP	2A' $\sigma\sigma^*$	17 140	0.005	13 680	35 520	3.60
2e	BHLYP	2A' $\sigma\sigma^*$	16 620	0.008	13 860	36 260	3.23
2e	RIADC(2)	2A' $\sigma\sigma^*$	13 780	0.017	12 990	39 060	1.88
2e	RICC2	2A' $\sigma\sigma^*$	14 880	0.014	13 320	37 970	2.32

^a The TZVP basis set was used to obtain S₁ stationary points in conjunction with methods listed.

^b This state is of high Rydberg character and thus calculations were done using the aug-cc-pVDZ basis set.

While the BHLYP and ab initio excited state vibrational calculations for the Si-Si bond stretch minimum, **2a**, indicated the S₁ stationary points to be transition states, the calculated emission energies when compared to the emission energies of Si-Si bond stretch minimum in longer

oligosilanes follow the experimental trend of decreasing emission energy with decreasing chain length.¹¹⁶ The first excited state ($1A_u$) of structure **2a** corresponds to a HOMO (a_g) to LUMO (a_u) transition ($\sigma\sigma^*$). The calculated vertical emission energy is 25 470 cm^{-1} , computed with the B3LYP/Def2-TZVP method for the minimum obtained with TDDFT using the PBE0 functional and TZVP basis set. There is a large energy gap (15 050 cm^{-1}) between S_1 and S_2 which is typical for the excited state minima in this work. The electronic transition dipole moment between the ground and the $1A_u$ state for **2a** lies along the Si-Si bond. While the S_1 state corresponds mainly to a transition between Si-Si bonding to Si-Si antibonding orbitals (Figure 2.29), the molecular orbital coefficients of the hybrid orbitals between atoms Si(1) and C(1) and Si(2) and C(6) have significant weight in the σ^* orbital but are in the plane of symmetry for which the nature of state is labeled. The RICC2/TZVP **2a** structure gave a very similar NHO coefficient description of the MOs (Figure 2.30).

The canonical molecular orbitals involved in the lowest electronic excitation for the minima **2a** are shown in Figure 2.31. The nature of the excited state S_1 minima is always described by a single excitation from the HOMO to LUMO. The **2a** structure has a considerable site distortion energy of 9 590 cm^{-1} . The calculated Stokes shift for the **2a** minimum is 27 310 cm^{-1} . The S_1 dipole moment for this state is zero.

The C-Si bond stretch minimum (**2b**), found to be a S_1 minimum with the TDDFT B3LYP/TZVP method, has an unusual HOMO which is maximized on the stretched Si(1)-C(1) bond. The LUMO is mainly located between the silicon atoms as shown in Figure 2.31. This excited state is of $\sigma\mu^*$ nature, when the local planes of symmetry are assigned as those formed by the C(1)Si(1)Si(2) and Si(1)Si(2)C(6) atoms (Figure 2.32).

The vertical emission energy of **2b** calculated with B3LYP/Def2-TZVP method is 17 100 cm^{-1} , as shown in Table 2.19. This molecule has a slightly smaller site distortion energy (8 890 cm^{-1}) than **2a**, but has a larger Stokes shift (35 560 cm^{-1}) due to a greater ground state destabilization at the relaxed S_1 geometry. This can be seen in Figure 2.33 which shows energies of the S_1 minima and their respective ground states relative to the $\sigma\pi^*$ state of the ground state equilibrium structure

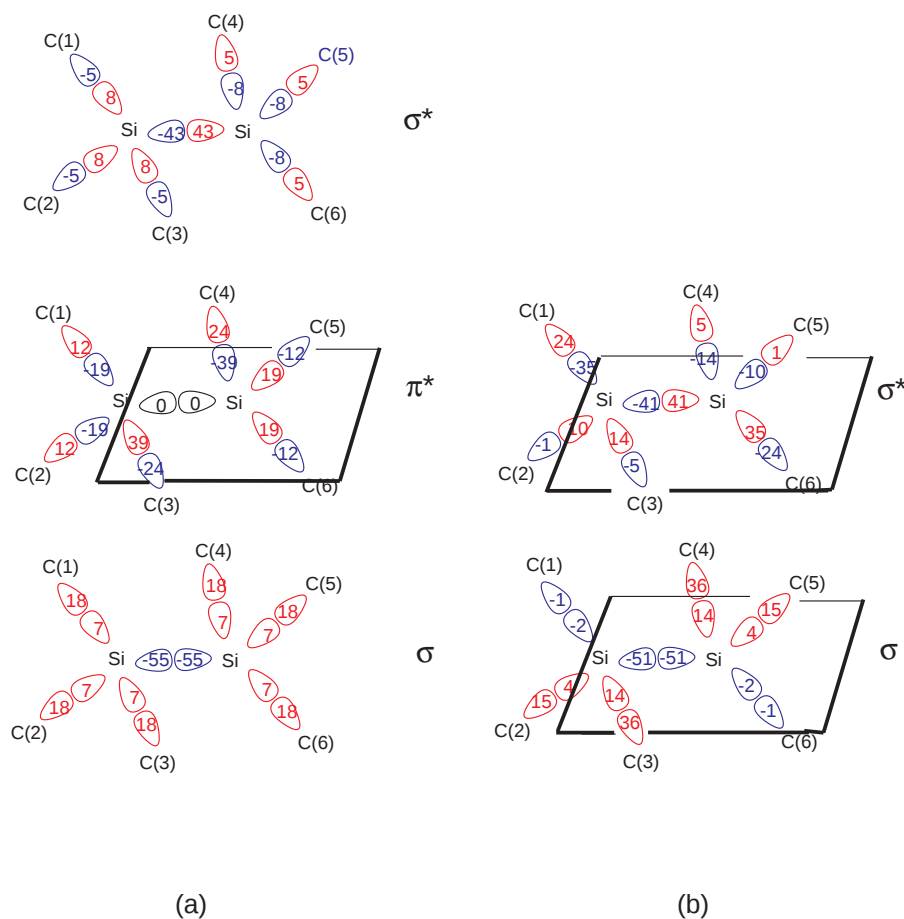


Figure 2.29: Molecular orbitals of **2G**, (a), and **2a**, (b), expressed in the NHO basis. NHO coefficients are shown multiplied by 100. NHO coefficients were obtained with the HF/6-311G(d,p) method.

2G. The S_1 state of **2b** has a dipole moment of 2.79 Debye and a weak S_0 - S_1 oscillator strength of 0.003.

The structure **2c**, the diffuse Si-Si bond stretch minimum, has the largest excitation energy (29 960 cm^{-1}) of the minima when calculated with the B3LYP/Def2-TZVP method. This state is of $\sigma\sigma^*$ nature, as the NHOs on each methyl group have the same sign and amplitude (Figure 2.34). The diffuse Si-Si bond stretch minimum has a relatively sizeable S_0 - S_1 oscillator strength of 0.049 and a large S_1 dipole moment of 3.3 Debye. The transition dipole moment lies along the Si-Si bond or z axis. The structure **2c** has a large site distortion energy of 11 100 cm^{-1} , but a relatively small Stokes shift of 22 700 cm^{-1} . This valence state no longer represents S_1 if diffuse functions are used,

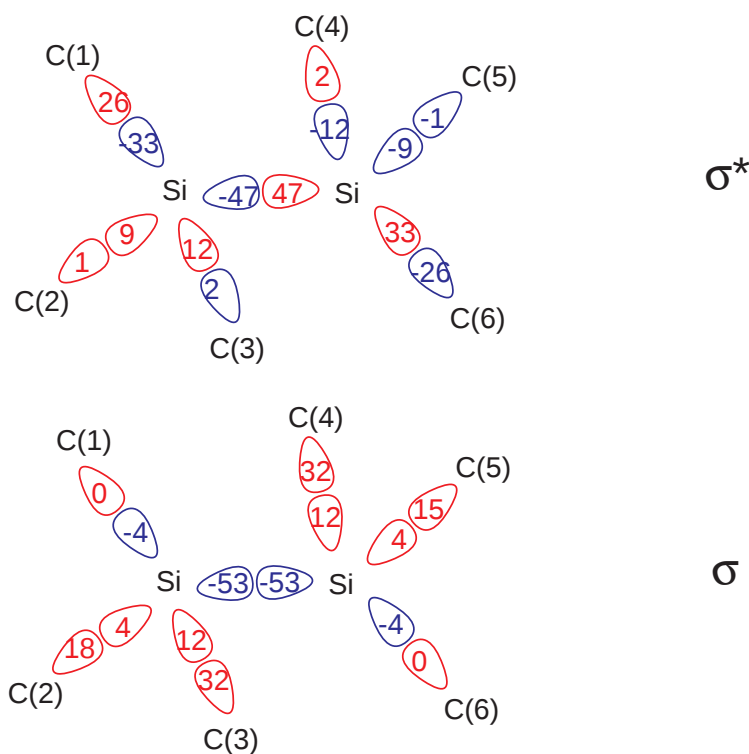


Figure 2.30: Molecular orbitals of **2a** (RICC2/TZVP structure), expressed in the NHO basis. NHO coefficients are shown multiplied by 100. NHO coefficients were obtained with the HF/6-311G(d,p) method.

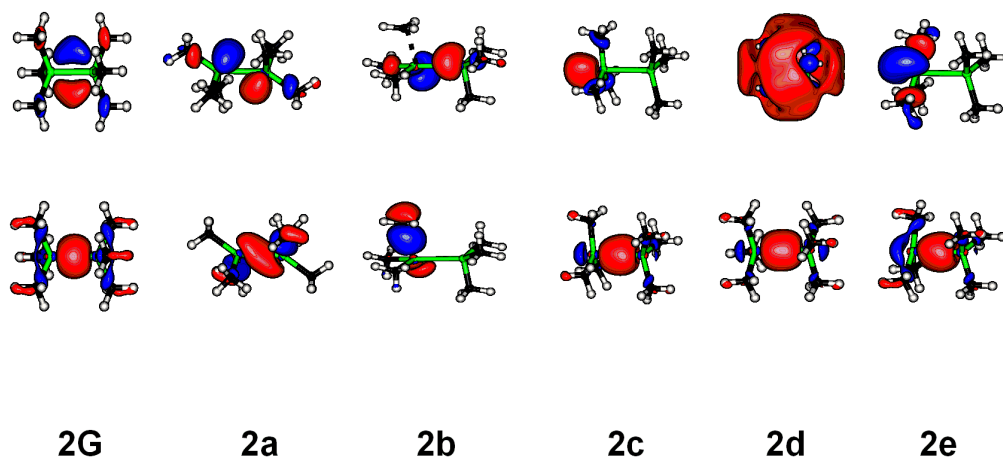


Figure 2.31: HOMO and LUMO for **2a-e** relaxed S_1 structures. The σ and π^* orbitals are shown for **2G**. Orbitals (B3LYP/Def2-TZVP) are plotted on the 0.06 isodensity contour value, with the exception of the LUMO orbital of the Rydberg minimum, **2d**, for which the 0.014 isodensity contour was used.

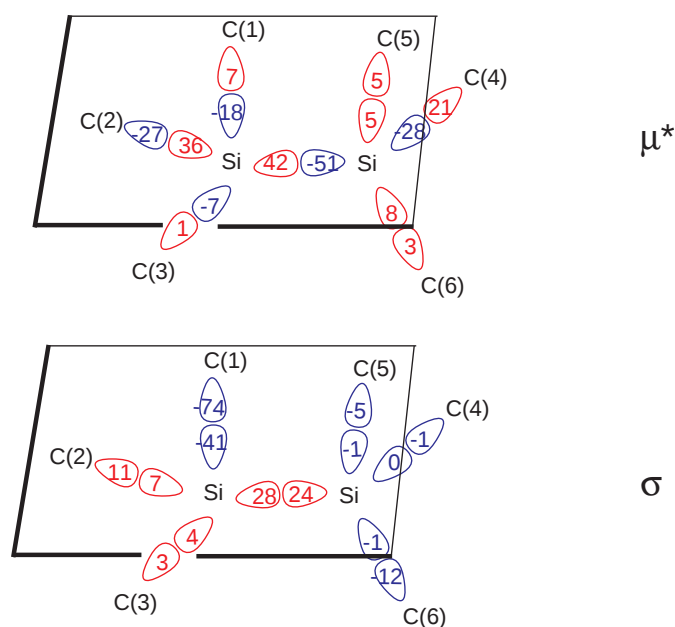


Figure 2.32: Molecular orbitals of **2b** expressed in the NHO basis. NHO coefficients are shown multiplied by 100. NHO coefficients were obtained with the HF/6-311G(d,p) method.

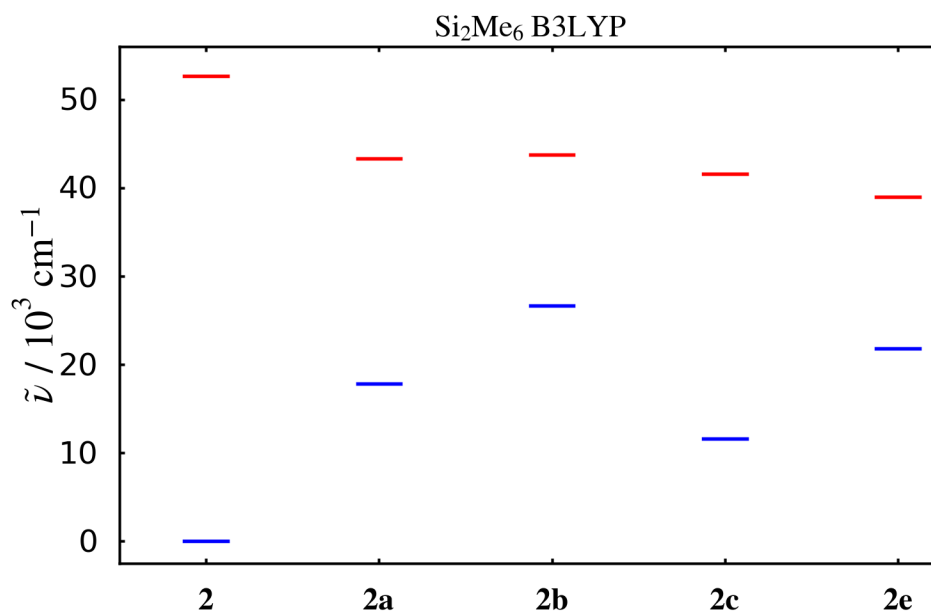


Figure 2.33: S_0 (blue) and S_1 (red) energies of **2** valence S_1 minima relative to **2G**. Structures **2G** and **2a**, **2b**, **2c**, and **2e** were optimized with the B3LYP/TZVP method and the relative energies are calculated with the B3LYP/Def2-TZVP method.

as S_1 is replaced by a Rydberg excited state.

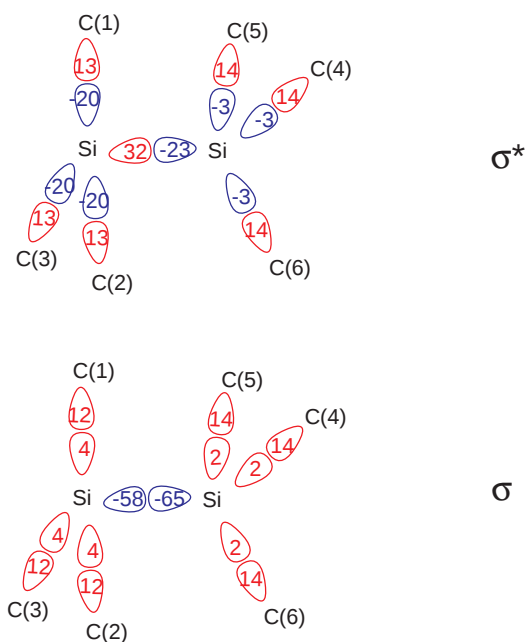


Figure 2.34: Molecular orbitals of **2c** expressed in the NHO basis. NHO coefficients are shown multiplied by 100. NHO coefficients were obtained with the HF/6-311G(d,p) method.

If the diffuse Si-Si bond stretch minimum **2c** structure is optimized with diffuse functions, the structure changes from C_3 to D_3 symmetry to give **2d**, a Rydberg minimum, where the relaxed structure has similar geometrical parameters to the cation (**2C**). The large orbital in Figure 2.31 is of 4s nature. This state has a zero transition dipole moment and a negligible S_1 dipole moment. The site distortion is $7\,530\text{ cm}^{-1}$ and the calculated Stokes shift is $16\,390\text{ cm}^{-1}$.

The polarization minimum **2e** structure gives different vertical emission energies depending on the S_1 optimization method. TDDFT S_1 relaxed structures give vertical emission energies (calculated with the B3LYP/Def2TZVP method) from $16\,620\text{ cm}^{-1}$ (BHLYP/TZVP structure) to $17\,700\text{ cm}^{-1}$ (PBE0/TZVP structure). **2e** structures optimized with ab initio methods gave lower emission energies (calculated with the B3LYP/Def2TZVP) of $13\,780\text{ cm}^{-1}$ for the RIADC(2)/TZVP structure and $14\,880\text{ cm}^{-1}$ for the RICC2/TZVP structure. On the other hand, the nature of the excited state is similar for all methods and involves excitation from the HOMO which is localized on the Si-Si bond to the LUMO, which is localized between the C(1)-Si(1) and Si(1)-C(3) bonds (Figure 2.31). The expression of these orbitals in the NHO basis is seen in Figure 2.36. When the

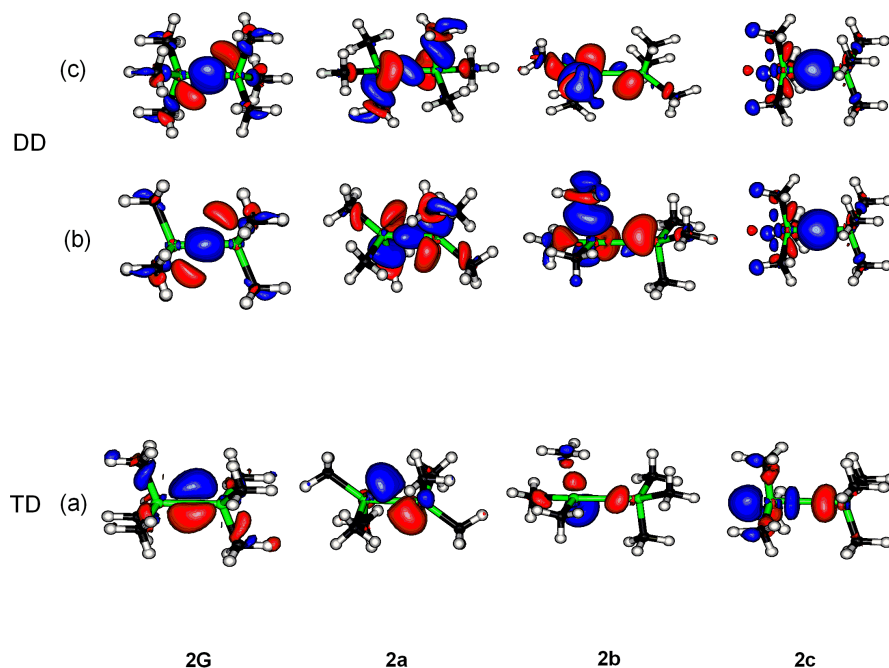


Figure 2.35: The S_0 - S_1 transition density (TD), (a), and S_0 - S_1 difference density (DD), (b) and (c), for **2G** as well as for **2a-c** relaxed S_1 structures obtained from (a) B3LYP/TZVP S_1 optimization and (b) RIADC(2)/Def2TZVP-mD S_1 optimization. The vantage point has been rotated for (c) with respect to (a) and (b). MOs are plotted on the ± 0.06 isodensity contour value, the TD and DD is plotted on the ± 0.004 isodensity contours, and all are calculated with the CIS/6-31G(d) method.

MOs are expressed in the NHO basis is becomes clear that the excitation is of the $\sigma\sigma^*$ nature, as a plane of symmetry exists between the C(2), Si(1), Si(2) and C(6) atoms. Differences between the polarization minima can be seen in the NHO analysis of the hybridization and the NHO occupancies in the S_1 state (section 2.3.2.5).

The structure **2e** is referred to as a polarization minimum as this it has the largest S_1 dipole moment (3.60 Debye, Table 2.19) of all **2** minima. The value of the S_1 dipole moments for **2e** does vary however. The TDDFT S_1 structures have larger S_1 dipole moments (~ 3 Debye) than the structures obtained with the ab initio methods (~ 2 Debye). The TDDFT structures have weaker S_0 - S_1 oscillator strengths ranging from 0.005 (PBE0/TZVP structure) to 0.008 (BHLYP/TZVP structure) and the ab initio minima have larger S_0 - S_1 oscillator strengths, 0.014 (RICC2/TZVP structure) and 0.017 (RIADC(2)/TZVP structure). This weak transition is polarized along the Si-

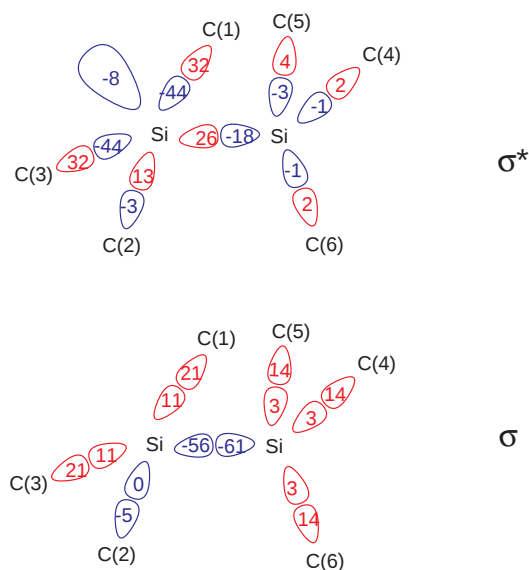


Figure 2.36: Molecular orbitals of **2e** (RICC2/TZVP structure) expressed in the NHO basis. NHO coefficients are shown multiplied by 100. NHO coefficients were obtained with the HF/6-311G(d,p) method.

Si bond. The ab initio minima also have slightly smaller site distortion energies, e.g., 13 780 cm^{-1} for the **2e** PBE0/TZVP structure versus 12 990 cm^{-1} for the **2e** RIADC(2)/TZVP structure. The ab initio **2e** minima have correspondingly larger ground state distortion (destabilization) energies, e.g., 21 310 cm^{-1} for the **2e** PBE0/TZVP structure versus 26 070 cm^{-1} for the **2e** RIADC(2)/TZVP structure.

The emission energies of the S_1 minima were checked with various methods because the TDDFT method is known to underestimate the excitation energies of Rydberg and charge transfer (CT) excited states.⁴⁵ The results for the vertical emission energies calculated with the diverse testing set are summarized in Table 2.20.

The different methods used to verify the emission energies include calculations to test the effects of diffuse basis functions and asymptotically corrected functionals. TDDFT energies and S_0 - S_1 oscillator strengths are compared to the results of the ab initio method, RICC2, which are better suited for the description of Rydberg and CT states.^{45,168} It should be noted that the RICC2 method tends to overestimate excited state excitation energies when compared to experiment for

Table 2.20: Vertical emission energy (E_{VE}) dependence on method (indicated below) for **2** S₁ minima.

E_{VE} Calc. Method	2a PBE0	2b B3LYP	2c B3LYP	2d B3LYP	2e PBE0	2e B3LYP	2e RIADC(2)
B3LYP-AC/ccpVTZ ^a	24 920	16 480	29 680	32 730	17 060	16 090	13 520
B3LYP-AC/maug-ccpVTZ ^a	24 840	16 530	26 100	28 040	16 590	15 620	13 060
B3LYP/Def2TZVP-mD	25 330	17 020	26 290	28 310	17 340	16 270	13 440
CAMB3LYP/Def2TZVP-mD	27 140	20 490	30 540	32 970	19 740	18 380	14 800
LC-BLYP/Def2TZVP-mD	27 210	21 860	32 020	34 670	20 400	18 970	15 190
LC'-BLYP/Def2TZVP ^b	25 300	18 700	31 180	34 590	18 260	17 080	13 920
LC'-BLYP/Def2TZVP-mD ^b	25 220	18 690	28 090	30 241	17 980	17 000	13 650
RICC2/Def2TZVP	28 350	21 430	33 390	38 400	21 230	18 970	15 550
RICC2/Def2TZVP-mD	28 190	21 350	29 550	32 280	20 770	19 320	15 160
RICC2/aug-cc-pVTZ	28 130	21 400	29 640	32 330	20 940	19 760	15 400

^a The μ parameter is set to $0.23 a_0^{-1}$ for this LC-BLYP calculation, as opposed to the default value of $0.33 a_0^{-1}$.

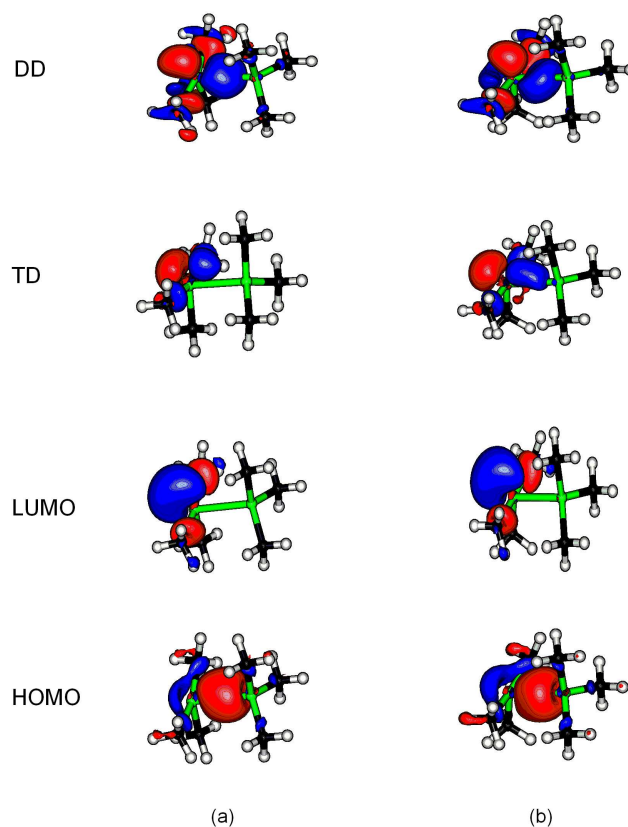


Figure 2.37: HOMO-LUMO, transition density (TD) and S_0 - S_1 difference density (DD) for **2e** relaxed S_1 structure obtained from (a) B3LYP/TZVP S_1 optimization and (b) RIADC(2)/Def2TZVP-mD S_1 optimization. MOs (B3LYP/Def2-TZVP) are plotted on the ± 0.06 isodensity contour value and the TD and DD are plotted on the ± 0.004 isodensity contours.

oligosilanes (Table 2.21). The asymptotically corrected TDDFT methods were used with the default parameters. Additional calculations with the LC-BLYP functional were carried out where the μ parameter was optimized to a value of $0.23 a_0^{-1}$ (as opposed to the default value of $0.33 a_0^{-1}$). This value of the μ parameter closely reproduced the experimental absorption of the $\sigma\pi^*$ state of **2G**.

Table 2.21: Vertical absorption energy (E_{VA}) and oscillator strength (f) dependence of **2G** on the method of calculation.

Structure	Method	State	E_{VE} / cm^{-1}	f
2G	B3LYP/Def2TZVP	$1E_u \sigma\pi^*$	52 660	0.143
2G	B3LYP-AC/cc-pVTZ ^a	$1E_u \sigma\pi^*$	51 990	0.146
2G	CAMB3LYP/Def2TZVP	$1E_u \sigma\pi^*$	55 400	0.178
2G	LCBLYP/Def2TZVP	$1E_u \sigma\pi^*$	55 330	0.173
2G	LCBLYP/Def2TZVP ^b	$1E_u \sigma\pi^*$	52 340	0.144
2G	RICC2/Def2TZVP	$1E_u \sigma\pi^*$	56 740	0.214
2G	Experiment ^c	$1E_u \sigma\pi^*$	52 300	0.151

^a This calculation is similar (functional and basis set) to previous calculations on **2**.¹³⁹ ^b The μ parameter is set to $0.23 a_0^{-1}$ for this LC-BLYP calculation, as opposed to the default value, $0.33 a_0^{-1}$. ^c The experimental E_{VA} value is for **2** at 77 K.¹⁰¹

For excited state minima of **2**, the Def2-TZVP-mD basis set gave results closer to RICC2/aug-cc-pVTZ than to RICC2/Def2-TZVP, with the exception of **2b** where the emission energies for all RICC2 calculations are degenerate and for the **2e** RIADC(2) structure where the RICC2/Def2-TZVP-mD slightly underestimates the vertical emission energy in comparison to the RICC2 calculations with the other basis sets. The advantage of the Def2-TZVP-mD basis set is apparent in **2c** and **2d** where diffuse excited states are relevant. For these minima, diffuse functions alter the S_1 vertical emission energy significantly. For **2c**, the emission energy dropped by $3\,840 \text{ cm}^{-1}$ when using the Def2-TZVP-mD basis in place of the Def2-TZVP basis set for the RICC2 method (Table 2.20). This shift was even more drastic for the emission energy of **2d**, which dropped by $6\,120 \text{ cm}^{-1}$ with the aforementioned basis set change when the RICC2 method was used for emission energies. For **2c**, S_1 is of a different nature depending on the basis set. If the Def2-TZVP-mD basis set is used, the first excited state is of strongly Rydberg character, and if the diffuse functions are not added and the Def2-TZVP basis set is used, a valence excited state as shown in Figure 2.31 is obtained. The Rydberg minimum **2d** has strong Rydberg character regardless of the basis set used and emission energies vary greatly depending on the basis set used. Despite having diffuse functions and asymptotically corrected functionals, the B3LYP-AC/maug-ccpVTZ method seems to underestimate emission energies for **2c** and **2d**. The other S_1 minima (**2a**, **2b**, **2e**) do not change

in nature, nor do their emission energies vary significantly upon the addition of diffuse basis set functions.

The difference in emission energies for the bond stretch minimum **2a** (structure obtained with the TDDFT PBE0/TZVP method) between standard TDDFT (25 330 cm^{-1}) and LC-BLYP (25 220 cm^{-1}) was only 110 cm^{-1} . The LC-BLYP/Def2-TZVP-mD calculation used the the optimized value of long-range cutoff parameter μ , 0.23 a_0^{-1} . Other minima, **2b**, **2c**, **2d**, did however show disparities between the standard TDDFT and LC-TDDFT emission energies, with differences of 1 670, 1 800, and 1 930 cm^{-1} , respectively. The **2e** minimum energy structures show smaller differences between LC-TDDFT and TDDFT. RICC2, CAM-B3LYP and the LC-BLYP method with the default μ parameter give the highest emission energies while B3LYP-AC method give the lowest emission energies.

There are also trends in the S_0 - S_1 oscillator strengths of the S_1 minima when calculated with various methods. These values are given in Table 2.22. Standard TDDFT gave the lowest S_0 - S_1 oscillator strengths for **2a-d**, and the second lowest for **2e**, where the LC functionals gave slightly lower values (0.014 versus 0.015) for this minimum. The RICC2 method consistently gave the largest S_0 - S_1 oscillator strengths for all minima. The TDDFT-AC method gave intermediate oscillator strengths for **2e**. For **2b**, on the other hand the TDDFT-AC method gave similarly low S_0 - S_1 oscillator strengths (0.003) as the standard TDDFT method, and the LC-TDDFT method gave intermediate S_0 - S_1 oscillator strengths (0.005-0.010).

The Λ parameter is related to the integral of the product of the moduli of the orbitals involved in the transitions which describe the excited state.⁶⁵ The Λ parameter is therefore an indicator of CT and Rydberg excited states. **2c** and **2d** showed a large variation in Λ depending on the basis set used (Table 2.23).

The **2a** Si-Si bond stretch minimum has the largest average Λ value (0.59) which is characteristic for this minimum irrespective of basis set or method (TDDFT and LC-TDDFT values are comparable). The **2b** C-Si bond stretch minimum has a lower average value of 0.46, which is also independent of basis set or method. The diffuse Si-Si bond stretch minimum **2c** and Rydberg min-

Table 2.22: S_0 - S_1 oscillator strength (f) calculated with various methods (indicated below) for the **2** S_1 minima.

f Calc. Method	2a PBE0	2b B3LYP	2c B3LYP	2d B3LYP	2e PBE0	2e B3LYP	2e RIADC(2)
B3LYP-AC/ccpVTZ ^a	0.047	0.003	0.050	0.000	0.006	0.009	0.017
B3LYP-AC/maug-ccpVTZ	0.049	0.003	0.015	0.000	0.005	0.008	0.016
B3LYP/Def2TZVP-mD	0.045	0.003	0.013	0.000	0.004	0.007	0.015
CAMB3LYP/Def2TZVP-mD	0.055	0.007	0.022	0.000	0.004	0.007	0.015
LC-BLYP/Def2TZVP-mD	0.056	0.010	0.030	0.000	0.004	0.007	0.014
LC'-BLYP/Def2TZVP ^a	0.045	0.005	0.060	0.000	0.005	0.007	0.015
LC'-BLYP/Def2TZVP-mD ^a	0.045	0.005	0.020	0.000	0.004	0.007	0.014
RICC2/Def2TZVP	0.066	0.008	0.093	0.000	0.008	0.013	0.027
RICC2/Def2TZVP-mD	0.068	0.008	0.024	0.000	0.007	0.011	0.025
RICC2/aug-cc-pVTZ	0.067	0.008	0.025	0.000	0.007	0.012	0.026

^a The μ parameter is set to $0.23 a_0^{-1}$ for this LC-BLYP calculation, as opposed to the default value of $0.33 a_0^{-1}$.

Table 2.23: Lambda values for TDDFT and LC-TDDFT emission energy calculations for the following Si_2Me_6 S_1 minima.

A Calc. Method	2a PBE0	2b B3LYP	2c B3LYP	2d B3LYP	2e PBE0	2e B3LYP	2e RIADC(2)
B3LYP/Def2TZVP	0.62	0.46	0.51	0.38	0.49	0.52	0.60
B3LYP/Def2TZVP-mD	0.61	0.46	0.37	0.29	0.48	0.51	0.59
CAMB3LYP/Def2TZVP-mD	0.59	0.47	0.29	0.24	0.44	0.47	0.55
LC-BLYP/Def2TZVP-mD	0.53	0.48	0.28	0.37	0.48	0.52	0.59
LC'-BLYP/Def2TZVP ^a	0.61	0.46	0.49	0.25	0.43	0.46	0.54
LC'-BLYP/Def2TZVP-mD ^a	0.58	0.46	0.30	0.25	0.43	0.46	0.54

^a The μ parameter is set to 0.23 for this LC-BLYP calculation, as opposed to the default value of $0.33 a_0^{-1}$.

imum **2d** show a strong basis set dependence. Without diffuse basis set functions their respective Λ values are 0.51 and 0.38. These values drop to 0.28 and 0.23, respectively, when calculated with the LC-B3LYP/Def2-TZVP-mD method.

An intriguing trend appears with the polarization minimum **2e**. The average Λ values increased for the structures obtained with more Hartree-Fock (HF) exchange. For the **2e** structure obtained with the least amount of HF exchange PBE0, the average Λ value was 0.44 when the transition was calculated with different methods (Table 2.23). For structural optimization with functionals which included intermediate exchange, the average Λ value was 0.47 for the BHLYP structure. The ab initio structure (obtained with RIADC(2)) gave the largest average Λ value (0.55). The B3LYP-AC method gave similar emission energy values to those of standard TDDFT, but underestimated emission energies in comparison to the LC-TDDFT values for the **2e** structures.

Interestingly, the **2e** structure obtained with the B3LYP/aug-cc-pVDZ yielded much higher emission energies (18 980 cm⁻¹ and 18 290 cm⁻¹ with the LC'-BLYP/Def2-TZVP and B3LYP/Def2-TZVP methods, respectively) than the B3LYP/TZVP **2e** structure (17 850 and 17 140 cm⁻¹ with the LC'-BLYP/Def2-TZVP and B3LYP/Def2-TZVP methods, respectively). Additional augmentation of the basis set with diffuse functions had a smaller effect on the emission energies (less than 400 cm⁻¹ differences were obtained) when the S₀-S₁ emission energy of one structure was calculated with different methods (Table 2.24).

Table 2.24: TDDFT and LC-TDDFT emission energy calculations for **2e**.

Structure	Emission Calc.	E_{VE} / cm^{-1}	f
2e B3LYP/aug-cc-pVDZ	B3LYP/Def2-TZVP	18 290	0.006
	B3LYP/aug-cc-pVDZ	18 480	0.006
	LC'-BLYP/Def2-TZVP ^a	18 980	0.006
	LC'-BLYP/Def2-TZVP-mD ^a	18 650	0.006
2e B3LYP/TZVP	B3LYP/Def2-TZVP	17 140	0.005
	B3LYP/aug-cc-pVDZ		0.005
	LC'-BLYP/Def2-TZVP ^a	17 850	0.005
	LC'-BLYP/Def2-TZVP-mD ^a		0.005

^a The μ parameter is set to 0.23 for this LC-BLYP calculation, as opposed to the default value of 0.33 a_0^{-1} .

2.3.2.7 Hexamethyldisilane Vibrational Modes and Barriers on the S_1 Surface

The Si-Si bond stretch minimum and polarization minimum, **2a** and **2e**, respectively, structurally rearrange to find similar funnels **2Fa** and **2Fe**. For **2a**, this primarily involves a widening of the C(2)Si(1)C(3) valence angle, and for **2e**, the primary motion involves a widening of the C(2)Si(1)Si(2) valence angle. This is shown schematically in Figure 2.38.

Distortions along the $1a_u$ and $1a'$ S_1 vibrational modes of **2a** and **2e**, respectively, can lead to the funnel **2Fa**. The $1a_u$ vibration decreases the C(1)Si(1)Si(2) valence angle and increases the C(6)Si(2)Si(1) angle, as shown in Figure 2.39. As wide SiSiC valence angles are reached, the funnel **2Fa** becomes more accessible. For the **2e** minimum, increasing the large C(1)Si(1)C(3) angle leads to S_0 - S_1 funnel regions, as will be shown in this section. The $1a'$ vibration on the S_1 electronic surface of **2e** varies the C(1)Si(1)C(3) valence angle as shown in Figure 2.40.

A sloped funnel is reached if the **2e** structure is distorted along the $1a'$ vibrational mode (Figure 2.41). The effective barrier to go from the S_1 minimum to a structure with an S_0 - S_1 energy gap less than $4\,000 \text{ cm}^{-1}$ according to distortion along the $1a'$ vibrational mode is approximately $7\,000 \text{ cm}^{-1}$. This is large but still much less than the E_{SD} ($14\,000 \text{ cm}^{-1}$), and if structural relaxation is allowed (with exception of the C(2)Si(1)Si(2) valence angle), the barrier becomes much lower (350 cm^{-1}) as seen in Figure 2.42.

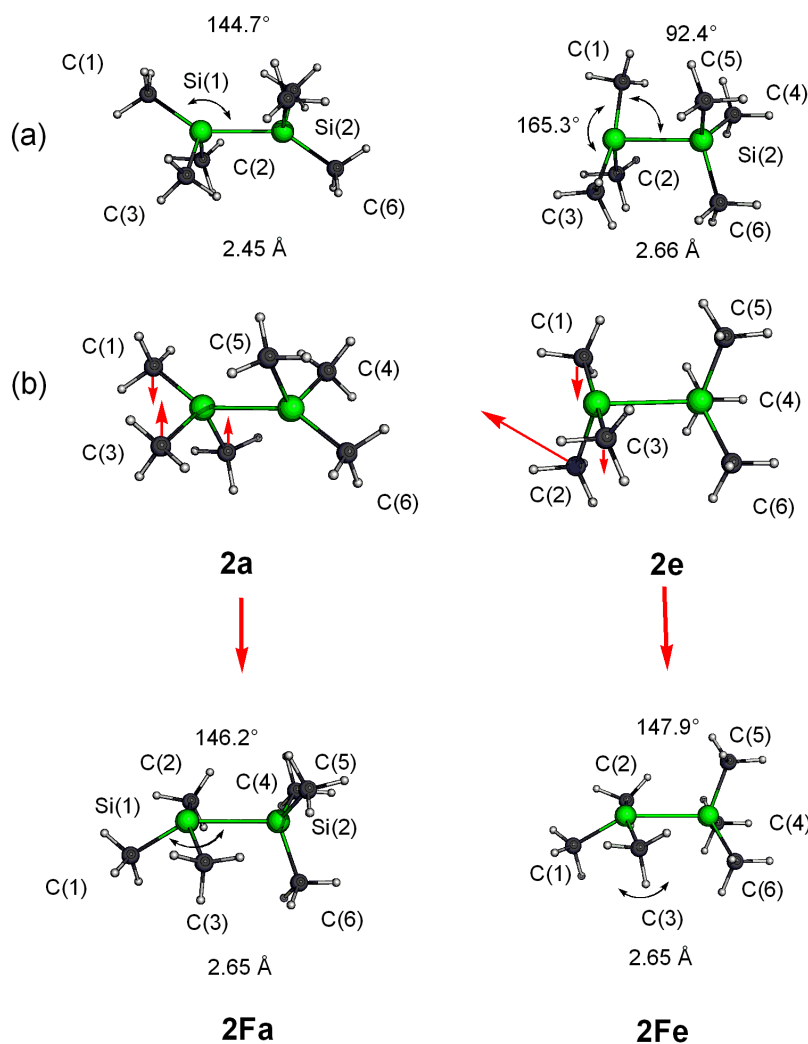


Figure 2.38: Schematic for the **2a** and **2e** structural rearrangement to the funnel **2Fa** (RI-ADC(2)/TZVP). Geometries are shown for the minima, (a), and forces (red arrows) needed for rearrangement are indicated in part (b).

As the C(2)Si(1)Si(2) angle increases, the vertical emission energy and the S₀-S₁ oscillator strength both decrease. These values, as well as the relative energy differences along the S₁ and S₀ surfaces, $\Delta S_{1Min}S_1$ and $\Delta S_{0Min}S_0$, respectively, are shown in Table 2.25. As the strength of the distortion along the 1a' vibrational mode is decreased (from 350 K to 300 K), the minimum E_{VE} value increases to 5 430 cm⁻¹ (Table 2.26). Calculation of the emission energies with TDDFT (PBE0/TZVP, TDA) greatly increases the S₀-S₁ energy gap (Table 2.27), but is useful for compar-

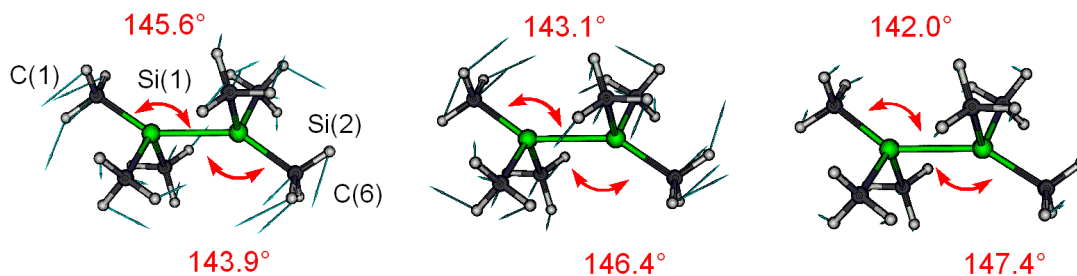


Figure 2.39: Selected frames along the $1a_u$ vibration of **2a**. Vibrational amplitudes (light blue arrows) are shown for geometries indicated by the C(1)Si(1)Si(2) and Si(1)Si(2)C(6) valence angles for the $1a_u$ vibration (PBE0/TZVP).

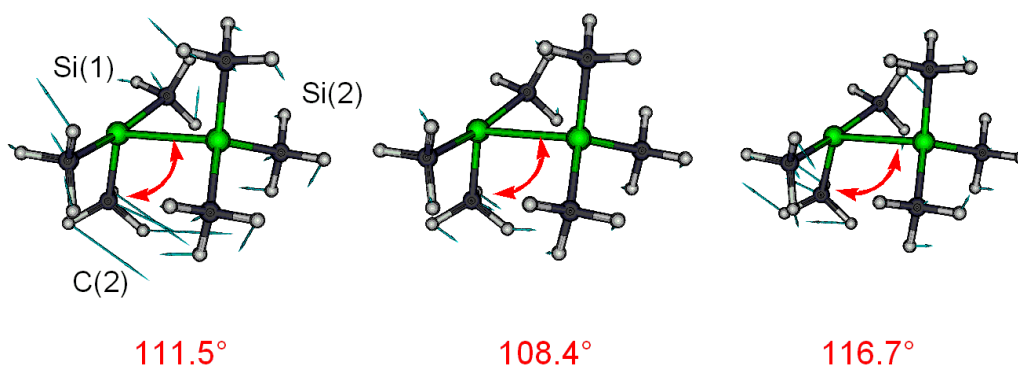


Figure 2.40: Selected frames along the $1a'$ vibration of **2e** on the S_1 surface. Vibrational amplitudes (light blue arrows) are shown for structures characterized by C(2)Si(1)Si(2) valence angles (red) for the $1a'$ vibration (PBE0/TZVP).

ison with relaxed scans (where all geometrical variables are optimized except for the SiSiC angle) which are carried out with the TDA TDDFT method.

The C(2)Si(1)Si(2) valence angle relaxed scan (all other geometrical parameters are optimized) shows an extremely flat S_1 relaxation pathway (Figure 2.42). After an approximately 134° distortion of the C(2)Si(1)Si(2) valence angle, a S_0 - S_1 funnel is reached. From Table 2.28, it can be seen that the S_0 - S_1 oscillator strength remains relatively constant (until the funnel region), but the E_{VE} drops as the C(2)Si(1)Si(2) valence angle is increased (Table 2.28).

The C(2)Si(1)C(3) valence angle relaxed scan, without additional constraints, is shown in Figure 2.43. The S_1 surface appears to be very flat, even decreasing in energy until a funnel is reached around the C(2)Si(1)C(3) valence angle of 140° . Table 2.29 shows there is a slight barrier

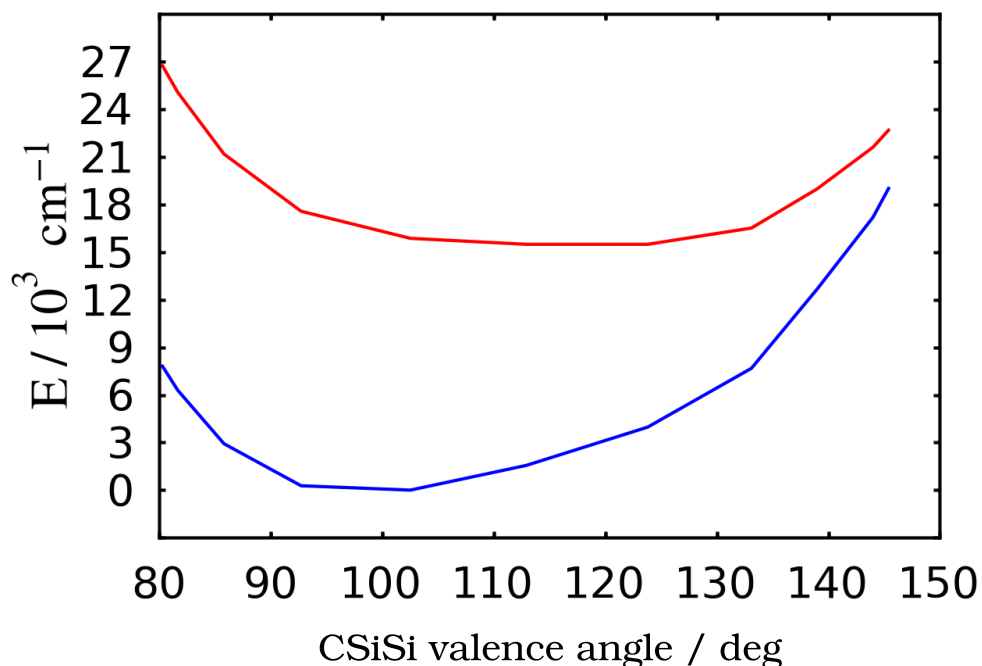


Figure 2.41: S_0 (blue) and S_1 (red) energies (LC'-BLYP/Def2TZVP) along the $1a'$ vibration (350 K) of **2e** plotted as function of the C(2)Si(1)Si(2) valence angle. Geometrical parameters change for all atoms according to $1a'$ vibrational normal mode distortion.

Table 2.25: S_0 and S_1 energies as well as the relative energy differences along the S_1 and S_0 surfaces, $\Delta S_{1Min}S_1$ and $\Delta S_{0Min}S_0$, respectively (LC'-BLYP/Def2TZVP), for the $1a'$ vibration (350 K) of **2e**.

$\angle$ C(2)Si(1)Si(2) /deg	E_{VE} / cm^{-1}	f	$\Delta S_{0Min}S_0$ / cm^{-1}	$\Delta S_{1Min}S_1$ / cm^{-1}
80.3	18 930	0.027	7 810	11 250
81.6	18 780	0.026	6 290	9 580
85.8	18 250	0.024	2 920	5 690
92.7	17 300	0.021	280	2 085
102.5	15 870	0.018	0	380
112.9	13 930	0.015	1 560	0
123.8	11 520	0.012	3 970	1
133.1	8 840	0.008	7 680	1 030
139.0	6 320	0.005	12 670	3 500
144.0	4 420	0.003	17 190	6 120
145.4	3 670	0.002	1 9010	7 190

(10 cm^{-1}) around 113° in the relaxed C(2)Si(1)C(3) valence scan. The oscillator strength for the first electronic transition decreases along with the E_{VE} value as the C(2)Si(1)C(3) angle is

Table 2.26: S_0 and S_1 energies along the $1a'$ vibration (300 K) of **2e**. Energies calculated with LC-TDDFT (LC'-BLYP/Def2TZVP).

$\angle$ C(2)Si(1)Si(2) /deg	E_{VE} / cm^{-1}	f	$\Delta S_{0Min}S_0$ / cm^{-1}	$\Delta S_{1Min}S_1$ / cm^{-1}
82.6	18 660	0.026	5 520	8 610
83.8	18 520	0.025	4 520	7 460
86.1	18 220	0.024	2 890	5 530
89.6	17 740	0.023	1 250	3 420
94.2	17 080	0.021	190	1 700
99.8	16 230	0.019	0	660
106.1	15 180	0.017	610	210
112.9	13 930	0.015	1 700	60
119.7	12 500	0.013	3 080	0
126.0	10 930	0.011	4 810	170
131.6	9 310	0.009	7 060	790
136.2	7 770	0.007	9 760	1 950
139.6	6 440	0.005	12 550	3 410
142.0	5 430	0.004	14 860	4 720

Table 2.27: S_0 and S_1 energies along the $1a'$ vibration (300 K) of **2e**. Energies calculated with TDDFT (PBE0/TZVP, TDA).

$\angle$ C(2)Si(1)Si(2) /deg	E_{VE} / cm^{-1}	f	$\Delta S_{0Min}S_0$ / cm^{-1}	$\Delta S_{1Min}S_1$ / cm^{-1}
82.6	20 950	0.049	6 000	9 020
83.8	20 790	0.049	4 930	7 790
86.1	20 470	0.047	3 190	5 730
89.6	19 970	0.045	1 430	3 470
94.2	19 290	0.043	250	1 610
99.8	18 430	0.040	0	500
106.1	17 390	0.037	600	70
112.9	16 190	0.034	1 740	0
119.7	14 840	0.032	3 180	90
126.0	13 380	0.030	4 990	450
131.6	11 920	0.028	7 330	1 320
136.2	10 550	0.025	10 150	2 780
139.6	9 410	0.022	13 050	4 530
142.0	8 590	0.020	15 460	6 120

increased.

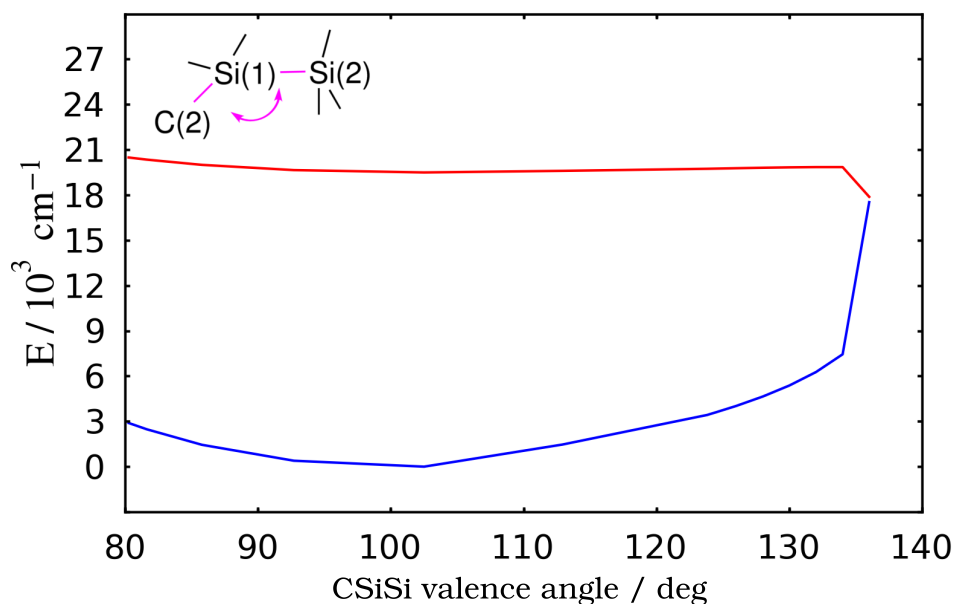


Figure 2.42: Relaxed structure scan (all other geometrical parameters optimized) along the C(2)Si(1)Si(2) valence angle coordinate on the S_1 surface of **2e**. Energies calculated with TDDFT (PBE0/TZVP). The S_1 energy is shown in red, S_0 in blue.

Table 2.28: Relaxed scan (all other geometrical parameters optimized) along the C(2)Si(1)Si(2) valence angle coordinate on the S_1 surface of **2e**. Energies calculated with TDDFT (PBE0/TZVP, TDA).

$\angle$ C(2)Si(1)Si(2) /deg	E_{VE} / cm^{-1}	f	$\Delta S_{0Min}S_0$ / cm^{-1}	$\Delta S_{1Min}S_1$ / cm^{-1}
80.4	17 590	0.008	2 900	990
81.6	17 870	0.008	2 480	850
85.8	18 550	0.009	1 450	500
92.7	19 252	0.010	390	160
102.5	19 500	0.011	0	0
112.9	18 140	0.014	1 460	100
123.8	16 310	0.012	3 420	240
124.5	16 140	0.012	3 610	250
126.0	15 750	0.012	4 030	280
128.0	15 160	0.011	4 650	310
130.0	14 450	0.011	5 380	340
132.0	13 580	0.010	6 270	350
134.0	12 410	0.009	7 450	350
136.0	354	0.000	17 530	-1 610

2.3.3 Octamethyltrisilane

To briefly summarize the results for the S_1 excited state relaxation for **3**, eight minima were located. Analogs of the minima located for **2** were found and are similarly named. For the analog

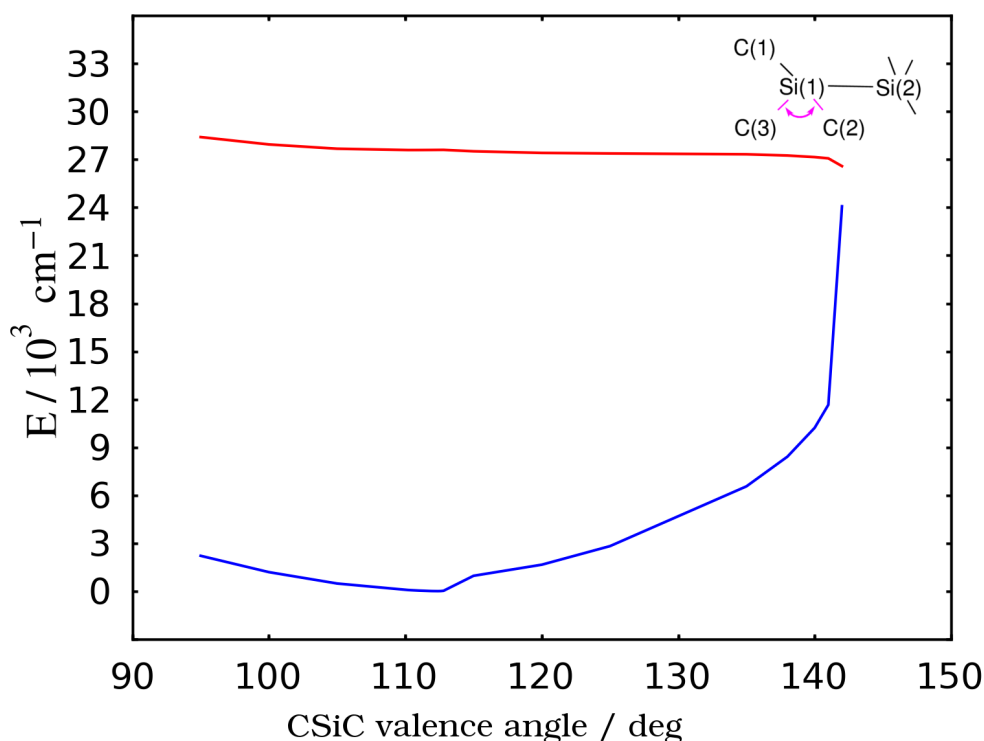


Figure 2.43: Relaxed structure scan (all other geometrical parameters optimized, PBE0/TZVP, TDA) along the C(2)Si(1)C(3) valence angle on the S_1 surface of **2a**. The S_1 energy is shown in red and S_0 in blue.

of **2e**, both the terminal Si polarization minimum (**3e**) and internal Si polarization minimum (**3f**) were located. Additional S_1 minima, not directly related to those of **2**, were located as well. These include a wide SiSiSi valence angle minimum (**3g**) and a narrow SiSiSi valence angle minimum (**3h**). The **3f** and **3g** minima can both also lead to a new funnel **3Ff**, and the minimum **3h** can structurally rearrange to find the **3Fh** funnel. Finally, an additional funnel, **3p**, was found from the direct optimization (with both TDDFT and ab initio methods) of the S_1 state ($\sigma\pi^*$) of the ground state equilibrium structure of octamethyltrisilane, **3G**.

Starting from an octamethyltrisilane structure derived from **2a** led to different minima depending on the method of excited state optimization. One minimum, **3a** (Figure 2.44 and Table 2.30), was obtained with both the BHLYP/TZVP and ab initio methods. The PBE0 and B3LYP functionals both led to the wide SiSiSi valence angle minimum **3g**. S_1 optimization with the

Table 2.29: Relaxed scan (all other geometrical parameters optimized) along the C(2)Si(1)C(3) valence angle on the S₁ surface of **2a**. Energies calculated with TDDFT (PBE0/TZVP, TDA).

$\angle$ C(2)Si(1)C(3) /deg	E_{VE} / cm ⁻¹	f	$\Delta S_{0Min}S_0$ / cm ⁻¹	$\Delta S_{1Min}S_1$ / cm ⁻¹
95.0	26 200	0.052	2 210	810
100.0	26 760	0.060	1 190	350
105.0	27 210	0.063	480	80
110.2	27 530	0.066	70	0
111.0	27 570	0.066	30	1
111.8	27 600	0.066	8	5
112.0	27 600	0.066	4	6
112.4	27 610	0.065	0	8
112.6	27 610	0.065	4	10
112.8	27 590	0.064	20	11
115.0	26 560	0.052	960	-80
120.0	25 770	0.047	1 650	-180
125.0	24 570	0.041	2 820	-210
135.0	20 780	0.028	6 560	-270
138.0	18 840	0.023	8 410	-340
140.0	16 940	0.020	10 220	-440
141.0	15 420	0.018	11 660	-520
142.0	2 510	0.002	24 080	-1 000

B3LYP/TZVP method from an octamethyltrisilane structure derived from **2b** led to the **3b** minimum. The B3LYP/TZVP S₁ minimization of the **2c** analog resulted in the **3c** minimum. This is interesting as the **2c** minimum was only obtained with the B3LYP/TZVP minimization. The Rydberg minimum **3d** was located with the aug-cc-pVDZ optimization of **3c**. The polarization minimum **3e** was located with the B3LYP/TZVP, PBE0/TZVP, B3LYP/TZVP and RIADC(2)/TZVP methods. Ab initio methods returned this structure to the **3Fa** funnel. The internal Si polarization minimum was only found with the B3LYP/TZVP method. Ab initio methods took the **3f** structure to the **3Ff** funnel. The minima **3e** and **3f** were found with starting structures derived from **2e**.

S₁ TDDFT optimization (PBE/SVP) on a set of stochastically kicked structures derived from **3G** led to the **3e**, **3h**, and **3g** minima as well as to the funnels **3Fa** and **3Fb**. The narrow SiSiSi valence angle minimum was located with the PBE0/TZVP, B3LYP/TZVP and B3LYP/TZVP methods. RIADC(2)/TZVP and RICC2/TZVP optimization of **3h** resulted in the funnel **3Fh**.

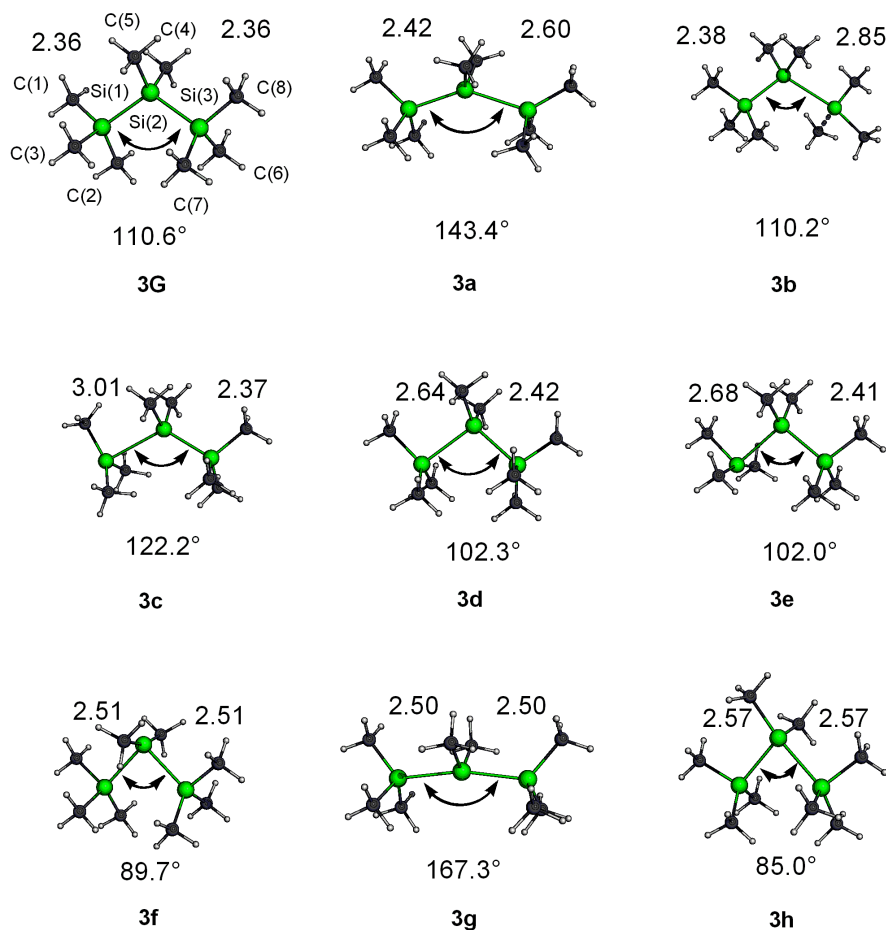


Figure 2.44: Geometries for ground state equilibrium structure **3G** (RIMP2/TZVP) and S_1 minima: **2a** (BHLYP/TZVP), **2b** (B3LYP/TZVP), **2c** (BHLYP/TZVP), **2d** (B3LYP/aug-cc-pVDZ), **2e** (B3LYP/TZVP), **2f** (B3LYP/TZVP), **2g** (B3LYP/TZVP) and **2h** (BHLYP/TZVP). The SiSiSi valence angles are in degrees and Si-Si bond lengths are given in Å. See **3G** for numbering.

The relaxed S_1 state structures are given in Table 2.30.

The Si-Si bond stretch minimum **3a** was found with the BHLYP/TZVP, RIADC(2)/TZVP and RICC2/TZVP S_1 optimizations of **3G**. This structure corresponds to a Si-Si bond stretch minimum where one Si-Si bond has been preferentially stretched (the longest Si-Si bonds are 2.590, 2.609, and 2.576 Å for BHLYP, RIADC(2) and RICC2 calculations, respectively). Si-C bond lengths and angles follow a pattern similar to that of **2a**. The **3a** BHLYP/TZVP, RPA optimized geometry gave a very long Si-Si bond (Figure 2.45) which is not similar to the ab initio bond lengths. For this

Table 2.30: Optimized S_1 geometries for Si_3Me_8 minima **3a-d**.

Structure	$\omega\text{CSiSiSi}$ /deg	$\angle\text{SiSiSi}$ /deg	$\angle\text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle\text{C}_i\text{Si}_i\text{Si}_t$ /deg	$\angle\text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	Si_iC_i /Å	Si_tC_t /Å
Si_3Me_8 BHLYP/TZVP C_1 3a	-179.7 -172.0	143.4	113.5	88.7 109.2 94.6 106.2	95.8 100.2 132.2 107.7 119.3 106.6	2.590 2.419	1.929 1.909	1.906 1.895 1.901 1.894 1.907 1.895
Si_3Me_8 RIADC(2)/TZVP C_1 3a	-179.3 -170.9	134.9	112.5	89.6 112.4 94.5 110.8	90.5 95.1 144.3 107.1 119.4 106.6	2.609 2.372	1.914 1.902	1.920 1.908 1.910 1.898 1.909 1.900
Si_3Me_8 RICC2/TZVP C_1 3a	180.0 -171.7	137.5	112.5	89.1 111.1 95.3 109.4	90.7 96.6 142.8 107.0 119.8 106.3	2.576 2.379	1.924 1.907	1.923 1.907 1.911 1.899 1.910 1.901
Si_3Me_8 B3LYP/TZVP C_1 3b	166.9 157.2	110.2	104.8	91.8 129.1 108.9 109.1	95.3 99.1 159.3 111.6 111.4 110.2	2.848 2.379	1.940 1.924	2.370 1.916 1.940 1.910 1.907 1.911
Si_3Me_8 BHLYP/TZVP C_1 3c	165.1 169.9	122.2	107.9	102.6 103.1 110.1 109.9	88.8 91.2 91.1 108.6 111.6 109.9	3.011 2.371	1.903 1.904	1.872 1.855 1.852 1.899 1.888 1.889
Si_3Me_8 B3LYP/aug-cc-pVDZ C_1 3d	164.1 164.1	102.3	112.3	105.8 114.6 104.7 115.5	106.3 102.9 97.5 100.4 108.0 111.7	2.636 2.421	1.886 1.887	1.876 1.877 1.882 1.900 1.888 1.887

reason and in view of the discussion of RPA failures for TDDFT optimizations in the introductory chapter, the RPA version of TDDFT was not used for structural optimization.

The C-Si bond stretch minimum **3b** found with the TDDFT B3LYP/TZVP method is struc-

Table 2.31: Optimized S_1 geometries for Si_3Me_8 minima **3e-f**.

Structure	$\omega\text{CSiSiSi}$ /deg	$\angle\text{SiSiSi}$ /deg	$\angle\text{CSiC}^a$ /deg	$\angle\text{C}_i\text{Si}_i\text{Si}_t$ /deg	$\angle\text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	Si_iC_i /Å	Si_tC_t /Å
Si_3Me_8 B3LYP/TZVP C_s 3e	180.0 180.0	102.0	165.4	110.8 112.4 110.8 112.4	94.0 94.0 96.2 104.6 111.3 111.3	2.681 2.412	1.900 1.900	2.015 2.015 1.927 1.909 1.893 1.893
Si_3Me_8 PBE0/TZVP C_s 3e	180.0 180.0	98.7	165.8	112.4 112.1 112.4 112.1	94.9 94.9 92.9 103.3 111.3 111.3	2.573 2.402	1.889 1.889	2.001 2.001 1.926 1.901 1.882 1.882
Si_3Me_8 BHLYP/TZVP C_s 3e	180.0 180.0	105.3	167.7	114.0 107.1 114.0 107.1	106.1 110.9 110.9 90.3 90.3 111.1	2.374 2.706	1.887 1.887	1.895 1.882 1.882 1.974 1.974 1.909
Si_3Me_8 B3LYP/TZVP C_2 3f	-166.2 -166.2	89.7	164.2	96.0 95.2 95.2 96.0	114.1 118.0 97.6 97.6 118.0 114.1	2.505 2.505	2.053 2.053	1.898 1.899 1.916 1.916 1.899 1.898

^a The CSiC valence angle given corresponds to largest value. For **3e** this is Si(1) and for **3f** this is Si(2).

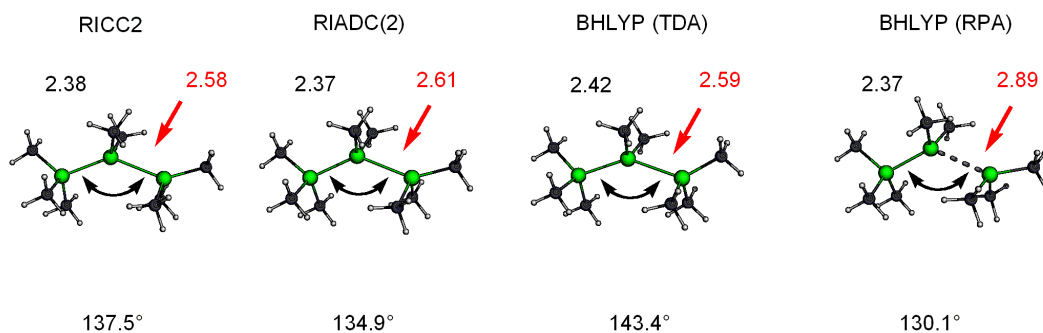


Figure 2.45: Trisilane Si-Si bond stretch minima. Structures have been optimized with various methods, all with the TZVP basis set. TDA and RPA refer to TDDFT calculations. Bond lengths are given in Å (above structures) and SiSiSi valence angles are given below in degrees.

Table 2.32: Optimized S_1 geometries for Si_3Me_8 , minima **3f-g**.

Structure	$\omega\text{CSiSiSi}$ /deg	$\angle\text{SiSiSi}$ /deg	$\angle\text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle\text{C}_i\text{Si}_i\text{Si}_t$ /deg	$\angle\text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	Si_iC_i /Å	Si_tC_t /Å
Si_3Me_8 PBE0/TZVP C_s 3g	-167.0 167.0	168.7	125.2	92.9 92.9 92.3 92.3	103.5 107.3 121.6 103.5 107.3 121.6	2.462 2.462	1.991 1.978	1.903 1.900 1.908 1.903 1.900 1.908
Si_3Me_8 B3LYP/TZVP C_s 3g	-174.1 174.1	167.3	120.4	93.2 93.2 93.2 93.2	103.6 106.2 123.0 103.6 106.2 123.0	2.501 2.501	2.016 2.000	1.913 1.910 1.919 1.913 1.910 1.919
Si_3Me_8 BHLYP/TZVP C_1 3h	168.8 164.9	85.0	98.1	102.8 97.3 108.0 156.9	99.8 110.4 113.6 133.4 107.6 94.0	2.565 2.567	1.911 1.948	1.891 1.879 1.875 1.917 1.896 1.911
Si_3Me_8 PBE0/TZVP C_1 3h	-178.5 169.6	94.1	98.8	97.9 99.3 99.8 155.4	105.1 108.4 105.5 136.8 107.3 92.4	2.611 2.558	1.914 1.952	1.885 1.878 1.877 1.931 1.905 1.919
Si_3Me_8 B3LYP/TZVP C_1 3h	-171.2 170.9	97.6	99.7	95.6 100.4 94.5 155.3	108.1 108.4 102.8 137.7 104.9 93.7	2.715 2.688	1.924 1.960	1.891 1.887 1.890 1.941 1.915 1.922
Si_3Me_8 BP86/TZVP C_1 3h	-170.9 167.9	100.9	100.5	93.4 101.8 94.3 152.1	111.0 107.7 100.5 142.0 103.1 91.9	2.689 2.668	1.929 1.957	1.896 1.892 1.899 1.954 1.921 1.929

turally similar to its disilane analog **2b**. The C-Si bond stretch is 2.370 Å, which is slightly longer than that of **2b** (2.358 Å). The diffuse Si-Si bond stretch minimum **3c** has a slightly longer Si-Si bond (3.011 Å) than its disilane analog, **2c** (2.797 Å), but it should be noted that these minima

were found with different methods. Only the B3LYP/TZVP method gave **2c**, whereas only the B3LYP/TZVP TDDFT calculation resulted in **3c** (Table 2.30).

While all methods found the polarization minimum **2e** to be stable on the S_1 surface, **3e** was only found with the TDDFT B3LYP/TZVP, PBE0/TZVP and B3LYP/TZVP calculational approaches (Table 2.31). Ab initio methods returned **3e** to the **3Fa** funnel. The **3e** structures have SiSiSi valence angles close to the ground state equilibrium structure, **3G**. Geometrical differences, such as wide CSiC valence angle (165.4° for the B3LYP/TZVP terminal Si polarization minimum) are concentrated on the Si(1) atom and connected atoms (Table 2.31). The internal Si polarization minimum **3f** has a narrower SiSiSi valence angle (89.7°). Geometrical differences for the internal Si polarization minimum are concentrated on Si(2). The large CSi(2)C valence angle for **3f** is 164.2° .

The TDDFT optimization of **3G** with the PBE0/TZVP method and with the B3LYP/TZVP methods led to a symmetrically distorted structure of the C_s symmetry group, **3g** in Figure 2.44. The **3g** structure has a wide SiSiSi valence angle of 168.7° and symmetrically stretched Si-Si bond lengths ($2.462 \text{ \AA}$ at the PBE0/TZVP level, Table 2.32). Structure **3g** is very close to having C_{2v} symmetry (in fact PBE0/SVP S_1 optimization finds the minimum to correspond to this symmetry group), and would attain this symmetry if not for slight methyl rotations and Si-C bond stretches. The **3g** structure obtained with B3LYP/TZVP also has C_s symmetry and similar geometrical parameters to the **3g** structure from the PBE0/TZVP level of theory.

Starting from a structure derived from **3G** with a narrow SiSiSi valence angle of 90° , an additional S_1 stationary point was located, **3h** (Figure 2.44) with the B3LYP/TZVP method. **3h** is characterized by a small SiSiSi valence angle of 85.0° (B3LYP/TZVP). Both Si-Si bonds are stretched to $2.57 \text{ \AA}$ (B3LYP/TZVP). PBE0/TZVP and B3LYP/TZVP **3h** structures have much wider SiSiSi valence angles than the B3LYP/TZVP **3h** structure.

Excited state frequencies were calculated for S_1 optimized structures. The lowest vibrational frequencies on the S_1 surface are reported in Table 2.33. Table 2.33 shows **3a-h** to be minima on the S_1 surface. Subsequent optimization of the narrow SiSiSi valence angle minimum, **3h**, with the RIADC(2)/TZVP method led to the traditional silylene extrusion funnel,¹³³ **3Fh**, Figure 2.46.

Table 2.33: Lowest frequencies for stationary points on S_1 surface for various TDDFT and ab initio methods for Si_3Me_8 .

Structure	Method	Lowest Frequency Vibration
3a	BHLYP/TZVP	24.0
3a	RIADC(2)/TZVP	17.3
3a	RICC2/TZVP	10.9
3b	B3LYP/TZVP	17.0
3c	BHLYP/TZVP	27.4
3d	B3LYP/aug-cc-pVDZ	14.8
3e	BHLYP/TZVP	24.3
3e	PBE0/TZVP	16.2
3e	B3LYP/TZVP	13.8
3f	B3LYP/TZVP	42.00
3g	PBE0/TZVP	25.2
3g	B3LYP/TZVP	23.0
3h	BHLYP/TZVP	37.6
3h	PBE0/TZVP	24.5
3h	B3LYP/TZVP	22.1
3h	BP86/TZVP	23.8

Subsequent optimization of the wide SiSiSi valence angle minimum, **3g**, led to a large SiSiSi angle (165.1°) funnel, **3Ff**, Figure 2.46. The geometries for the new funnels (differing from the analogs of **2**) calculated with RIADC(2)/TZVP are listed in Table 2.34.

2.3.3.1 Octamethyltrisilane Radical Anion Geometries

Additional calculations were undertaken to rationalize the wide SiSiSi valence angle minimum **3g** and the narrow SiSiSi valence angle minimum **3h** minima. Optimization of the radical anion for each case gave similar structures; these are analogously named **3Ag** and **3Ah**. The optimization of **3Ag** also led to a C_{2v} symmetric structure with wide (132.1°) SiSiSi and CSiSi valence angles (131.1°) (Table 2.35). The former valence angle is smaller than in **3g**, and the latter is larger than those found in **3g**, giving the radical anion a similar but more delocalized distortion pattern close to **3g**. The large CSiSi angles in both cases are described by the C-Si bond located in the plane of symmetry defined by the Si backbone.

The **3Ah** radical anion also has somewhat less extreme distortions than its singlet excited

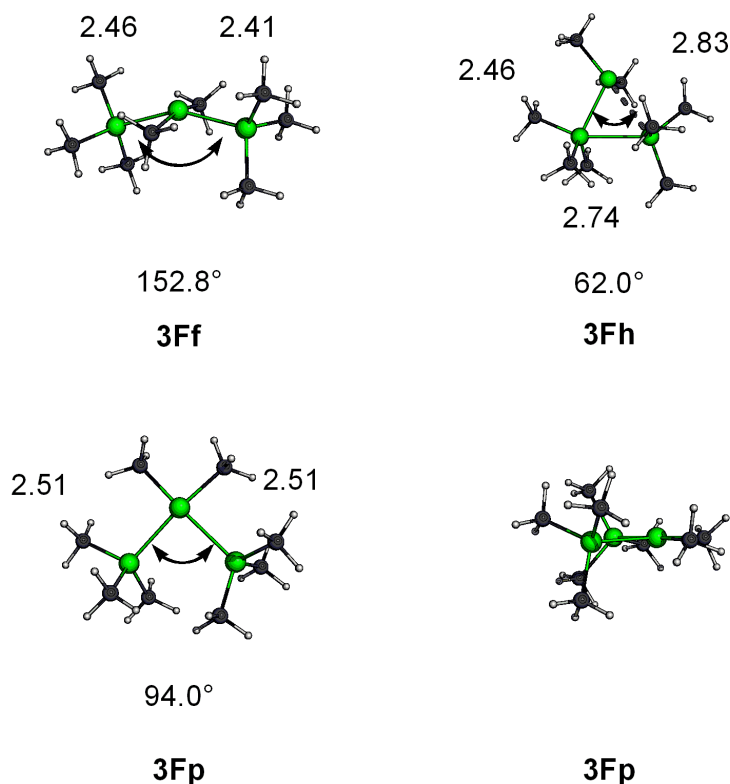


Figure 2.46: S_0 - S_1 funnel structures for octamethyltrisilane. Structures found with the RI-ADC(2)/TZVP method. Selected SiSiSi valence angles and Si-Si bond lengths (Å) are noted.

state counterpart. The **3Ah** structure has a slightly wider SiSiSi valence angle (98.3°) than **3h** (85.0° , BHLYP/TZVP). The **3Ah** structure also retained wide SiSiC valence angles, which were calculated to be 147.0° , larger than in **3G**, but smaller than in **3h** (156.9° , BHLYP/TZVP). Interestingly, unlike the highly distorted but delocalized **3Ag** structure, the structural changes are more localized on the Si(2)-Si(3) bond and substituents (Table 2.35), similar to the **3h** minimum.

2.3.3.2 Octamethyltrisilane Natural Bond Orbital Analysis

As many minima and funnels resemble those of **2**, only non-analogous minima are treated in this section. The Si-Si bond stretch minimum **3a** shows (Figure 2.47 and Figure 2.48) reduced NHO occupancies throughout the Si backbone relative to the ground state equilibrium structure Si-Si NHO occupancies ($\sim 1 e^-$). There is very little difference between the NHO occupancies of

Table 2.34: S₀-S₁ funnel geometries (RIADC(2)/TZVP) for Si₃Me₈.

Structure	$\angle$ SiSiSi / deg	$\angle$ CSiC ^a / deg	$\angle$ SiSiC _i / deg	SiSi / Å	Si _i C _i / Å	Si _t C _t / Å
3Ff	152.8	165.1	88.7	2.459	2.050	1.897
			87.9	2.408	2.046	1.895
			85.0			1.897;
			91.8			1.898
						1.899
3Fh	62.3	100.3	158.7	2.495	1.907	1.923
			114.5	2.676	1.926	1.903
			99.2			1.891
			97.4			1.935
						1.900
3Fp	87.7	94.0	173.6	2.518	1.966	1.899
			89.3	2.530	1.973	1.897
			88.4			1.894
			173.7			1.893
						1.897
3Fp^b	94.0	88.1	177.3	2.507	1.961	1.907
			88.2	2.510	1.959	1.903
			89.6			1.905
			176.2			1.910
						1.903
						1.910

^a CSiC angles given for terminal Si atom in Si₂Me₆ with large methyl distortions and for the central Si atom for Si₃Me₈. ^b This funnel was found with the PBE0/TZVP TDDFT TDA method to give a S₀-S₁ splitting of 860 cm⁻¹.

the TDDFT and ab initio structures of the Si-Si bond stretch minimum **3a**. The Si hybrid orbitals between Si(2) and Si(3) have high p character and low occupancy (0.70 e⁻). There are higher occupancies in the Si NHOs between Si(1) and Si(2). Si(2) has an sp² hybridized orbital with a large occupancy (1.14 e⁻) that points towards Si(1). The central Si atom has a drastically reduced atomic charge (+0.81) (Figure 2.47). The main difference between the BHLYP/TZVP and RICC2/TZVP optimized **3a** structures are the relative weights of the resonance structures. The BHLYP/TZVP geometry favored an internal dimethylsilylene extrusion resonance structure, whereas the RICC2/TZVP geometry favored a terminal dimethylsilylene extrusion resonance struc-

Table 2.35: Radical anion geometries (RIUMP2/Def2-TZVP) for Si_3Me_8^- .

Structure	$\angle \text{SiSiSi}$ /deg	$\angle \text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle \text{CSiC}$ /deg	$\angle \text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC_i /Å	SiC_t /Å
3Ag	132.1	104.1	106.2	106.8	2.401	1.917	1.909
		104.1	102.2	106.8	2.401	1.917	1.909
		104.1	102.2	131.1			1.931
		104.1	102.1	106.8			1.909
			102.2	131.1			1.931
			105.5	106.8			1.909
			105.5				
3Ah	98.3	104.9	95.9	112.8	2.342	1.940	1.908
		98.4	105.2	113.1	2.400	1.974	1.904
		106.5	105.3	115.1			1.900
		147.0	102.6	128.6			1.934
			105.1	110.3			1.906
			101.5	106.5			1.912
			104.4				

ture.

The NHO analysis of **3g** revealed another novel bonding pattern in oligosilane singlet excited states. The excited state bonding pattern of **3g** is different from the polarization minimum. Both the polarization minimum and the wide SiSiSi valence angle minimum have five valence orbitals on one of the Si atoms, but in the latter case the extra nonbonding orbital resides in a wide SiSiSi valence angle as opposed to being located in a wide CSiC angle. In the wide SiSiSi valence angle minimum, the Si hybrids on the central Si atom, Si(2), pointing towards neighboring Si atoms have high p character (sp^5), and the Si(2) atom has higher s character hybrids pointing towards its Me groups. There is a reduced occupancy between Si atoms and also between Si(2) and C(4) and C(5) atoms. Remarkably, the fifth hybrid orbital on Si(2) is of nonbonding character and is made from Si 4p and 3d orbitals. The nonbonding orbital has an occupancy of 0.35 e^- (Figure 2.49). In contrast to the nonbonding orbital analysis of **2e**, the 3d atomic orbitals play a larger role than the 4p atomic orbitals in the nonbonding hybrid orbital in **3g** (Table 2.36).

The NHO analysis of the wide SiSiSi valence angle minimum PBE0/TZVP **3g** structure is very similar to that of the B3LYP/TZVP **3g** structure. Slightly more electron occupation (0.42 e^- ,

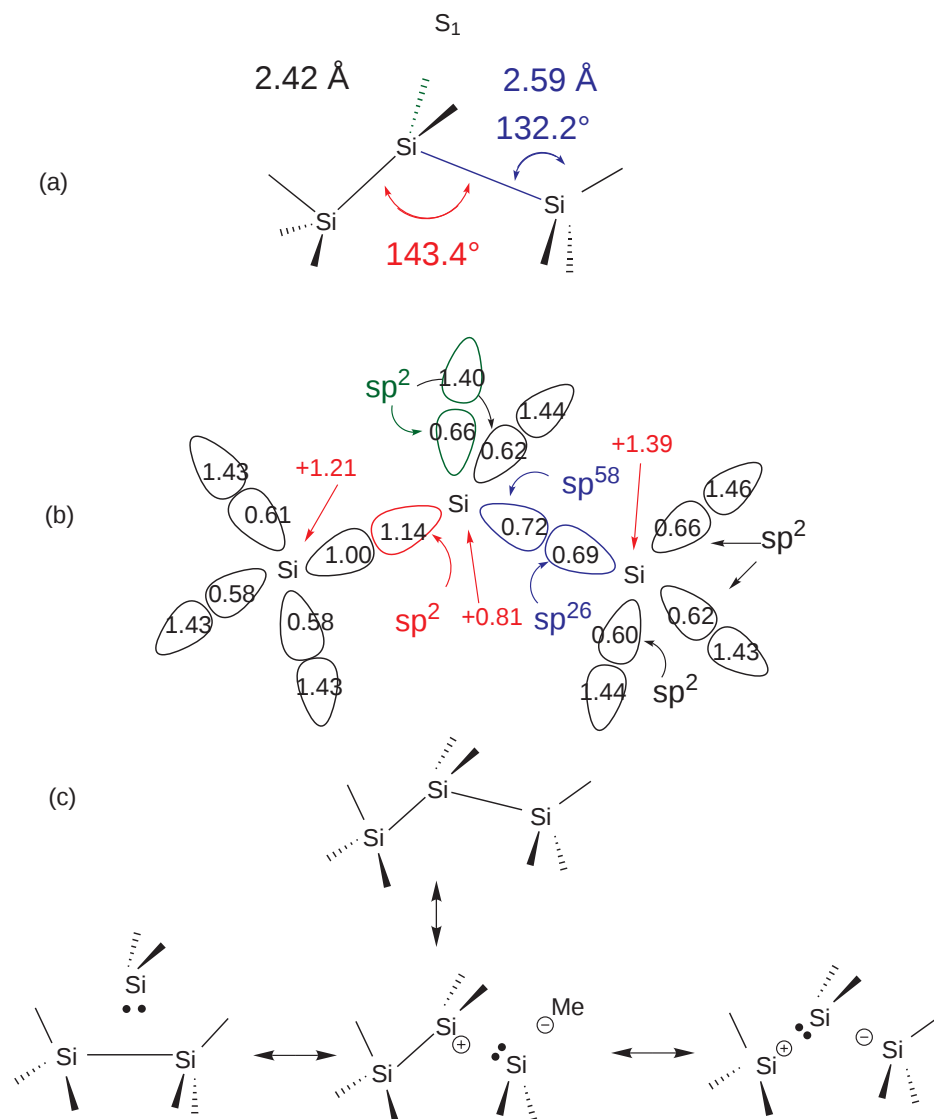


Figure 2.47: NHO analysis for **3a** (BHLYP/TZVP structure) S_1 density, selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

Figure 2.50) is partitioned into the nonbonding orbital on Si(2), which is also made of Si atomic 4p and 3d contributions (Table 2.36). The central atom has a similar natural charge of +0.53, which indicates that the Si(2) atom has more electron density than normal (in comparison to the ground state equilibrium structure).

Due to the large differences in E_{VE} between **3h** structures optimized with different functionals, NHO analysis was carried out on each structure. The BHLYP/TZVP **3h** structure has a

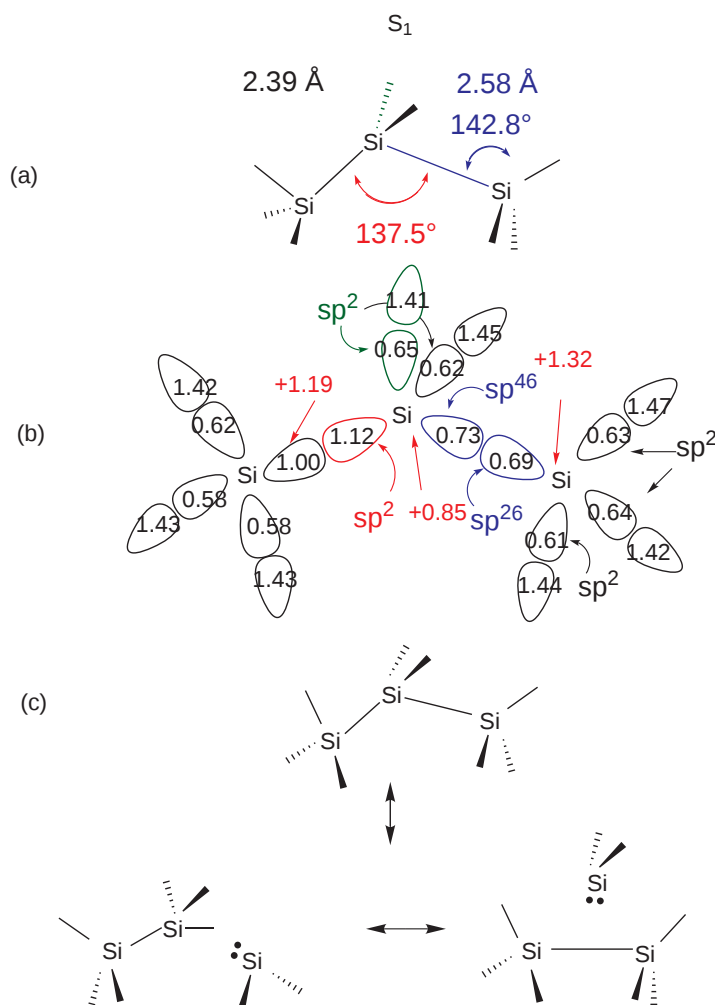


Figure 2.48: NHO analysis for **3a** (RICC2/TZVP structure) S_1 density, selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

sp^3 and an sp^2 hybrid orbital pointing away from Si(2) toward the terminal Si atoms, Figure 2.51. Density has been removed from the Si-Si bonds and relocated between the Si and C atoms, namely the NHO populations between atoms Si(2)-C(4) and Si(3)-C(6). The Si(2) atom carries natural charge of +0.80, again slightly less positive than usual. The NHO analysis of the **3h** PBE0/TZVP structure shows a reversal of the hybridization pattern on Si(2) with respect to the B3LYP/TZVP structure. Now the NHO pointing from Si(2) to Si(3) is of essentially pure p character and the hybrid pointing towards Si(1) is sp hybridized, Figure 2.52. The high p character orbital has a lower occupancy ($0.59 e^-$) and the high s character orbital has a higher occupancy than usual, $1.27 e^-$.

Table 2.36: The **3g** nonbonding orbital composition (structures obtained with the PBE0/TZVP and B3LYP/TZVP methods). NAO orbitals with a weight exceeding 1 % are included below. NAO type (valence or Rydberg orbital) is defined by the principal quantum number. NHO analysis was performed with the CIS/6-311G(d,p) method.

Structure	%	NAO	Type
3g B3LYP/TZVP	41.8	p _z	Val(3p)
	24.8	p _z	Ryd(4p)
	30.0	d _{x²-y²}	Ryd(3d)
	2.2	d _{z²}	Ryd(3d)
3g PBE0/TZVP	50.7	p _z	Val (3p)
	19.8	p _z	Ryd (4p)
	26.8	d _{x²-y²}	Ryd (3d)
	1.5	d _{z²}	Ryd (3d)

The central Si atom has a similar overall natural charge, +0.79, as in the B3LYP/TZVP structure. The NHO analysis of the **3h** B3LYP/TZVP structure (Figure 2.53) is similar to that of the **3h** PBE0/TZVP structure. The slight differences are the higher occupancy of the sp hybridized Si(2) orbital (1.36 e⁻) and higher p character in the adjacent Si(2) hybrid which points toward Si(3). This orbital has a lower occupancy (0.54 e⁻). The Si(2) atom has the same natural charge (+0.79) as in the analysis of the PBE0/TZVP structure. The NHO analysis of the **3h** BP86/TZVP structure (Figure 2.54) is similar to that of the **3h** PBE0/TZVP and B3LYP/TZVP structures. The structure is slightly more polarized with natural atomic charges on the Si(1), Si(2) and Si(3) atoms of +1.60, +0.81, and +1.19, respectively.

2.3.3.3 Octamethyltrisilane Vertical Emission Energies

The vertical emission energy (E_{VE}) of each relaxed S₁ minimum of **3** was calculated with the B3LYP/Def2-TZVP method and is listed in Table 2.37. The vertical emission energies calculated with TDDFT (B3LYP/Def2-TZVP) for the different excited state minima showed a dependence on the method used to optimize the structure.

For the Si-Si bond stretch minimum, **3a**, these values ranged from 25 230 cm⁻¹ (structure obtained with the RIADC(2)/TZVP method) to 27 600 cm⁻¹ (structure obtained with the BH-

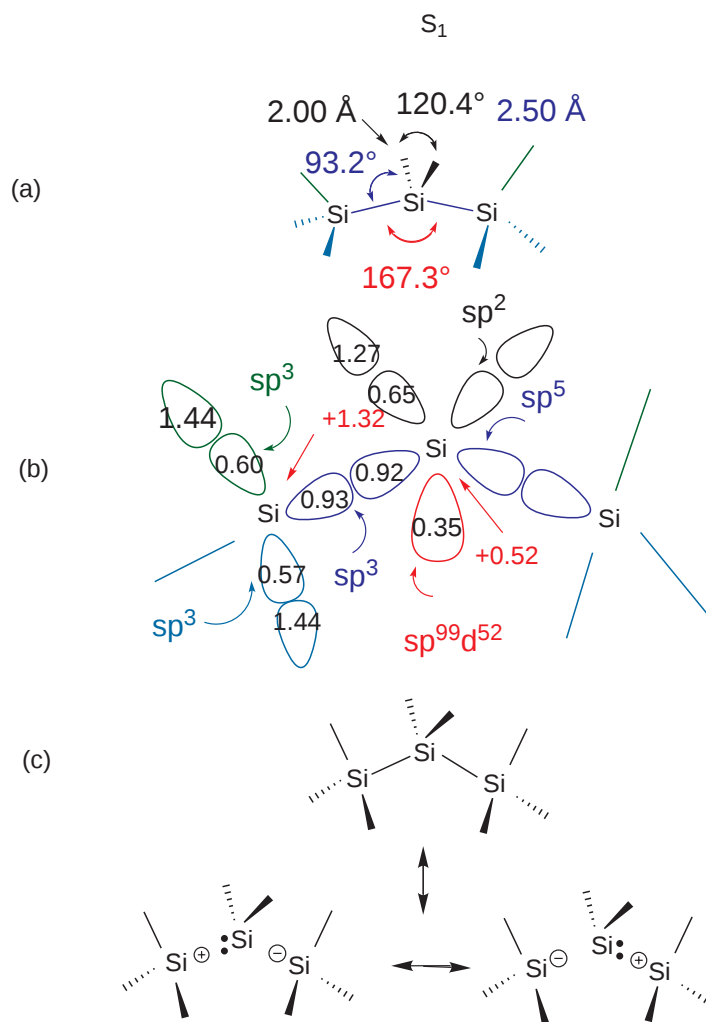


Figure 2.49: NHO analysis for **3g** (B3LYP/TZVP structure) S_1 density, selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

LYP/TZVP method). The 2A state of **3a** is characterized by HOMO to LUMO transitions of $\sigma\sigma^*$ nature (*vide infra*). The S_0 - S_1 oscillator strength was calculated for the B3LYP/TZVP S_1 optimized **3a** structure to be 0.139, which is large compared to most other **3** minima. The transition dipole moments were directed along the z axis (long molecular axis) for the ground to S_1 state transition for **3a**. To describe the nature of states, the MOs were examined in the NHO basis. The coefficients of the NHO orbitals which describe the canonical MOs of the ground state structure **3G** are shown in Figure 2.55. The π^* orbital has zero amplitude in the plane of the Si atoms

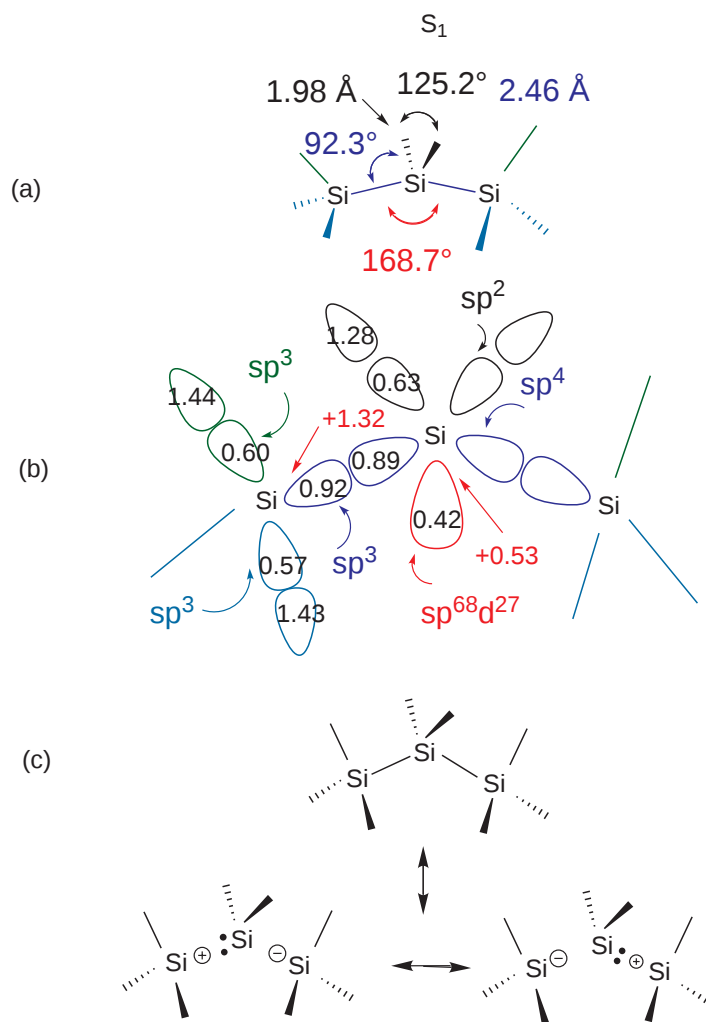


Figure 2.50: NHO analysis for **3g** (PBE0/TZVP structure) S_1 density, selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

and larger coefficients (with alternating signs across the local plane of symmetry) between the Si-C bonds. The σ^* orbital has the absolute value of its coefficients maximized along the Si backbone. The coefficients between the central Si atom and internal methyl groups are also large. They carry the same sign with respect to reflection across the plane of symmetry created by the Si backbone.

For the Si-Si bond stretch minimum, **3a**, the MOs involved in the S_0 - S_1 transition, expressed in the NHO basis, are shown in Figure 2.56. There are high absolute value amplitudes in the σ orbital between Si(2) and Si(3) and negligible coefficients between Si(1) and Si(2). The σ^* orbital

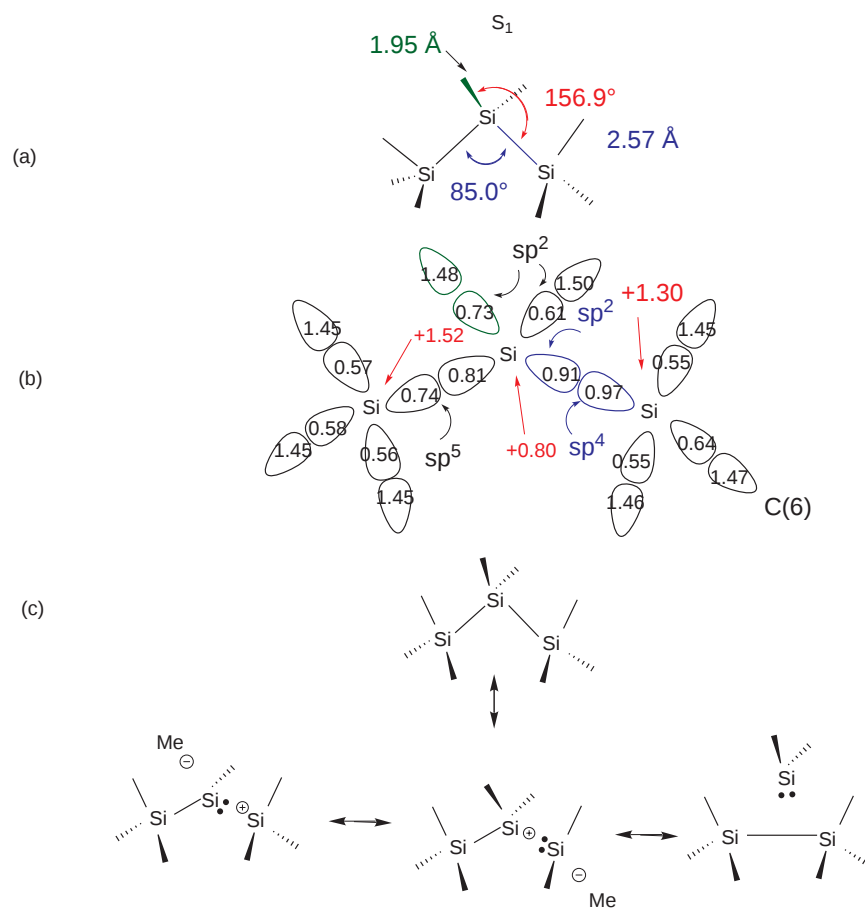


Figure 2.51: NHO analysis for **3h** (BHLYP/TZVP structure) S_1 density, selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

has large coefficients across the Si backbone, and the coefficients of the NHOs pointing to the internal C atoms carry similar signs, indicating strong σ^* character.

The C-Si bond stretch minimum, **3b**, has a slightly lower E_{VE} ($17\,380 \text{ cm}^{-1}$) than **2b** ($18\,700 \text{ cm}^{-1}$) when calculated with the LC'-BLYP/Def2-TZVP method. The E_{SD} decreases greatly for **3b** ($2\,920 \text{ cm}^{-1}$) in comparison to **2b** ($8\,890 \text{ cm}^{-1}$) when the values are calculated with standard TDDFT (B3LYP/Def2-TZVP). When the distortion energy is calculated with the LC'-BLYP method, it is actually inverted by 500 cm^{-1} (Table 2.38). The site distortion energy of $2\,920 \text{ cm}^{-1}$ is the smallest value for the S_1 minima of **3**.

The vertical emission energy for **3c** is $23\,210 \text{ cm}^{-1}$ and is less than that for **2c** ($29\,960 \text{ cm}^{-1}$).

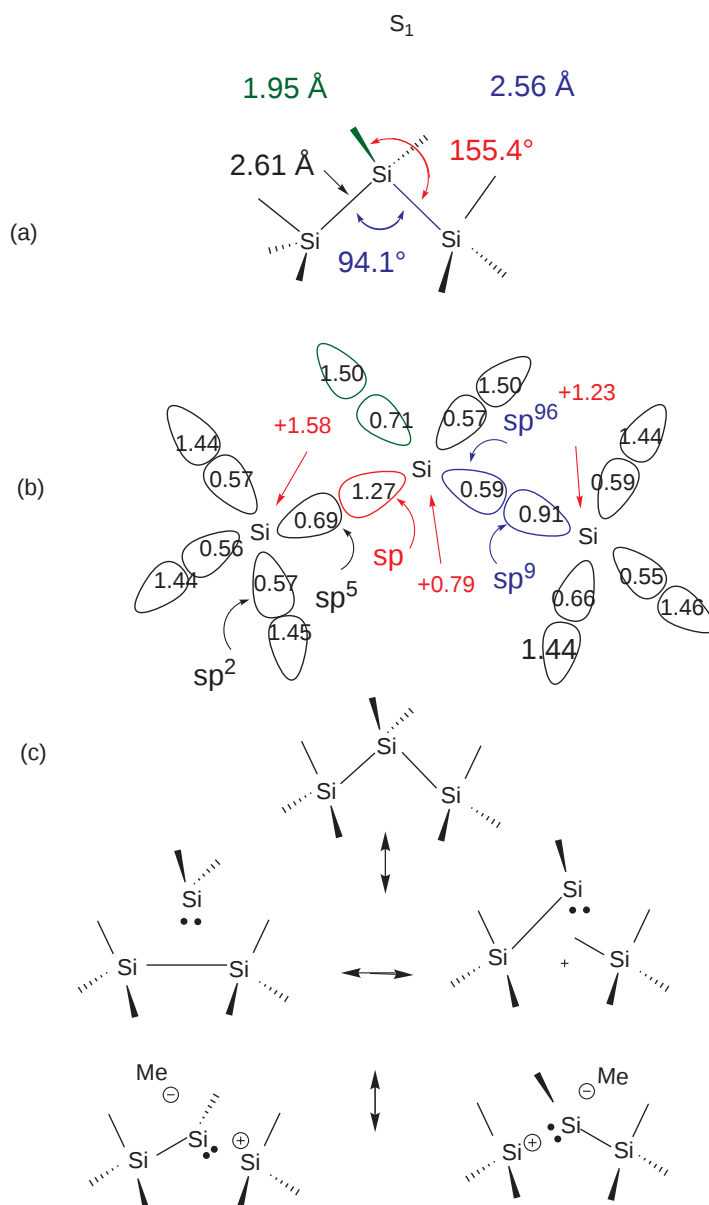


Figure 2.52: NHO analysis for **3h** (PBE0/TZVP structure) S_1 density, selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

The site distortion energy also dropped to 5 770 cm^{-1} in comparison with 11 100 cm^{-1} for **2c**. The S_1 dipole moment of **3c** (1.00 D) decreased in comparison to **2c** (3.26 D).

The Rydberg minimum **3d** has a similar emission energy (30 730 cm^{-1}) to the Rydberg minimum **2d** (29 960 cm^{-1}) when calculated with the TDDFT (B3LYP/aug-cc-pVDZ) method. Similar

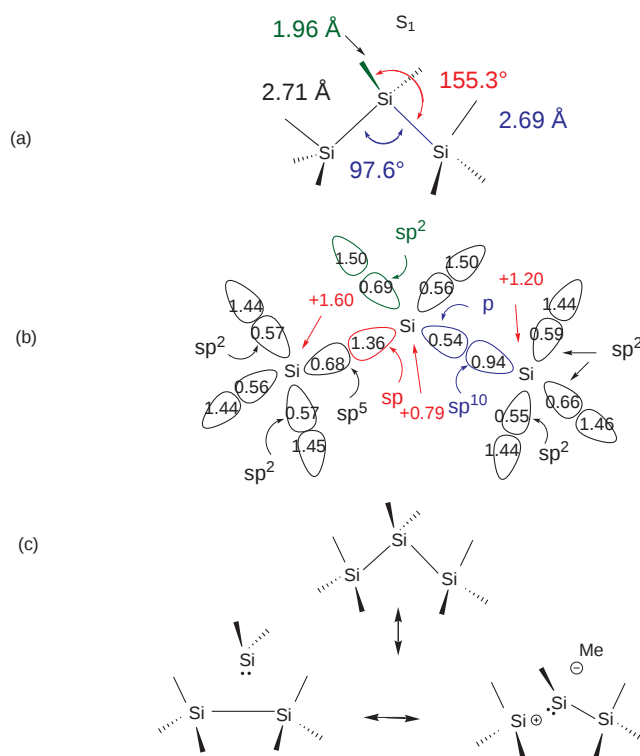


Figure 2.53: NHO analysis for **3h** (B3LYP/TZVP structure) S_1 density, selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

observations are obtained for the site distortion energy (around 7 000 cm^{-1} for both molecules). The S_1 dipole of **3d** increased (1.36 D) with respect to **2d** (0.02 D).

The vertical emission energy of the terminal Si polarization minimum **3e** (16 810 cm^{-1} for the B3LYP and BHLYP structures) decreased slightly in comparison to the polarization minimum **3e** (17 140 cm^{-1} for the B3LYP structure) when calculated with the B3LYP/Def2-TZVP method. The LC'-BLYP E_{VE} value (18 040 cm^{-1}) for **3e** is similarly blue shifted (with respect to the standard TDDFT emission energy) as was the case with **2e**. The S_0 - S_1 oscillator strength for structures which were optimized with higher amounts of HF exchange were greater (0.014 vs. 0.007 for the BHLYP and B3LYP structures, respectively), Table 2.37. Another trend appears with the value of the S_1 dipole moment where it increases with decreasing HF exchange. The site distortion values E_{SD} for **3e** were approximately 8 000 cm^{-1} , roughly half of the **2e** E_{SD} value.

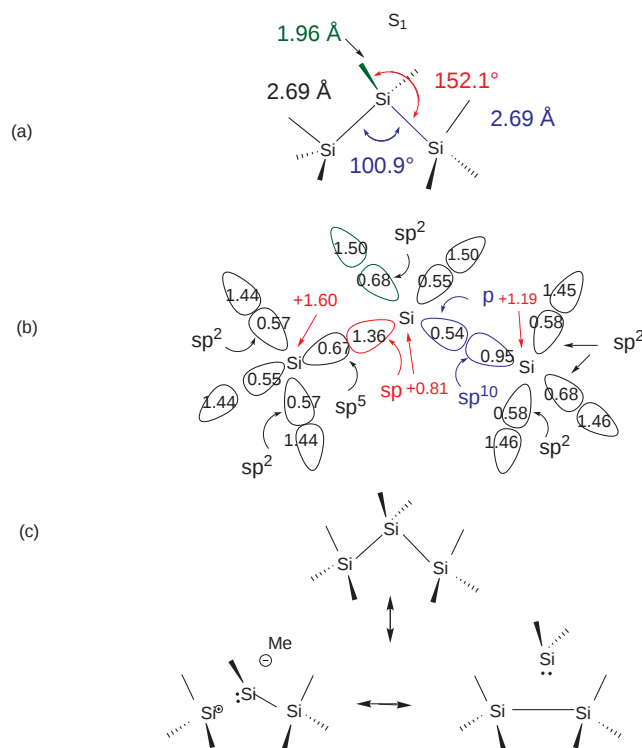


Figure 2.54: NHO analysis for **3h** (BP86/TZVP structure) S_1 density, selected geometrical parameters (a), NHO hybridization and NHO occupancies (b) and predominant natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method.

The vertical emission energy of the internal Si polarization minimum **3f** ($17\,290\text{ cm}^{-1}$) is slightly higher compared to the terminal Si polarization minimum **3e** ($16\,810\text{ cm}^{-1}$) value when calculated with the B3LYP/Def2-TVZP method, but slightly lower ($17\,880\text{ cm}^{-1}$ versus $18\,040\text{ cm}^{-1}$) when calculated with the LC'-BLYP method, although it should be noted that the transitions for **3e** and **3f** are degenerate within the accuracy of the method (approximately $1\,600\text{ cm}^{-1}$).¹⁶⁹ The site distortion energy is slightly less for **3f** ($7\,060\text{ cm}^{-1}$) compared to the terminal Si polarization minimum **3e**.

The wide SiSiSi valence angle minimum **3g** obtained with PBE0/TZVP and B3LYP/TZVP methods gives practically identical emission energies for both structures ($22\,850\text{ cm}^{-1}$ and $23\,360\text{ cm}^{-1}$, respectively) when the emission energies are computed with the B3LYP/Def2-TZVP method (Table 2.37). This transition is also characterized as a HOMO to LUMO promotion. In this case, the HOMO differs from that of the other minima for **3**, and is more related to the second least stable

Table 2.37: Vertical emission energies, E_{VE} , and S_0 - S_1 oscillator strengths (B3LYP/Def2-TZVP), f , for stationary points on S_1 surface for various TDDFT and ab initio methods for Si_3Me_8 . S_1 site distortion and Stokes shift energies, E_{SD} and E_{SS} , respectively, are calculated with respect to the $\sigma\pi^*$ state at the ground state structure, optimized with a similar method as indicated by the Method column.

Structure	Method	State	E_{VE} / cm^{-1}	f	E_{SD} / cm^{-1}	E_{SS} / cm^{-1}	S_1 Dipole Debye
3a	BHLYP/TZVP	$2A \sigma\sigma^*$	27 600	0.139	5 580	18 790	1.62
3a	RIADC(2)/TZVP	$2A \sigma\sigma^*$	25 230	0.141	5 240	20 890	1.05
3a	RICC2/TZVP	$2A \sigma\sigma^*$	25 430	0.127	5 300	20 690	1.14
3b	B3LYP/TZVP	$2A \sigma\mu^*$	15 580	0.003	2 920	30 730	2.74
3c	BHLYP/TZVP	$2A \sigma\sigma^*$	23 210	0.184	5 770	23 180	1.00
3d	B3LYP/aug-cc-pVDZ	$2A \sigma 4s$	30 730	0.004	6 860	13 460	1.36
3e	BHLYP/TZVP	$2A' \sigma\sigma^*$	16 810	0.014	8 040	30 120	3.21
3e	PBE0/TZVP	$2A' \sigma\sigma^*$	16 780	0.007	7 850	29 450	4.04
3e	B3LYP/TZVP	$2A' \sigma\sigma^*$	16 810	0.007	8 080	29 500	3.90
3f	B3LYP/TZVP	$1B \sigma\sigma^*$	17 290	0.006	7 060	29 020	2.57
3g	PBE0/TZVP	$2A' \sigma\sigma^*$	22 850	0.002	5 600	22 850	0.93
3g	B3LYP/TZVP	$2A' \sigma\sigma^*$	23 360	0.001	5 750	23 360	0.96
3h	BHLYP/TZVP	$2A \sigma\mu^*$	18 190	0.006	10 120	28 200	2.60
3h	PBE0/TZVP	$2A \sigma\mu^*$	17 730	0.004	10 250	28 500	3.69
3h	B3LYP/TZVP	$2A \sigma\mu^*$	15 140	0.003	10 390	31 170	4.10
3h	BP86/TZVP	$2A \sigma\mu^*$	14 880	0.003	10 000	31 240	4.35

molecular orbital of **3G**. Excitation remains into the σ^* orbital. The transition dipole moment for **3g** is along the short molecular axis (which would be the C_2 rotational symmetry axis if the molecule contained full C_{2v} symmetry. In the case of C_{2v} symmetry, this state would be the $2A_1$ state and the transition dipole moment would be along the z axis, as the labels of the axes change between point groups). The oscillator strength for this transition is very low (0.002), although it is allowed by symmetry. This structure has a relatively small site distortion energy for **3** (5 600 and 5 750 cm^{-1} for the PBE0/TZVP and B3LYP/TZVP structures, respectively). From inspection of the **3g** MOs in the NHO basis (Figure 2.57) the transition is characterized as being of $\sigma\sigma^*$ nature. In fact, the NHO coefficients of the σ^* molecular orbital have increased along the σ backbone for this minimum in comparison to **3G** (Figure 2.55).

The narrow SiSiSi valence angle minimum **3h** structure (obtained with the BHLYP/TZVP optimization) has an emission energy of 18 190 cm^{-1} . This transition is also very weak and the

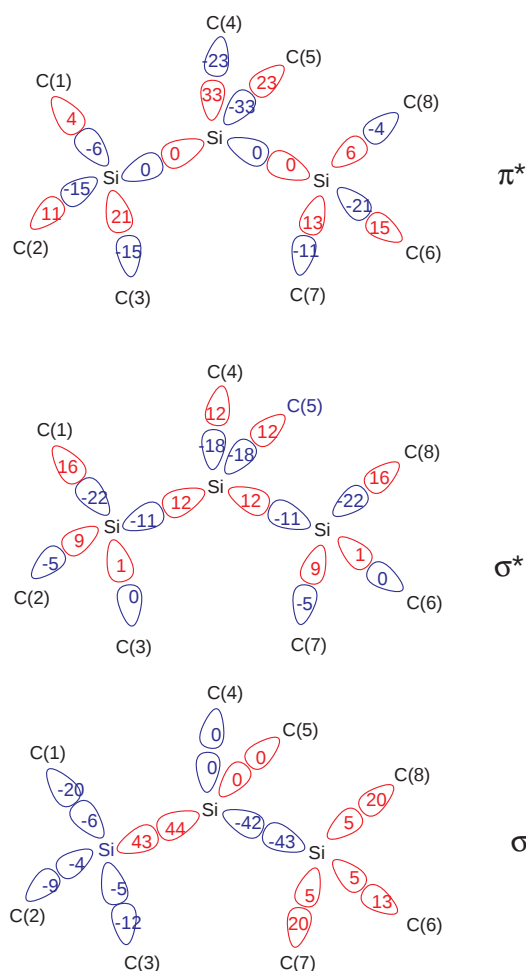


Figure 2.55: Molecular orbitals of **3G** (RIMP2/TZVP structure) expressed in the NHO basis. NHO coefficients are shown multiplied by 100. NHO coefficients were obtained with the HF/6-311G(d,p) method.

oscillator strength is calculated to be 0.006. The properties (E_{VE} , f , E_{SD} , E_{SS} , S_1 dipole moment, and Λ value) of **3h** seem to be heavily influenced by the amount of HF exchange included in the TDDFT structural optimization (Table 2.38). For example, the vertical emission energy dropped by $3\,310\text{ cm}^{-1}$ (to $14\,880\text{ cm}^{-1}$) when the BP86/TZVP (no HF exchange) method was used in the B3LYP/Def2-TZVP emission energy calculation. Additionally, the S_1 dipole moment increased to 4.35 D (BP86/TZVP structure) in comparison to the 2.60 D dipole moment for the B3LYP/TZVP structure. The **3h** structure has the largest site distortion energies, ranging from $10\,120\text{ cm}^{-1}$ to $10\,000\text{ cm}^{-1}$ (Table 2.37). The Λ value also decreases from 0.58 to 0.47 with decreasing HF

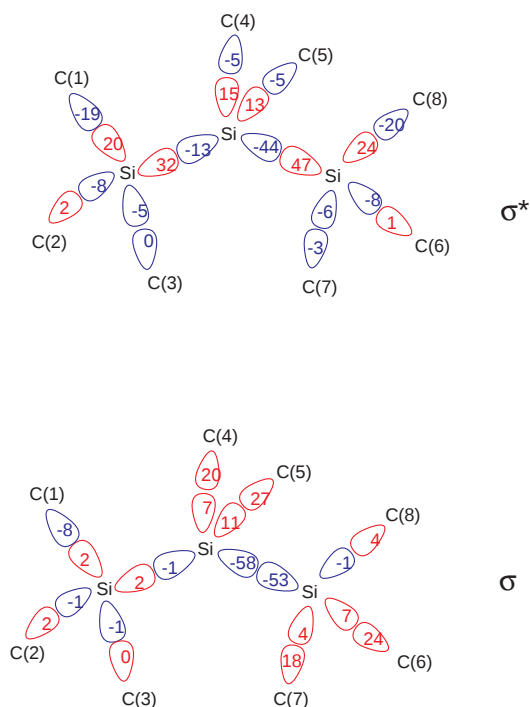


Figure 2.56: Molecular orbitals of the Si-Si bond stretch minimum **3a** (RICC2/TZVP structure) expressed in the NHO basis. NHO coefficients are shown multiplied by 100. NHO coefficients were obtained with the HF/6-311G(d,p) method.

exchange.

The S_0 - S_1 transition for **3h** is shown pictorially in Figure 2.58. From this figure it is apparent that the LUMO is of mixed σ^* and π^* character (μ^*). From the weight of the NHO coefficients, the LUMO is localized between C(4), Si(2), Si(3) and C(6) atoms. It should be re-emphasized that the nature of the hybrid orbitals involved slight changes regarding the optimization method for the **3h** structures (section 2.3.3.2).

The transition densities of the $\sigma\sigma^*$ and $\sigma\pi^*$ states of **3G** and the HOMO and LUMO for **3a-g** are shown in Figure 2.60. The transition density for **3a** appears to be similar to the $\sigma\sigma^*$ transition density of **3G**. The S_0 - S_1 transition density of the **3h** structures optimized with different methods is shown in Figure 2.61. This figure shows that the optimization method affects the structure and these differences can be visualized via the transition density. The different structures also have decreasing Λ values when optimized with functionals that included decreasing amounts

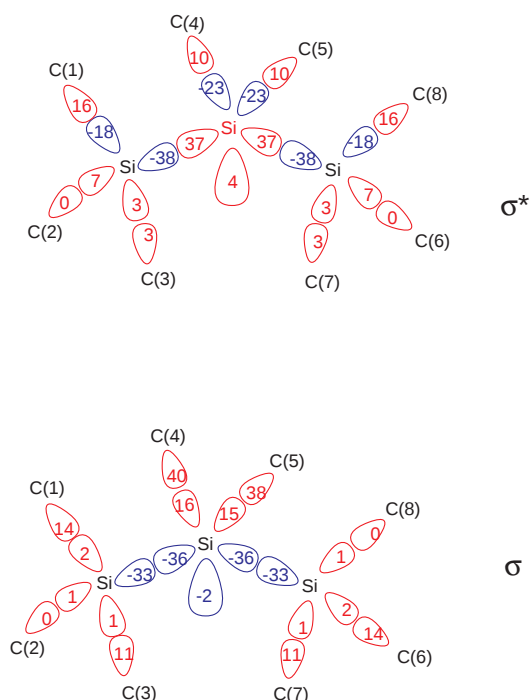


Figure 2.57: Molecular orbitals of **3g** (PBE0/TZVP structure) expressed in the NHO basis. NHO coefficients are shown multiplied by 100. NHO coefficients were obtained with the HF/6-311G(d,p) method.

Table 2.38: Vertical emission energies and S_0 - S_1 oscillator strengths of **3** calculated with the LC'-BLYP/Def2-TZVP method (and the LC'-BLYP/Def2-TZVP-mD methods for selected minima,^a) for stationary points on S_1 surface obtained with various TDDFT and ab initio methods.

Structure	Method	State	E_{VE} / cm^{-1}	f	E_{SD} / cm^{-1}	E_{SS} / cm^{-1}	Λ
3a	BHLYP/TZVP	2A $\sigma\sigma^*$	27 460	0.140	5 270	18 760	0.67
3a	RIADC(2)/TZVP	2A $\sigma\sigma^*$	25 280	0.127	5 170	20 890	0.67
3b	B3LYP/TZVP	2A $\sigma\mu^*$	17 380	0.005	-500	28 800	0.49
3c ^a	BHLYP/TZVP	2A $\sigma\sigma^*$	22 640	0.136	4 640	22 570	0.49
3e	B3LYP/TZVP	2A' $\sigma\sigma^*$	18 040	0.006	7 040	28 140	0.43
3f	B3LYP/TZVP	1B $\sigma\sigma^*$	17 880	0.006	7 470	28 300	0.41
3g	PBE0/TZVP	2A' $\sigma\sigma^*$	22 950	0.003	5 690	23 110	0.66
3g	B3LYP/TZVP	2A' $\sigma\sigma^*$	23 530	0.002	5 440	22 650	0.65
3h	BHLYP/TZVP ^c	2A $\sigma\mu^*$	18 220	0.007	10 590	28 000	0.58
3h	PBE0/TZVP	2A $\sigma\mu^*$	18 180	0.005	9 840	27 880	0.52
3h	B3LYP/TZVP	2A $\sigma\mu^*$	16 020	0.004	8 870	30 160	0.49
3h	BP86/TZVP	2A $\sigma\mu^*$	15 950	0.004	8 874	30 160	0.47

^a The LC'-BLYP/Def2-TZVP-mD method was used for this structure.

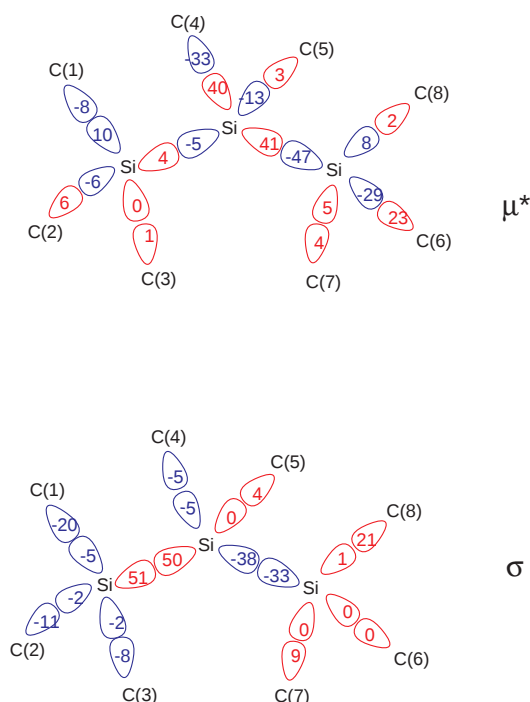


Figure 2.58: Molecular orbitals of **3h** (BHLYP/TZVP structure) expressed in the NHO basis. NHO coefficients are shown multiplied by 100. NHO coefficients were obtained with the HF/6-311G(d,p) method.

of HF exchange (Table 2.38). For the **3h** minima, the TDDFT BHLYP/TZVP method yielded the largest S_0 - S_1 Λ value (0.58).

2.3.3.4 Octamethyltrisilane S_1 Barriers

Previously, in section 2.3.2.7, critical vibrational and geometrical distortions were identified as important coordinates for excited state relaxation to the ground state. In this section, similar distortions are investigated for the slightly longer silane, octamethyltrisilane, **3**.

The C(7)Si(3)C(6) angle (see Figure 2.44 for numbering) was scanned (while all other geometrical variables were optimized) in the S_1 state with TDDFT (BHLYP/TZVP, TDA). The results of this scan are shown in Figure 2.62. The surface is slightly less flat than that for hexamethyldisilane (Figure 2.43).

These ground and excited state energy differences are tabulated in Table 2.39. A funnel is

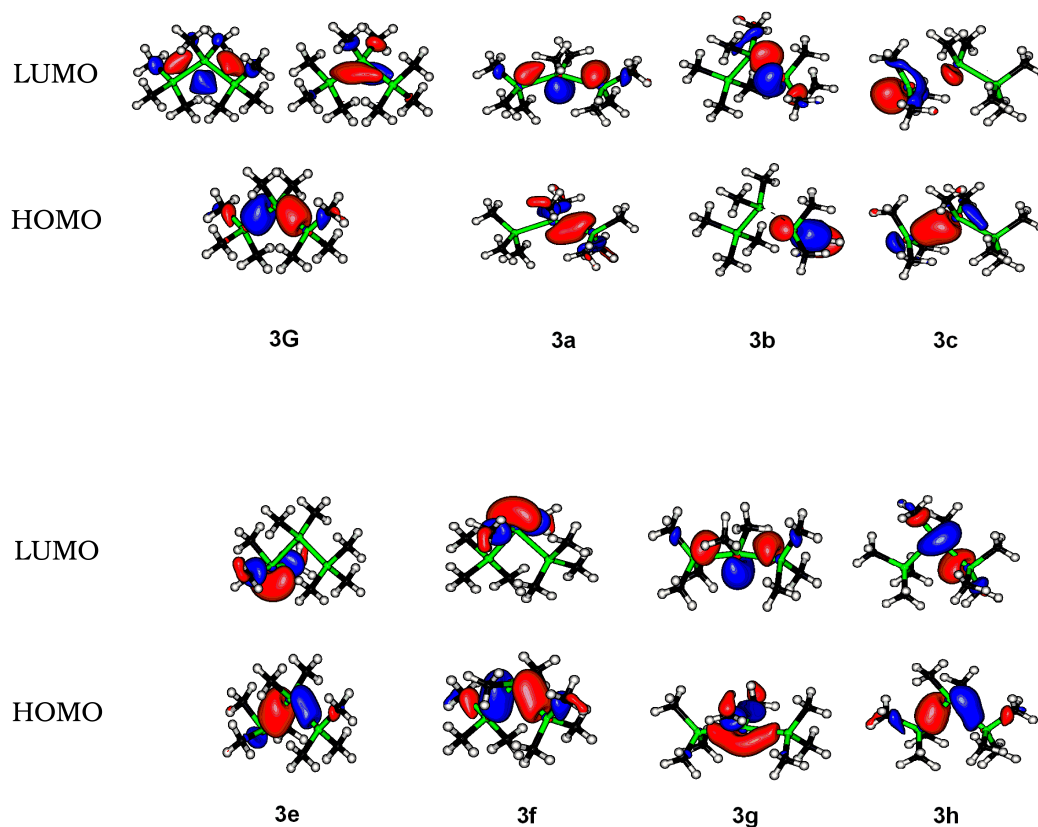


Figure 2.59: HOMO and LUMO for **3a-h** valence excited state relaxed S_1 structures. The σ^* and π^* orbitals are shown for **3G**. The B3LYP/Def2TZVP orbitals are plotted on the 0.06 isodensity contour value.

reached once the C(7)Si(3)C(6) valence angle approaches 142° . The barrier for this process is approximately 630 cm^{-1} . The oscillator strength of the S_0 - S_1 transition also decreases with increasing C(7)Si(3)C(6) valence angle. This is similar to the results obtained for the CSiC distortion of **2**.

2.3.4 Hindered Peralkylated Trisilanes

Extrusion of internal dimethylsilylene provides an efficient radiationless pathway from the S_1 state to the S_0 state. The SiSiSi bending mode gives access to this pathway; therefore, if the bending mode is hindered and extrusion becomes infeasible, then decay from S_1 to S_0 might occur via fluorescence. With the above considerations in mind, some new peralkylated trisilanes have

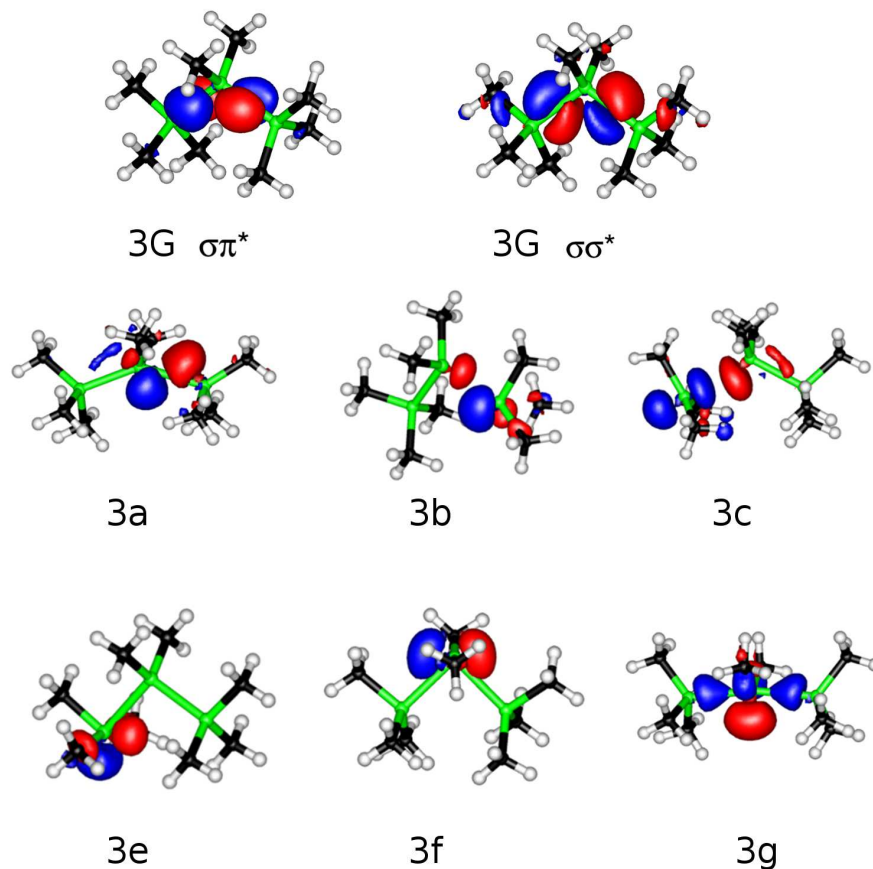


Figure 2.60: S_0 - S_1 transition densities (CIS/6-31G(d)) for **3G** and valence excited state minima, **3a-g**. All transition densities are plotted on the ± 0.004 isodensity contour.

Table 2.39: Relaxed scan (all other geometrical parameters were optimized) along the C(7)Si(3)C(6) valence angle on the S_1 surface of **3**. Energies calculated with TDDFT(BHLYP/TZVP, TDA).

$\angle \text{C(7)Si(3)C(6)}$ /deg	E_{VE} / cm^{-1}	f	$\Delta S_{0Min} S_0$ / cm^{-1}	$\Delta S_{1Min} S_1$ / cm^{-1}
112.0	32 050	0.248	160	0.0
114.0	32 210	0.261	20	20
116.0	32 270	0.268	0	60
120.0	30 730	0.254	1 610	130
130.0	27 910	0.157	4 790	490
135.0	25 410	0.107	7 430	630
142.0	18 910	0.050	13 840	540
144.0	130	0.000	30 460	-1 620

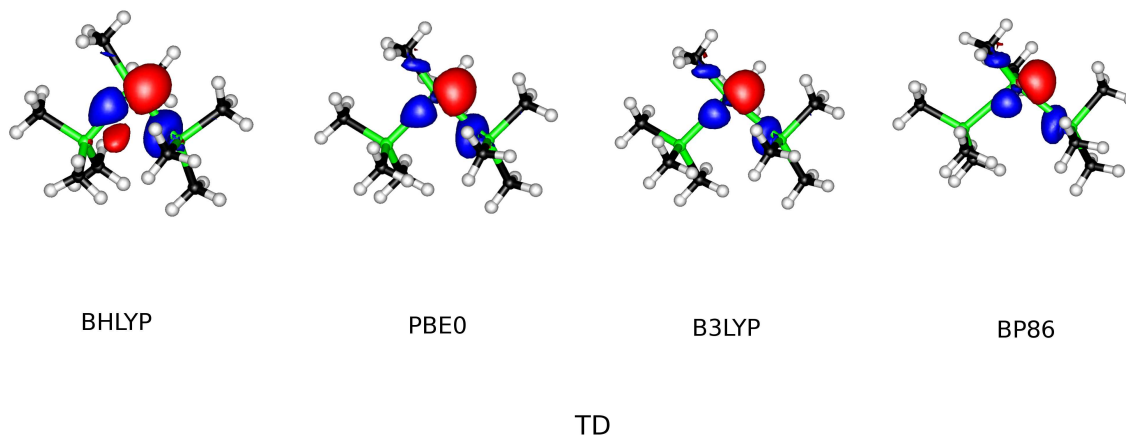


Figure 2.61: S_0 - S_1 transition densities (CIS/6-31G(d)) for **3h** structures optimized with various methods (see labels in figure). All transition densities are plotted on the ± 0.004 isodensity contour.

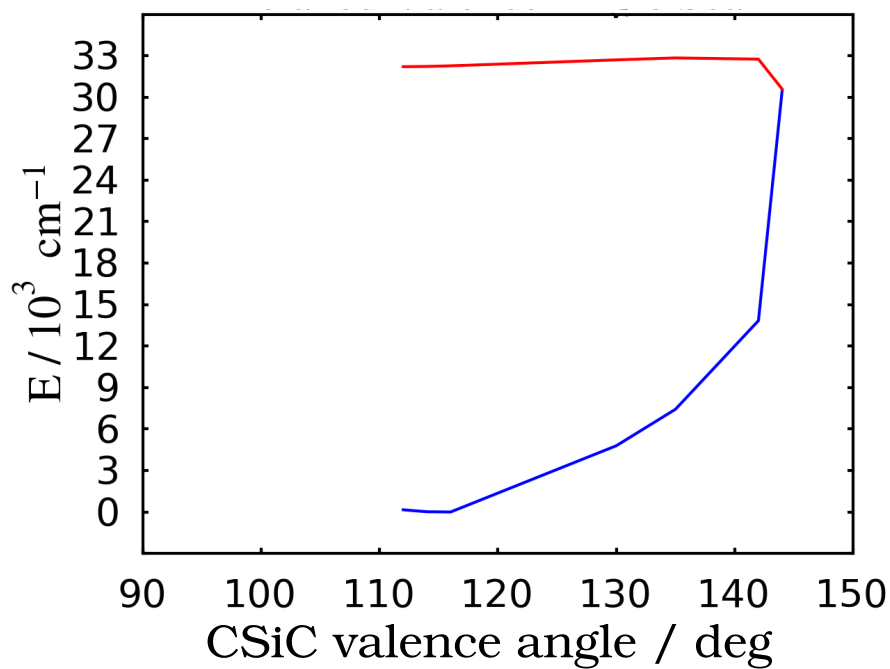


Figure 2.62: Relaxed structure scan (all other geometrical parameters were optimized) along the C(7)Si(3)C(6) valence angle on the S_1 surface (BHLYP/TZVP, TDA). The S_1 energy is shown in red, S_0 in blue.

been designed with the help of Mr. Lukáš Kobl, a synthetic chemist. Table 2.40 gives the ground state geometries for the peralkylated trisilanes optimized with several methods. These substituted trisilanes include an isopropyl derivative, **21** and a *t*-butyl derivative, **22**, Figure 2.63. Another important parameter in the design is the proposed facile synthesis of these compounds.

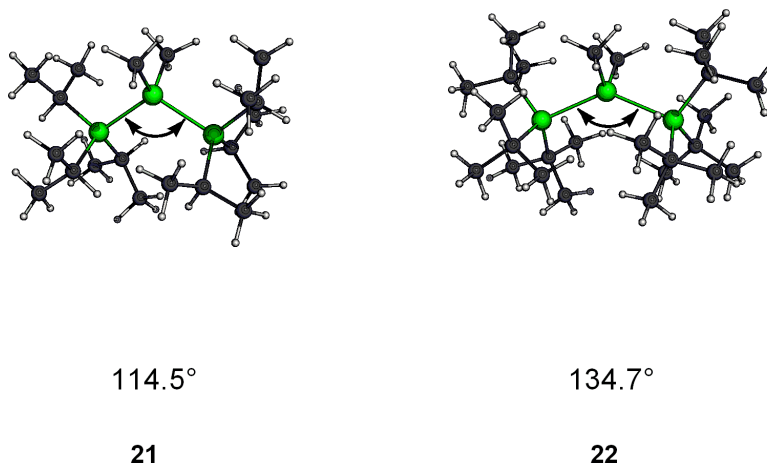


Figure 2.63: Optimized S_0 minima (RIMP2/TZVP) for hindered trisilanes, **21** and **22**.

There are multiple conformations accessible to **21** due to rotations of the isopropyl groups. The structure analyzed here has the isopropyl hydrogen pointing inwards (towards the central Si atom), and is the structure with the smallest SiSiSi angle of the conformations, within 2 kcal/mol from the lowest minimum energy conformer (MM3 calculation). The structure used for **21** has C_1 symmetry which can be seen in Table 2.40. According to the RIMP2/TZVP method, the SiSiSi valence angle is only slightly wider than in **3G** (114.5° versus 110.6°). The Si-Si bonds are also only slightly longer in **21** (2.398 Å) versus **3G** (2.357 Å).

The largest SiSiSi valence angle (134.7°) in the ground state was found for **22** with the RIMP2/TZVP method. This structure has C_2 symmetry. The Si-Si bonds are greatly stretched (2.492 Å), and resemble those of the excited state minimum **3a**. The SiSiSi valence angle of **22** is also fairly insensitive to optimization method and varied less than a degree, from 135.6° to 134.7° for PBE0/SVP and RIMP2/TZVP results, respectively. The DFT methods yield slightly longer

Table 2.40: Optimized S_0 minima (PBE0/SVP, BHLYP/SVP and RIMP2/TZVP methods) for hindered trisilanes **21** and **22**.

Structure	$\angle \text{SiSiSi}$ / deg	$\angle \text{CSiC}^a$ / deg	SiSi / Å	Si _i C _i / Å	Si _t C _t / Å
21 S_0 PBE0/SVP	118.0	104.6	2.415 2.406	1.911 1.910	1.933 1.939 1.934 1.933 1.939 1.934
21 S_0 BHLYP/SVP	118.0	105.5	2.416 2.409	109.5 109.7	1.925 1.925 1.931 1.929 1.928 1.933
21 S_0 RIMP2/TZVP ^b	114.5	105.6	2.398 2.390	1.914 1.914	1.920 1.920 1.924 1.927 1.933 1.926
22 S_0 PBE0/SVP	135.6	105.4	2.521 2.521	1.917 1.917	1.999 1.979 1.975 1.999 1.979 1.975
22 S_0 BHLYP/SVP	134.8	105.5	2.523 2.523	1.912 1.912	1.995 1.976 1.972 1.995 1.976 1.972
22 S_0 RIMP2/TZVP ^b	134.7	104.7	2.492 2.492	1.926 1.926	1.976 1.957 1.960 1.976 1.957 1.960

^a CSiC angles given for internal Si atom. ^bRIMP2/TZVP optimizations performed by Lukáš Kobr.

Si-Si bonds (2.52 Å) compared to the Si-Si bond length of 2.49 Å from the RIMP2/TZVP optimized

geometry.

To gain a better feeling for the efficiency with which the bulky substituents of **21** and **22** exclude geometries with small SiSiSi valence angles, molecular dynamics simulations^b were performed by Mr. Lukáš Kobr. The isopropyl groups of **21** still allowed for fairly small SiSiSi valence angles (101.8°) compared to the minimum SiSiSi valence angle of **22**, 127.1°. The standard deviations decreased as bulkier substituents were added to the trisilane.

Vertical absorption calculations were done with TDDFT (B3LYP/Def2-TZVP) on the RIMP2/TZVP ground state structures of **3**, **21** and **22**. The results (Table 2.41) show that the $\sigma\sigma^*$ state indeed moves down in energy as the bulkier substituents are added to the trisilane backbone.

Table 2.41: Vertical absorption energies, oscillator strengths and polarizations (B3LYP/Def2-TZVP) for ground state optimized RIMP2/TZVP structures of compounds **2**, **3** and **4**. Transition dipole moment direction (Pol.) is given in the C_2 symmetry frame, with the long molecular axis oriented along the y axis.

Structure	State	E_{VA} / 10^3cm^{-1}	f	Pol.
2	2A $\sigma_1\pi_1^*$	46 120	0.000	z
	1B $\sigma_1\sigma_1^*$	46 450	0.083	y
	2A $\sigma_2\sigma_1^*$	52 730	0.014	z
3	2A $\sigma_1\sigma_1^*$	44 520	0.173	y
	3A $\sigma_1\pi_1^*$	46 300	0.006	z
	4A $\sigma_2\sigma_1^*$	49 660	0.012	z
4	1B $\sigma_1\sigma_1^*$	44 000	0.572	y
	2A $\sigma_2\sigma_1^*$	47 260	0.003	z
	3A $\sigma_1\pi_1^*$	47 290	0.001	z

For **3G**, the vertical absorption energy of the $\sigma\sigma^*$ state is $46\,450\text{ cm}^{-1}$. This transition energy decreased for **21** and **22** to $44\,520\text{ cm}^{-1}$ and $44\,000\text{ cm}^{-1}$, respectively. As the $\sigma\sigma^*$ excitation decreased in energy, the oscillator strength also grew from 0.083 for **3G** to 0.572 for **22**.

The structures **21** and **22** were optimized in the excited state to test if structures similar to the previously found minima for **3** could be located. Indeed, TDDFT (PBE0/SVP) optimization of **21** led to a structure similar to the C-Si bond stretch minimum (**3b**) and the analogous structure of

^b Structural properties for peralkylated trisilanes from NVE molecular dynamics run at 300 K equilibrium temperature with 0.5 fs time steps and 10 ps trajectories. These dynamics were run at the BLYP/6-31G* level of theory.

21 also has a large Si-C bond length (2.310 Å), (Table 2.42). TDDFT optimization of **21** with the BHLYP/SVP functional led to a structure similar to **3a**, the Si-Si bond stretch minimum. Here the Si-Si bond is stretched to 2.704 Å. Similar results were obtained for **22**. The PBE/SVP optimization led to a C-Si bond stretch minimum type structure with a large Si-C bond length (2.550 Å), and the BHLYP/SVP optimization led to a Si-Si bond stretch minimum type structure with a Si-Si bond stretched even more to 3.257 Å. The SiSiSi valence angle also increased in comparison to the ground state starting geometry. For **21** the increase is only slight (to a maximum of 136.9°), but for **22** it is more dramatic (153.3 and 150.7° for the PBE0/SVP and BHLYP/SVP structures, respectively). Due to the large size of **21** and **22**, vibrational frequency analysis was not performed.

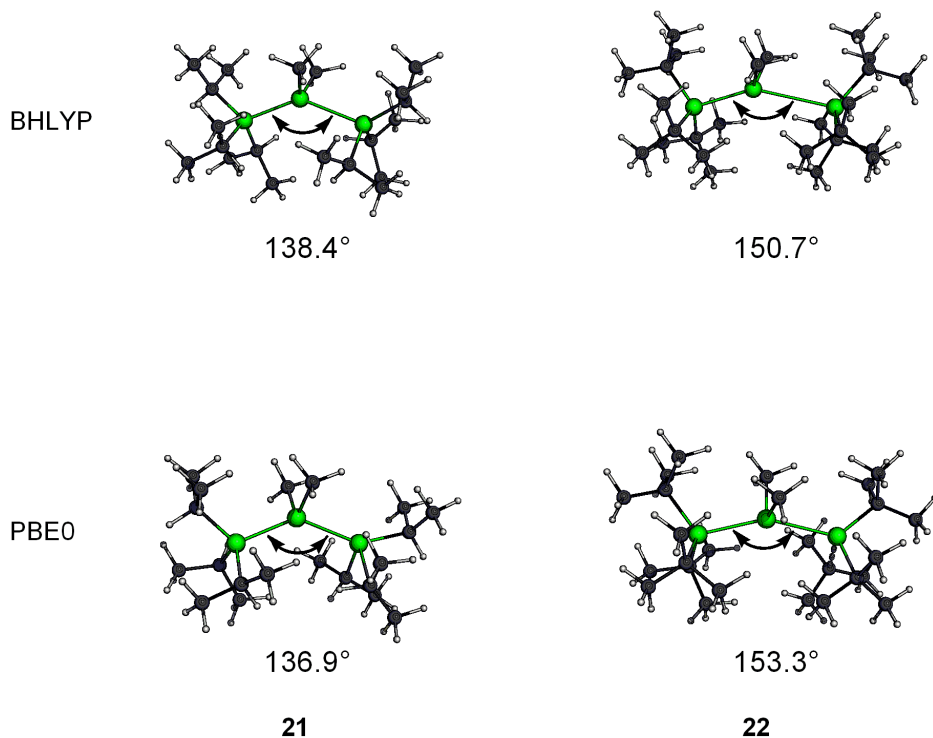


Figure 2.64: Optimized S_1 minima (PBE0/SVP and BHLYP/SVP) for the hindered trisilanes **21** and **22**. SiSiSi valence angle shown in degrees.

The E_{VE} for the **21** C-Si bond stretch minimum type structure was calculated (B3LYP/Def2-

Table 2.42: Optimized S_1 minima (PBE0/SVP and BHLYP/SVP TDDFT methods) for the hindered trisilanes **21** and **22**.

Structure	$\angle \text{SiSiSi}$ / deg	$\angle \text{CSiC}^a$ / deg	SiSi / Å	Si _i C _i / Å	Si _t C _t / Å
21 S_1 PBE0/SVP	136.9	103.3	2.608 2.414	1.918 1.918	2.310 1.955 1.943 1.939 1.931 1.935
21 S_1 BHLYP/SVP	138.4	106.9	2.704 2.434	1.908 1.895	1.936 1.945 1.941 1.936 1.921 1.931
22 S_1 PBE0/SVP	153.3	102.7	2.683 2.534	1.926 1.926	2.550 2.002 1.973 1.985 1.994 1.978
22 S_1 BHLYP/SVP	150.7	105.6	3.257 2.456	1.893 1.895	1.986 1.979 1.972 1.965 1.969 1.989

^a CSiC angles given for internal Si atom.

TZVP) to be 16 030 cm^{-1} , slightly blue shifted in comparison to **3b** (15 580 cm^{-1}). The S_0 - S_1 oscillator strength is similar (0.004), but the E_{SD} value increased (from 2 920 to 9 340 cm^{-1}) and the S_1 dipole moment also increased (from 2.79 to 4.78 D) upon derivatization of **3**. Similar results were obtained for the PBE0/SVP structure of **22**. Here the S_1 dipole moment increased to 5.46 D, the E_{SD} value to 11 480 cm^{-1} , and the vertical emission dropped to 13 210 cm^{-1} .

The E_{VE} value for the Si-Si bond stretch minimum type structure of the hindered trisilanes (optimized with the BHLYP/SVP method) is similar for **21** (27 590 cm^{-1}) and **2a**. The E_{VE} value decreased to 23 390 cm^{-1} for the **22** Si-Si bond stretch minimum type structure. Notably, the S_0 - S_1

oscillator strength increases for the hindered trisilanes and is calculated to be 0.231 and 0.487 for the **21** and **22** S₁ relaxed structures, respectively.

Table 2.43: Vertical emission energies E_{VE} and S₀-S₁ oscillator strengths (B3LYP/Def2-TZVP) for S₁ optimized PBE0 and BHLYP structures of **21** and **22**.

Structure	Opt. Method	State	E_{VE} / cm ⁻¹	f	E_{SD} / cm ⁻¹	E_{SS} / cm ⁻¹	S ₁ Dipole Debye
21	PBE0/SVP	2A $\sigma\mu^*$	16 030	0.003	9 340	28 450	4.78
21	BHLYP/SVP	2A $\sigma\sigma^*$	27 590	0.231	6 540	16 960	1.78
22	PBE0/SVP	2A $\sigma\mu^*$	13 210	0.006	11 480	29 270	5.46
22	BHLYP/SVP	2A $\sigma\sigma^*$	23 390	0.487	9 740	19 770	0.90

2.4 Discussion

2.4.1 Dimethylsilylene

Dimethylsilylene is one of the smallest silylenes for which both experimental absorption and emission signals are known.^{130,131} Dimethylsilylene is also a known photoproduct of larger oligosilanes.⁹⁹ The electronic excitation of **1** involves the excitation of a lone pair electron and therefore is not at all similar to excitations in oligosilane chains which do not have lone pairs in the ground state but which usually involve the excitation of the Si backbone. A large amount of theoretical work has been done on silylenes.^{96,97,166} CSiC valence angles for the ground state equilibrium structure **1G** and the S₁ equilibrium structure **1a** are in close agreement.⁹⁶

The ground state structure and TDDFT methods seem to reproduce the experimental absorption band maximum of **11** quite well, but this is not so for the relaxed excited state (1¹B₁) structure which gave a much lower vertical emission energy (around 12 100 cm⁻¹) compared to the experimental fluorescence band maximum (15 270 cm⁻¹). The disagreement between theory and experiment for the emission energies is most likely related to the fact that decreasing the CSiC valence angle more drastically increases both the oscillator strength and emission energy for the 1¹A₁ to 1¹B₁ transition (Table 2.4) for **1G** more than for **1a** (?). The behavior of the oscillator strength with increasing CSiC valence angle can therefore cause a larger blue shift of the emission

band with respect to the vertical emission energy from the S_1 equilibrium geometry. A simulation of the emission spectrum that involves a distribution of geometries is likely to show the red shift of the calculated emission energy for **1a** with respect to the band maximum.

As the CSiC angle is increased, the lone pair and p_x orbitals become degenerate at the 180° limit of the CSiC valence angle. At this geometry both the lone pair and p_x orbitals become atomic Si p_z and p_x orbitals (Figure 2.65), which accounts for the decrease in transition energy.

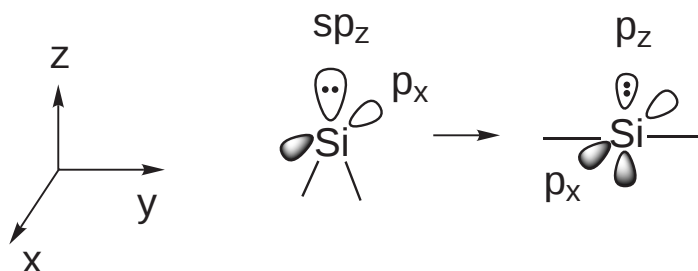


Figure 2.65: Rehybridization upon CSiC valence angle increase for SiMe_2 .

Only the 3s contribution of the lone pair orbital (and not the 3p part) is able to contribute to the transition moment by symmetry. As the valence angle approaches 180° , the 3s contribution to the transition dipole moment goes to zero. The S_0 - S_1 oscillator strength and transition energy for **1G** are less affected by CSiC valence angle variation than **1a**. This most likely occurs because the CSiC valence angle distortions are centered around different equilibrium structures for each state: the S_1 equilibrium geometry is centered around a 120° CSiC valence angle, whereas the ground state is centered around a 97° CSiC valence angle. Similar CSiC valence angle perturbations cause larger excitation energy differences for the S_1 structure because the **1a** structure is closer to the 180° CSiC limit.

The members of the oligosilane series which emit green (Chapter 4) have transitions in emission which are from the Si framework to π_{SiC} orbitals outside the backbone and are therefore expected to exhibit valence angle dependence of the transition energy and oscillator strength. For longer oligosilanes, the valence angles and associated geometrical perturbations of relaxed structures are more complicated and their effect on the emission spectra is less straightforward due to

the increased number of degrees of freedom.

2.4.2 Hexamethyldisilane

2.4.2.1 Excited State Relaxed Geometries

To summarize the results for **2**, several minima were located on the S_1 surface, **2a-e**. The stationary point **2a** resembles the Si-Si bond stretch minima of longer oligosilane chains found in Chapter 3. The nature of the **2a** stationary point differed depending on the optimization method. The PBE0 functional with various basis sets found this structure to be a minimum while the other methods found one imaginary frequency on the S_1 surface, indicating **2a** to be a transition state. Distortion along the imaginary frequency led to a new funnel **2Fa**. The remaining minima (and their analogs in longer permethylated oligosilanes) had not been found until this work. The C-Si bond stretch minimum **2b** was located with the B3LYP functional which also was the sole functional to yield **2c**. The B3LYP functional was the only functional to locate the analog of the **2c** minimum for **3**. The **2c** structure has excitation localized at one Si terminal end when diffuse functions are not present, but gradually acquires Rydberg character as diffuse functions are added to the basis set. Further optimization of **2c** with diffuse basis sets yielded the minimum **2d**, which has 4s Rydberg character. The polarization minimum **2e** was found to be a minimum with all excited state optimization methods used in this work.

From Table 2.7 it is apparent that there are large geometrical rearrangements at both Si and C atoms for the **2a** relaxed structures. These rearrangements are a red flag that the methyl groups are an important part of the chromophore. The omission of these groups when modeling how permethylated oligosilanes relax after light absorption leads to very different results, namely that S_1 minima are much more difficult to find. This claim was met with skepticism,^c and additional S_1 optimizations were carried out with the RICC2/TZVP method on Si_2H_6 structures which were derived from the permethylated S_1 stationary states for **2**. The Si_2H_6 optimizations of the analogs of **2a** and **2e** led to funnels similar to the permethylated disilane funnel **2Fa** and **2Fe**, respectively.

^c Private communication with Josef Michl

While these funnels were very similar in the permethylated disilane, in disilane there are larger structural differences between the **2Fa** and **2Fe** analogs (Figure 2.66). This is most likely due to the short Si-H bonds which allow for larger van der Waals interactions between the Si-H and neighboring bonds. Other calculations on slightly bigger systems, such as 2-methyltrisilane, also led to S_0 - S_1 funnel regions.¹³³

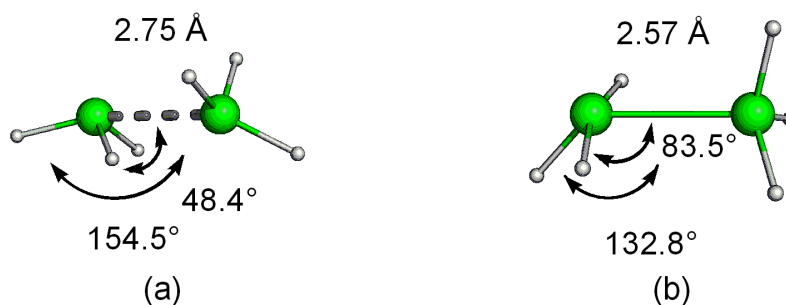


Figure 2.66: Disilane analogs of the **2Fa** (a) and **2Fe** (b) funnel structures. The Si-Si bond length is indicated as well as various HSiSi valence angles.

From the geometrical parameters and from orbital analysis of the lowest transition, the S_1 state of **2a** is of $\sigma\sigma^*$ nature. The large methyl rearrangements in **2a** allow the S_1 energy to drop significantly in energy without extreme Si-Si bond-stretching. Indeed, an early constrained scan along the Si-Si bond stretching coordinate in which the SiSiC angles were not relaxed predicted the $\sigma\sigma^*$ state minimum to be located at Si-Si bond lengths greater than 3.0 Å.¹²⁴ The structure from the TDDFT PBE0/TZVP method shows more involvement of the Si-C bonds, as is evident from the large Si-C bond lengths of **2a** and difference in NHO populations with respect to the RICC2/TZVP **2a** structure. There is also a difference in Si-Si bond lengths and populations and the PBE0/TZVP structure has a shorter Si-Si bond length than those obtained with other methods.

This difference could explain the tendency of the PBE0 functional to describe the stationary state **2a** as a minimum. The **2a** transition state structures, on the other hand, have longer Si-Si bond lengths, as does the funnel **2Fa**. These structures are therefore geometrically closer to the funnel and this could explain the why the other structures are identified as transition states on the S_1 surface.

The NHO analysis of the Si-Si bond stretch minimum **2a** shows the development of fragments which have rehybridized to an electronic structure similar to that of dimethylsilylene on each Si atom. As these zwitterionic fragments oppose one another due to the molecular symmetry, no overall excited state dipole moment results. Symmetry breaking coordinates (*e.g.*, the 1a' vibration on the S_1 surface) disrupt this symmetry and result in the asymmetric **2Fa** funnel. This funnel is mostly described by only one resonance structure which indicates the structure is not close to the conical intersection. The analysis of funnel structures, however, is much less trustworthy as these structures are not well described by single reference methods, see the D_2 values in Table 2.44.

A single Si-C bond is stretched to 2.358 Å, (approximately 125% of the ground state Si-C bond length) in the Si-C bond stretch minimum **2b**. The LUMO is localized on Si(1) and adjoining methyl groups and appears to be of Si-C antibonding nature. The large Si-Si bond stretch also characterizes **2b**. This relaxed structure is lower than the starting geometry in energy on the S_1 surface obtained with multiple methods. It is troubling that the optimization of the **2b** (B3LYP/TZVP) minimum with other methods led to different results. This is can be an indication of the inaccuracy of the TDDFT B3LYP method or simply an indication of the ease of geometrical rearrangement and low barriers in excited states for oligosilanes.

The **2c** structure also was obtained solely with the B3LYP/TZVP TDDFT S_1 optimization. This structure has somewhat flattened (reduced) C-Si-Si bond angles, characterized by the small C-Si(1)-Si(2) valence angles (95.2°) and a long Si-Si bond (2.797 Å). NHO analysis of this excitation shows that the HOMO is predominantly located across the Si-Si bond and that the LUMO consists of Si(1)-C antibonding orbitals as well as a diffuse orbital located on Si(1). While this structure appears to be of a diffuse nature and therefore **2c**, which was obtained without diffuse functions,

might appear to be artificial, a similar situation is actually encountered for the structure **2G**. The $\sigma\pi^*$ state of **2G** only appears to be of valence nature if no diffuse functions are added, and as soon as they are this valence state becomes highly mixed (contaminated) with Rydberg character. In solution, however, Rydberg orbitals are pushed to higher energies and the $\sigma\pi^*$ transition is believed to be located at a similar energy as predicted by TDDFT calculations without diffuse functions. Isolated molecule calculations with diffuse functions seriously underestimate the experimentally observed absorption energies for hexamethyldisilane.^d

The **2d** structure is obtained by optimizing the σ -4s Rydberg state. This structure is referred to as a Rydberg minimum and has a large Si-Si bond stretch and slight twisting of the methyl groups resulting in a structure of D_3 symmetry. This structure is very close to that obtained for the ground state optimization of **2C**. This radical cation structure is also of D_3 symmetry, with Si-Si bond length at 2.666 Å, the Si-C bond lengths at 1.853 Å, the CSiSi valence angles at 101.5°, and the CSiC valence angles at 116.2° when calculated at the RIUMP2/Def2-TZVP level.

The **2e** structure deviates from the ground state **2G** (sp^3 hybridized) structure with regard to the geometrical parameters connected with Si(1), which appears to be hypervalent (pentavalent). There is significant rehybridization of the NHOs connected to Si(1), and the **2e** structure is referred to as a polarization minimum. The Si(1) hybrids pointed towards C(2) and C(3) are approximately sp^2 hybridized and the hybrid pointed towards Si(2) is sp hybridized (RIADC(2)/Def2-TZVP-mD structure). NBO analysis of this excitation shows electron density being transferred from the Si-Si bond to a fifth (nonbonding) orbital located on Si(1). This orbital is made of 4s, 4p and some 3d contributions. This nonbonding orbital does not have full occupation which is reflected in the mixture of resonance structures that describe the S_1 density. The large weight of the covalent natural resonance structure indicates that while the σ framework may be polarizable, it does not like to lose its electrons. The other resonance structures for **2e** indicate that the molecule also tries to keep the positive and negative parts of the exciton together. The small amount of density that is deposited into the nonbonding orbital does, however, have a large effect on structure; for example,

^d Absorption energies are red-shifted by roughly 10 000 cm^{-1} when diffuse basis sets are used for **2G**.

2e has a large CSiC valence angle of approximately 168° .

Another explanation of the low nonbonding orbital occupancy could be the fact that the CIS wave function does not include sufficient electron correlation. This is less likely as the UMP2 density analysis results were very similar to the UHF density analysis for **2Ae**. It could also be the case that the NBO procedure preferentially tries to localize electrons between bonds—a good idea for the ground state, but less ideal for excited states. Evidence for this behavior is the increasing electron density (from NHO analysis) in between the Si(1)-C(1) and Si(1)-C(3) bonds with decreasing nonbonding orbital occupation (TDDFT structures). The disparity between the occupation of the nonbonding orbital in ab initio and TDDFT structures is troubling as the transition density appears very similar for both structures. On the other hand, properties such as the emission energies, oscillator strengths and Λ values differ for the ab initio and TDDFT sets of **2e** structures. This finding seems to support such differences in electronic structure as hybridization and different NHO occupations between the sets of **2e** geometries.

The polarization minimum **2e** can also be thought of as a collapsed Rydberg minimum. There is diffuse character mixed into the Si(1) NHOs directed toward neighbors in addition to the diffuse orbital directed between C(1) and C(3). Interestingly, diffuse basis sets do not significantly alter the properties (for example E_{VE} and f) of **2e** (Table 2.22). Clearly, the S_1 state of **2e** is already sufficiently described at the Def2-TZVP level of basis set and more diffuse orbitals are not required to properly describe the wave function. The S_1 bonding of **2e** represents a highly localized way of dealing with electronic excitation in σ bonded systems and has not been previously recognized. Analogs of **2e** in longer oligosilanes are discussed in Chapter 4.

Atoms that have been traditionally labeled as hypervalent in molecules such as SF_4 , are thought to participate in 3-center 4-electron (3c-4e) bonding.¹⁷⁰ The polarization minimum **2e** has some similarities to such systems with hypervalent atoms that should be pointed out. A large valence angle is typical for trigonal bipyramidal coordination, as seen in SF_4 .¹⁷¹ For **2e** there is a large CSiC angle (Figure 2.67). Geometric hypervalency does not require electronic hypervalency and vice versa, as pointed out by Schleyer.¹⁷² 3c-4e bonding is defined as having a strong preference

of the electron density to be described by the X: A-X $\leftrightarrow$ X-A :X resonance structures for a central atom (A) and substituents (X). In the case of **2e** a 3c-4e bond was not found with the 3c-4e bond search in NBO program. This could be because the Si atom (A) is more electronegative in the S_1 state than in the S_0 state, as witnessed by the less positive natural charge, thus lowering the preference for the 3c-4e description which gives the X substituents more electrons than the central atom. Another reason why the NBO search failed to locate a 3c-4e bond could be that the covalent resonance structure still has a higher weight than the 3c-4e resonance structures and the default threshold for determining the 3c-4e bond was too high. Nevertheless, **2e** has some characteristics of the 3c-4e bonding. Besides the large C-Si-C valence angle (168°) and large Si-C bond lengths (1.97 Å), there is also a high σ^* C-Si antibonding occupation of 0.24 e^- (light blue colored atoms in Figure 2.67). This is expected from the high NHO occupations between the Si and C atoms (which totaled over 2 e^-). Examination of the occupations in the **2e** polarization minima obtained from various optimizations shows there is a competition involving where to place the electron upon $\sigma\sigma^*$ excitation: into the C-Si σ^* orbitals or into the nonbonding NHO. Usually, the central atom in the 3c-4e bond has hybrid orbitals with higher p character than what was observed for **2e** (sp^2). This can be explained by the higher than normal electron occupations in these hybrids ($\sim 0.8 e^-$), as higher occupations induce higher s character to the hybrid orbitals, in general. The polarization minimum **2e** does have resonance structures which correspond to the 3c-4e description, and thus the bonding can be regarded as having at least partial 3c-4e character.

2.4.2.2 S_0 - S_1 Funnels

According to the single reference methods utilized in this work, the disilane can reorganize to find the funnels **2Fa**, **2Fb**, **2Fc**, and **2Fe**. An asymmetric distortion of hexamethyldisilane clearly disrupts the equal weights of the zwitterionic hole pair valence bond description of the **2a** $\sigma\sigma^*$ state, giving rise to a heterosymmetric biradicaloid. These types of reactive intermediates are expected to be found in conical intersections,²² and in the case of **2** the funnel is represented by **2Fa** and **2Fe**. This can be visualized by the difference in the natural atomic charges of the Si atoms.

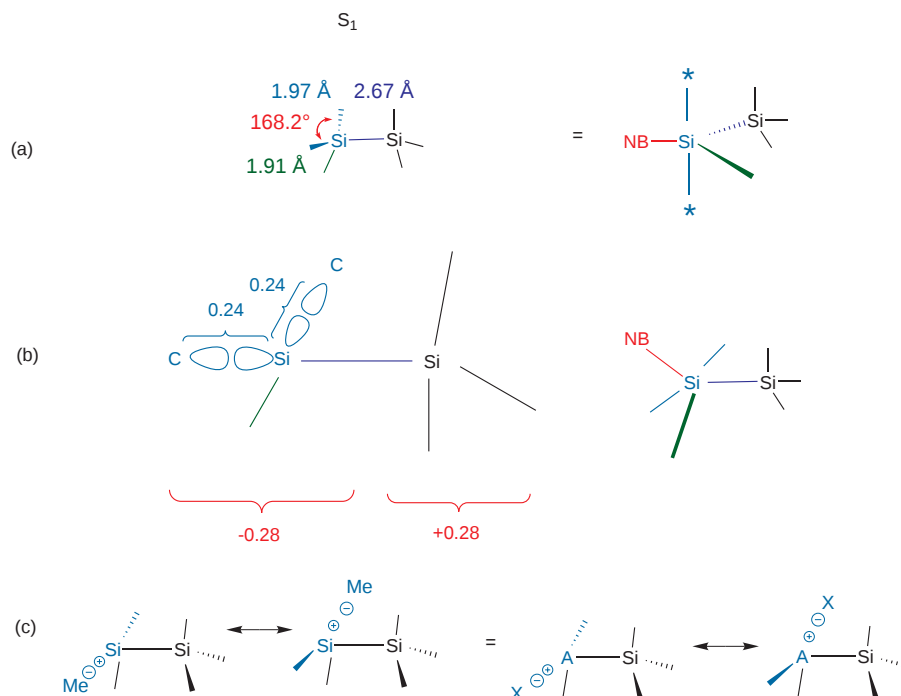


Figure 2.67: NHO analysis for **2e** S_1 density of the RICC2/TZVP structure, selected geometrical parameters with asterisks indicating axial substituents (a), selected NBO antibonding (σ^*) occupations (b), and natural resonance structures (c). NHO calculations were performed with the CIS/6-311G(d,p) method. Si atoms of the proposed 3-center 4-electron bond are shown in light blue color.

Additionally, according to the NHO analysis of the BHLYP/TZVP structure, there is considerable occupation ($0.26 e^-$) in a fifth orbital, which is of nonbonding character. Ground state (CASSCF) optimization on the stochastically perturbed funnel structures returned the molecules to **2G** with a strikingly large probability, most likely due to the high weight of the covalent resonance structure in the natural resonance theory description of the S_0 density.

The rearrangement products that were also located via optimization of CASSCF S_0 wave function were the homolytic Si-Si bond cleavage product **17**, a silylene extrusion plus tetramethyldisilane product **18**, methyl dissociation product **19** and the ethane plus silylene product **20**. Overall, these products seem quite reasonable. The silylene in product **20** is known to rapidly convert to silene.¹³⁶ Products **17** and **18** are expected from known processes in larger oligosilane chains.¹⁰⁰ Silylene is the known major thermal decomposition product for Si_2H_6 .^{173,174} Product

19, on the other hand, has been searched for but never observed in the (GC-MS, NMR) analysis of the photolysis products of oligosilanes.^{100,136} Product **20** is a known minor product in the thermal decomposition of Si_2H_6 .^{173,174} It should be stressed that with the stochastic search of the ground state funnel region, these products appear to be rare events, but the product branching ratios should not be taken seriously unless nonadiabatic molecular dynamics methods are used. The method used here simply yields various products that are possible in the molecular relaxation process. Various kick sizes to different groups were modeled on the molecular rearrangements of the excited state minima. The results of the large kicks might be more realistic than small kicks as the disilane will have a large amount of kinetic energy, as evident from the large site distortion energies. If the S_0 - S_1 energy gap is very small, small kicks might more appropriate to simulate ground state return of the molecules. The S_0 - S_1 energy gap was less than $4\,000\text{ cm}^{-1}$ in all cases, but this is still rather large. Finally, it should be noted that two of the products, **18** and **20**, were predicted by the analysis of the natural resonance structures in section 2.3.2.5.

The geometries of the funnel structures in Table 2.12 are very approximate as the methods used for excited state optimization do not contain multireference wave functions, and structures located near funnels or conical intersections are intrinsically multireference in nature. The need for static as well as dynamic correlation is indicated by the D_1 and D_2 diagnostics, respectively.

The structures **2Fa** and **2Fe** resemble those of the alkene analog, the twisted monopyramidalized conical intersection for ethylene which has been found with multireference configuration interaction with singles and doubles (MR-CISD)¹⁷⁵ and MSCASPT2 methods.¹⁷⁶ As long as these funnel structures (**2Fa**, **2Fb** and **2Fc**) still exist with higher levels of theory (that include both static and dynamic correlation), the exact geometries of the conical intersection are not so important as internal conversion takes place throughout the general vicinity of a conical intersection.

2.4.2.3 Excited States

For **2a**, the vertical emission energies of the structures obtained with RIADC(2) and RICC2 are in line with experimental fluorescence energy extrapolation of band maxima ($24\,700\text{ cm}^{-1}$)

Table 2.44: D₁ and D₂ diagnostics (calculated for S₀ with the RIADC(2)/TZVP method) for **2** S₁ minima and S₀-S₁ funnels.

Structure	Method	D ₁	D ₂
1a	PBE0	0.023	0.21
2a	B3LYP	0.023	0.21
2a	BHLYP	0.023	0.21
2a	RIADC(2)	0.025	0.22
2a	RICC2	0.025	0.21
2b	B3LYP	0.027	0.30
2c	B3LYP	0.025	0.26
2d	B3LYP ^a	0.022	0.22
2e	PBE0	0.025	0.25
2e	B3LYP	0.025	0.25
2e	BHLYP	0.027	0.25
2e	RIADC(2)	0.062	0.26
2e	RIADC(2) ^a	0.032	0.28
2e	RICC2	0.030	0.26
2Fa	RIADC(2)	0.1097	0.51
2Fb	RIADC(2)	0.0548	0.38
2Fc	RIADC(2)	0.0987	0.50

^a This structure originates from the RIADC(2)/Def2-TZVP-mD S₁ optimization.

from longer oligosilanes,¹¹⁶ even though these structures are not calculated to be minima on the S₁ surfaces. The experimental extrapolation is also in good accord with the minimum energy structure **2a** obtained with the PBE0/TZVP method (25 470 cm⁻¹). This emission energy carries the most credibility as it was found that only the PBE0 functional characterized the **2a** structure as a minimum. Nevertheless other **2a** stationary points gave similar energies, with the exception of that obtained with the BHLYP/TZVP method which gave an emission energy which is too large and could be due to an excessively stabilized ground state energy at the BHLYP/TZVP **2a** transition state geometry. For the **2a** structure obtained with PBE0/TZVP method, both B3LYP/Def2-TZVP-mD and the LC-BLYP/Def2-TZVP-mD methods gave very similar emission energies (25 330 and 25 220 cm⁻¹, respectively). This close agreement is likely due to the high Λ value for the transition, indicating accurate reproduction of the emission energy with standard TDDFT methods.

Calculated emission from the Si-C bond stretch minimum, structure **2b**, can be described as

having some charge transfer character as electron density moves from the stretched Si-C bond into the Si-Si framework. This can be visualized by plotting the difference density in Figure 2.37 where blue color indicates loss of electron density and red color indicates a gain of electron density upon excitation to the S_1 state. The NHO analysis shows Si(1) to be of silylene hybridization with a quasi-lone pair pointed towards Si(2) and a p orbital of reduced occupation pointing towards the stretched bond to the methyl group of C(1). While this charge transfer is not over a large distance, there is a lowering of the Λ parameter value when compared to **2a**, and B3LYP/Def2-TZVP-mD and LC-BLYP/Def2-TZVP-mD emission energies now vary significantly (by 1 670 cm^{-1}). As diffuse functions do not significantly change the emission energy, this difference is attributed to partial charge transfer character of the transition.

The calculated emission from the structure **2c** has a large basis set dependence. If no diffuse basis functions are used, a valence excited state is obtained, as evidenced from Figure 2.31 and the high Λ value of 0.51. S_1 is of strong Rydberg character. This is evident from the large change in emission energy as diffuse functions are added to the basis set. A lower S_0 - S_1 oscillator strength and Λ parameter value also result when diffuse functions are added to the basis set. It seems the B3LYP-AC/maug-cc-pVTZ calculation seriously underestimates the emission energy of this transition, as the difference between the emission energy between that obtained with the LC-BLYP/Def2-TZVP-mD method (with $\mu=0.23 a_0^{-1}$) differ greatly (1 990 cm^{-1}). Diffuse basis functions had a much smaller effect on the simple valence S_0 - S_1 transition of **2a**: the emission energy difference was only 380 cm^{-1} .

While the basis set choice had a large impact on the emission energy of the Rydberg minimum **2d**. Even in the absence of diffuse functions, the first excited state had Rydberg character. This is partially evident from the consistently low Λ value for **2d**. In **2d**, the LC-BLYP value varies slightly more (2 040 cm^{-1}) from the RICC2 value than in **2c** (1 460 cm^{-1}). This can be due to the μ parameter which was optimized to reproduce a valence excited state and not a Rydberg excited state. Unfortunately, the optimal μ parameter can be different for different excited states in a molecule.¹⁷⁷

Examination of the S_1 emission energies, oscillator strengths and Λ values of the various structures of **2e** is very instructive concerning the origin of emission energy differences between ab initio **2e** and TDDFT **2e** structures. The large difference between B3LYP and LC-BLYP emission energies is likely caused by artificial CT contamination from TDDFT. As seen in **2b**, diffuse functions do not significantly change the emission energy. Additional HF exchange helps to correct the artificial CT problem (the PBE0 functional contains 25 % HF exchange, and the BHLYP functional contains 50% HF exchange). In this case, emission energies from the ab initio RIADC(2) and RICC2 **2e** structures are lower than that of the PBE0 TDDFT **2e** structure. Emission energies from various methods for the **2e** structure obtained with BHLYP functional are between those of the PBE0 and RIADC(2) **2e** structures. A similar trend is followed with the S_0 - S_1 oscillator strengths and Λ values, where the PBE0 **2e** structure consistently gave lower values, the RIADC(2) structure higher values and the BHLYP structure intermediate values. Lower S_0 - S_1 oscillator strengths and Λ values are indicative of transitions of increased CT character. Because the emission calculations were done with various methods, including ab initio methods, the differences in E_{VE} (and other properties) indicate that artificial CT has been built into the optimized structures. The Λ values for the **2e** PBE0 structure are not very low on average,⁶⁵ but result in greatly different emission energies from those of the ab initio structures. The **2e** PBE0 structures had an average emission of 19 100 cm^{-1} whereas the average emission energy for the **2e** RIADC(2) structure is much less at 14 550 cm^{-1} . For the **2e** RIADC(2) structure, the standard TDDFT excitation energy does not vary significantly from the LC-BLYP result, most likely because artificial CT has not been built into this structure.

2.4.2.4 Hexamethyldisilane Barriers

Why does **2** not emit? Small barriers, as suggested by low vibrational frequencies for excited state minima in section 2.3.2.7, as well as large site distortion energies, indicate that easily accessed funnels are likely to play a large role. The site distortion energy represents a loss of electronic potential energy that is converted into kinetic energy and allows the small silane to find funnels.

While minima might be accessed it may only be momentarily. Given the weak S_0 - S_1 oscillator strengths of the minima, this could explain the lack of fluorescence even at low temperatures.

Using relaxed geometry scans along a distinct coordinate as a method of barrier calculation is very crude and is only used to obtain a rough estimate of the barrier size that molecules encounter on the way to a S_0 - S_1 funnel. This method is susceptible to corner cutting on the potential energy surface;¹⁷⁸ and therefore vibrational scans were calculated to get a higher energy value for the barrier. For **2e**, the relaxed C(2)Si(1)Si(2) valence angle scan gave a barrier of approximately 350 cm^{-1} . The S_0 - S_1 funnel region is located around 134° for the C(2)Si(1)Si(2) valence angle. From the vibrational scan of **2e**, an increase from 132° to 136° costs about 1 000 cm^{-1} . This value can be added to the relaxed scan barrier to estimate a higher limit of the barrier of about 1 400 cm^{-1} . This is still much less than the E_{SD} value of approximately 38 000 cm^{-1} .

The approximated barrier for **2a** is very small, on the order of 10 cm^{-1} , and this probably is the reason why the other methods of calculation did not characterize this structure as an energy minimum on the S_1 surface. These methods (ab initio and TDDFT functionals other than BHLYP) characterized **2a** as a saddle point, indicating a barrierless path to **2Fa**. According to Figure 2.43, the PBE0/TZVP potential along the C(2)Si(1)C(3) valence angle bend is also very flat and the molecule finds the **2Fa** funnel around 140° . If the C(1)Si(1)Si(2) angle is constrained, this is not the case and instead a barrier of 1 200 cm^{-1} is encountered, which represents a higher energy on the pathway to the **2Fa** funnel for **2a**. Again, this is much less than the E_{SD} , estimated to be 27 300 cm^{-1} for **2a**.

The barriers involved for access from **2a** and **2e** to the **2Fa** funnel are therefore less than 1 600 cm^{-1} , the accuracy of the TDDFT method.¹⁶⁹ The nudged elastic band (NEB) method¹⁷⁸ would be an ideal choice for the calculation of more accurate barriers, but as this method would still need to utilize TDDFT due to system size, the accuracy of the barriers would still be in question.

2.4.3 Octamethyltrisilane

For **3**, eight excited state minima were located with the approximate methods used. The minima **3a-e** largely resemble their analogs in **2**. The new minima **3f-h** are unique to **3**.

The Si-Si bond stretch minimum **3a** structures have a similarly distorted disilane fragment as that of **2a**, and are now characterized as minima with BHLYP/TZVP, RICC2/TZVP and RI-ADC(2)/TZVP methods. This suggests that the trisilane Si-Si bond stretch minimum structure is stabilized with respect to the disilane analog. In the case of **3**, there is a longer silicon backbone along which a plane of symmetry can very easily be defined. With respect to this plane of symmetry, the S_1 state of **3a** has strong $\sigma\sigma^*$ character (Figure 2.56).

The overall assignment of the $\sigma\sigma^*$ state of **3a** is strengthened by examination of the transition density which appears to be more like that of the $\sigma\sigma^*$ state than that of the $\sigma\pi^*$ state of **3G** (Figure 2.60). The extrapolated octamethyltrisilane emission value is $25\,400\text{ cm}^{-1}$.¹¹⁶ This value agrees more closely with E_{VE} value calculated for the ab initio **3a** structures than the BHLYP/TZVP **3a** structure. The emission energy value for the BHLYP/TZVP **3a** is similarly blue-shifted to the experimental estimate of the extrapolated emission energy. This blue shift is similar for the of the BHLYP/TZVP **2a** structure.

The structure **3g** has a well defined $\sigma\sigma^*$ state. This minimum was obtained with PBE0/TZVP and B3LYP/TZVP methods. This structure appears to be similar to the polarization minimum in that a large space has been made for a nonbonding orbital in this case via a SiSiSi valence angle distortion, as opposed to the CSiC valence angle distortion which occurs on a terminal Si atom and on an internal Si atom for **3e** and **3f**, respectively. The basis set size was important for obtaining the **3g** minimum with the TDDFT method, as the BHLYP optimization with the SVP basis set gave rise to **3Ff**, the large SiSiSi valence angle funnel.

Finally, **3h**, found with all the TDDFT functionals tested, shows strong $\sigma^*\pi^*$ mixing in the S_1 state. From Table 2.37 it is also apparent that some CT contamination is built into the relaxed structure via the TDDFT optimizations. In this case, the effect on the transition density is strong

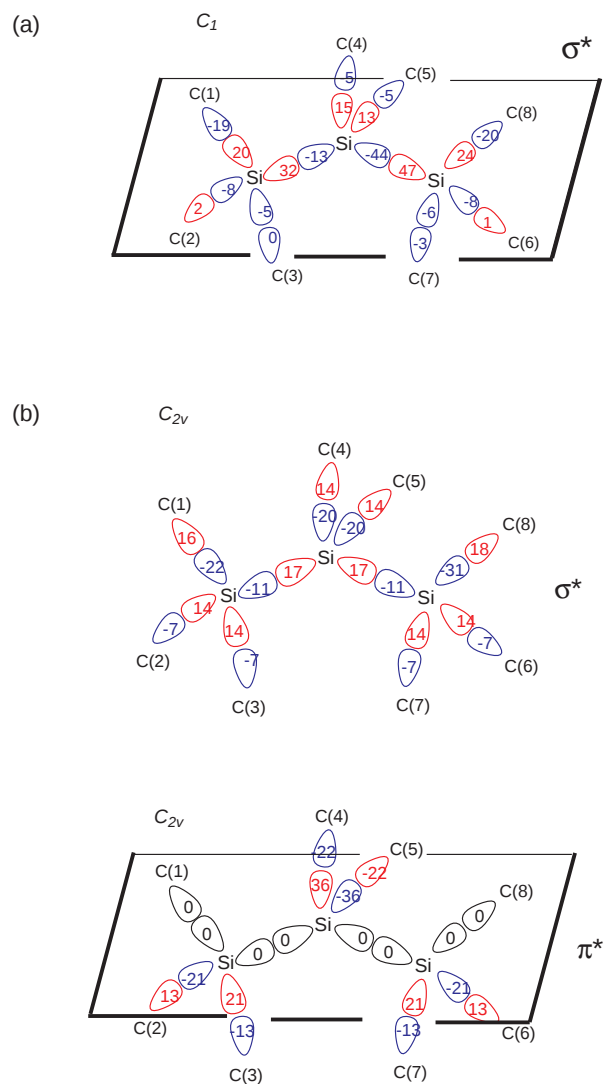


Figure 2.68: Illustration of orbital symmetry in **3a** (BHLYP/TZVP structure). The reference C_{2v} **3** structure is shown as well. MOs are expressed in the NHO basis. NHO coefficients (CIS/6-311G(d,)) are shown multiplied by 100.

and is visualized in Figure 2.61. This minimum seems to be a trisilane analog of that found by Teramae et al.¹²⁶ for tetrasilane. The minimum energy tetrasilane structure found with CASSCF methods also has small SiSiSi valence angles (90°) and a pair of large SiSiC valence angles (153°). The exciton in the aforementioned tetrasilane was found to be localized between the central Si atoms and the Si-C bonds. Considering that this minimum (**3h**) has the largest E_{SD} ($10\,000\text{ cm}^{-1}$), it is not surprising that it was found earlier in analogous oligosilanes.

2.4.3.1 Funnels

For **3**, the silylene extrusion funnel **3Fh** is similar to those found earlier for 2-methyltrisilane.¹³³ Indeed, internal silylene extrusion is a common synthetic method for decreasing oligosilane chain length.¹²⁸ Computationally, there seems to be little or no S_1 barrier to access this funnel, as ab initio RICC2 and RIADC(2) optimization of **3h** leads directly to **3Fh**. This barrier seems to increase in longer oligosilanes as RIADC(2) optimization of a similarly structured tetrasilane molecule (**4h2**, Chapter 4) led to a minimum energy structure.

According to the TDDFT (BHLYP) and ab initio methods used in this work there also can be a large angle funnel **3Ff**. The driving force for this structure can be rationalized by simple minimization of the antibonding interactions in the σ^* orbital, shown in Figure 2.69. Ground state optimization of this funnel and stochastically perturbed structures derived from **3Ff**, returned the molecules to the C_2 symmetric ground state minimum structure **3G**. The optimizations show possible inversion of the center Si atom, and rotation of terminal methyl groups, but in the absence of atomic labels these structures are indistinguishable.

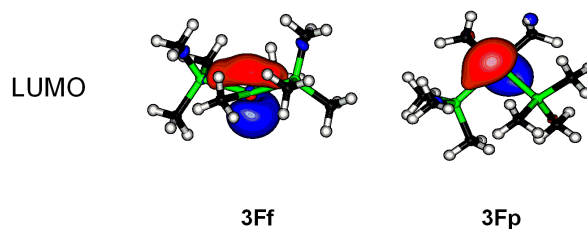


Figure 2.69: LUMO orbital (B3LYP/Def2-TZVP) for the **3Fg** and **3Fp** funnel structures.

There is no barrier in access from the ground state equilibrium geometry to the **3Fp** funnel as it results from direct optimization of the $\sigma\pi^*$ state of **3G**. This was found using both TDDFT and ab initio methods. This represents an extremely efficient way for **3G**, and possibly larger oligosilanes, to return to the ground state after vertical excitation. Safe return to **3G** is predicted from the NHO analysis of the ground state density of **3Fp**, which resembles that of the ground state equilibrium structure, although the entire vicinity of the funnel has not been examined and

this could simply be the result having a structure which lies strongly to one side of the conical intersection. The driving force for structural reorganization of the $\sigma\pi^*$ state of **3G** to **3Fp** seems to be a minimization of the Si-C antibonding interactions. These interactions are decreased if the Si-C bonds rotate into the plane of symmetry defined by the Si backbone as this plane of symmetry represents a node for the π^* orbital (Figure 2.69).

Methyl and larger substituents seem to stabilize the excited S_1 state and allow minima to exist. In the parent trisilane and in 2-methyltrisilane, no minima were located. In contrast to the work of Robb and coworkers⁷ which was done with the CASSCF/6-31G(d) method, multiple funnels were located for 2-methyltrisilane. Structures derived from the geometrical parameters of **3a**, **3e**, **3g**, and **3h** were relaxed with the RIADC(2)/TZVP method and are shown in Figure 2.70. No S_1 minima were located and these structures correspond to S_0 - S_1 funnels. With the exception of the Si_3H_8 **3a** analog, the trisilane and 3-methyltrisilane funnel analogs are very similar to their octamethyltrisilane counterparts. The trisilane **3a** analog has a larger rearrangement of the internal substituents as opposed to the terminal substituents in **3Fa**.

2.4.3.2 Proposed Hindered Oligosilanes for Possible Fluorescence Detection

Constrained oligosilanes have been used to alter conformational populations and barriers, leading to new fluorescence quantum yields.⁹⁹ The bulky substituents of **21** and **22** will hopefully hinder the silylene extrusion process and allow the $\sigma\sigma^*$ minima to be accessed and experimentally verified via fluorescence detection.

The isopropyl groups in **21** do not greatly alter the SiSiSi valence angle in the ground state, but in the excited state optimization narrow valence angle minima were not directly located in the excited state optimization. Additionally, an extremely large SiSiSi valence angle might not be desired as it could lead to an increased likelihood of encountering the wide SiSiSi valence angle funnel, analogous to that of **3Ff**. The S_1 ($\sigma\sigma^*$) state of **21** is located at 44 520 cm^{-1} , much lower than in **3G**. The synthesis of **21** should be extremely facile, and thus this hypothesis should be tested.

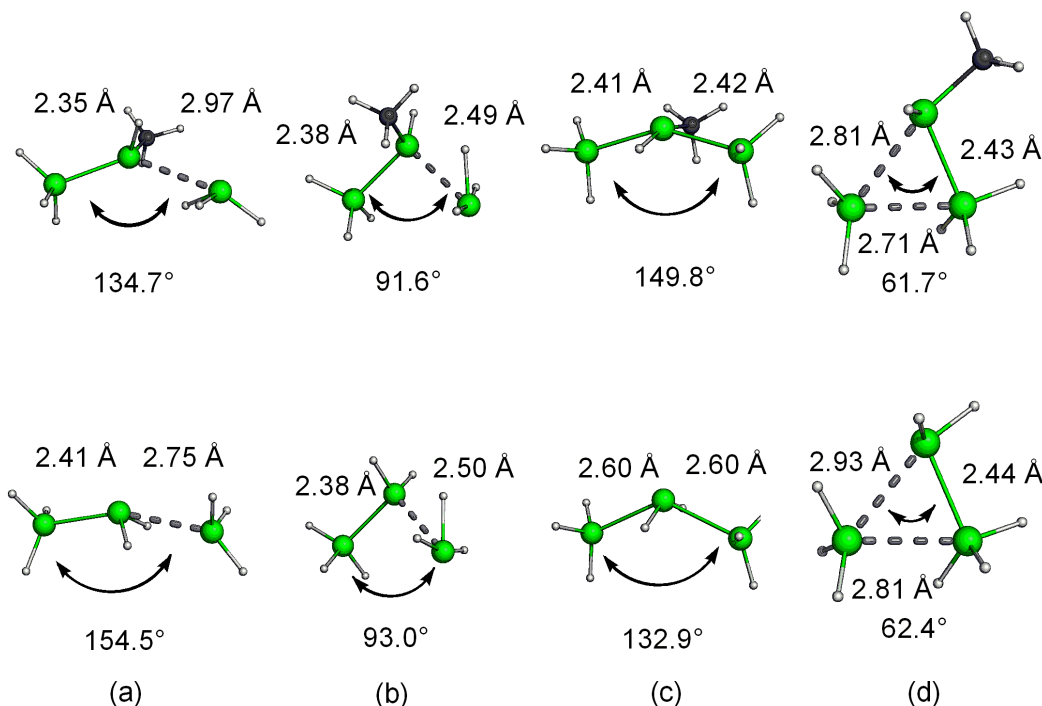


Figure 2.70: Parent trisilane and 2-methyltrisilane analogs of the **3Fa** (a), **3Fe** (b), **3Fg** (c), and **3Fh** (d) funnel structures. The Si-Si bond length is indicated as well as various HSiSi valence angles.

The *t*-butyl groups should keep the SiSiSi valence angle fairly wide in **22**, most efficiently discouraging internal silylene extrusion and possibly promoting fluorescence. The ground state SiSiSi valence angle of 134.7° (RIMP2/TZVP) of **22** is very close to that of the **3a**, 134.9° (RI-ADC(2)/TZVP). The bond lengths of these structures are also similar, thus possibly allowing for more direct access of **22** to the $\sigma\sigma^*$ state. Indeed, the vertical absorption energy of the S_1 ($\sigma\sigma^*$) state is calculated to be 44 000 cm^{-1} .

The trend in vertical S_0 - S_1 absorption energies and oscillator strengths for both **21** and **22** will help to increase the quantum yield to the $\sigma\sigma^*$ states. Also promising is the increased S_0 - S_1 oscillator strength of the relaxed S_1 structures. If emission is observed, variation of the solvent should be carried out as the $\sigma\mu^*$ state was calculated for the Si-C bond stretch structures of **21** and **22** (PBE0/SVP) to have a much larger S_1 dipole moment than the $\sigma\sigma^*$ state of the Si-Si bond stretch structures (BHLYP/SVP) of **21** and **22**.

The $\sigma\pi^*$ deactivation mechanism is likely to be hampered in **21** and **22**. Access to the funnel **3Fp**, found from optimization of the $\sigma\pi^*$ state, will be mitigated as the $\sigma\sigma^*$ is now the lowest vertical excited state reached from ground state equilibrium geometries.

Until now, the main funnel for the octamethyltrisilane return from S_1 to S_0 was believed to be that of the internal dimethylsilylene extrusion funnel **3h**. The bulky groups are meant to hinder relaxation via this funnel. If fluorescence is detected from these trisilanes, besides being the first detected emission from a trisilane, it would support the idea that this funnel is a major part of the excited state quenching mechanism. If emission is not detected, it would also be interesting as this would, albeit indirectly, support the existence of the new funnels found in this work, especially the wide SiSiSi valence angle funnel **3Ff**.

The limits of localization and trends of the properties (E_{VE} , f etc.) of these minima in longer oligosilanes will be addressed in later chapters. The Si-Si bond stretch minima appear in longer chains and are addressed in Chapter 3. The analogs of the other minima found in this chapter will be examined in Chapter 4.

2.5 Conclusions

Calculations on the vertical emission of **1** showed that excited state structure can strongly influence S_0 - S_1 emission energy and oscillator strength. Specifically, the CSiC valence angle strongly influences Si hybridization. The CSiC angle also directly affects the electronic transition energy and oscillator strength as the 1^1A_1 to 1^1B_1 transition involves lone pair electronic excitation to orthogonal p_x Si orbital. The relaxed CSiC valence angle scans in disilane and trisilane also showed a similar emission energy dependence on valence angle. A decrease of E_{VE} and f with increasing CSiC angle was found.

For **2**, five new minima on the S_1 surface have been found. These minima correspond to a Si-Si bond stretch minimum, **2a**, a C-Si bond stretch minimum, **2b**, a diffuse Si-Si bond stretch minimum, **2c**, a Rydberg minimum **2d** and a polarization minimum, **2e**. The Si-Si bond-stretch minima are predicted to emit in the blue spectral region, **2b** and **2e** in the green spectral region,

and **2c** and **2d** in the UV ($30\,000\text{ cm}^{-1}$). These minima have not been previously identified their analogs could also be present in longer oligosilanes, as will be shown in later chapters. The lack of fluorescence is attributed to small barriers on the way to funnel structures and extremely large site distortion energies. The barrier for **2a** to access **2Fa** is predicted to be nonexistent (or very small, 10 cm^{-1}), via a relaxed CSiC valence angle scan. The barrier for **2e** to access the **2Fa** funnel was calculated to be 350 cm^{-1} via a SiSiC relaxed valence angle scan, also inconsequential compared to the site distortion energies of the minima.

For **3**, eight new minima have been located. The analogs of the **2** minima were located as well as three minima that are unique to longer oligosilanes. The new minima correspond to an internal Si polarization minimum **3f**, a wide SiSiSi valence angle minimum **3g**, and a narrow SiSiSi valence angle minimum **3h**. These new minima also provide access to new funnels such as a wide SiSiSi valence angle funnel **3Ff**. The barrier to the **3Fa** funnel from the **3a** relaxed CSiC valence angle scan is predicted to be 540 cm^{-1} , significantly larger than in the disilane analog (10 cm^{-1}). An efficient deexcitation mechanism that only involves twisting of the internal methyl groups into the Si backbone plane of symmetry (**3Fp**) has been identified. Finally, hindered molecules that have significantly larger S_0 - S_1 oscillator strengths and are likely to prevent access to the **3Fh** funnel have been proposed and experimentalists are challenged to observe fluorescence from these small oligosilanes.

How do σ bonds accommodate $\sigma\sigma^*$ excitation? The valence minima appear to belong to two classes: (i) Minima resulting from an excited state which contain high $\sigma^*\pi^*$ mixing, and (ii) Minima resulting from excited states which have structurally reorganized to minimize antibonding interactions in the LUMO. This is also referred to as minimization of the (electronic) kinetic energy in the literature.¹¹⁹ All minima have electronic rehybridization with respect to the typical ground state sp^3 reference point.

Class (i) includes **2b**, **3b** and **3h**. These structures usually have little or no symmetry and large orbital amplitudes between Si atoms and between Si and C atoms that are arranged in a way that indicates mixing between σ and π orbitals. The rehybridization is from sp^3 towards sp and p

hybridization, the silylenic limit.

Class (ii) includes **2c**, **3c**, **2e**, **3e** and **3g**. These minima tend to have more symmetry and less electronic mixing of the $\sigma\sigma^*$ and $\sigma\pi^*$ states. In these minima, a Si atom can become pentavalent and localize an electron into a nonbonding orbital. Interestingly, the 4s and 4p orbitals are preferentially used rather than the 3d orbitals to add a nonbonding orbital to accommodate excitation in at least one case (**2e**) in σ bonded systems, although the 3d orbitals seem to also be involved to some extent and are more important than the 4s and 4p orbitals in the nonbonding orbital of **3g**. While the nonbonding orbital has typically low occupation ($< 0.5 e^-$), this orbital seems to have a profound effect on structure, creating large CSiC (**2e** and **3e**), large SiSiSi (**3g**) and large SiSiC (**2Fa** and **3Fa**) valence angles. If the funnels were to be characterized as well, they would also nicely fit into class (ii) in terms of having a driving force that seems to minimize the kinetic energy of the antibonding orbital that helps to characterize the state. The **2Fa**, **3Fa**, **2Fc** and **3Ff** funnels can also become hypervalent.

2.5.1 Practical Considerations

S_1 structures **2b**, **2c** and **2d** obtained with TDDFT results varied greatly depending upon the functional used and only sometimes gave similar results to the ab initio methods (RICC2 and RIADC(2), *e.g.*, **2e**). Therefore, numerous functionals and basis sets should be tested. Analysis of the S_0 - S_1 transition density and Λ parameter value for the various excited state minima shows TDDFT excited state optimizations can be dangerous as artificial CT can be built into the structure when an excited state is optimized. This seems to only be a minor problem for hexamethyldisilane, but it could become serious if the size of the oligosilane is increased.

2.5.2 Future Work

S_1 optimizations with LC-TDDFT within the TDA approximation and using various functionals should be carried out as analytical gradients become available. Another promising approach is to test the metafunctional of Truhlar and coworkers, M06-2x and M06-HF. These functionals

contain a high amount of HF exchange and should be tested as soon as analytical gradients are available. Nudged elastic band (NEB) calculations can be done to confirm various barrier heights. Finally, nonadiabatic molecular dynamics calculations and transient absorption spectroscopy can be carried out to estimate the time scales involved for the deactivation mechanisms proposed in this work.

Chapter 3

The Normal and Blue Emission in Oligosilanes

3.1 Introduction

A hallmark of delocalization phenomena is size dependence of a given property. In this chapter, delocalization effects in linear permethylated oligosilanes will be examined. This will include how properties scale with chain length in the normal and blue emitters. The normal emitters are defined as those which give rise to Franck-Condon allowed fluorescence and the blue emitters are those which give rise to Stokes-shifted fluorescence in the blue spectral region. The properties of primary focus in this chapter have to do with the chain-length-dependent shift of the electronic absorption and emission spectra and are the topic of this chapter.

It has been postulated for many years that the highly Stokes shifted emission in the blue spectral region from peralkylated oligosilanes is due to bond stretch isomers with highly localized excitation.¹²⁴ Until now, electronic structure calculations have not been able to locate geometrically relaxed excited singlet states structures whose emission energies correlate with experiment. This chapter aims to elucidate the extent of localization in the blue exciton. Other questions will be addressed as well. These include: What do the blue excitons look like? Can they exist in larger oligosilanes?

Little is known about how saturated molecules (containing only σ bonds) relax upon electronic excitation. From an extremely oversimplified viewpoint, structural relaxation upon electronic excitation can be thought to take place either over the entire molecule (Figure 3.1 (a)) or in localized regions (Figure 3.1 (b-d)). We will see that situations (b)-(c) in Figure 3.1 correspond to slightly

more localized excitation, whereas in situation d, excitation is even more localized and geometrical rearrangements reside in a twisted region of the molecule.

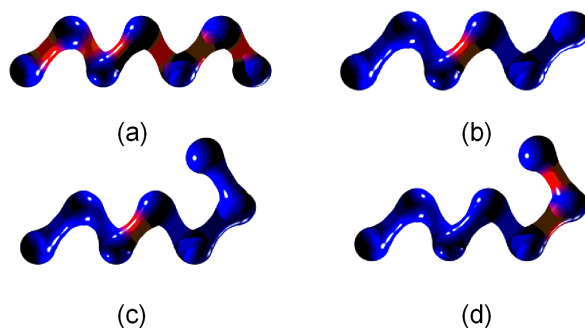


Figure 3.1: Schematic showing structural relaxation (red) in delocalized excited states (a), and in localized excited states (b-d).

This chapter will contrast the delocalized excitation of longer silanes with that of the more localized excitation which is believed to be responsible for Franck-Condon forbidden emission in the blue spectral region in shorter oligosilanes. Finally, this chapter will demonstrate that blue emission may be possible from very long oligosilanes, if the correct conformations are excited.

3.1.1 Experimental Observations

Blue emission from permethylated oligosilanes was first reported in 1992 by Sun and Michl for **6**.¹²³ These authors reported a distinctly Stokes-shifted, Franck-Condon forbidden emission centered at $28\,600\text{ cm}^{-1}$ with a width at half-maximum of $5\,350\text{ cm}^{-1}$ at 77 K, unlike the narrow band typical of the Franck-Condon allowed emission found in longer oligosilanes. The authors noted that the fluorescence quantum yield of **6** was strongly temperature dependent. At low temperatures (77 K) they reported a quantum yield of 0.45 ± 0.05 which at room temperature decreased to be less than 10^{-4} . At low temperatures the fluorescence quantum yield was independent of excitation energy. The authors fitted the fluorescence decay (measured at 77 K) with a single exponential function to yield a fluorescence lifetime of $1.2 \pm 0.1\text{ ns}$, which was longer than the authors expected from the integrated absorption intensities. The activation energy for a dark channel, leading to diminishing fluorescence quantum yield, was estimated to be 2.1 kcal/mol. Measurements were

carried out in 3-methylpentane. At 77 K, the fluorescence polarization was measured to be 0.35 ± 0.03 for **6**, and was independent of excitation energy.

Raymond and Michl reported the absorption and fluorescence of the linear permethylated $\text{Si}_n\text{Me}_{2n+2}$ oligosilane series in which $2 \leq n \leq 16$ (**2-16**).¹¹⁶ By comparing the temperature dependence of the absorption spectra of the oligosilane series, the authors concluded that at 77 K and below low-energy absorption is due to the extended conformers for $n < 7$ and mostly due to these extended conformers in longer oligosilanes. Comparison of the absorption curves for the permethylated oligosilanes to those of conformationally constrained oligosilanes also played a role in the assignment of the low-energy region of the absorption band to extended conformers.¹¹⁶ The fluorescence found by Raymond and Michl was attributed to relaxed species of these extended chains after the excitation. The absorption and fluorescence spectra at or below 298 K are shown in Figure 3.2. This figure shows the Franck-Condon allowed emission for $n \geq 7$ and a highly Stokes-shifted blue emission ($26\,000\text{ cm}^{-1}$) for $4 \leq n \leq 6$. The Franck-Condon forbidden emission blue-shifted upon cooling for $4 < n \leq 6$ (Table 3.1).

Table 3.1: Summary of experimental fluorescence peak maxima (E_{VE}) from the work of Raymond and Michl.¹¹⁶ The E_{SS} and temperature of the experiment are given below.

Compound	T / cm^{-1}	E_{VE} / K	E_{SS} / cm^{-1}
4	17 ^a	26 300	16 800
5	120	26 000	14 100
	30	27 600	12 500
6	120	26 800	11 300
	30	29 600	8 500
7^b	132	27 200	10 000
7	77	35 100	1 500
8	77	34 700	800
10	77	33 500	600
16^c	77	31 300	350

^a Experiment carried out on neat compound. ^b Data from Raymond et al.¹²² ^c In 3-methylpentane.¹²³

Above 100 K, a very broad emission peak was observed for permethylated heptasilane (Figure 3.3). It was decomposed by using Gaussian fitting, and the difference between the emission spectra

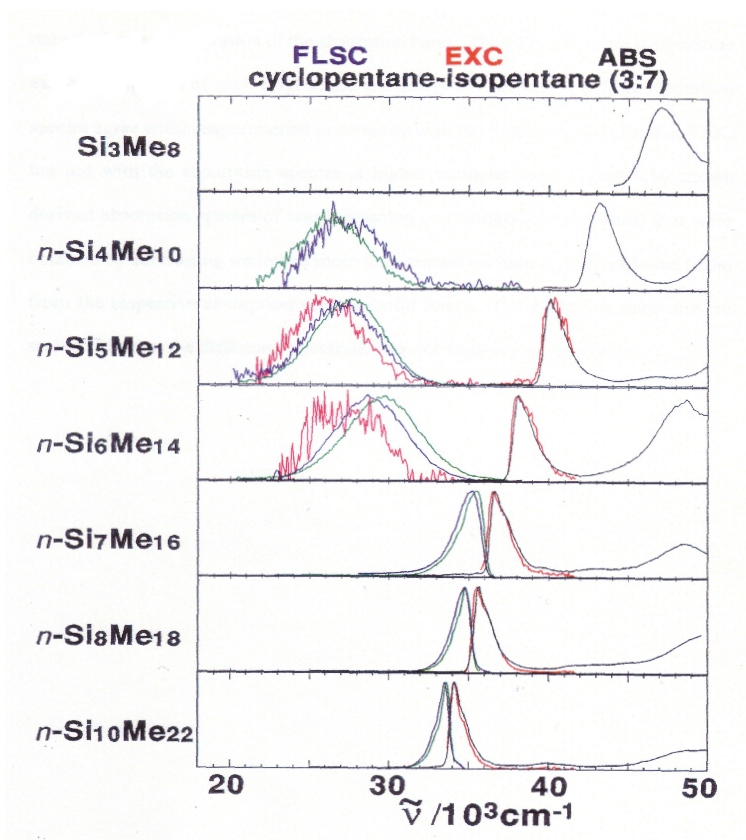


Figure 3.2: Reproduced from Raymond and Michl.¹¹⁶ Absorption, and excitation (red) spectra of $\text{Si}_n\text{Me}_{2n+2}$ at 77 K in isopentane:cyclopentane (7:3). Emission for **4** measured at 17 K (green) and 60 K (purple). Emission for **5** measured at 30 K (green), 78 K (purple) and 100 K (red). Emission for **6** measured at 30 K (green), 74 K (purple) and 298 K (red). The peak maxima were normalized to unity.

taken at 40 K and 132 K yielded a peak with a width at half-height of about $7\,600\text{ cm}^{-1}$ centered around $29\,000\text{ cm}^{-1}$, corresponding to a Stokes shift of about $10\,000\text{ cm}^{-1}$.¹²²

In a cyclopentane:isopentane (3:7) solvent mixture, the fluorescence lifetime, fitted to a single exponential, was 700 ps at 108 K for **6**. This is slightly longer than that of the normal emission of the permethylated octasilane (530 ps for decay at 106 K).

Mazières et al.¹²⁸ measured the fluorescence from a constrained hexasilane, **6-r2**, shown in Figure 3.4. This compound also showed multiple emission signals in the blue spectral region. The Franck-Condon forbidden emission peak blue-shifted (from $27\,000\text{ cm}^{-1}$ to $29\,600\text{ cm}^{-1}$) upon cooling from 128 K to 31 K. The staffane rod in the racked compound **6-r2** (Figure 3.4), is believed

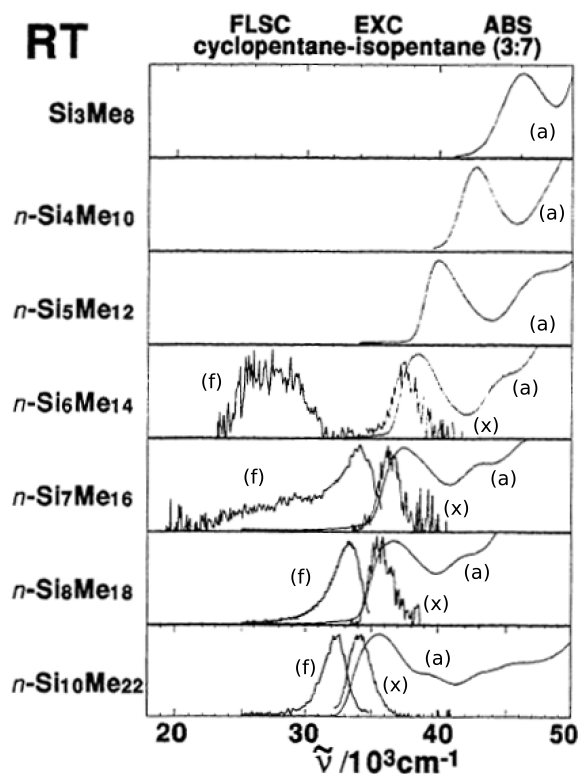


Figure 3.3: Reproduced from Raymond¹⁷⁹ Emission (f), absorption (a), and excitation (x) spectra of $\text{Si}_n\text{Me}_{2n+2}$ measured at room temperature (RT). The peak maxima were normalized to unity.

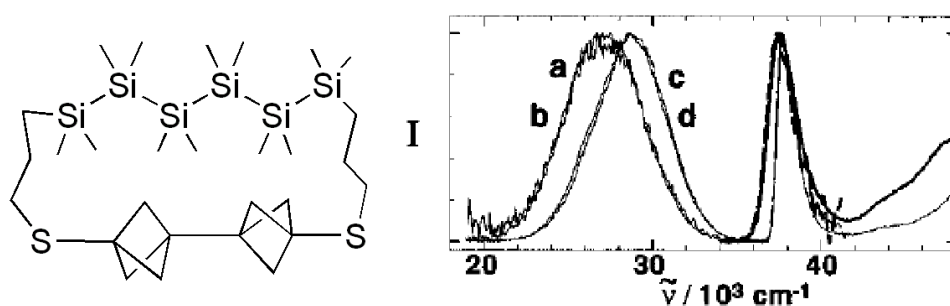


Figure 3.4: Reproduced from Mazières et al.¹²⁸ Emission at 134 (a), 110 (b), 56 (c), and 37 (d) K. The absorption curve (full line) and excitation (dashed) spectra at 298 K (fat line) and 77 K (thin line) of **6-r2** (left).

to stretch the molecule to favor extended (all-anti) conformations. Work by Fogarty¹²⁵ shows that this is often the case, but not always, as a slight twist of the Si backbone can be introduced at a marginal cost, according to MM3 calculations. Nevertheless, all-anti conformations are still believed to be the most stable.¹²⁵

Fogarty measured similar trends in the emission for similarly racked silanes, consisting of differing numbers of Si atoms in the silane backbone ($4 \leq n \leq 7$).¹²⁵ Notably for **4-r2** (the tetrasilane version of **6-r2**), a blue shift in the emission energy peak maxima (from 24 950 cm⁻¹ to 26 530 cm⁻¹) was observed upon cooling from 98 K to 34 K (Table 3.2). This trend was also observed for the analogous racked heptasilane **7-r2** where the emission peak maximum energy shifted from 27 770 cm⁻¹ to 29 140 cm⁻¹ upon cooling from 173 K to 35 K. Fluorescence quantum yields were very small for **4-r2** (0.025 at 74 K) and increased as the Si chain grows. For **6-r2** the fluorescence quantum yield at 27 K was reported to be 0.71 ± 0.03 .¹²⁵ The emission from a racked heptasilane with three bicyclo[1.1.1]pentane units, **7-r3**, was also measured. For this compound, both temperature independent dual emission (blue and normal types) was observed until 120 K, where upon additional cooling the fluorescence quantum yield of the blue emission dropped and at 70 K was no longer observable. For the racked compounds containing two bicyclo[1.1.1]pentane units, Fogarty found another even more Stokes-shifted emission, centered around 20 000 cm⁻¹ and green in color, which will be discussed in Chapter 4. Excitation into the low-energy absorption band edge increased the blue fluorescence quantum yield, while the green emission was maximized by excitation directed more into the center of the absorption band.

Fogarty also recorded the fluorescence polarization anisotropy of selected compounds.¹²⁵ The polarization of the emission is given by:

$$P = \frac{(3 \cos^2 \theta - 1)}{(\cos^2 \theta + 3)} \quad (3.1)$$

where θ is the angle between absorption and emission transition dipole moments. If the transition dipole moments are collinear, $P=1/2$, and if they are orthogonal, $P=-1/3$. This equation assumes only one absorption transition moment and one emission transition dipole moment are involved.

Table 3.2: Summary of experimental fluorescence peak maxima (E_{VE}) from the work of Fogarty.¹²⁵ The excitation energy (E_{EX}) and temperature of the experiment (in cyclopentane:isopentane (3:7)) are given below.

Compound	E_{EX} / cm^{-1}	T / K	E_{VE} / cm^{-1}
4-r2	42 920	98	24 950
	42 920	74	26 020
	42 920	34	26 530
	42 550	133	26 190
	42 550	74	26 130
	42 550	34	26 530
6	37 890	233	27 770
	37 890	87	27 500
6-r2	37 890	233	27 620
	37 890	88	27 580
	37 890	27	28 670
7-r2	38 310	153	27 770
	38 310	77	27 990
	38 310	35	29 140

Molecular torsions in the excited state can alter the polarization values by reorienting the transition moment directions. The data in Table 3.3 show that the reorientation is relatively minor.

Table 3.3: Summary of observed fluorescence anisotropy.¹²⁵ The blue emission polarization P_b and angle between transition dipole moments (Θ_b) are given.

Compound	P_b	Θ_b / deg
4	0.50 ± 0.04	0 ± 5
4-r2	0.48 ± 0.02	10 ± 2
5	0.40 ± 0.05	23 ± 5
5-r2	0.46 ± 0.01	15 ± 1
6	0.47 ± 0.02	13 ± 2
6-r2	0.48 ± 0.02	10 ± 2

3.1.2 Past Computational Efforts to Describe Normal and Blue Emission

Blue emission was attributed to bond-stretch minima almost two decades ago.¹²⁴ The conclusion was based on simple bonding theory and early work that involved the calculation of unrelaxed (rigid D_{3d} symmetry) scan of the Si-Si stretching coordinate of Si_2H_6 , which, at the MR-SDCI/cc-VDZ level of theory, yielded an S_1 minimum when Si-Si bond length reached approximately 3.4 Å.¹²⁴

The normal emission for the all-transoid conformations of **8-10** were optimized with the BP86/SV(P) RPA method.¹²⁵ The calculated emission energies (BP86/SV(P), RPA) for **8-10** were reported as 22 550 cm^{-1} , 24 140 cm^{-1} , and 22 930 cm^{-1} , respectively. These values are strongly red-shifted in comparison to experiment where emission peaks for **8** and **10** were measured to be 34 790 cm^{-1} , and 33 600 cm^{-1} respectively, at 35 K.¹¹⁶ Perhaps most disturbing was the fact that the calculated emission energy of **8** was red-shifted compared to that of **9** and **10**. Similar calculations on **7** resulted in highly distorted structures with very low emission energies (15 720 cm^{-1}). More calculations on longer oligosilanes were suggested.¹²⁵

3.1.3 Blue Exciton Hypothesis

As this chapter will show, the Franck-Condon forbidden emission in the blue spectral region is believed to originate from Si-Si bond stretch minima, which have now been located with computational means. For **6**, there are three Si-Si bond stretch minima: a terminal Si-Si bond stretch minimum **6a1**, an internal Si-Si bond stretch minimum **6a2**, and a central Si-Si bond stretch minimum **6a3** (Figure 3.14).

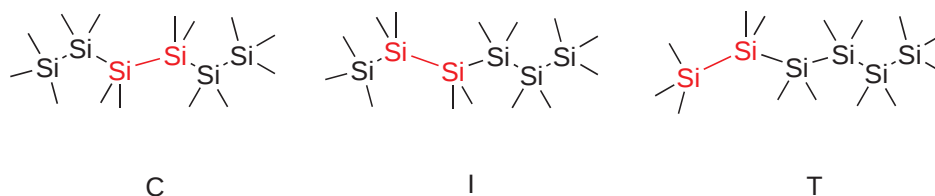


Figure 3.5: S_1 Si-Si bond stretch minima, for which red denotes central (C), internal (I), and terminal (T) bond stretching.

Excitation localization is limited to part of the oligosilane and is not dependent upon the relative conformational changes in the remaining part of the molecule. As more strongly Stokes-shifted emission has been located in the green spectral region, the blue emission is expected to be of an intermediately localized character. As will be shown, this is played out in the fact that the blue exciton requires a small portion of the molecule to be extended and is not found in highly twisted conformers. Also, the blue exciton seems to have a maximum finite length of six Si atoms, and does not delocalize over more atoms even if they are present in the molecule. Once the chain has reached a length of seven Si atoms, delocalization and Franck-Condon allowed emission are favored if the Si backbone is in an extended conformation (defined by all-transoid or anti dihedral angles). To summarize, the observed blue emission from linear silanes has been a mysterious and long standing problem in this field. The work presented in this chapter rationalizes the experimental results.

3.2 Computational Methods

The methods used in this chapter are analogous to those used in Chapter 2. Only exceptions are therefore noted. To assess the accuracy of the methods used in the longer oligosilanes, additional calculations were carried out for **4**. Vertical excitation energies, for ground state absorption (E_{VA}) and for excited state vertical emission (E_{VE}), were calculated with the B3LYP/Def2-TZVP method and compared with values from the multi-state complete active space method with perturbative corrections (MSCASPT2) from the MOLCAS 6.0 program suite.¹⁸⁰ These calculations were performed with the ANO-L basis set¹⁸¹ for the following atoms: Si:ANO-L[5S4P2D], C:ANO-L[3S2P1D], H:ANO-L[2S1P]. The ANO-L' notation refers to a slightly larger basis set: Si:ANO-L[5S4P2D], C:ANO-L[4S3P2D], H:ANO-L[2S1P]. An active space of 6 electrons and 10 orbitals was chosen. Improved virtual orbitals as described in the MOLCAS program were utilized in defining the active space. Unless otherwise noted, nine states were diagonalized in the MSCASPT2 procedure.

The search for localized excitation and blue excitons in longer oligosilanes ($n \geq 8$) was carried out on structures derived from the blue emitters, *e.g.*, **6a2**, which had additional permethylated

silicon atoms added in a direction orthogonal to the main chain. These calculations were not meant to exhaustively search all of the possible conformational space, which is huge for **12**, but to merely demonstrate that blue emission is possible in longer oligosilanes.

3.3 Results

The main focus of this chapter is to examine the normal and blue emission. But before this is done, it is useful to reproduce the trends in absorption energies in the extended (all-transoid) conformations of linear oligosilanes. This is also necessary if the computed Stokes shift is to be compared to experimental results.

3.3.1 Delocalized Excitation

Electronic excitation in oligosilanes is delocalized, as evidenced by strong dependence of the absorption energy on chain length. In fact, one of the strongest supporting pieces of evidence for σ conjugation is the striking red shift in absorption energy with increasing chain length.⁷⁵ Even the most simplistic quantum mechanical models (*e.g.*, particle in a box) predict a decrease in excitation energy with increasing delocalization (box size). The values shown in Figure 3.6 are tabulated in Table 3.4.

The asymptotic correction to the DFT potential of Casida and Salahub¹⁵⁴ combined with the Dixon shift¹⁵⁵ (here simply referred to as TDDFT-AC) improves the calculated excitation energies, as noted in the literature.¹³⁹ The calculated E_{VE} values are red-shifted with respect to the experimental absorption peaks for chain lengths above $n = 10$ (Table 3.5). The E_{VA} (B3LYP-AC/TZVP) for **16** is 31 260 cm⁻¹ and still is very close to the experimental absorption maximum¹¹⁶ of 31 900 cm⁻¹. The TDDFT-AC calculation is currently very expensive for large oligosilanes, and for localized excited states, is of questionable value as pointed out in Chapter 2.

Usually, the all-transoid (SiSiSiSi dihedral angles) conformers are the most stable. These conformations have higher populations at lower temperatures.¹⁰⁶ At higher temperatures however,

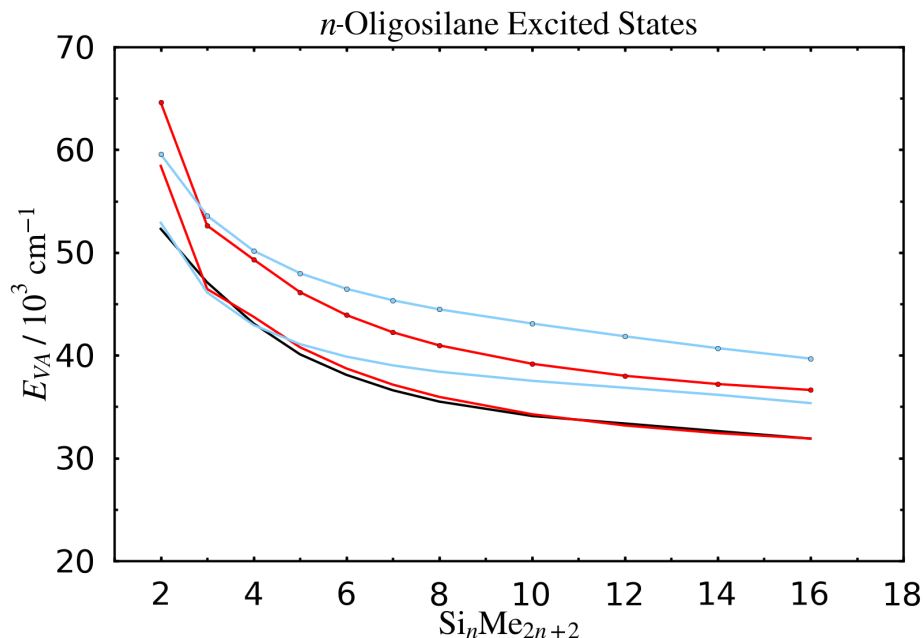


Figure 3.6: S_1 experimental (black line) and calculated B3LYP/Def2-TZVP $\sigma\sigma^*$ (red line) and $\sigma\pi^*$ (blue line) excitation energies of permethylated n -oligosilanes **2-12**, as well as calculated orbital energy gaps ($\sigma\sigma^*$ (red line with dots) $\sigma\pi^*$ (blue line with dots)).

Table 3.4: Vertical excitations in the series of linear permethylated all-transoid oligosilanes calculated with B3LYP/Def2-TZVP (TDDFT). Structures were optimized in the ground state with the RIMP2/TZVP method.

Compound $\text{Si}_n\text{Me}_{2n+2}$	$E_{VA} \sigma\sigma^*$ / 10^3 cm^{-1}	f	$E_{VE} \sigma\pi^*$ / 10^3 cm^{-1}	f	σ / eV	π^* / eV	σ^* / eV	Experiment ^a / 10^3 cm^{-1}
2	58.43	0.075	52.90	0.140	-6.568	0.816	1.445	52.3
3	46.45	0.083	46.12	0.000	-6.257	0.387	0.267	47.1
4	43.75	0.304	42.94	0.003	-5.996	0.225	0.120	43.1
5	40.79	0.467	41.09	0.000	-5.811	0.139	-0.090	40.1
6	38.72	0.662	39.87	0.000	-5.679	0.083	-0.234	38.1
7	37.15	0.857	39.02	0.000	-5.580	0.043	-0.343	36.6
8	35.96	1.054	38.40	0.000	-5.505	0.009	-0.425	35.5
10	34.27	1.452	37.52	0.000	-5.400	-0.057	-0.543	34.1
12	33.18	1.838	36.85	0.000	-5.332	-0.143	-0.620	NA
14	32.43	2.216	36.16	0.000	-5.286	-0.240	-0.673	NA
16	31.90	2.592	35.35	0.000	-5.253	-0.333	-0.713	31.9

^aExperimental absorption peaks from solution, cyclopentane:isopentane (3:7), with the exception of the **2** and **16** which were measured in 3-methylpentane. Spectra recorded at 77 K.¹⁰²

less stable conformers can be populated, in which excitation is less delocalized. Oligosilane chains

Table 3.5: The vertical $\sigma\sigma^*$ excited state absorption energies ($\text{cm}^{-1} \times 10^3$) in the all-transoid series of linear oligosilanes.

Compound $\text{Si}_n\text{Me}_{2n+2}$	B3LYP/TZ ^a E_{VA} / f	B3LYP/Def2-TZVP E_{VA} / f	B3LYP+AC /TZVP E_{VA} / f	Experiment ^b E_{VA} / f
3	48.6 0.09	46.5 0.08	46.7 0.12	47.1 0.13
4	45.2 0.32	43.8 0.30	43.5 0.34	43.1 0.16
5	42.2 0.49	40.8 0.47	40.5 0.52	40.1 0.18
6	40.0 0.69	38.7 0.66	38.4 0.73	38.1 0.23
7	38.4 0.89	37.1 0.86	36.8 0.94	36.6 0.31
8	37.3 1.08	36.0 1.06	35.5 1.16	35.5 0.39
10	35.8 1.49	34.3 1.45	33.8 1.59	34.1 0.55

^a Calculations done with the TDDFT method according to Rooklin et al.¹⁰² ^b Spectra in solution at 77 K.¹⁰²

with alternating cisoid and anti dihedral angles imposed by added alkane chains are known to have electronic spectra which do not show a decrease in absorption energy with increasing chain length.¹⁰⁹ Twisted conformations also give rise to more localized excited states, which are addressed in Chapter 4. The all-transoid conformers also have large transition dipole moments and are believed to be responsible for the so-called normal and blue emission.¹¹⁶

3.3.2 Normal Emission

3.3.2.1 Summary of the Results

It has long been known that absorption energies in permethylated oligosilanes are well reproduced with standard TDDFT methods.¹⁰² Although DFT ground-state structures differ slightly from the superior MP2 results, the vertical absorption energy calculated from these structures is still quite accurate when compared to experimental absorption energies. Similarly, normal emission is also well reproduced with standard TDDFT methods. This is not surprising as relaxed S_1 geometries differ very little from the S_0 equilibrium structures. As the molecules relax on the S_1 surface, Si-Si bond stretching occurs throughout the backbone. All-Si valence and dihedral angles also increase. While these structural changes happen throughout the molecule, they are maximized in the central region of the chain. The calculated emission energy differences for these structures

are given later in this section. The PBE0/SVP method gives an astonishingly close reproduction of the experimental emission energies for the normal emission.

3.3.2.2 Relaxed S_1 Geometries and Emission Energies

In normal emission, the relaxed S_1 geometry of the emitter resembles that of the ground state. The ground state equilibrium conformers are denoted with a **G** appended to the compound name and the relaxed S_1 geometry of the normal emitters are denoted with an appended **N**.

Table 3.6: Optimized S_0 **7G** and S_1 **7N** geometries (using the BHLYP/SVP methods) for $\text{Si}_7\text{Me}_{16}$.

Structure	$\omega\text{SiSiSiSi}$ /deg	$\angle\text{SiSiSi}$ /deg	$\angle\text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle\text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle\text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC_i /Å	SiC_t /Å
7G	164.0	111.7	110.4	108.1	111.4	2.366	1.899	1.889
	164.3	111.0	108.4	108.1	109.5	2.370	1.899	1.891
	164.3	111.5	108.0	108.3	110.2	2.370	1.899	1.889
	164.1	111.0	110.8	108.1	111.4	2.370	1.899	1.889
		111.7	110.4	108.1	109.5	2.370	1.899	1.891
			108.1	108.8	110.2	2.366	1.899	1.889
			108.1	108.4			1.899	
			110.4	108.4			1.899	
			108.4	108.8			1.899	
			110.4	108.4			1.899	
			110.8	108.4				
			108.0					
7N	169.8	113.5	110.8	108.8	110.2	2.388	1.893	1.887
	169.7	114.8	106.3	109.1	111.4	2.407	1.892	1.895
	169.7	117.7	108.5	108.9	109.2	2.461	1.889	1.887
	169.8	114.8	107.2	109.1	110.2	2.461	1.888	1.887
		113.5	108.0	108.8	111.4	2.407	1.888	1.895
			107.1	109.3	109.2	2.388	1.888	1.887
			107.1	108.2			1.889	
			108.0	108.5			1.888	
			106.3	109.3			1.892	
			110.8	108.2			1.893	
			107.2	108.5				
			108.5					

The largest Stokes shift for the normal emission was found for **7** to be $1\,500\text{ cm}^{-1}$ at 77 K.¹¹⁶ Similarly, the largest changes in ground and excited (S_1) state equilibrium structures are found

for **7**, and are given in Figure 3.7 and Table 3.6. Changes in SiSiSi valence angle correspond to a maximum increase in the S_1 state of 6.2° according to the BHLYP/SVP method. The Si-Si bond lengths increase $0.09 \text{ \AA}$ in the excited state according to this method. The all-Si dihedral angles extend to 169.3° in the center of the chain when the S_1 state is optimized by the BHLYP/SVP method. The structural changes between **7G** and **7G** are similar according to the PBE0/SVP (Table 3.7) and B3LYP/SVP (Table 3.8) methods.

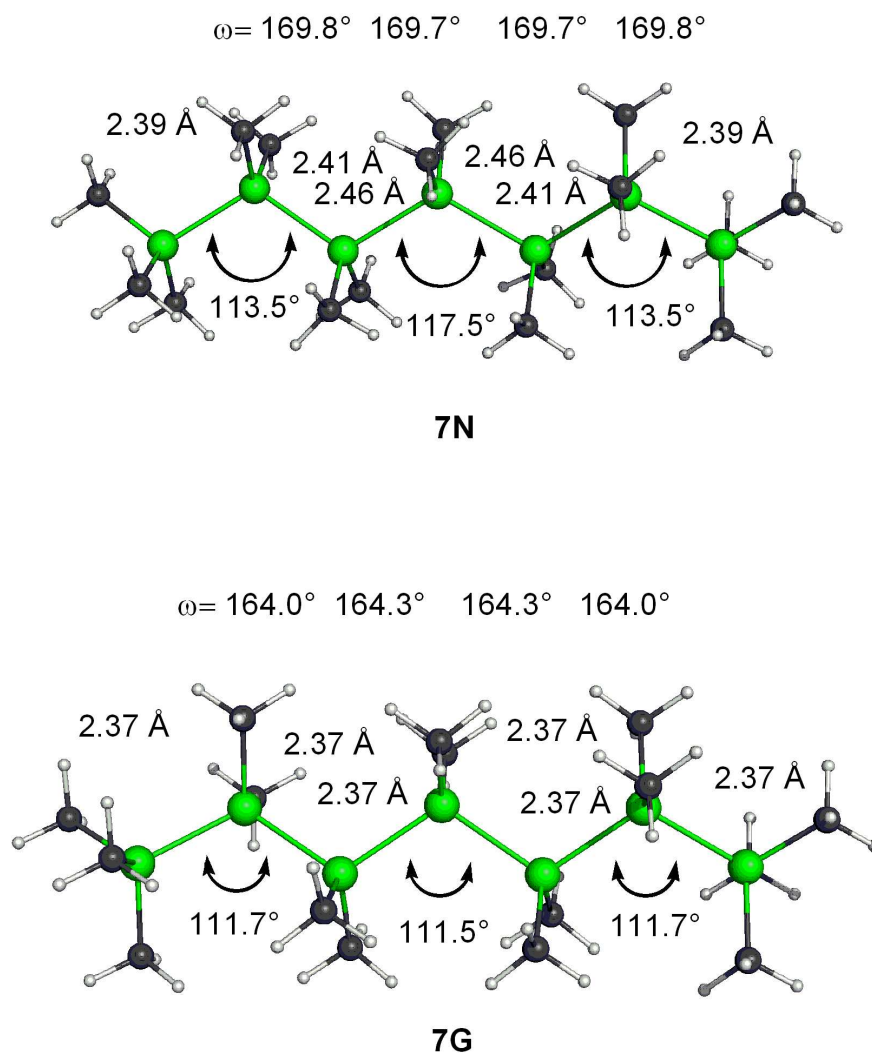


Figure 3.7: The all-transoid S_0 minimum **7G** and S_1 minimum **7G** (BHLYP/SVP). All-Si dihedrals and valence angles given in degrees and Si-Si bond lengths in $\text{\AA}$.

The HOMO to LUMO ($\sigma\sigma^*$) transition density and difference density also resemble those

Table 3.7: Optimized S_0 **7G** and S_1 **7N** geometries (using the PBE0/SVP methods) for $\text{Si}_7\text{Me}_{16}$.

Structure	$\omega\text{SiSiSiSi}$ /deg	$\angle\text{SiSiSi}$ /deg	$\angle\text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle\text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle\text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC_i /Å	SiC_t /Å
7G	163.3	111.3	110.5	108.5	111.3	2.365	1.902	1.893
	163.9	110.5	108.4	108.6	109.4	2.367	1.903	1.895
	164.0	111.2	108.0	108.9	110.1	2.367	1.902	1.893
	163.2	110.5	110.8	108.6	111.3	2.367	1.902	1.893
		111.3	110.3	108.5	109.4	2.367	1.902	1.895
			108.1	109.0	110.1	2.365	1.902	1.893
			108.1	108.5			1.902	
			110.3	108.5			1.902	
			108.4	109.0			1.903	
			110.5	108.5			1.902	
			110.8	108.5				
			108.0					
7N	167.6	112.7	110.8	109.2	110.0	2.389	1.895	1.890
	168.0	113.4	106.9	109.7	111.5	2.396	1.895	1.899
	168.0	115.5	108.1	109.7	108.7	2.428	1.893	1.891
	167.6	113.4	107.9	109.7	110.0	2.428	1.892	1.890
		112.7	108.6	109.2	111.5	2.396	1.892	1.899
			107.2	109.6	108.7	2.389	1.892	1.891
			107.2	108.3			1.893	
			108.6	108.8			1.892	
			106.9	109.6			1.895	
			110.8	108.3			1.895	
			107.9	108.8				
			108.0					

of the transition from the relaxed ground state. These orbitals and densities are shown in Figure 3.8 for **8N**. The NHO populations are shown for ground and excited states of **8** for the relaxed ground (a) and S_1 (b) structures in Figure 3.9. The figure shows that the NHO occupation does not change significantly between ground and excited state (S_1) relaxed structures. The largest changes in occupation occur toward the center of the molecule, but in the NHO basis this only corresponds to occupancy differences of 0.03 e^- (electrons) at most.

Analysis of the ground and excited state occupations in the NAO basis set is quite useful for describing excited state absorption and Franck-Condon allowed (normal) emission. This is because the σ and σ^* orbitals are predominantly described by the Si $3p_z$ and $3p_y$ orbitals, respectively.

Table 3.8: Optimized S_0 **7G** and S_1 **7N** geometries (using the B3LYP/SVP methods) for $\text{Si}_7\text{Me}_{16}$.

Structure	$\omega\text{SiSiSiSi}$ /deg	$\angle\text{SiSiSi}$ /deg	$\angle\text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle\text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle\text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC_i /Å	SiC_t /Å
7G	164.2	112.2	110.4	107.9	111.7	2.380	1.912	1.902
	164.7	111.4	108.3	107.9	109.4	2.384	1.913	1.904
	164.7	112.0	107.8	108.1	110.4	2.385	1.912	1.902
	164.2	111.4	110.9	107.9	111.7	2.385	1.912	1.902
		112.2	110.4	107.9	109.4	2.384	1.912	1.904
			108.0	108.7	110.4	2.380	1.912	1.902
			107.9	108.3			1.912	
			110.4	108.3			1.912	
			108.3	108.7			1.913	
			110.4	108.3			1.912	
			110.9	108.3				
			107.8					
7N	170.4	114.3	110.1	108.6	110.2	2.409	1.905	1.899
	170.4	115.5	106.8	108.8	111.2	2.422	1.905	1.909
	170.4	118.1	108.0	108.7	109.3	2.464	1.903	1.899
	170.4	115.5	107.5	108.8	110.2	2.464	1.903	1.899
		114.3	107.9	108.6	111.2	2.422	1.903	1.909
			107.0	109.4	109.3	2.409	1.903	1.899
			107.0	108.2			1.903	
			107.9	108.5			1.903	
			106.8	109.4			1.905	
			110.1	108.2			1.905	
			107.5	108.5				
			108.0					

The electron occupation does not change significantly in the other atomic orbitals. The maximum change in occupation for the delocalized absorption in **8G** is 0.17 e^- , where it has slightly increased in the center of the molecule (to 0.19 e^-) for the relaxed excited state emitter **8N** (Figure 3.10).

The trend of increased $\sigma\sigma^*$ transition density towards the center of the molecule can be seen in Figure 3.11. This figure shows the $\sigma\sigma^*$ transition density for the ground state all-transoid equilibrium structures (**8G** (a) and **12G** (b)), bottom row, and for the relaxed excited state (S_1) structures **8N** and **12N**. The $\sigma\sigma^*$ transition densities at ground and excited state relaxed structures appear very similar, as expected for a delocalized excitation.

The optimized geometries of the ground state equilibrium structure of the permethylated

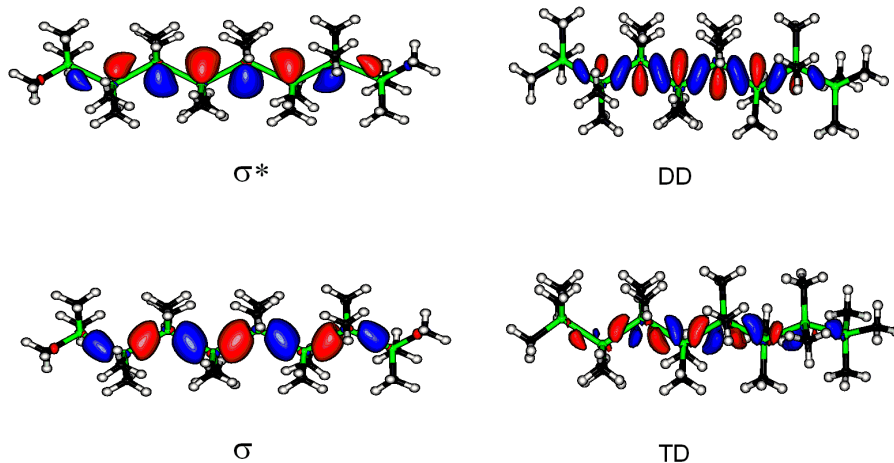


Figure 3.8: The σ and σ^* molecular orbitals (B3LYP/Def2-TZVP) are given as well as the ground and $\sigma\sigma^*$ state transition density (TD) and difference density (DD) for S_1 relaxed structure (B3LYP/SVP) **8N**. Orbitals are plotted on the ± 0.06 isodensity contours, the TD (CIS/6-31G(d)) is plotted on the ± 0.004 isodensity contours and the DD (B3LYP/Def2-TZVP) is plotted on the ± 0.02 isodensity surface values.

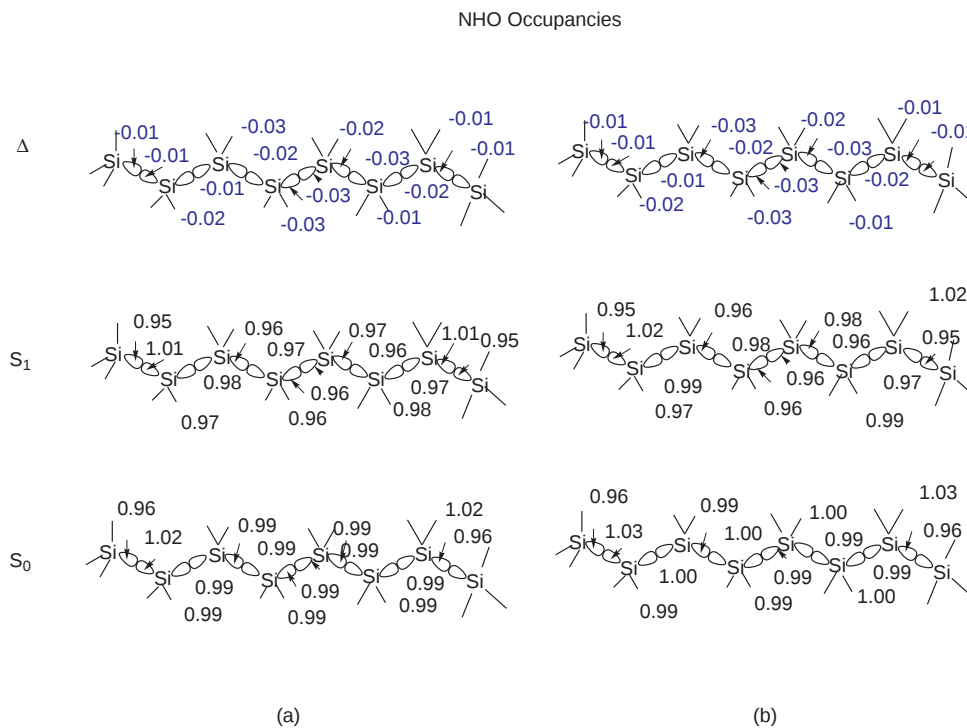


Figure 3.9: NHO populations for the ground (S_0) and excited state (S_1) of the S_0 and S_1 all-transoid relaxed structures for **8**, (a) and (b) respectively. Extended (all-transoid) structures optimized with DFT and TDDFT (B3LYP/SVP).

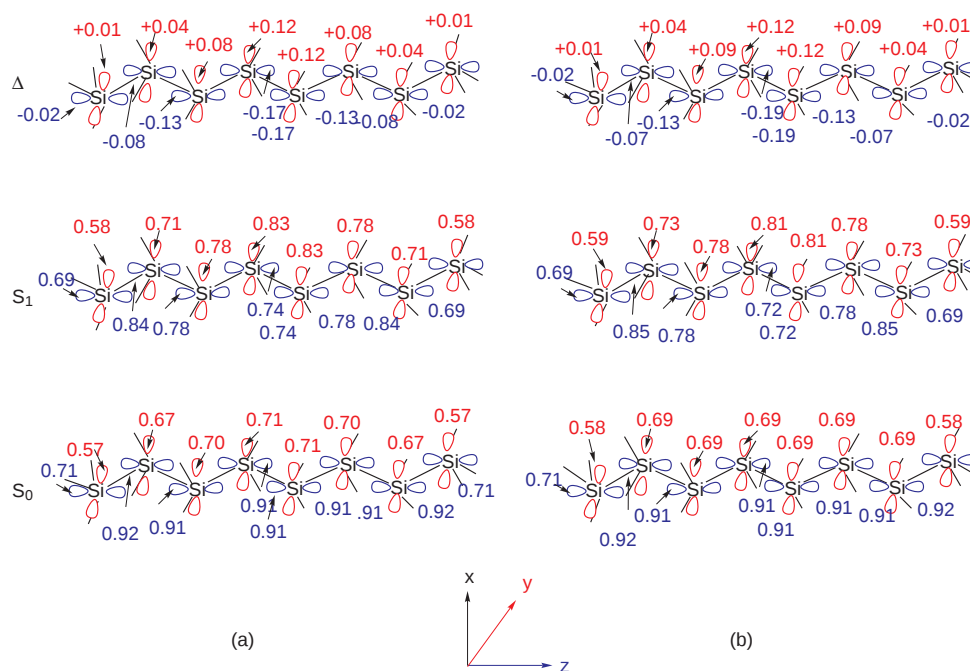


Figure 3.10: 8 NAO populations for the ground and excited (S_1) state of the S_0 and S_1 relaxed structures, (a) and (b) respectively. Si $3p_z$ orbitals (blue) and Si $3p_y$ orbitals (red) are shown with NAO occupations for extended (all-transoid) structures optimized with DFT and TDDFT (BHLYP/SVP).

octasilane, **8G**, with various methods give similar results. To note, the B3LYP/SVP method gave the longest Si-Si bond lengths (*e.g.*, 2.386 Å, Table 3.9) and the BHLYP/SVP gave a shorter Si-Si bond at 2.371 Å (Table 3.10). The RIADC(2)/SVP and RIMP2/TZVP methods gave virtually identical Si-Si bonds lengths (2.357 Å, Table 3.11). The dihedral angles defined by the Si atoms varied as well; the B3LYP/SVP method gave more extended dihedrals (165.4°), while *ab initio* methods gave slightly less extended dihedrals, *e.g.*, 163.1°, Table 3.11.

Table 3.12 lists the difference in vertical absorption energies between the DFT and MP2 structures. The E_{VA} differences between the various **8G** structures are very small. Of these structures, the B3LYP/SVP structure yielded an S_0 - S_1 absorption energy (35 580 cm^{-1}), that is practically identical to the experimental absorption band maximum value¹¹⁶ (35 500 cm^{-1}). The calculated S_0 - S_1 oscillator strengths are, however, too high. For **8**, the experimental oscillator

Table 3.9: Optimized S_0 geometries (using DFT methods) of **8G**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ C _i Si _i C _i /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
PBE0/SVP	163.8	111.3	110.4	108.5	111.3	2.366	1.903	1.893
	163.8	110.8	108.3	108.7	109.4	2.367	1.903	1.895
	163.2	110.7	107.9	108.8	110.1	2.368	1.902	1.893
	163.8	110.7	110.6	108.8	111.3	2.369	1.902	1.893
	163.8	110.8	110.4	108.7	109.4	2.368	1.902	1.895
		111.3	108.1	108.5	110.2	2.367	1.902	1.893
			108.1			2.366	1.902	
			110.7				1.902	
			108.1				1.902	
			110.4				1.902	
			110.7				1.903	
			108.1				1.903	
			110.6					
			107.9					
			108.3					
			110.4					
B3LYP/SVP	165.4	112.2	110.4	107.9	111.6	2.380	1.912	1.902
	164.8	111.7	108.2	108.0	109.4	2.384	1.913	1.904
	164.1	111.5	107.9	108.0	110.5	2.386	1.912	1.902
	164.8	111.5	110.7	108.0	111.6	2.386	1.912	1.902
	165.3	111.7	110.5	108.0	109.4	2.386	1.912	1.904
		112.2	108.0	107.9	110.5	2.384	1.912	1.902
			108.0			2.380	1.912	
			110.7				1.912	
			108.0				1.912	
			110.5				1.912	
			110.7				1.912	
			108.0				1.913	
			110.7					
			107.9					
			108.2					
			110.4					

Table 3.10: Optimized S_0 geometry for **8G** (structure obtained using the BHLYP/SVP method).

ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ C _i Si _i C _i /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
164.9	111.7	110.4	108.1	111.3	2.367	1.899	1.889
164.5	111.2	108.3	108.2	109.5	2.369	1.899	1.891
164.0	111.1	108.1	108.2	110.4	2.371	1.899	1.889
164.5	111.1	110.6	108.3	111.3	2.371	1.899	1.889
164.9	111.2	110.4	108.2	109.5	2.371	1.899	1.891
	111.7	108.2	108.1	110.4	2.369	1.899	1.889
		108.2			2.367	1.899	
		110.6				1.899	
		108.2				1.899	
		110.4				1.899	
		110.6				1.899	
		108.2				1.899	
		110.6					
		108.1					
		108.3					
		110.4					

Table 3.11: Optimized S_0 geometries for **8G** (structures obtained using the RIADC(2)/SVP and RIMP2/TZVP methods).

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ C _i Si _i C _i /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
RIADC(2)/SVP	162.9	110.2	110.9	108.6	110.5	2.357	1.903	1.894
	163.3	109.7	108.7	108.7	110.1	2.357	1.904	1.895
	163.1	109.8	108.4	108.9	109.8	2.357	1.903	1.893
	163.3	109.8	110.4	108.9	110.5	2.357	1.903	1.894
	162.9	109.7	110.4	108.7	110.1	2.357	1.903	1.895
		110.2	108.4	108.6	109.8	2.357	1.903	1.893
			108.6			2.357	1.903	
			110.7				1.903	
			108.4				1.903	
			110.4				1.903	
			110.7				1.903	
			108.6				1.904	
			110.4					
			108.4					
			108.7					
			110.9					
RIMP2/TZVP	163.3	110.3	110.4	108.6	110.5	2.357	1.907	1.898
	163.6	110.1	108.7	108.7	110.3	2.357	1.908	1.898
	163.5	110.1	108.7	108.8	109.8	2.357	1.907	1.897
	163.6	110.1	110.2	108.8	110.5	2.357	1.907	1.898
	163.3	110.1	110.3	108.7	110.3	2.357	1.907	1.898
		110.3	108.5	108.6	109.8	2.357	1.907	1.897
			108.7			2.357	1.907	
			110.4				1.907	
			108.5				1.907	
			110.3				1.907	
			110.4				1.907	
			108.7				1.908	
			110.2					
			108.7					
			108.7					
			110.4					

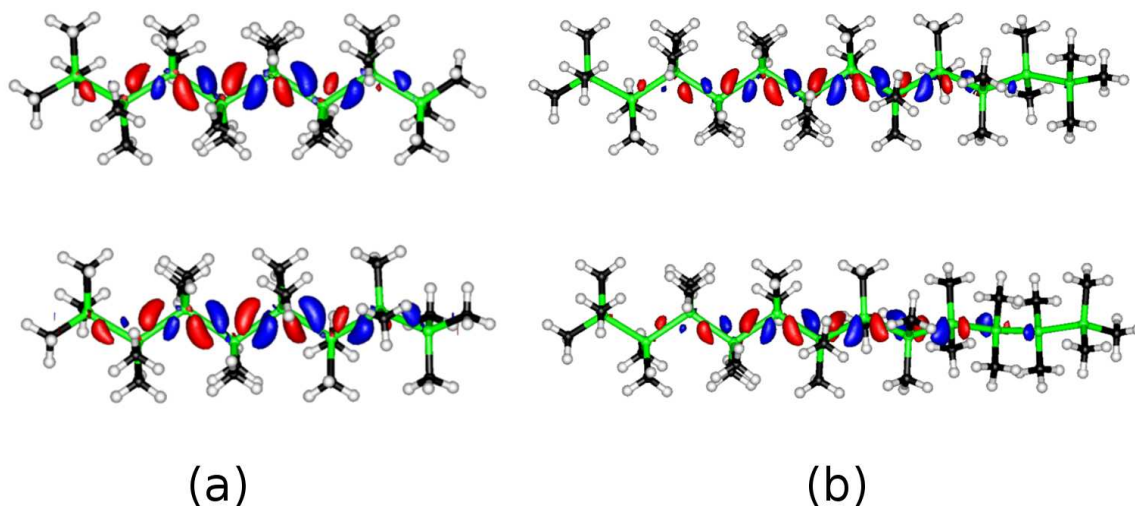


Figure 3.11: The $\sigma\sigma^*$ transition density for the ground state all-transoid structures (**8G** (a) and **12G** (b)), bottom row, and for the relaxed excited state (S_1) structures **8N** and **12N**, top row.

strength for the S_0 - S_1 transition is 0.39,¹⁰² while the TDDFT method based on the RIMP2/TZVP **8G** structure estimates the oscillator strength of this transition to be 1.06.

Table 3.12: Vertical absorption energies for **8G** DFT and RIMP2 structures. Theoretical values are calculated with TDDFT (B3LYP/Def2-TZVP) with excitation energies are expressed in $\tilde{\nu}/\text{cm}^{-1}$.

Structure	E_{VA}	f
PBE0/SVP	35 750	1.07
B3LYP/SVP	35 580	1.15
BHLYP/SVP	35 700	1.11
RIADC(2)/SVP	35 900	1.02
RIMP2/TZVP	35 960	1.06

The relaxed S_1 structure for the permethylated octasilane, **8N**, shows that the dihedral angles increase upon excited state relaxation. This amount varied from method to method, *e.g.*, the B3LYP/SVP method gave the upper limit (170.2°, Table 3.13) and the RIADC(2)/SVP method gave the lower limit (165.5°, Table 3.14). The Si-Si bond lengths increased as well in the relaxed S_1 structures (BHLYP/SVP: 2.450 Å, RIADC(2)/SVP: 2.413 Å). The Si-C bond lengths did not

change significantly from the ground state equilibrium structure. The SiSiSi valence angles increased in comparison to their ground state equilibrium values. The RIADC(2)/SVP method yielded an increase from 109.8° to 113.1° for the ground and excited state equilibrium SiSiSi valence angles, respectively, for **8**.

Table 3.15 lists the excited state vertical emission energy differences between the approximate DFT and RIADC(2)/SVP structures. The calculated Stokes shift, reported as the difference between vertical absorption and emission energies, is slightly overestimated with respect to experimental values. The experimental Stokes shift for **8** is approximately 800 cm^{-1} , while the computed value is $1\,870\text{ cm}^{-1}$ (B3LYP/SVP). The agreement with absorption band maxima is quite good, so the difference is attributed to the calculated value of the emission energy, which is slightly underestimated ($33\,710\text{ cm}^{-1}$) with respect to experiment ($34\,700\text{ cm}^{-1}$). This trend is reversed for the RIADC(2)/SVP ab initio method, which gave a larger error for the absorption energy.

The B3LYP/SVP S_0 optimized structures give a slightly better agreement with the experimental absorption peak maximum, though all methods are well within the calculational uncertainty ($1\,600\text{ cm}^{-1}$).¹⁶⁹ The RIADC(2)/SVP S_1 relaxed structure gave the closest reproduction of the fluorescence peak maximum ($34\,700\text{ cm}^{-1}$).¹¹⁶ Of the TDDFT S_0 optimized structures, the PBE0/SVP structure gave the closest experimental reproduction of the fluorescence band maximum for **8N**.

As the linear oligosilane chain length increases, some structural trends are noted. The differences between the ground state equilibrium structures and the excited state S_1 relaxed geometries decrease. For example, the B3LYP/SVP method for **12G** yielded: a maximum SiSiSiSi dihedral angle at 169.0° , a maximum SiSiSi valence angle at 113.4° , and a maximum Si-Si bond length at $2.415\text{ \AA}$, Table 3.16, and for **12N** the B3LYP/SVP method yielded: a maximum SiSiSiSi dihedral angle at 169.0° , a maximum SiSiSi valence angle at 113.4° , and a maximum Si-Si bond length at $2.415\text{ \AA}$ (Table 3.17). For **16**, the **16N** values were close to the S_0 relaxed structure (Table 3.18). The **16N** maximum Si-Si bond, all-Si valence and dihedral angle values were reduced to 168.0° , 112.7° and $2.404\text{ \AA}$, respectively, Table 3.19.

As shown, the geometry differences between excited state and ground state optimized struc-

Table 3.13: Optimized S₁ geometries of **8N** using TDDFT PBE0/SVP and B3LYP/SVP methods.

Structure	ω_{SiSiSiSi} /deg	$\angle \text{SiSiSi}$ /deg	$\angle \text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle \text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle \text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
PBE0/SVP	166.6	112.2	111.0	109.0	110.3	2.383	1.897	1.891
	167.7	112.4	107.2	109.5	111.0	2.391	1.896	1.898
	168.4	114.0	108.0	109.7	109.0	2.411	1.894	1.891
	167.7	114.0	108.8	109.7	110.3	2.415	1.894	1.891
	166.6	112.4	109.5	109.5	111.0	2.411	1.893	1.898
		112.2	107.3	109.0	109.0	2.391	1.893	1.891
			107.5			2.383	1.893	
			108.8				1.893	
			107.3				1.894	
			109.5				1.894	
			108.8				1.897	
			107.5				1.896	
			108.8					
			108.0					
			107.2					
			111.0					
B3LYP/SVP	169.4	113.6	110.3	108.4	110.5	2.402	1.907	1.899
	169.9	114.2	107.2	108.7	110.7	2.414	1.906	1.908
	170.2	116.2	107.9	108.7	109.6	2.441	1.905	1.900
	169.9	116.2	108.4	108.7	110.5	2.449	1.904	1.899
	169.4	114.2	109.0	108.7	110.7	2.441	1.904	1.908
		113.6	107.3	108.4	109.6	2.414	1.904	1.900
			107.3			2.402	1.904	
			108.2				1.904	
			107.3				1.904	
			109.0				1.905	
			108.2				1.907	
			107.3				1.906	
			108.4					
			107.9					
			107.2					
			110.3					

Table 3.14: Optimized S_1 geometry of **8N** structure obtained using the TDDFT (BHLYP/SVP) and RIADC(2)/SVP methods.

Structure	ω_{SiSiSiSi} /deg	$\angle \text{SiSiSi}$ /deg	$\angle \text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle \text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle \text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
BHLYP/SVP	168.5	113.0	110.8	108.6	110.5	2.383	1.894	1.887
	169.5	113.4	107.0	109.0	110.9	2.399	1.893	1.894
	169.8	115.5	108.2	109.0	109.5	2.427	1.891	1.888
	169.5	115.5	108.4	109.0	110.5	2.450	1.890	1.887
	168.5	113.4	109.4	109.0	110.9	2.427	1.889	1.894
		113.0	106.9	108.6	109.5	2.399	1.889	1.888
			107.8			2.383	1.889	
			108.0				1.889	
			106.9				1.890	
			109.4				1.891	
			108.0				1.894	
			107.8				1.893	
			108.4					
			108.2					
			107.0					
			110.8					
RIADC(2)/SVP	165.5	110.7	111.8	109.2	109.9	2.370	1.898	1.892
	167.2	111.2	107.1	109.8	112.0	2.379	1.898	1.898
	168.2	113.1	108.3	110.1	108.5	2.398	1.894	1.892
	167.2	113.1	108.6	110.1	109.9	2.413	1.894	1.892
	165.5	111.2	109.9	109.8	112.0	2.398	1.892	1.898
		110.7	107.0	109.2	108.5	2.379	1.892	1.892
			108.1			2.370	1.892	
			108.6				1.892	
			107.0				1.894	
			109.9				1.894	
			108.6				1.898	
			108.1				1.898	
			108.6					
			108.3					
			107.1					
			111.8					

Table 3.15: Vertical absorption and emission energies and oscillator strengths for **8** using various functionals and S_0 and S_1 optimized structures. The Stokes shift is reported as the difference between vertical absorption and emission energies. All theoretical excitations are calculated with TDDFT (B3LYP/Def2-TZVP). The ab initio RIADC(2) results are also given. Experimental values are indicated in the footnote.^a

Method	E_{VA} / cm^{-1}	f	E_{VE} cm^{-1}	f	E_{SS} cm^{-1}
PBE0/SVP	35 750	1.072	34 270	1.185	1 480
B3LYP/SVP	35 580	1.154	33 710	1.300	1 870
BHLYP/SVP	35 700	1.113	33 850	1.251	1 850
RIADC(2)/SVP	35 900	1.020	34 430	1.136	1 470

^a Experimental values for vertical absorption and emission (77 K)¹¹⁶ are 35 500 and 34 700 cm^{-1} respectively, yielding an experimental Stokes shift of 800 cm^{-1} .

tures decrease as the chain length is increased. The calculated Stokes shift for large silanes also follows this trend *i.e.*, as the chain grows, the vertical absorption and emission energies move closer together. A decrease in the Stokes shift energy with increasing chain length is also observed experimentally.¹¹⁶ The calculated Stokes shift was determined with BHLYP/SVP (Table 3.20), PBE0/SVP (Table 3.21), and B3LYP/SVP (Table 3.22) structures.

Table 3.16: Optimized S_0 geometry DFT (BHLYP/SVP) of **12G**.

ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ C _i Si _i C _i /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
164.5	111.7	108.0	108.1	111.4	2.367	1.899	1.889
164.1	111.2	110.7	108.1	109.5	2.369	1.899	1.890
164.2	111.2	110.4	108.3	110.3	2.371	1.899	1.889
163.9	111.1	108.4	108.2	111.4	2.371	1.899	1.889
164.1	111.1	108.1	108.3	109.5	2.372	1.899	1.890
163.9	111.1	110.7	108.3	110.3	2.372	1.899	1.889
164.2	111.1	110.4	108.2		2.372	1.899	
164.1	111.2	108.2	108.3		2.371	1.899	
164.5	111.2	108.1	108.1		2.371	1.899	
	111.7	110.6	108.1		2.369	1.899	
		110.6			2.367	1.899	
		108.1				1.899	
		108.1				1.899	
		110.6				1.899	
		110.6				1.899	
		108.1				1.899	
		108.1				1.899	
		110.6				1.899	
		110.6				1.899	
		108.1				1.899	
		108.1				1.899	
		110.6				1.899	
		110.6				1.899	
		108.1				1.899	
		108.2				1.899	
		110.4				1.899	
		110.7				1.899	
		108.1				1.899	
		110.7				1.899	
		108.0				1.899	
		108.4				1.899	
		110.4				1.899	

Table 3.17: Optimized S₁ geometry TDDFT (BHLYP/SVP) of **12N**.

ω_{SiSiSiSi} /deg	$\angle \text{SiSiSi}$ /deg	$\angle \text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle \text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle \text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
165.8	112.2	108.1	108.3	111.0	2.373	1.897	1.888
166.4	111.8	109.9	108.5	110.0	2.381	1.897	1.892
167.8	112.4	110.7	108.8	110.0	2.391	1.895	1.888
168.8	112.9	107.7	108.9	111.0	2.401	1.895	1.888
169.0	113.4	108.0	108.9	110.0	2.411	1.893	1.892
168.8	113.4	109.6	108.9	110.0	2.415	1.894	1.888
167.8	112.9	110.5	108.9		2.411	1.892	
166.4	112.4	107.5	108.8		2.401	1.892	
165.8	111.8	107.9	108.5		2.391	1.891	
	112.2	109.4	108.3		2.381	1.891	
		110.2			2.373	1.891	
		107.4				1.891	
		107.7				1.892	
		109.4				1.892	
		109.8				1.894	
		107.5				1.893	
		107.5				1.895	
		109.8				1.895	
		109.4				1.897	
		107.7				1.897	
		107.4					
		110.2					
		109.4					
		107.9					
		107.5					
		110.5					
		109.6					
		108.0					
		109.9					
		108.1					
		107.7					
		110.7					

Table 3.18: Optimized S_0 geometry DFT (BHLYP/SVP) of **16G**.

ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ C _i Si _i C _i /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
164.4	111.7	108.0	108.1	110.2	2.367	1.899	1.889
164.0	111.2	110.7	108.1	111.4	2.370	1.899	1.890
164.1	111.2	110.4	108.3	109.5	2.371	1.899	1.890
164.0	111.2	108.3	108.2	110.2	2.371	1.899	1.889
163.9	111.1	108.1	108.2	111.4	2.372	1.899	1.889
164.0	111.2	110.7	108.3	109.5	2.372	1.899	1.891
163.9	111.1	110.5	108.2		2.372	1.899	
163.9	111.1	108.1	108.2		2.372	1.899	
163.8	111.2	108.0	108.2		2.372	1.899	
164.0	111.1	110.7	108.2		2.372	1.899	
164.0	111.2	110.6	108.2		2.372	1.899	
164.0	111.2	108.1	108.3		2.371	1.899	
164.3	111.2	108.1	108.1		2.371	1.899	
	111.7	110.7	108.1		2.369	1.899	
		110.7			2.366	1.899	
		108.0				1.899	
		108.0				1.899	
		110.7				1.899	
		110.7				1.899	
		108.0				1.899	
		110.7				1.899	
		108.0				1.899	
		108.0				1.899	
		110.7				1.899	
		108.0				1.899	
		110.7				1.899	
		110.7				1.899	
		108.0				1.899	
		110.7				1.899	
		108.0				1.899	
		108.0				1.899	
		110.7				1.899	
		110.7				1.899	
		108.1				1.899	
		...					

Table 3.19: Optimized S₁ geometry TDDFT (BHLYP/SVP) of **16N**.

ω_{SiSiSiSi} /deg	$\angle \text{SiSiSi}$ /deg	$\angle \text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle \text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle \text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
164.9	112.0	108.1	108.2	110.2	2.369	1.898	1.889
165.1	111.5	110.3	108.3	111.2	2.375	1.898	1.889
165.8	111.7	110.5	108.5	109.7	2.380	1.897	1.891
166.7	111.9	108.1	108.6	110.2	2.386	1.897	1.889
167.4	112.2	108.1	108.7	111.2	2.392	1.896	1.889
168.0	112.5	110.2	108.8	109.7	2.397	1.896	1.891
168.2	112.7	110.5	108.8		2.402	1.895	
168.0	112.7	107.8	108.8		2.404	1.895	
167.4	112.5	108.1	108.8		2.402	1.894	
166.7	112.2	110.0	108.7		2.397	1.894	
165.8	111.9	110.6	108.6		2.392	1.893	
165.1	111.7	107.7	108.5		2.386	1.893	
164.9	111.5	108.0	108.3		2.380	1.892	
	112.0	109.9	108.2		2.375	1.892	
		110.5			2.369	1.892	
		107.6				1.892	
		107.9				1.893	
		109.8				1.893	
		110.3				1.894	
		107.6				1.894	
		110.0				1.895	
		107.7				1.895	
		107.8				1.896	
		109.9				1.896	
		107.7				1.897	
		110.0				1.897	
		109.9				1.898	
		107.8				1.898	
		109.8					
		107.9					
		107.6					
		110.3					
		109.9					
		108.0					
		...					

Table 3.20: Vertical absorption and emission energies (B3LYP/Def2-TZVP) and oscillator strengths for $\text{Si}_n\text{Me}_{2n+2}$ using S_1 and S_0 optimized structures (B3LYP/SVP).

$\text{Si}_n\text{Me}_{2n+2}$ n	E_{VA} / cm^{-1}	f	E_{VE} / cm^{-1}	f	E_{SS} / cm^{-1}
7	36 950	0.90	34 610	1.06	2 340
8	35 700	1.11	33 850	1.25	1 850
9	34 760	1.32	33 180	1.44	1 580
10	33 990	1.52	32 590	1.62	1 400
12	32 880	1.91	31 730	1.99	1 150
14	32 100	2.30	31 130	2.35	970
16	31 580	2.68	30 710	2.72	870

Table 3.21: Vertical absorption and emission (B3LYP/Def2-TZVP) energies and oscillator strengths for $\text{Si}_n\text{Me}_{2n+2}$ using S_1 and S_0 optimized structures (PBE0/SVP).

$\text{Si}_n\text{Me}_{2n+2}$ n	E_{VA} / cm^{-1}	f	E_{VE} / cm^{-1}	f	E_{SS} / cm^{-1}
7	36 970	0.87	35 180	1.00	1 790
8	35 750	1.07	34 270	1.19	1 480
9	34 800	1.28	33 520	1.37	1 280
10	34 040	1.47	32 910	1.55	1 130
12	32 920	1.86	31 990	1.91	930
14	32 160	2.25	31 350	2.28	810

Table 3.22: Vertical absorption and emission (B3LYP/Def2-TZVP) energies and oscillator strengths for $\text{Si}_n\text{Me}_{2n+2}$ using S_1 and S_0 optimized structures (B3LYP/SVP).

$\text{Si}_n\text{Me}_{2n+2}$ n	E_{VA} / cm^{-1}	f	E_{VE} / cm^{-1}	f	E_{SS} / cm^{-1}
7	36 830	0.94	34 510	1.11	2 320
8	35 580	1.15	33 710	1.30	1 870
9	34 640	1.36	33 020	1.49	1 620
10	33 880	1.57	32 440	1.68	1 440
12	32 770	1.97	31 570	2.05	1 200

3.3.3 Blue Emission

3.3.3.1 Summary of the Results

The purpose of this section is to illustrate structures which could be responsible for the Franck-Condon forbidden blue emission. These structures are referred to collectively as Si-Si bond stretch minima, but it should always be noted that these structures have many other important structural distortions such as wide SiSiSi valence angles and narrow SiSiC valence angles. To summarize the results, two blue-emitting structures have been found for **4** and **5**. For **6** there are three Si-Si bond stretch minima.

Various methods were tested to ensure accurate calculations for the emission energies of the Si-Si bond stretch minima of **4**. The LC'-BLYP/Def2-TZVP method gave close agreement with MSCASPT2(6,10)/ANO-L' and experimental emission energies. Standard TDDFT gave acceptable results as well.

From experimental work,¹²² **7** is known as the borderline case, *i.e.*, it is the longest permethylated oligosilane for which both Franck-Condon forbidden and Franck-Condon allowed emission has been observed. As previously mentioned, the all-transoid conformer of **7** was found to relax in the S_1 state to give only a slightly Stokes-shifted emission (section 3.3.2). In this section three additional S_1 minima were located that are believed to be responsible for the blue emission of **7**. As the chain length is increased, many more conformations are available, many of which could give rise to blue emission. All of the possible emitters were not searched for, only a small subset to demonstrate that blue emission could be possible from longer chain lengths, if the correct conformations are accessed. The longest chain length which could give rise to blue emission found here is $n = 12$ (**12**). This is by no means a limiting chain length, only the longest conformer examined here. Emission from longer chains is possible if highly twisted conformations accompany a short extended segment of the chain in which the blue exciton can reside. Twisting is necessary to suppress the effects of σ delocalization and effectively reduce the chromophoric unit to sizes for which blue emission is favored. Emission energies do not change significantly as the chain length is increased

for these longer ($n > 6$) blue emitters.

3.3.3.2 Geometries of the Blue Emitters

The excited state optimized structures responsible for the blue emission in shorter chains ($n \leq 7$) differ from the normal emitter structures in that at least one bond is greatly stretched, however the overall structures differ throughout the entire molecule as can be seen from analysis of the geometric parameters. For the permethylated tetrasilane, two blue emitters were found: a terminal and a central bond stretch minimum, **4a1** and **4a2**, respectively (Figure 3.12).

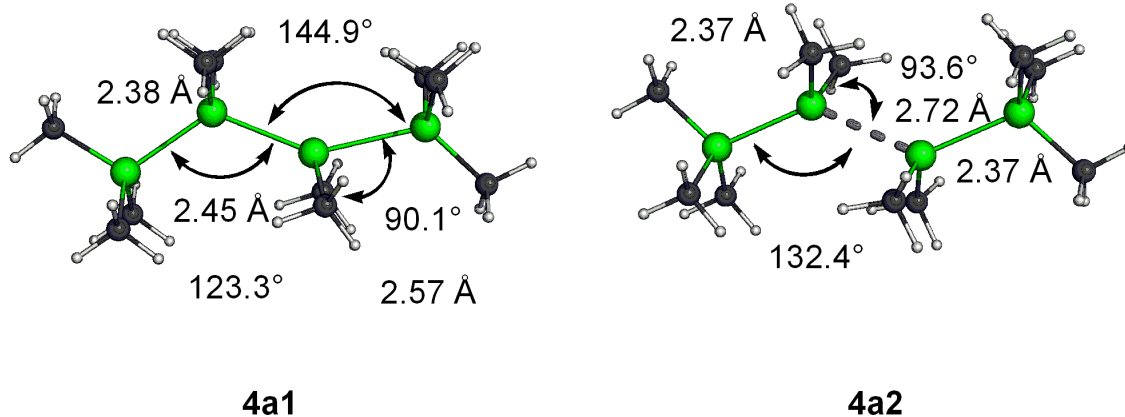


Figure 3.12: $\text{Si}_4\text{Me}_{10}$ terminal Si-Si bond stretch minimum **4a1** and central Si-Si bond stretch minimum **4a2**. Structures from S_1 optimization (BHLYP/SVP) with Si-Si bond lengths (Å) and selected valence angles (degrees).

Table 3.23 shows the relaxed excited state geometries (for PBE0/SVP and RIADC(2)/SVP structures). Table 3.24 includes the Si-Si bond stretch minima obtained with the BHLYP functional and various basis sets. The terminal Si-Si bond stretch minimum **4a1** has a symmetry plane along the Si backbone, which is perfectly anti (180° SiSiSiSi dihedral angle). The BHLYP/TZVP method gave the longest terminal Si-Si bond length at 2.588 Å and the PBE0/SVP method the shortest

one (2.477 Å). There is a large SiSiSi valence angle (147.9°, RIADC(2)/SVP structure) associated with the terminal Si-Si bond and adjacent internal Si atoms. Likewise there is a large SiSiC valence angle (128.6°, RIADC(2)/SVP structure) which is defined by the terminal (stretched) Si-Si bond and the in-plane C atom.

The central Si-Si bond stretch isomer **4a2** is of C_i symmetry according to the PBE0/SVP method and C_{2h} symmetry according to other methods. The lowering of symmetry is due to slight twisting of the internal methyl groups (on substituent positions 2 and 3) in the case of the PBE0/SVP structure. This symmetry lowering can also be seen in the disparity between CSiSi valence angles in Table 3.23. The **4a2** structure has an elongated central Si-Si bond, ranging from 2.473 Å (PBE0/SVP) to 2.741 Å (BHLYP/TZVP). This tetrasilane conformer has two equally large SiSiSi valence angles; these values range from 130.5° (BHLYP/TZVP) to 138.2° (PBE0/SVP). The PBE0/SVP structure also has elongated Si-C bonds (1.951 Å) associated with the narrow CSiSi valence angle (89°) defined by the stretched C-Si bond adjacent to the internal Si-Si bond.

The pentasilane **5** also has two Si-Si bond stretch minima: a terminal Si-Si bond stretch minimum **5a1** and an internal Si-Si bond stretch minimum **5a2** (Figure 3.13). Compared to the tetrasilane terminal Si-Si bond stretch minimum, the Si-Si bond length increases slightly (to 2.493 Å for the PBE0/SVP structure, and to 2.583 Å in the case of the BHLYP/SVP optimized structure). The SiSiSi valence angles decreases slightly (to 139.5° for the PBE0/SVP structure and to 140.1° for the BHLYP/SVP structure), cf. Table 3.25. The internal Si-Si bond stretch minimum, **5a2**, has an elongated Si-Si bond at 2.510 Å according to the PBE0/SVP method and at 2.686 Å according to the BHLYP/SVP method. The **5a2** structure also has a wide SiSiSi valence angle (139.8° PBE0/SVP) and narrow internal CSiSi angles (<100°), cf. Table 3.25.

The three Si-Si bond stretch minima that were found for the permethylated hexasilane.^a These include a terminal Si-Si bond stretch minimum **6a1**, an internal Si-Si bond stretch mini-

^a PBE0/SVP optimization indicate all three minima to have no imaginary frequencies on the S_1 surface. The BHLYP/SVP method indicate **6a2** and **6a1** to be minima, but **6a1** was only found with the BHLYP/SVP method when the structure was partially optimized and then the terminal SiSiSi valence angle was constrained and all other variables were optimized. Without the former constraint, at the BHLYP/SVP level, the **6a1** structure rearranges to the **6a2** minimum. This indicates a low barrier to rearrangement at the BHLYP/SVP level of theory.

Table 3.23: Optimized S_1 geometries TDDFT (PBE0/SVP) and RIADC(2)/SVP for the terminal (**4a1**) and central (**4a2**) bond stretch minima of $\text{Si}_4\text{Me}_{10}$.

Structure	$\omega\text{SiSiSiSi}$ /deg	$\angle\text{SiSiSi}$ /deg	$\angle\text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle\text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle\text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC_i /Å	SiC_t /Å
4a1 PBE0/SVP C_s	180.0	146.8 127.8	106.6 106.6 102.2 102.2	114.2 108.1	121.7 102.1 102.1 108.8 108.8 116.0	2.477 2.473 2.378	1.927 1.927 1.910 1.910	1.889 1.890 1.890 1.902 1.902 1.905
4a1 RIADC(2)/SVP C_s	180.0	147.9 121.6	108.1 108.1 104.5 104.5	114.0 108.7	128.6 97.7 97.7 109.4 109.4 114.3	2.566 2.417 2.363	1.918 1.918 1.905 1.905	1.891 1.894 1.894 1.897 1.897 1.901
4a2 PBE0/SVP C_i	180.0	138.2 138.1	89.0 101.5 101.5 89.0	109.2 109.2	108.2 117.7 106.4 117.7 106.4 108.2	2.394 2.473 2.393	1.951 1.900 1.900 1.951	1.894 1.904 1.895 1.904 1.895 1.894
4a2 RIADC(2)/SVP C_{2h}	180.0	134.7 134.7	91.0 91.0 91.0 91.0	111.0 111.0	108.3 115.8 108.3 115.8 108.3 108.3	2.351 2.686 2.351	1.899 1.899 1.899 1.899	1.893 1.903 1.893 1.903 1.893 1.893

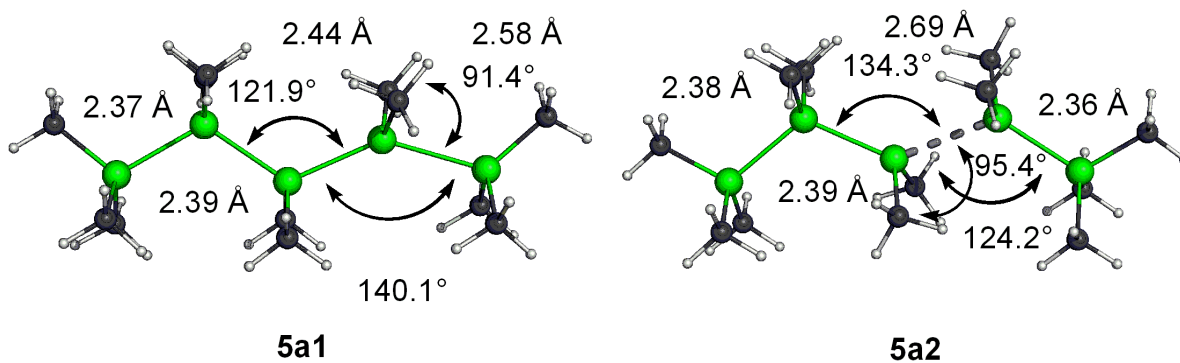


Figure 3.13: $\text{Si}_5\text{Me}_{12}$ terminal Si-Si bond stretch minimum **5a1** and internal Si-Si bond stretch minimum **5a2**. Structures from S_1 optimization (BHLYP/SVP) with Si-Si bond lengths (Å) and selected valence angles (degrees).

Table 3.24: Optimized S_1 geometries TDDFT (BHLYP/SVP and BHLYP/TZVP structures) for the terminal (**4a1**) and central (**4a2**) Si-Si bond stretch minima of Si_4Me_{10} .

Structure	$\omega SiSiSiSi$ /deg	$\angle SiSiSi$ /deg	$\angle C_iSi_iSi_i$ /deg	$\angle C_iSi_iC_i$ /deg	$\angle Si_iSi_tC_t$ /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
4a1 BHLYP/SVP C_s	180.0	144.9 123.3	90.1	113.5	123.6	2.570	1.912	1.886
			90.1	108.0	100.5	2.450	1.912	1.888
			107.9		100.5	2.377	1.901	1.888
			107.9		109.8		1.901	1.897
					109.8			1.891
					113.6			1.891
4a1 BHLYP/TZVP	180.0	143.7 122.5	108.7	113.8	124.1	2.588	1.915	1.893
			108.7	108.0	100.5	2.444	1.915	1.893
			105.1		100.5	2.383	1.904	1.893
			105.1		110.0		1.904	1.895
					110.0			1.895
					113.3			1.901
4a2 BHLYP/SVP C_{2h}	180.0	132.4 132.4	93.6	111.9	109.0	2.369	1.892	1.888
			93.6	111.9	114.4	2.721	1.892	1.899
			93.6		109.0	2.369	1.892	1.888
			93.6		109.0		1.892	1.888
					114.0			1.889
					109.0			1.888
4a2 BHLYP/TZVP C_{2h}	180.0	130.5 130.5	94.0	111.5	109.0	2.375	1.895	1.892
			94.0	111.5	114.4	2.741	1.895	1.903
			94.0		109.0	2.375	1.895	1.892
			94.0		114.4		1.895	1.903
					109.0			1.892
					109.0			1.892

mum **6a2**, and a central Si-Si bond stretch minimum **6a3** (Figure 3.14). All of these conformers are of extended nature (all-anti or transoid Si dihedral angles). Both TDDFT PBE0/SVP and BHLYP/SVP optimization of the terminal Si-Si bond stretch minimum resulted in the smallest Si-Si bond stretch distances (2.512 Å, and 2.586 Å, respectively). The longest Si-Si bond distance according to the PBE0/SVP method was found for the internal Si-Si bond stretch minimum (2.544 Å), while the BHLYP/SVP method relaxed the central Si-Si bond to a greater extent (2.734 Å). SiSiSi valence angles decrease (varying from 131° to 132° according to the PBE0/SVP method) relative to the bond stretch minima of the permethylated pentasilane. The internal CSiSi angles for the hexasilane bond stretch minima are similar to those of the pentasilane bond stretch minima

Table 3.25: Optimized S₁ geometries TDDFT (PBE0/SVP and BHLYP/SVP) for the central and terminal Si-Si bond stretch minima of Si₅Me₁₂.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ C _i Si _i C _i /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
5a1 PBE0/SVP	179.7	139.5	102.4	112.9	119.9	2.493	1.909	1.884
	177.4	126.4	108.3	108.2	101.8	2.445	1.910	1.890
		119.4	102.4	107.8	101.7	2.391	1.908	1.891
			108.0		109.9	2.372	1.908	1.896
					110.1		1.906	1.896
					113.3		1.906	1.902
5a2 PBE0/SVP	176.8	120.5	107.9	108.5	109.2	2.374	1.903	1.895
	174.4	139.8	97.6	111.4	109.3	2.410	1.905	1.896
		127.7	108.8	109.8	114.1	2.510	1.904	1.901
			89.2		108.5	2.364	1.934	1.892
					113.5		1.896	1.900
					109.3		1.912	1.892
5a1 BHLYP/SVP	179.1	140.1	104.6	112.2	122.3	2.583	1.903	1.884
	174.5	121.9	108.8	108.1	100.5	2.440	1.903	1.885
		116.2	104.5	107.8	100.4	2.387	1.900	1.885
			108.2		110.2	2.373	1.900	1.890
					110.8		1.900	1.890
					111.4		1.900	1.895
5a2 BHLYP/SVP	173.4	116.4	110.2	108.6	109.6	2.379	1.896	1.889
	174.2	134.3	95.4	111.2	109.9	2.386	1.897	1.890
		124.2	111.9	110.4	112.5	2.686	1.894	1.895
			91.6		108.6	2.362	1.901	1.887
					113.3		1.884	1.896
					109.5		1.888	1.887

(103.3° vs. 102.4°, respectively, calculated as the lowest CSiSi valence angle for the terminal Si-Si bond stretch minima according to the PBE0/SVP method).

The permethylated heptasilane, which experimentally shows both normal and blue emission,¹²² does not have bond stretch minima in its extended form according to calculations in this work. Instead, a delocalized emitter is preferred if the extended conformations of various bond stretch minimum-type heptasilane analogs are optimized. If a methyl group is substituted with a trimethylsilyl group in an orthogonal manner to the extended Si backbone in *e.g.*, **6a2**, the **7a2a** minimum (Table 3.28) is found in both PBE0 and BHLYP TDDFT optimizations. A similar strategy resulted in Si-Si bond stretch minima derived from the blue pentasilane emitter (**5a2**) and in **7**,

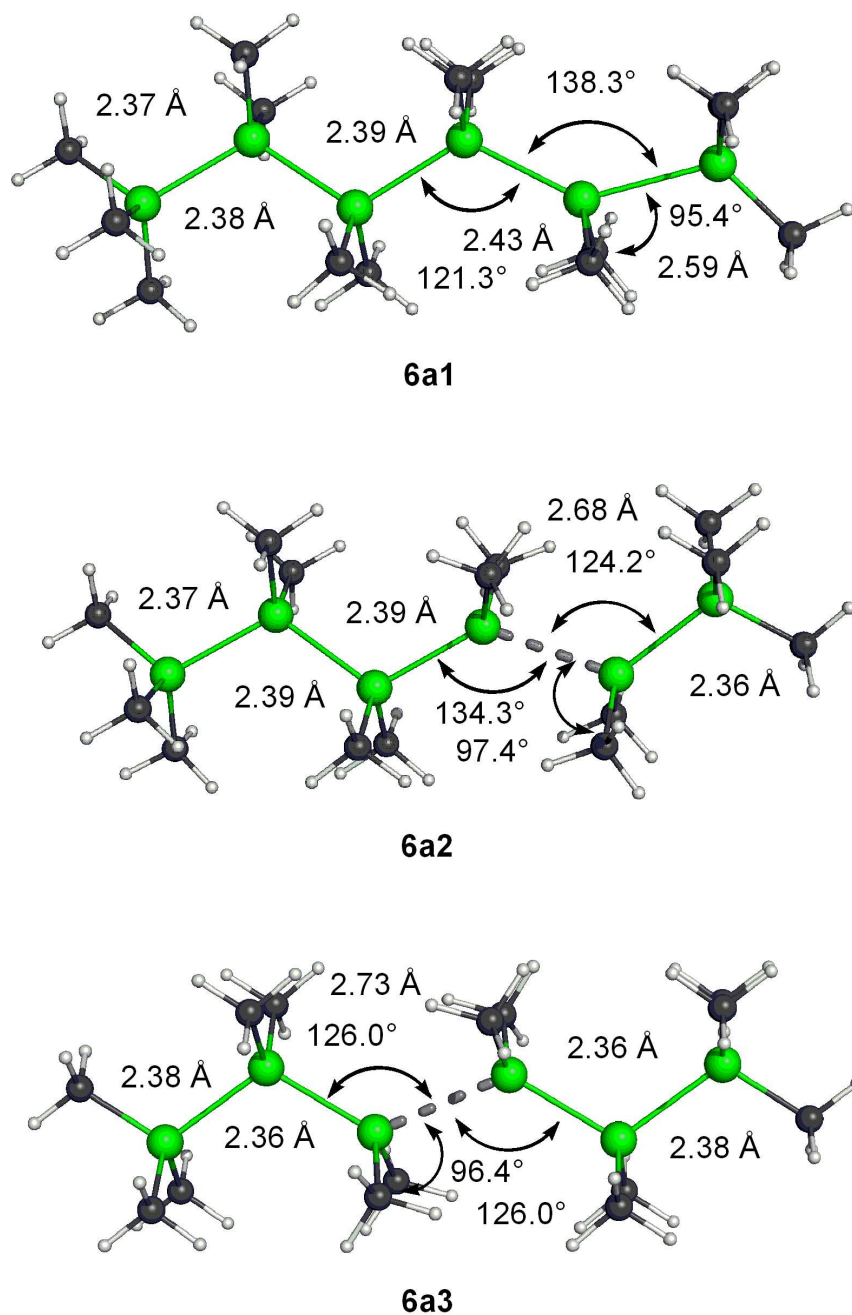


Figure 3.14: $\text{Si}_6\text{Me}_{14}$ terminal Si-Si bond stretch minimum **6a1**, internal Si-Si bond stretch minimum **6a2**, and central Si-Si bond stretch minimum **6a3**. Structures from S_1 optimization (BHLYP/SVP) with Si-Si bond lengths (Å) and selected valence angles (degrees).

these are named **7a2b** (Table 3.29) and **7a2c** (Table 3.30). These conformers are shown in Figure 3.15.

Table 3.26: Optimized S₁ geometries TDDFT (PBE0/SVP) for the Si-Si bond stretch minima of Si₆Me₁₄.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ C _i Si _i C _i /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
6a1	179.7	132.2	103.4	112.3	117.9	2.512	1.899	1.881
	173.0	124.4	108.0	108.4	101.5	2.415	1.898	1.886
	167.6	119.7	103.3	107.9	101.7	2.400	1.907	1.886
		116.2	108.4	107.9	112.4	2.380	1.907	1.901
			106.8		109.8	2.369	1.906	1.896
			107.0		110.5		1.905	1.896
			106.2				1.905	
			108.8				1.906	
6a2	172.3	117.1	107.8	108.1	112.6	2.372	1.904	1.901
	177.5	121.1	104.9	108.7	110.4	2.387	1.904	1.895
	174.7	134.2	108.6	112.3	109.7	2.410	1.905	1.895
		122.1	105.3	109.9	110.1	2.544	1.904	1.890
			110.0		108.7	2.361	1.902	1.890
			94.4		111.4		1.903	1.897
			110.5				1.894	
			93.9				1.895	
6a3	176.2	115.6	110.9	109.0	112.4	2.375	1.902	1.899
	180.0	131.1	92.4	110.4	109.2	2.373	1.901	1.893
	-176.2	131.1	110.8	110.4	109.9	2.536	1.915	1.894
		115.6	99.2	109.0	112.4	2.373	1.896	1.899
			92.4		109.9	2.375	1.915	1.894
			110.9		109.2		1.896	1.893
			99.2				1.901	
			110.8				1.902	

The geometrical parameters for the blue chromophore in the heptasilane change very little in comparison to the shorter silane analogs. The **7a2a** minimum has a slightly shortened longest Si-Si bond length (2.777 Å) in comparison to the hexasilane analog (2.684 Å, Table 3.28) . The **7a2b** minimum has a slightly elongated Si-Si bond (2.713 Å, Table 3.29) in comparison to its parent structure **5a2** (2.583 Å). The **7a2c** minimum structure also has an elongated longest Si-Si bond length (2.682 Å, Table 3.30) in comparison to its parent structure **5a2** (2.583 Å).

As the chain length of the linear oligosilane increases, more conformations are available and many bond stretch minima might exist in twisted conformations. Again, if the silane is extended, the delocalized emitters are preferred. Two examples of blue emitters in long oligosilane chains

Table 3.27: Optimized S₁ geometries TDDFT (BHLYP/SVP) for the Si-Si bond stretch minima of Si₆Me₁₄.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ C _i Si _i C _i /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
6a1	178.9	138.3	105.1	111.3	120.8	2.586	1.899	1.883
	170.9	121.3	107.9	108.3	100.9	2.431	1.899	1.884
	166.7	115.2	105.1	107.9	100.9	2.394	1.900	1.884
		113.6	108.6	107.9	110.5	2.379	1.900	1.893
			108.5		111.1	2.370	1.899	1.890
			107.5		110.2		1.898	1.890
			107.7				1.900	
			109.9				1.899	
6a2	171.8	114.7	108.2	108.2	110.9	2.374	1.898	1.894
	173.0	115.1	107.3	108.8	110.9	2.389	1.898	1.889
	174.6	130.9	109.6	110.5	110.0	2.385	1.896	1.889
		122.2	107.7	110.4	109.8	2.684	1.895	1.886
			110.6		108.6	2.364	1.891	1.886
			96.5		112.8		1.895	1.896
			112.4				1.886	
			93.8				1.883	
6a3	179.9	113.2	112.9	108.8	111.6	2.382	1.894	1.894
	179.8	126.0	96.3	110.3	109.8	2.363	1.894	1.888
	179.4	126.0	112.9	110.3	109.8	2.734	1.888	1.888
		113.2	96.3	108.8	111.6	2.363	1.888	1.894
			96.4		109.7	2.382	1.887	1.888
			112.8		109.8		1.888	1.888
			96.3				1.894	
			112.9				1.895	

are given: Table 3.31 for the permethylated octasilane **8a2a** and Table 3.32 for the permethylated dodecasilane **12a2a**. The structure **8a2a** is related to **6a2** with the additional Si atoms and their methyl groups added in a orthogonal fashion (ortho and gauche Si dihedral angles). In **12a2a**, the blue exciton is located in the center of the molecule as twisted dihedral angles exist on both ends of the molecule (Figure 3.16 and Table 3.32).

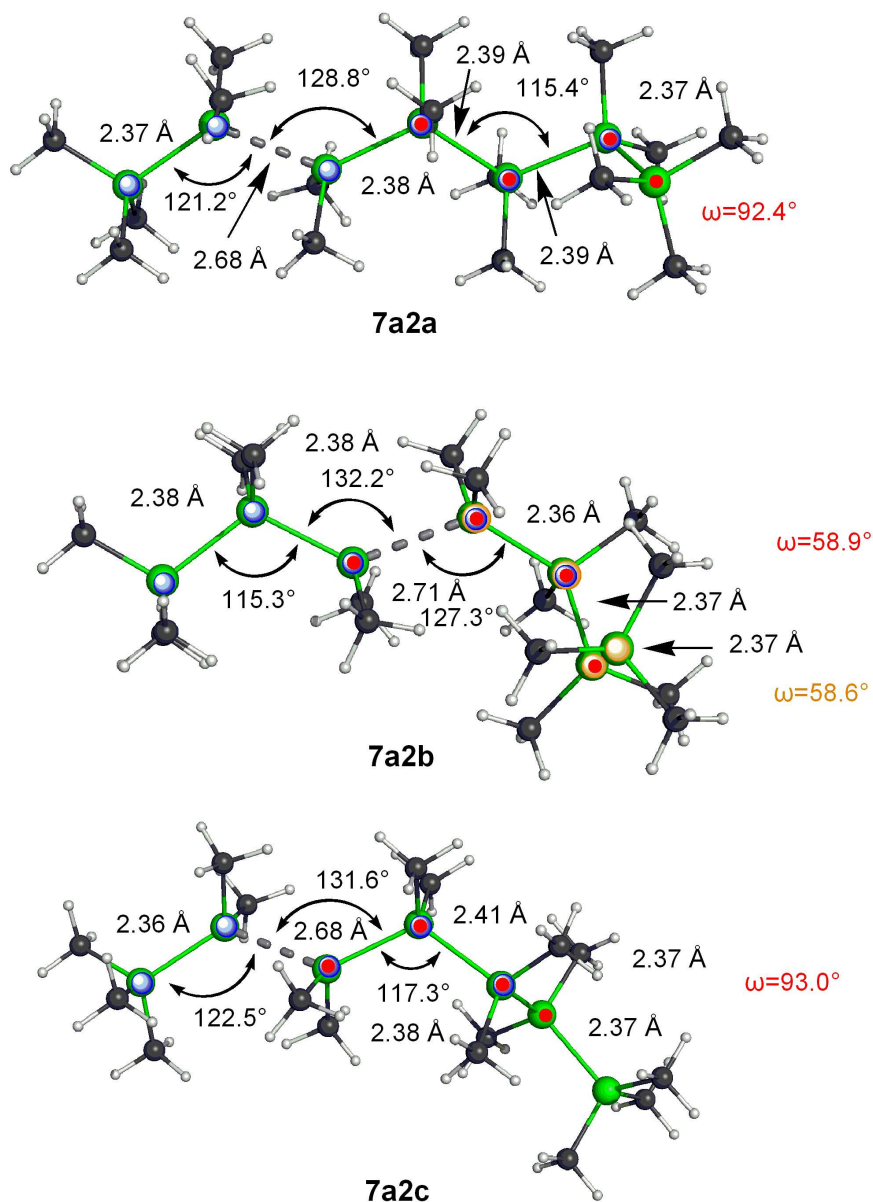


Figure 3.15: $\text{Si}_7\text{Me}_{16}$ blue emitters **7a2a**, **7a2b** and **7a2c**. Structures from S_1 optimization (BHLYP/SVP) with Si-Si bond lengths (Å) and selected valence and dihedral angles (degrees). The Si atoms of the blue emitter are outlined with blue spheres.

Table 3.28: Optimized S_1 geometries TDDFT (BHLYP/SVP and PBE0/SVP) for the **7a2a** Si-Si bond stretch minimum of $\text{Si}_7\text{Me}_{16}$.

Structure	$\omega\text{SiSiSiSi}$ /deg	$\angle\text{SiSiSi}$ /deg	$\angle\text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle\text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle\text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
7a2a BHLYP/SVP	92.4	113.0	109.5	106.8	109.1	2.366	1.903	1.891
	-174.5	115.4	109.2	107.6	111.9	2.390	1.898	1.888
	-173.4	114.9	107.6	108.9	110.4	2.394	1.897	1.889
	-174.3	128.8	107.3	110.2	112.7	2.384	1.898	1.896
		121.2	109.9	110.3	109.9	2.677	1.894	1.886
			107.6		108.6	2.365	1.895	1.886
			107.8				1.890	
			107.6				1.893	
			110.9				1.883	
			97.4				1.886	
			112.4					
			95.2					
7a2a PBE0/SVP	92.2	112.8	109.0	106.3	109.3	2.364	1.911	1.897
	-176.8	118.1	108.2	107.3	112.0	2.387	1.905	1.894
	-177.9	120.5	106.8	108.9	110.5	2.393	1.903	1.894
	-173.9	131.1	106.9	112.1	111.0	2.401	1.906	1.897
		120.4	108.8	110.0	110.3	2.552	1.903	1.889
			105.5		108.6	2.361	1.904	1.889
			107.6				1.898	
			105.3				1.899	
			110.7				1.892	
			95.4				1.892	
			111.2					
			94.7					

Table 3.29: Optimized S_1 geometries TDDFT (BHLYP/SVP and PBE0/SVP) for the **7a2b** Si-Si bond stretch minima of $\text{Si}_7\text{Me}_{16}$.

Structure	ω_{SiSiSiSi} /deg	$\angle \text{SiSiSi}$ /deg	$\angle \text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle \text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle \text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
7a2b BHLYP/SVP	175.3	115.3	110.9	108.8	112.2	2.379	1.896	1.895
	167.9	132.2	96.3	111.1	109.5	2.378	1.896	1.889
	58.9	127.3	112.1	109.7	110.0	2.713	1.891	1.889
	58.6	115.6	91.9	106.3	108.3	2.363	1.898	1.890
		116.0	95.7	107.2	111.3	2.369	1.887	1.889
			115.7		111.9	2.369	1.889	1.889
			94.7				1.899	
			111.0				1.908	
			106.2				1.902	
			107.8				1.897	
			112.4					
			108.1					
7a2b PBE0/SVP	176.1	118.7	108.3	108.7	113.6	2.374	1.904	1.901
	166.2	137.3	98.1	111.4	109.2	2.396	1.903	1.894
	53.1	130.8	109.6	110.1	109.5	2.532	1.902	1.895
	62.6	114.7	90.3	106.6	107.8	2.360	1.925	1.895
		116.0	95.7	107.3	111.2	2.367	1.906	1.892
			112.9		112.5	2.369	1.904	1.893
			96.2				1.905	
			109.2				1.911	
			106.1				1.907	
			107.4				1.901	
			113.8					
			107.9					

Table 3.30: Optimized S_1 geometries TDDFT (BHLYP/SVP and PBE0/SVP) for the blue emitting **7a2c** minimum of $\text{Si}_7\text{Me}_{16}$.

Structure	$\omega\text{SiSiSiSi}$ /deg	$\angle\text{SiSiSi}$ /deg	$\angle\text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle\text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle\text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC_i /Å	SiC_t /Å
7a2c BHLYP/SVP	-166.2	111.7	110.3	108.2	109.5	2.369	1.898	1.891
	93.0	112.1	108.5	106.3	111.4	2.369	1.899	1.889
	-175.5	117.3	109.3	107.7	110.3	2.408	1.898	1.889
	-173.9	131.6	110.2	110.4	112.9	2.384	1.904	1.896
		122.5	106.5	110.4	109.7	2.682	1.899	1.887
			107.2		108.6	2.364	1.895	1.886
			109.8				1.892	
			108.0				1.896	
			111.0				1.884	
			96.2				1.887	
			111.7					
			93.7					
7a2c PBE0/SVP	-164.3	111.5	110.1	108.5	109.7	2.369	1.902	1.896
	93.0	111.7	107.5	105.7	111.5	2.365	1.903	1.893
	179.9	121.6	109.3	107.6	110.0	2.404	1.905	1.894
	-173.7	134.4	112.4	111.9	112.0	2.402	1.911	1.898
		122.4	105.6	109.9	110.0	2.546	1.908	1.891
			105.3		108.7	2.361	1.902	1.890
			109.6				1.903	
			106.4				1.905	
			110.2				1.895	
			94.9				1.895	
			109.9					
			93.9					

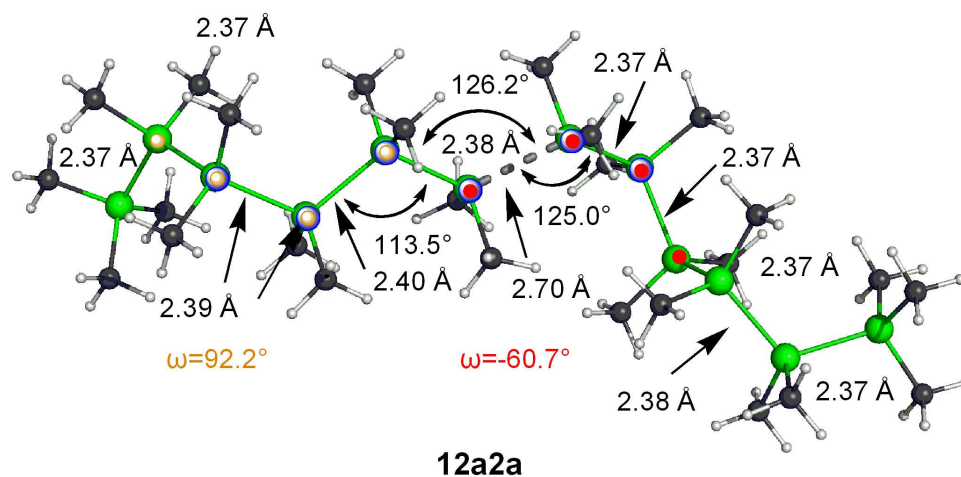


Figure 3.16: $\text{Si}_{12}\text{Me}_{26}$ blue emitter **12a2a**. Structures from S_1 optimization (BHLYP/SVP) with Si-Si bond lengths (Å) and selected valence and dihedral angles (degrees). The Si atoms of the blue emitter are outlined with blue spheres.

Table 3.31: Optimized S_1 geometries TDDFT (PBE0/SVP and BHLYP) for the selected Si-Si bond stretch minimum of $\text{Si}_8\text{Me}_{18}$.

Structure	ω_{SiSiSiSi} /deg	$\angle \text{SiSiSi}$ /deg	$\angle \text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle \text{C}_i\text{Si}_i\text{C}_i$ /deg	$\angle \text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
8a2a BHLYP/SVP	-174.0	120.9	97.5	110.3	108.6	2.366	1.883	1.886
	-173.5	128.4	111.0	110.2	112.6	2.675	1.886	1.896
	-174.9	114.8	95.4	109.0	109.9	2.385	1.890	1.886
	92.2	115.5	112.4	107.6	108.2	2.395	1.893	1.891
	69.5	115.1	107.6	106.1	111.0	2.392	1.894	1.889
		116.0	109.7	107.3	112.8	2.372	1.894	1.889
			107.6			2.373	1.898	
			108.1				1.896	
			107.5				1.900	
			107.2				1.902	
			108.7				1.902	
			110.1				1.898	
			109.3					
			107.0					
			109.6					
			109.4					
8a2a PBE0/SVP	-173.5	119.9	95.6	110.1	108.5	2.361	1.891	1.889
	-177.5	130.3	110.9	112.1	110.9	2.555	1.891	1.897
	-177.1	120.2	95.0	109.0	110.4	2.399	1.897	1.889
	93.0	118.2	111.4	107.4	108.2	2.394	1.898	1.896
	70.7	114.6	105.5	105.4	111.0	2.389	1.903	1.893
		115.7	108.4	107.2	112.9	2.368	1.904	1.893
			105.5			2.373	1.906	
			107.9				1.902	
			107.2				1.907	
			106.5				1.909	
			107.5				1.908	
			109.6				1.903	
			108.8					
			106.6					
			111.6					
			109.2					

Table 3.32: Optimized S_1 geometries TDDFT (BHLYP/SVP) for the selected Si-Si bond stretch minimum of $Si_{12}Me_{26}$.

Structure	$\omega_{SiSiSiSi}$ /deg	$\angle SiSiSi$ /deg	$\angle C_iSi_iSi_i$ /deg	$\angle C_iSi_iC_i$ /deg	$\angle Si_iSi_tC_t$ /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
12a2a	69.4	116.0	107.1	107.3	108.2	2.373	1.902	1.891
	92.2	115.1	109.3	106.1	111.0	2.372	1.898	1.888
	-174.8	115.0	109.5	107.7	112.8	2.392	1.900	1.888
	-174.4	113.5	109.3	109.2	108.8	2.395	1.902	1.890
	-165.5	126.2	107.4	109.7	113.1	2.377	1.898	1.888
	-60.7	125.0	107.4	109.0	109.5	2.696	1.895	1.889
	-57.9	117.3	110.1	106.0		2.373	1.893	
	-157.7	114.9	108.9	107.1		2.372	1.893	
	89.4	112.5	110.0	108.1		2.371	1.887	
		114.1	108.1	107.1		2.375	1.890	
			108.1			2.366	1.889	
			107.9				1.885	
			111.6				1.900	
			98.7				1.909	
			112.6				1.897	
			96.1				1.901	
			97.0				1.898	
			109.6				1.899	
			98.0				1.899	
			116.1				1.901	
			105.7					
			107.6					
			111.5					
			108.0					
			110.8					
			109.0					
			104.2					
			110.5					
			110.9					
			109.7					
			108.8					
			106.7					

Table 3.33: Optimized S_1 geometries TDDFT (PBE0/SVP) for the selected Si-Si bond stretch minimum of $\text{Si}_{12}\text{Me}_{26}$.

Structure	ω_{SiSiSiSi} /deg	$\angle_{\text{SiSiSi}}$ /deg	$\angle_{\text{C}_i\text{Si}_i\text{Si}_i}$ /deg	$\angle_{\text{C}_i\text{Si}_i\text{C}_i}$ /deg	$\angle_{\text{Si}_i\text{Si}_t\text{C}_t}$ /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
12a2a	70.2	115.8	106.7	107.3	108.2	2.373	1.907	1.896
	92.6	114.8	108.9	105.6	111.0	2.368	1.903	1.893
	-176.0	117.6	109.2	107.6	112.9	2.388	1.907	1.893
	-175.4	118.8	111.2	109.2	108.4	2.392	1.908	1.894
	-163.7	129.3	106.6	111.3	113.3	2.391	1.905	1.891
	-59.5	125.3	107.4	109.1	109.3	2.566	1.901	1.893
	-58.0	118.0	109.7	106.6		2.361	1.902	
	-159.2	114.4	107.6	107.4		2.369	1.903	
	90.1	111.9	108.6	108.2		2.368	1.896	
		113.9	106.1	107.3		2.373	1.898	
			107.9			2.366	1.899	
			106.0				1.891	
			110.8				1.903	
			96.7				1.911	
			111.6				1.900	
			95.5				1.904	
			95.2				1.901	
			109.4				1.902	
			99.4				1.902	
			116.0				1.905	
			105.9					
			108.0					
			110.0					
			107.8					
			110.7					
			109.4					
			103.9					
			110.7					
			111.1					
			109.9					
			108.7					
			106.9					

3.3.3.3 NHO Analysis

NHO analysis of the S_1 density for the terminal Si-Si bond stretch minimum **4a1** showed that the internal Si atom that is associated with the large Si-Si bond length is rehybridized. Instead of two sp^3 hybrid orbitals pointing to neighboring Si atoms, there is an sp^2 hybridized orbital pointing towards the neighboring internal Si atom, and a high p character orbital pointing towards the neighboring terminal Si.

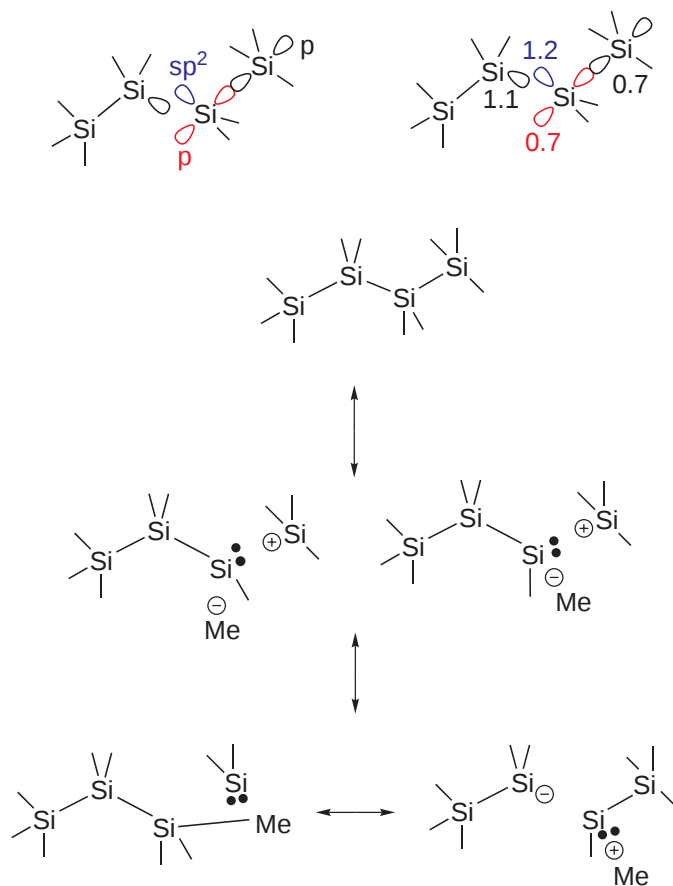


Figure 3.17: $\text{Si}_4\text{Me}_{10}$ terminal Si-Si bond stretch minimum (**4a1**) NHO populations for the excited state (S_1) density of the S_1 relaxed structure. Hybridization deviating from sp^3 is noted.

The remaining hybrid orbitals (pointing toward methyl groups) are sp^3 hybridized. The sp^2 hybridized orbital pointing towards the neighboring internal Si atom has higher than normal occupancy (1.2 electrons) and the latter orbital has less population than normal (0.7 electrons). Normal occupancy is defined as that in the ground state equilibrium structures, which have 1.0

electron per Si hybrid orbital. The covalent resonance structure (Figure 3.17) mostly describes the S_1 density, but secondary resonance structures are noted, one of which is related to chain abridgment via a terminal dimethylsilylene extrusion product.

NHO analysis of the S_1 density for the central Si-Si bond stretch minimum **4a2** indicates a symmetric rehybridization (from sp^3 to sp^2) of Si hybrid orbitals located on the internal Si atoms which point to the terminal Si atoms (Figure 3.18). The remaining Si hybrid orbitals are sp^3 hybridized. The sp^2 hybridized orbitals have slightly more occupancy (1.1 electrons) and the adjacent internal Si hybrids have slightly less population (0.9 electrons). The covalent resonance structure as well as zwitterionic resonance structures describe the S_1 density.

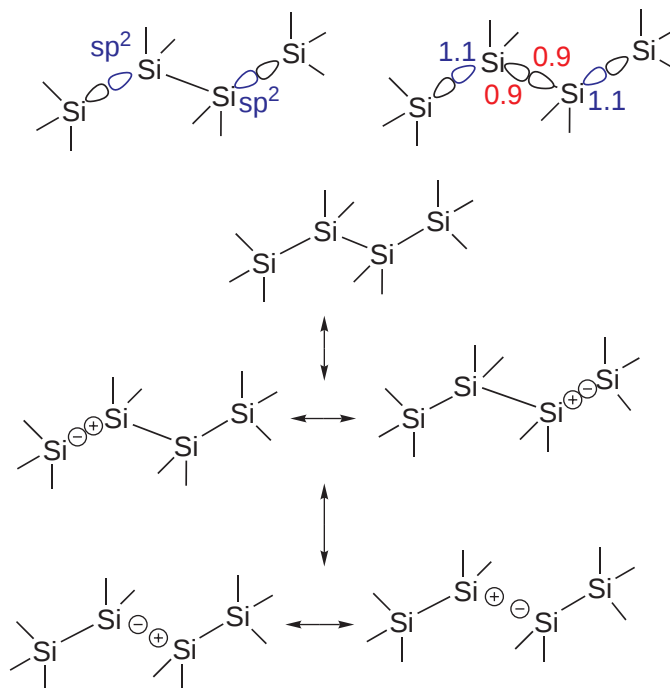


Figure 3.18: Si_4Me_{10} central Si-Si bond stretch minimum (**4a2**) NHO populations for the excited state (S_1) density of the S_1 relaxed structure. Hybridization deviating from sp^3 is noted.

3.3.3.4 Blue Emission for $\text{Si}_n\text{Me}_{2n+2}$ ($n = 4 - 6$)

The S_0 - S_1 transition for the terminal Si-Si bond stretch minimum **4a1** structure is similar to that of the smaller permethylated trisilane, **3a**, in Chapter 2. This transition is of $\sigma\sigma^*$ nature, and directed along the Si backbone, as can be seen from the transition density in Figure 3.19. The polarization of this transition is in agreement with fluorescence anisotropy experiments.¹²⁵ The $\sigma\sigma^*$ transition density and HOMO for the terminal Si-Si bond stretch minimum is localized on the elongated terminal Si-Si bond, whereas the LUMO and difference density are delocalized over the Si backbone, also shown in Figure 3.19.

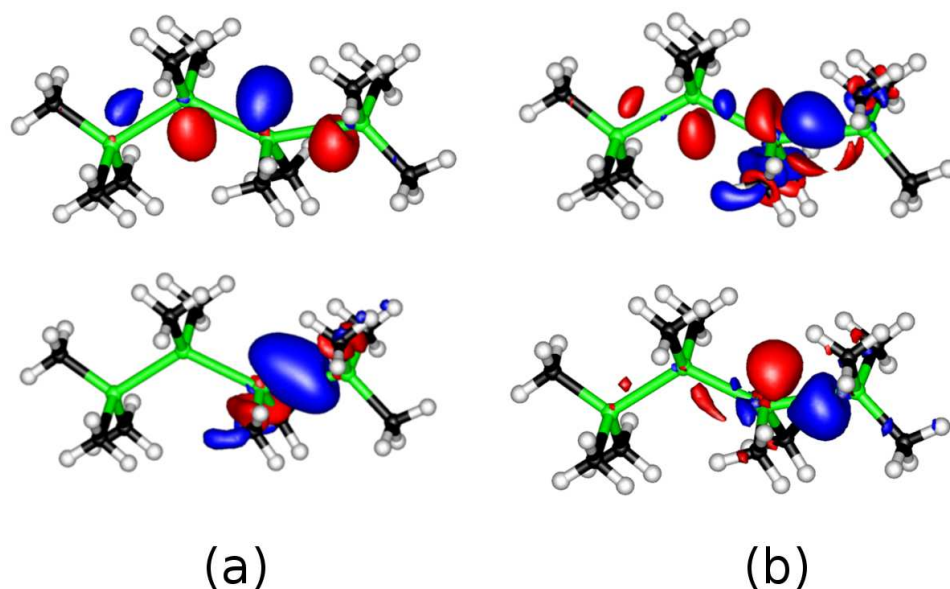


Figure 3.19: Molecular orbitals and densities for the terminal Si-Si bond stretch minimum, **4a1**. HOMO (bottom) and LUMO (top) are shown in column (a) and S_0 - S_1 transition density (bottom) and S_0 - S_1 difference density (top) are shown in column (b). Molecular orbitals are shown with the isodensity surface values of ± 0.06 , transition density is shown with the isodensity surface values of ± 0.004 and the difference density is shown isodensity surface values of ± 0.003 .

A similar situation is encountered for the central Si-Si bond stretch minimum, **4a2**. Here the transition density is localized along the central Si-Si bond, as is the HOMO. The LUMO is

delocalized over the Si backbone as can be seen in Figure 3.20. This transition also characterized as being of $\sigma\sigma^*$ nature, as the orbitals involved are symmetric with respect to reflection in a symmetry plane, which for both the central and terminal bond stretch minima can be easily defined by the plane of the Si backbone.

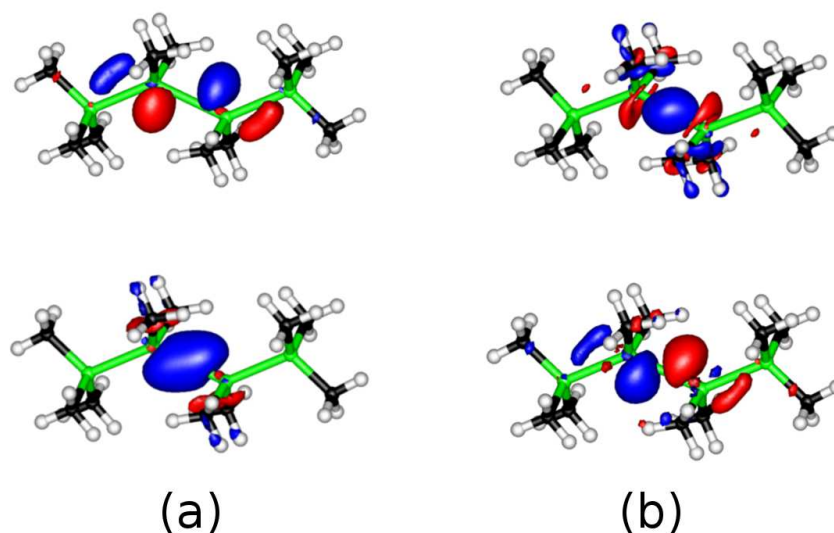


Figure 3.20: Molecular orbitals and densities for the central Si-Si bond stretch minimum, **4a2**. HOMO (bottom) and LUMO (top) are shown in column (a) and S_0 - S_1 transition density (bottom) and S_0 - S_1 difference density (top) are shown in column (b). Molecular orbitals are shown with the isodensity surface values of ± 0.06 , transition density is shown with the isodensity surface values of ± 0.004 and the difference density is shown isodensity surface values of ± 0.003 .

In order to calculate accurate emission energies, the μ parameter was optimized to reproduce experimental absorption energies. As the silane increases in length, the optimal μ value decreases as standard TDDFT reproduces the absorption energies with increasing accuracy (Table 3.34).

For the permethylated tetrasilane, the terminal Si-Si bond stretch minimum gives higher emission energies than that of the central Si-Si bond stretch minimum. This difference is minimal when the emission energy is calculated with the standard TDDFT method (B3LYP/Def2-TZVP). For the Si-Si bond stretch minima (PBE0/SVP, BHLYP/SVP and RIADC(2)/SVP structures)

Table 3.34: Theoretical vertical absorption energies calculated with the LC-BLYP/Def2TZVP method with various μ values for RIMP2/TZVP S_0 optimized $\text{Si}_n\text{Me}_{2n+2}$ structures. For $n \geq 4$, all-transoid structures are calculated.

$\text{Si}_n\text{Me}_{2n+2}$ n	State	μ / a_0^{-1}	E_{VE} / cm^{-1}	f
2	$\sigma\pi^*$	0.22	52 070	0.140
2*	$\sigma\pi^*$	0.23	52 400	0.144
2	$\sigma\pi^*$	0.24	52 730	0.148
3	$\sigma\sigma^*$	0.22	46 790	0.118
3*	$\sigma\sigma^*$	0.23	47 164	0.124
3	$\sigma\sigma^*$	0.24	47 530	0.131
4	$\sigma\sigma^*$	0.19	42 930	0.282
4*	$\sigma\sigma^*$	0.20	43 260	0.289
4	$\sigma\sigma^*$	0.21	43 578	0.297
5	$\sigma\sigma^*$	0.17	39 660	0.416
5*	$\sigma\sigma^*$	0.18	40 000	0.428
5	$\sigma\sigma^*$	0.19	40 340	0.440
6	$\sigma\sigma^*$	0.16	37 570	0.582
6*	$\sigma\sigma^*$	0.17	37 900	0.596
6	$\sigma\sigma^*$	0.18	38 570	0.611

Experimental values at 77 K¹⁰² show absorption peak maxima at 52 300, 47 100, 43 100, 40 100, 38 100 cm^{-1} for $n = 2, 3, 4, 5, 6$, respectively. ^a n^* refers to optimal μ value which reproduces experimental absorption.

the TDDFT (B3LYP/Def2-TZVP) emission energy differences were 1 130 cm^{-1} , 280 cm^{-1} , and 630 cm^{-1} , respectively. Using the LC'-BLYP method ($\mu = 0.20$) the energy differences between bond stretch minima emission energies were 1 060 cm^{-1} and 1 280 cm^{-1} , respectively. A similar trend is observed with the RICC2 and MSCASPT2 emission energy differences between terminal and central bond stretch minima. The PBE0/SVP terminal stretch minimum has a much larger S_1 dipole moment (4.13 Debye) compared to the BHLYP and RIADC(2) minima (3.13 and 2.85 Debye, respectively), where the MSCASPT2(6,10)/ANO-L' S_1 dipole moments are compared. The S_0 - S_1 oscillator strengths (calculated with various methods) are also weakest for the PBE0/SVP structures. There is a larger variation for the S_0 - S_1 oscillator strengths of the central bond stretch isomer (0.12-0.54) than for the terminal Si-Si bond stretch minimum (0.12-0.35). The transition dipole moments for the S_0 - S_1 transition is along the long axis of the molecule. The lowest emission energy was calculated for the central bond stretch minimum (RIADC(2)/SVP structure), with

energies ranging from 23 480 cm^{-1} (MSCASPT2/ANO-L') to 25 770 cm^{-1} (RICC2/Def2-TZVP). The largest emission energies were calculated for the terminal bond stretch minimum, with emission energies ranging from 24 890 cm^{-1} (MSCASPT2/ANO-L') to 29 280 cm^{-1} (RICC2/Def2-TZVP). The values are tabulated in Table 3.35 for the structures obtained with the PBE0/SVP method. The vertical emission energies calculated for the BHLYP/SVP structures are listed in Table 3.36 and for the RIADC(2)/SVP structures, in Table 3.37.

On a final note, the reparametrized LC'-BLYP emission energy values agreed extremely well with MSCASPT2 values. For example, regarding the terminal Si-Si bond stretch minimum obtained from the BHLYP/SVP S_1 optimization, the LC'-BLYP emission energy is 26 880 cm^{-1} , which only differs by 60 cm^{-1} from the MSCASPT2/ANO-L' value (26 820 cm^{-1}). LC'-BLYP and MSCASPT2 emission energies were similar for the central Si-Si bond stretch minimum. These values are listed in Table 3.36.

Table 3.35: Calculated vertical emission energies for PBE0/SVP S_1 optimized Si-Si bond stretch $\text{Si}_4\text{Me}_{10}$ structures. Transition dipole moments are directed along the long axis of the molecule.

Structure	Method	E_{VE}	f	Weight	S_1 Dipole
4a1	TDDFT/Def2-TZVP	26 810	0.12	98.6	4.22
	LC'-TDDFT/Def2-TZVP	26 940	0.11	98.9	NA
	RICC2/Def2-TZVP	29 280	0.17	95.6	4.18
	MSCASPT2(6,10)/ANO-L	27 480	0.25	88.9	4.15
	MSCASPT2(6,10)/ANO-L'	27 140	0.25	88.9	4.13
4a2	TDDFT/Def2-TZVP	25 670	0.12	98.2	0.0
	LC'-TDDFT/Def2-TZVP	25 020	0.12	98.4	NA
	RICC2/Def2-TZVP	27 690	0.18	96.3	0.0
	MSCASPT2(6,10)/ANO-L ^a	25 680	0.38	90.4	0.0
	MSCASPT2(6,10)/ANO-L' ^b	25 380	0.35	91.1	0.0

^aThe ANO-L basis set refers to Si:ANO-L[5S4P2D]C:ANO-L[3S2P1D]H:ANO-L[2S1P]. ^bThe ANO-L' basis set refers to Si:ANO-L[5S4P2D]C:ANO-L[4S3P2D]H:ANO-L[2S1P].

Three Si-Si bond stretch minima that were found for the permethylated hexasilane are shown in Figure 3.21. The HOMO is localized over the Si-Si bond which is most stretched for each minimum. In all cases, the LUMO is delocalized over the entire Si backbone.

The trend of the blue shift of the excitation energy of the terminal bond stretch minimum

Table 3.36: Theoretical vertical emission energies for BHLYP/SVP S_1 optimized $\text{Si}_4\text{Me}_{10}$ structures.

Structure	Method	E_{VE} / cm^{-1}	f	Weight / %	S_1 Dipole Moment Debye
4a1	TDDFT/Def2-TZVP	26 982	0.17	98.4	3.67
	LC'-TDDFT/Def2-TZVP	26 880	0.17	98.9	NA
	RICC2/Def2-TZVP	29 170	0.25	95.6	3.64
	MSCASPT2(6,10)/ANO-L	27 180	0.33	85.2	3.17
	MSCASPT2(6,10)/ANO-L'	26 820	0.33	85.0	3.31
4a2	TDDFT B3LYP/Def2-TZVP	26 690	0.30	98.1	0.0
	LC'-TDDFT BLYP/Def2-TZVP	25 820	0.28	99.5	NA
	RICC2/Def2-TZVP	28 210	0.39	98.4	0.0
	MSCASPT2(6,10)/ANO-L	25 480	0.47	92.9	0.0
	MSCASPT2(6,10)/ANO-L'	25 850	0.54	92.5	0.0

Table 3.37: Theoretical vertical emission energies for RIADC(2)/SVP S_1 optimized $\text{Si}_4\text{Me}_{10}$ structures.

Structure	Method	E_{VE} / cm^{-1}	f	Weight / %	S_1 Dipole Moment Debye
4a1	TDDFT/Def2-TZVP	24 970	0.16	98.5	3.11
	LC'-TDDFT/Def2-TZVP	24 790	0.15	98.2	NA
	RICC2/Def2-TZVP	26 990	0.22	95.9	3.16
	MSCASPT2(6,10)/ANO-L	25 240	0.30	87.4	2.90
	MSCASPT2(6,10)/ANO-L'	24 890	0.31	87.2	2.85
4a2	TDDFT B3LYP/Def2-TZVP	24 340	0.25	98.4	0.0
	LC'-TDDFT BLYP/Def2-TZVP	23 520	0.23	99.6	NA
	RICC2/Def2-TZVP	25 770	0.33	96.8	0.0
	MSCASPT2(6,10)/ANO-L	23 920	0.45	89.3	0.0
	MSCASPT2(6,10)/ANO-L'	23 480	0.46	89.8	0.0

structure relative to that of the central bond stretch minimum is also observed for longer oligosilanes. Another trend, this time easily compared to that of experiment,¹¹⁶ is the red shift of blue exciton emission energies with decreasing oligosilane chain length, n , which is well reproduced with TDDFT calculations. The pentasilane structures (obtained with the BHLYP/SVP method) gave a small difference in emission energies for the terminal Si-Si and central Si-Si bond stretch minima: 27 650 cm^{-1} and 27 140 cm^{-1} , respectively. The pentasilane structures obtained with the PBE0/SVP method gave a larger difference of emission energies for the terminal Si-Si and central Si-Si bond

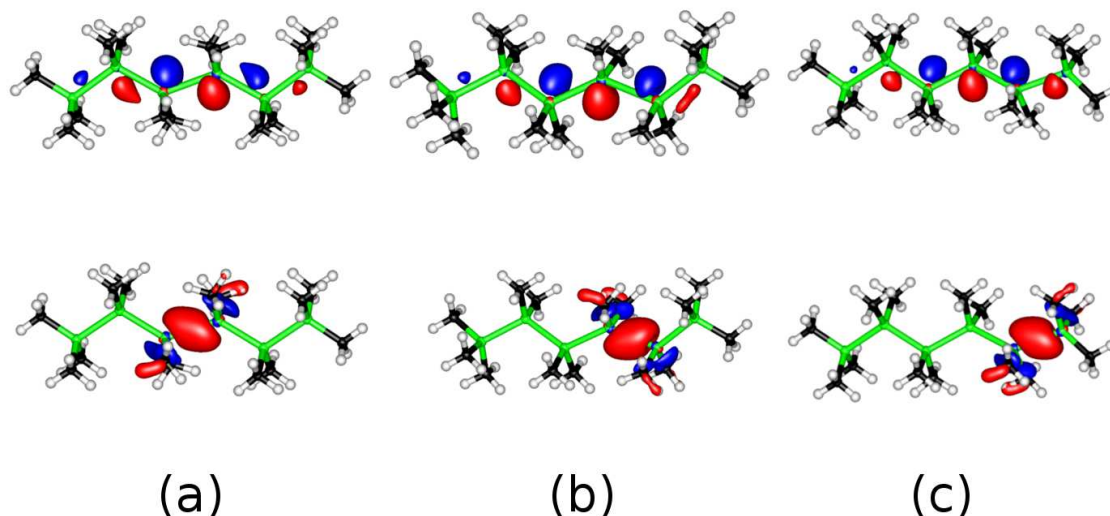


Figure 3.21: Molecular orbitals, HOMO (bottom) and LUMO (top) for **6a3** (a), **6a2** (b), **6a1** (c). Molecular orbitals are shown with the isodensity surface values of ± 0.06 .

stretch minima: $27\,640\text{ cm}^{-1}$ and $26\,620\text{ cm}^{-1}$, respectively. The differences in the calculated vertical emission follow a similar trend for the hexasilane bond stretch minima obtained with PBE0/SVP and BHLYP/SVP methods. In the former case, the emission energies vary over $1\,350\text{ cm}^{-1}$, but for the latter case these values only differ by a maximum of 360 cm^{-1} . These values are listed in Table 3.38 for structures obtained with the PBE0/SVP method and listed in Table 3.39 for structures obtained with the BHLYP/SVP method.

Table 3.38: Theoretical (B3LYP/Def2-TZVP) vertical emission energies for PBE0/SVP S_1 optimized **4** to **6** structures. Transition dipole moments are directed along the long axis of the molecule.

Structure	E_{VE} / cm^{-1}	f	S_1 Dipole Moment / Debye
4a1	26 810	0.12	4.22
4a2	25 670	0.12	0.00
5a1	27 640	0.20	6.49
5a2	26 620	0.22	2.13
6a1	28 890	0.32	8.81
6a2	27 770	0.36	4.55
6a3	27 540	0.40	0.00

Table 3.39: Theoretical (B3LYP/Def2-TZVP) vertical emission energies for B3LYP/SVP S_1 optimized **4** to **6** structures.

Structure	E_{VE} / cm^{-1}	f	S_1 Dipole Moment / Debye
4a1	26 980	0.17	3.67
4a2	26 690	0.30	0.00
5a1	27 650	0.26	5.35
5a2	27 140	0.39	1.57
6a1	28 340	0.36	6.58
6a2	28 190	0.54	2.61
6a3	27 980	0.65	0.00

3.3.3.5 Heptasilane Emission

Blue emission from permethylated heptasilanes has been calculated to result from various structures (**7a2a-7a2c**). The S_0 - S_1 state is described by a HOMO to LUMO excitation and these orbitals are shown in Figure 3.22. The active orbitals in the normal emitter, which are delocalized over the entire Si backbone, are shown for comparison.

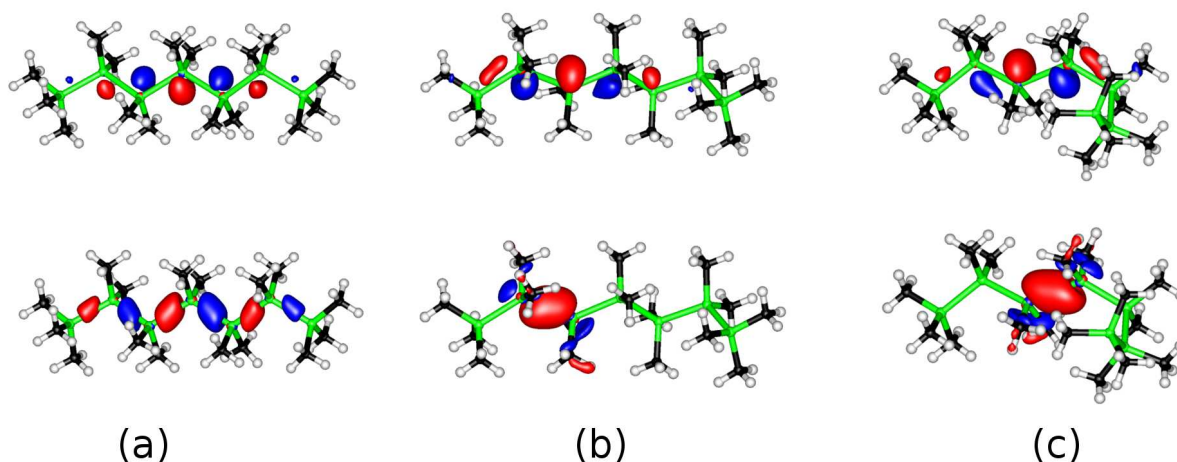


Figure 3.22: Molecular orbitals (B3LYP/Def2-TZVP) HOMO (bottom) and LUMO (top) for the delocalized emitter **7N** (a), and blue emitters: **7a2a** (b) and **7a2b** (c). All orbitals are shown with isodensity surface values of ± 0.06 .

Regarding the blue emission from the heptasilane, there are some differences in emission energies in comparison to the analogous chromophore subunit from which the structures were derived. For example, for **7a2a** the emission energy was slightly red-shifted ($26\,760\text{ cm}^{-1}$) for the PBE0/SVP **7a2a** structure (Table 3.38), in comparison to the PBE0/SVP **6a2** emission energy ($27\,770\text{ cm}^{-1}$) even though the emission energies should resemble those of **6a2**. For the BHLYP/SVP structure, this value was slightly blue-shifted ($29\,100\text{ cm}^{-1}$, Table 3.39) in comparison to the BHLYP/SVP **6a2** emission energy ($28\,190\text{ cm}^{-1}$).

Considering the series of blue emitters thus far, the S_0 - S_1 oscillator strengths increased (from 0.12 to 0.38) as the oligosilane chain length increased from the tetrasilane Si-Si bond stretch minima

to the heptasilane Si-Si bond stretch minima, cf. Table 3.40. The S_1 dipole moment also increased in a similar fashion (*e.g.*, from 3.72 Debye for **4a1** to 6.58 Debye for **6a1**, both calculated with the BHLYP/SVP TDDFT method, cf. Table 3.41).

Table 3.40: Theoretical (B3LYP/Def2-TZVP) vertical emission energies for PBE0/SVP S_1 optimized $\text{Si}_7\text{Me}_{16}$ structures.

Structure	E_{VE} / cm^{-1}	f	S_1 Dipole Moment / Debye
7a2a	28 470	0.44	5.32
7a2b	26 760	0.25	1.45
7a2c	28 450	0.38	3.39

Table 3.41: Theoretical (B3LYP/Def2-TZVP) vertical emission energies for BHLYP/SVP S_1 optimized $\text{Si}_7\text{Me}_{16}$ structures.

Structure	E_{VE} / cm^{-1}	f	S_1 Dipole Moment / Debye
7a2a	26 760	0.25	2.97
7a2b	26 840	0.41	0.78
7a2c	28 310	0.52	2.09

3.3.3.6 Blue Emission Predicted for Longer ($n \geq 8$) Oligosilane Chains

While blue emission has not been observed for permethylated oligosilanes longer than the heptasilane, according to calculations in this section, blue emission might be possible in longer oligosilanes if conformations similar to those presented here can be experimentally accessed. The blue excitons seem to be delocalized over a small number of silicon atoms. If the structure is partially distorted (with twisted cisoid-ortho all-Si dihedral angles), excited state minima which yield blue emission energies are found in even longer silanes ($n = 8 - 12$).

The blue emitter **8a2a** has a HOMO which is localized over the elongated Si-Si bond and a LUMO which is delocalized over the extended Si backbone. These orbitals can be seen in Figure 3.23, where they plotted on various isodensity surface values. The smaller isodensity value aids in visualization of the blue exciton, while the larger one is plotted for comparison to other orbitals in

this work.

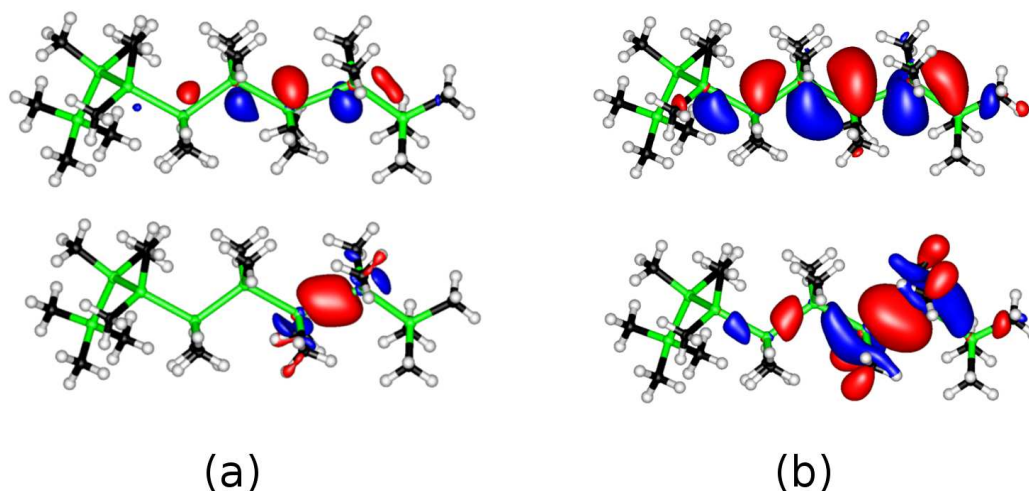


Figure 3.23: Molecular orbitals (B3LYP/Def2-TZVP) HOMO (bottom) and LUMO (top) for the blue emitter **8a2a** shown with isodensity surface values of ± 0.06 (a) and ± 0.03 (b).

The blue exciton found in **12a2a** also contains a HOMO which is localized on the elongated internal Si-Si bond. The LUMO is delocalized over the extended portion of the Si backbone, which consists of six Si atoms. These orbitals are shown in Figure 3.24.

The emission energies of the longer blue emitters are not very blue-shifted from those of **6a2**, indicating that the exciton in the longer chains is delocalized over a similar number of Si atoms (6). For the **8a2a** structure obtained with the PBE0/SVP method, the emission energy (B3LYP/Def2-TZVP) was $28\,680\text{ cm}^{-1}$, and for the even longer dodecasilane **12a2a**, this value was calculated to be $28\,760\text{ cm}^{-1}$. The parent hexasilane **6a2** gave an emission energy ($27\,770\text{ cm}^{-1}$). The S_0 - S_1 oscillator strengths do not change significantly either, and are 0.47 and 0.53 for **8a2a** and **12a2a**, respectively. These values are listed in Table 3.42.

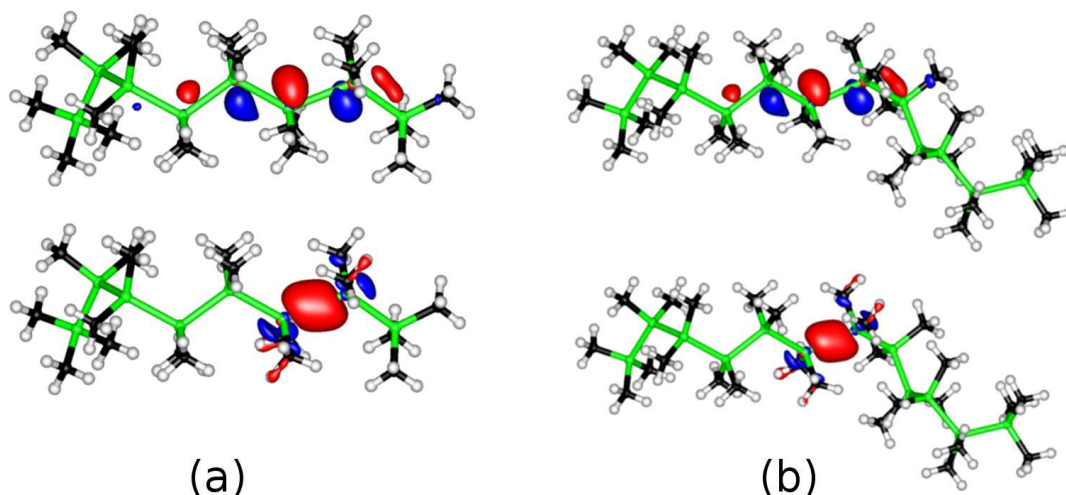


Figure 3.24: Molecular orbitals (B3LYP/Def2-TZVP) HOMO (bottom) and LUMO (top) for the blue emitters: **8a2a** (a) and **12a2a** (b). All orbitals are shown with isodensity surface values of ± 0.06 .

Table 3.42: Theoretical (B3LYP/Def2-TZVP) vertical emission energies for PBE0/SVP and BHLYP S_1 optimized $\text{Si}_8\text{Me}_{18}$ and $\text{Si}_{12}\text{Me}_{26}$ structures.

Structure	E_{VE}	f
8a2a (PBE0/SVP)	28 680	0.47
8a2a (BHLYP/SVP)	29 220	0.66
12a2a (PBE0/SVP)	28 760	0.53
12a2a (BHLYP/SVP)	29 220	0.77

3.4 Discussion

3.4.1 Delocalized Excitation

There has been extensive work on the absorption properties of linear oligosilanes.^{75,99,109} It is noted from this work that for long oligosilanes ($n \geq 7$), structures from the B3LYP/SVP DFT method closely reproduce experimental absorption peak energies for these systems when absorption energies were calculated with the TDDFT B3LYP/Def2-TZVP method. There is likely a large cancelation of errors responsible for this as DFT is known to produce less accurate structures than ab initio methods.¹⁰² Other structures, obtained with the PBE0/SVP, BHLYP/SVP, and RI-

ADC(2)/SVP methods yielded similar absorption energies. The standard TDDFT method predicts vertical absorption energies with increasing accuracy as the chain length is increased. Reasons for the chain-length dependence of the accuracy are difficult to ascertain for semi-empirical methods. A likely explanation for this is that in standard TDDFT the exchange potential has been parameterized and this does not take the system size into account. In oligosilanes this size-extensivity is not a severe problem, as compared to that found in polyenes.¹⁷

3.4.2 Normal Emission

TDDFT describes seems to describe delocalized excitation as well as the normal emission quite accurately and so it is not surprising that the normal emission is reproduced well, as relaxed geometries from the all-transoid conformers do not differ significantly. Since the goal of this work is to understand the emission in a large range of oligosilanes, the TDDFT based methods were chosen for excited state optimization. Table 3.15 lists the structures obtained with the PBE0/SVP method. This method seemed to reproduce the experimental emission energies best.

Upon excitation, SiSiSiSi dihedral angles relax to values closer to that of the anti conformations, and SiSiSi valence angles also increase. These structural rearrangements are largest for the permethylated heptasilane and decrease as the chain length is extended. The structural changes decrease as chain length is increased because of the increased excitation delocalization in longer chains.¹¹⁶ NBO analysis showed that the electron occupancy decreases between the Si atoms (described by the Si 3p_z orbitals) and increases on the Si atoms (Si 3p_y orbitals) upon delocalized excitation in extended oligosilane chains. This explains the increased bond lengths, as well as the increased SiSiSi valence angles.

3.4.3 Blue Emission

The blue $\sigma\sigma^*$ exciton is of mixed Si-Si antibonding and Si-C antibonding nature, and is of overall σ symmetry with respect to the Si backbone. The HOMO is localized on one Si-Si bond whereas the LUMO is delocalized over the Si chain and the in-plane terminal Si-C atoms. The

exciton length is related to the delocalization of the LUMO, as these blue emitters are found for extended conformations of a maximum of six silicon atoms, and emission energies blue-shift until this limit is reached. The different spatial arrangement of the HOMO and LUMO accounts for the relatively low S_0 - S_1 oscillator strengths in comparison to the delocalized emitters. The mixing of Si-Si antibonding orbitals with the in-plane Si-C antibonding orbitals stabilizes the state and leads to large geometry changes in not just the Si-Si bond lengths and angles but also those of the in-plane Si-C bond lengths and angles. This is in contrast to the normal emitters which have small lattice rearrangements, especially in the Si-C bonds upon relaxation of the ground state equilibrium structure. While the blue exciton seems to be limited to six Si atoms, it can exist in longer chains, when it can be localized over at most six Si atoms and when the additional Si atoms are connected by strongly twisted adjacent Si dihedral angles. If more than six Si atoms are arranged in an extended chain (transoid Si dihedral angles) a delocalized exciton is preferred, as witnessed in the S_1 optimizations.

Geometries of the blue emitters show bond-stretch isomerism, but they also show that the localized exciton is not just located on one pair of silicon atoms, as there are geometrical distortions throughout the chain. Namely, there are large SiSiSi valence angle increases (to $\sim 140^\circ$), as well as CSiSi valence angle distortions. The valence angle distortions are of similar importance as the Si-Si bond stretch, as the angles also deviate strongly from the standard tetrahedral values found in the ground state in oligosilanes.

Terminal Si-Si bond stretch minima seem to be less stable, as S_1 TDDFT optimizations with terminal Si-Si bond stretch minimum-type starting geometries sometimes rearranged to internal Si-Si bond stretch minimum. The barriers for this process are therefore also predicted to be very small. Bond stretch minima constructed from **4a2** and substitution of terminal gauche methyl groups with trimethylsilane resulted in rearrangement to the linear bond stretch minima. It is conceivable that additional bond stretch minima exist for the shorter silanes if there is heavy twisting in the Si backbone, but these minima were not found. In reality, these structures are probably less stable than the extended forms found in this work, but might be accessed in solution, due to solvation

stabilization and/or viscosity effects.

The NHO analysis of the **4a1** minimum energy structure showed a secondary resonance structure which indicates the possibility of the formation of a terminal dimethylsilylene extrusion product. This is a likely excited state deactivation mechanism for the terminal Si-Si bond stretch minimum, which could be responsible for the lower than unity experimental quantum yields for the blue emission, even at low temperatures.¹⁷⁹

The NHO analysis of the S₁ density for the central Si-Si bond stretch minimum **4a2** explains the reason for the differences in the Si-Si bond distances, namely that the central Si-Si bond has less electron density. There are a myriad of zwitterionic secondary resonance structures that help the molecule not to dissociate. These resonance structures also predict the central Si-Si bond stretch minimum to be quite stable, and not as prone to photochemical rearrangements as the terminal Si-Si bond stretch minimum.

There is a difference in the point group symmetry of the relaxed excited state central bond stretch minima obtained with different methods. The larger Si-Si bond lengths of the BHLYP and RIADC(2) methods (compared to those obtained with the PBE0/SVP method) could lead to less steric repulsions and be a possible explanation of the preference of *C*_{2h} symmetry for structures obtained with the BHLYP and RIADC(2) methods.

Empirical fitting of the μ parameter in the LC-TDDFT method (or any method for that matter) is not particularly desirable but it is perhaps acceptable since standard TDDFT is already heavily parameterized by the amount of HF exchange contained in the functional. Standard TDDFT excitation energies vary greatly if they are obtained with functionals without HF exchange (*e.g.*, BP86) or with those with more HF exchange (*e.g.*, BHLYP). Furthermore, the parameterization of μ is fairly robust for an oligosilane of a given length, as the parameterization was done for the ground state equilibrium structure and yet the emission energy of the blue emitter calculated with the reparameterized LC-BLYP method agreed extremely closely with that obtained with MSCASPT2 methods. This is remarkable as the blue emitter undergoes significant structural relaxation from the ground state equilibrium geometry upon excitation.

The trend in the S_0 - S_1 oscillator strengths and S_1 dipole moments of the PBE0/SVP bond stretch minimum in comparison to those of the BHLYP/SVP and RIADC(2)/SVP tetrasilane structures suggests that some artificial charge transfer character is built into the bond stretch minima. Optimization with ab initio methods or with TDDFT methods which include more HF exchange are therefore preferred. Nevertheless, the vertical emission energies did not vary significantly for the structures obtained with RIADC(2) and BHLYP methods.

The B3LYP/Def2-TZVP method is less ideal for calculation of the bond stretch minima as the LC'-BLYP emission energies resemble those of the MSCASPT2 method more closely. For longer silanes the B3LYP/Def2-TZVP method is much more feasible. The shift between B3LYP/Def2-TZVP emission energies and LC'-TDDFT/Def2-TZVP energies should be of a similar size for larger molecules as the exciton is localized. There are however shifts in the emission energy and the S_1 dipole moments increase between the PBE0/SVP and RIADC(2)/SVP structures, suggesting that ab initio methods or range-corrected TDDFT (LC-TDDFT) methods give more accurate results.

As section 3.3.3 showed, the S_1 dipole moment grows quite large for the terminal bond stretch minima as the chain length is increased. The blue emission should therefore have interesting solvent effects, as terminal Si-Si bond stretch isomers have larger dipole moments than the central Si-Si bond stretch minima. Structures with larger excited state dipole moments should interact more with the solvent, making for potentially interesting shifts of the blue emission band maxima in polar solvents.

A remarkable result is that the borderline case between delocalized and localized excitation is found to be heptasilane with both experimental and computational techniques. According to experiment, **7** gave both Franck-Condon allowed and forbidden emission.¹²² Calculations showed that delocalized excitation is preferred as the heptasilane backbone is extended, but that more localized Si-Si bond stretch minima can exist if twisting of the Si backbone occurs. Theory suggests that the blue exciton can be delocalized over a maximum of six Si atoms and in-plane methyl groups. More centralized Si-Si bond stretch minima are preferred and the maximum delocalization length is the most stable of the partially localized minima on the S_1 surface. This does not rule

out the possibility of emission from minima where the exciton is localized on shorter segments of the heptasilane, or on terminal Si-Si bond stretch minima. The energetic barriers between different minima are likely to be small.

3.4.4 Predicted Blue Emission

Excited state minima that also yield emission energies in the blue spectral region can occur for longer oligosilanes, but only if strong twisting of the backbone is present. Strong twisting of the Si backbone cuts off σ conjugation, giving the oligosilane the opportunity to localize the excitation energy in a smaller part of the molecule. According to this hypothesis, as the chain length grows, many more blue-emitting conformations will be available. The structures found in this work are by no means an exhaustive treatment for each oligosilane, but only are presented to prove the general feasibility of blue emission in longer oligosilanes. Blue emission was found to be possible in the permethylated dodecasilane, but again this is not a limit and more calculations can be done. Blue emitters constructed from the blue tetrasilane chromophore were not found in this work, but could possibly exist.

Considering that the emission has been known for such a long time, it may appear strange that the blue emitters were not found with computational methods until this work. There are several factors that made these structures difficult to locate. A crucial reason is that there are several minima that are lower in absolute energy than the blue emitters. Calculations in the past found these lower energy structures. The small SiSiSi valence angle minimum¹²⁶ believed to be responsible for the blue emission⁹⁹ is shown in the subsequent chapter to emit at much lower energies. Another reason for the difficulty in locating the blue emitters is that barriers are very low for oligosilane rearrangements, thus enabling rearrangements to lower energy minima or S_0 - S_1 funnels.

3.5 Conclusions

Delocalized emission is very well reproduced by TDDFT and ab initio methods. The relaxed excited state geometries are very similar to the ground state equilibrium structures. There is a slight extension of the dihedral angles (towards anti conformations), a widening of SiSiSi valence angles and stretching of Si-Si bonds upon excited state (S_1) relaxation. These structural differences decrease as the chain length is increased. NAO population differences between the S_0 and S_1 states rationalize these changes in structure.

Structures responsible for the blue emission have long been predicted. In this work new structures which indeed show bond stretch isomerism, have finally been found. Remarkably, these structures, found with ab initio and TDDFT methods, do not show extremely large Si-Si bond stretching, as predicted. These structures accurately reproduce the blue emission and its blue shift as the oligosilane chain length is increased.

It is remarkable how well theory reproduced the borderline nature of excitation localization in the heptasilane. As soon as this structure became extended, the delocalized exciton was found. Highly twisted dihedral angles toward the end of the molecule produced the blue exciton upon structural relaxation. There could exist multiple blue emitters, according to this work. These emitters can have extended pentasilane or hexasilane conformations.

Through an understanding of the nature of the blue exciton, namely that it exists in an extended conformation of up to six Si atoms, and armed with the knowledge that the effects of σ conjugation are suppressed by the introduction of small dihedral angles, new structures were built in predicted conformations and subsequently optimized. Franck-Condon forbidden emission in the blue spectral region from long ($n > 8$) permethylated oligosilanes has not been observed, but as shown in this chapter, could be realized, if the correct conformations are experimentally accessed.

Chapter 4

Green Emission in Oligosilanes

4.1 Introduction

This chapter explores how longer silanes rearrange and accommodate $\sigma\sigma^*$ excitation in a highly localized fashion. Recent experiments¹²⁵ show that in addition to the normal Franck-Condon allowed and the Franck-Condon forbidden blue emissions (attributed to vertical geometries and to bond stretch minima, respectively, as discussed in Chapter 3), there exists another emission band which is even more Stokes-shifted. This emission resides around 19 000 cm^{-1} to 21 000 cm^{-1} , and is the topic of this chapter.

Calculations have been performed in order to locate structures that could be responsible for the green emission. These calculations as well as a rationalization of the localized excited state structures will be presented.

4.1.1 Experimental Observations

Recently a weak broad emission (centered around 20 000 cm^{-1}) resulting from excitation of constrained oligosilanes has been experimentally observed.⁹⁹ The constrained compounds responsible for the green emission are shown in Figure 4.1. Green emission is believed to result from excitation of the ground state doubly twisted conformation ($o_+t_-t_-o_+$, where the conformation of the Si backbone is described in terms of dihedral angles, Table 1.4) of **7-r2**, the anti conformations of **4-r2** and **4-r2O**, and the gauche conformations of **4-r3** and **4-c4** (Figure 4.1).

The absorption and emission spectra for compounds **4-c4** and **4-r2** are shown in Figure 4.2.

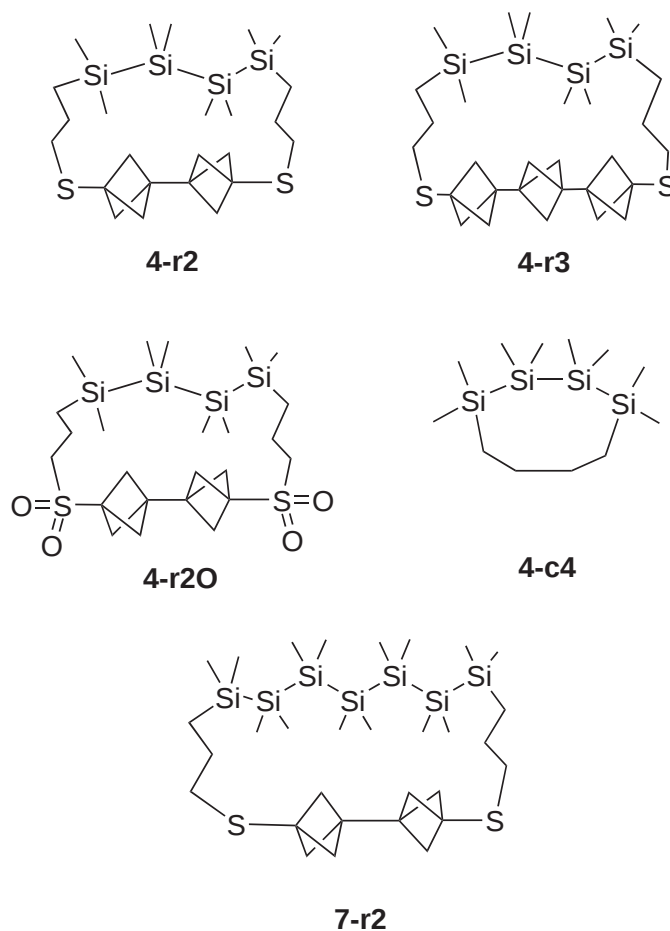


Figure 4.1: Compounds for which green emission has been observed.¹²⁵

For **4-c4**, (a) in Figure 4.2, blue emission was recorded from excitation at $40\,000\text{ cm}^{-1}$ (pink line). It should be noted that the authors attributed this emission to an impurity of unknown origin as the emission energy maximum of this peak was not found for any other compound and **4-c4** is not believed to absorb significantly at $40\,000\text{ cm}^{-1}$. This emission was not observed at higher excitation energies.¹²⁵ The more strongly Stokes-shifted emission centered at $20\,000\text{ cm}^{-1}$ resulted from excitation into the main part of the absorption band at $42\,550\text{ cm}^{-1}$. The tetramethylene moiety constrains the compound to gauche type conformations.^{125,182} The green emission broadens with decreasing temperature for **4-c4**, in contrast with the narrowing of the emission band observed for both the blue and normal emission. While for **4-r2** at 77 K the fluorescence quantum yield for the blue emission was slightly larger than that of the green emission, the relative peak intensities

were reversed for **4-r2O**. For **4-r2O** at 77 K, the green emission was more intense than the blue emission. Fogarty attributed this to the small differences in the conformations of **4-r2O** compared to **4-r2**, which were thought to be of a more twisted nature in the former compound.¹²⁵

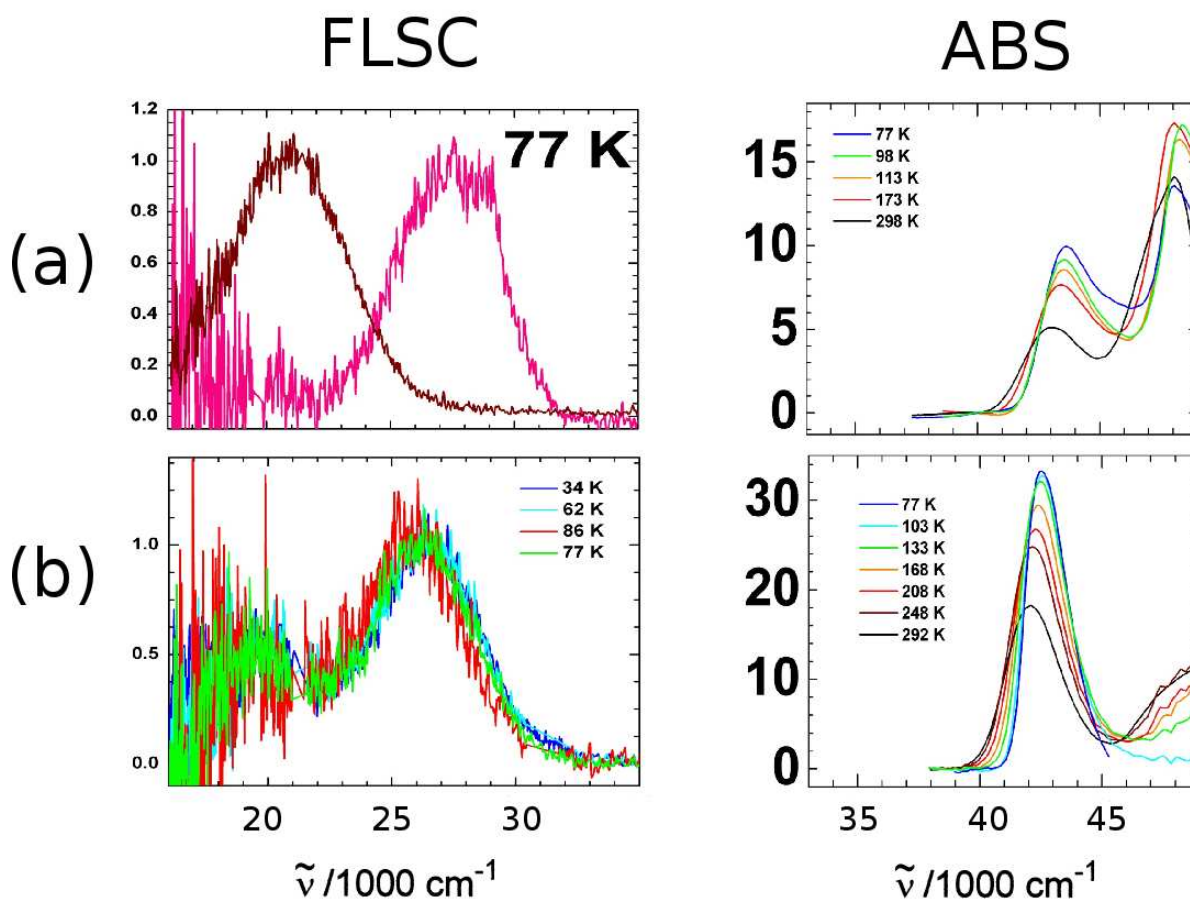


Figure 4.2: Absorption ($\epsilon / 10^3 \text{ cm}^{-1}\text{M}^{-1}$ vs. wavenumber) and emission spectra from Fogarty,¹²⁵ for **4-c4** (a) and **4-r2** (b). In the case of (a), emission is recorded for excitation at $40\,000 \text{ cm}^{-1}$ (pink line) and at $42\,550 \text{ cm}^{-1}$ (magenta line). In the case of (b) emission is recorded for excitation at $42\,500 \text{ cm}^{-1}$, at various temperatures (34–77 K).

Multiple emission bands were observed for **7-r2**. The normal emission, as well as the weak broad emission band, are shown in Figure 4.3, part (a). This emission resulted from excitation into the low energy side of the absorption band, at $36\,230 \text{ cm}^{-1}$, and is believed to result from the absorption of light by an extended ground state conformation of $t_+at_-t_+$ nature.¹²⁵ At an

intermediate excitation energy, $37\,590\text{ cm}^{-1}$, three emission peaks were observed, the most intense of which is centered around $20\,000\text{ cm}^{-1}$. The excitation at $37\,590\text{ cm}^{-1}$ is believed to primarily excite the $t_+t_+t_+o_-$ conformer.¹²⁵ Excitation farther into the absorption band led to more intense green emission, and from calculations of the relative absorption energies of the conformers, is believed to primarily excite the doubly twisted $o_+t_-t_-o_+$ conformation (Table 4.1). From time

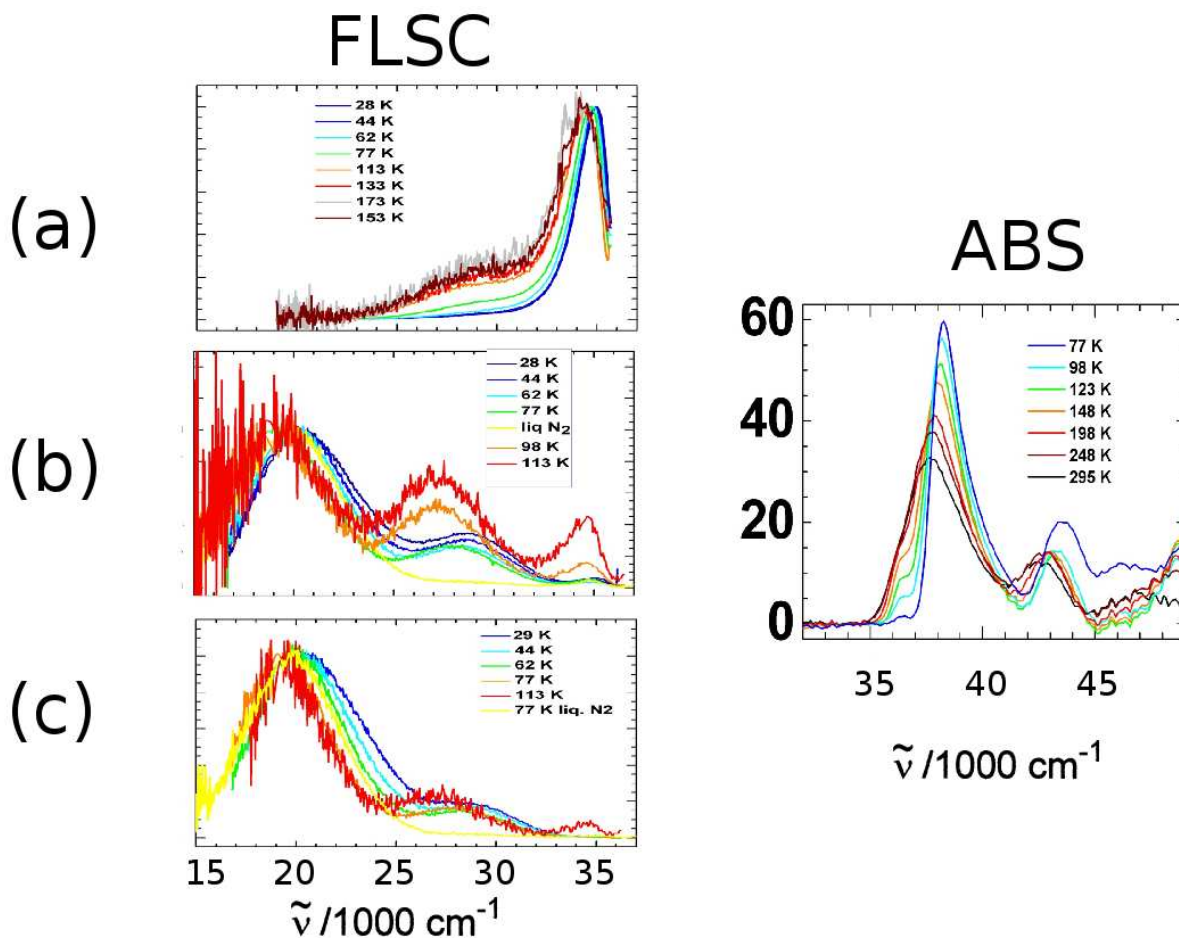


Figure 4.3: Absorption (ABS) ($\epsilon / 10^3\text{ cm}^{-1}\text{M}^{-1}$ vs. wavenumber) and emission (FLSC) spectra from Fogarty,¹²⁵ for **7-r2**. Fluorescence spectra are shown for excitation at $36\,230\text{ cm}^{-1}$ (a), $37\,590\text{ cm}^{-1}$ (b), and at $38\,500\text{ cm}^{-1}$ (c). Emission was measured at various temperatures: for (a) these varied from 28 K (black) to 173 K (dark maroon), for (b) and (c) temperatures ranged from 28 K (blue) to 113 K (red).

correlated single photon counting (TCSPC)¹⁸³ experiments, the fluorescence lifetime of the blue emission (measured at $28\,570\text{ cm}^{-1}$) from **7-r2** was determined to be 320 ps at 131 K. At this

temperature, the lifetime of the green emission (measured at $18\,180\text{ cm}^{-1}$) was determined to be much longer, $2\,100\text{ ps}$.¹²⁵

Table 4.1: Summary of experimental experimental fluorescence peak maxima (E_{VE}) from the work of Fogarty.¹²⁵ The excitation energy (E_{EX}), and temperture of the experiment are given below.

Compound	E_{EX} / cm^{-1}	T / K	E_{VE} / cm^{-1}
4-c4	42 920	86	20 900
	42 920	77	20 670
4-r2	42 920	98	18 910
	42 920	74	19 510
	42 920	34	19 870
	42 550	98	18 190
	42 550	74	19 170
	42 550	34	19 830
7-r2	38 310	173	20 820
	38 310	77	18 920
	38 310	35	20 290
	37 590	133	18 760
	37 590	98	18 970
	37 590	77	19 290
	37 590	35	20 290

The experimental fluorescence quantum yields of various emitters from the work of Fogarty¹²⁵ are summarized in Table 4.2. Fluorescence was not detected at temperatures above 77 K for **4-c4**, whereas for the other compounds fluorescence signal was first detected at slightly higher temperatures ($\sim 100\text{ K}$). For **4-r2**, fluorescence quantum yields increased for blue emission as lower excitation frequencies were used. For **7-r2** at excitation frequencies of $37\,590\text{ cm}^{-1}$, blue and green emission detection began at approximately 133 K. For **7-r2**, normal emission (which peaks at $34\,670\text{ cm}^{-1}$ when measured at 77 K), was detected when excitation frequencies on the low energy edge of the absorption band were used ($36\,230\text{ cm}^{-1}$).

4.1.2 Past Computational Efforts to Describe Green Emission

As the extremely Stokes-shifted emission in the green spectral region was found fairly recently by Fogarty, computational efforts to describe this emission specifically are fairly new. For **4**, ground

Table 4.2: Summary of experimental experimental fluorescence quantum yields from the work of Fogarty.¹²⁵ The excitation energy (E_{EX}), temperture of the experiment (in cyclopentane:isopentane (7:3) v:v) and fluorescene quantum yields for the blue (Φ_B) and green (Φ_G) emission are given below.

Compound	E_{EX} / cm^{-1}	T / K	Φ_B	Φ_G
4-c4	40 000 ^a	77	0.074	0.000
	42 920	86	0.000	0.000
	42 920	77	0.000	0.016
4-r2	42 920	98	0.009	0.012
	42 920	74	0.025	0.032
	42 920	34	0.040	0.057
	42 550	133	0.004	0.002
	42 550	74	0.059	0.035
	42 550	34	0.045	0.135
7-r2	38 310	153	0.002	0.001
	38 310	77	0.025	0.169
	38 310	35	0.031	0.319
	37 590	133	0.011	0.021
	37 590	77	0.058	0.238
	37 590	35	0.105	0.444
	36 230 ^b	233	0.002	0.000
	36 230 ^c	77	0.025	0.000
	36 230 ^d	35	0.022	0.000

^a Fluorescence at this excitation energy was determined to be due to an impurity. ^b At this excitation frequency and temperature, the fluorescence for this compound is dominated by the normal emission, for which the quantum yield was 0.001. ^c The normal emission quantum yield is 0.115 in this case. ^d The normal emission quantum yield was 0.194 here.

state minima were optimized on the S_1 surface with TDDFT (BP86/SV(P), RPA) methods by Fogarty.¹²⁵ From the *t*, *g* and *o* starting conformations (Table 1.4), structures with emission energies that were severely red-shifted with respect to experiment were found (14 000 cm^{-1} , 12 040 cm^{-1} , and 11 730 cm^{-1} , respectively). The *t* conformer optimized to a small SiSiSi valence angle (89.6°) minimum structure similar to that found by Teramae and Michl.¹²⁶ The *o* conformer optimized to another extended (177° all Si dihedrals) structure with a small SiSiSi valence angle (90°). The *g* conformer optimized to a new type of structure, with trigonal bipyramidal coordination on an internal Si atom, and an all Si dihedral angle of 88.4° and Si-Si bond lengths at 2.38 Å, 2.75 Å and 2.66 Å. The bonding of this structure was analyzed by the present author and analysis of similar

structures will be presented later in this chapter. Fogarty attributed the low emission energies to the inadequacies of the TDDFT (and DFT) approach to describing bond stretching. The Si-Si bond lengths for the S_1 minima located for **4** ranged from 2.38 Å to 2.75 Å. Fogarty also optimized the **4-c4** structure on the S_1 surface, and found the resulting minimum to be very similar to that found for the *g* conformation of the permethylated tetrasilane **4** (Si dihedral angle: 87.9°, Si-Si bond lengths: 2.38 Å, 2.74 Å and 2.66 Å). A similar approach was used for longer oligosilanes and similarly red-shifted emission energies were found.

4.1.3 Exciton Localization

The goal of this chapter is to rationalize the localized excited state structures possibly responsible for the observed green emission and to explore the limits of localization.

As mentioned in Chapters 1 and 3, absorption of light in long oligosilanes results in structural changes preferentially delocalized over all the Si-Si excitation sites, but for shorter oligosilanes large structural distortions localized over one Si-Si excitation site become preferable to the energy saving involved in delocalization. Once excitation has been localized, radiationless deactivation mechanisms begin to flourish. Just as shorter ($n < 3$) oligosilanes do not show fluorescence, shorter polyenes such as 1,3-butadiene and 1,3,5-hexatriene show negligible or weak fluorescence compared to longer polyenes.¹⁸⁴ For π -conjugated molecules, localization results in bond twisting and pyramidalization of the C atom and its substituents. As seen in Chapter 2, σ -bonded systems such as small oligosilanes can rearrange in many ways. This chapter will explore some of these distortion patterns in longer oligosilanes—for which fluorescence has been observed, albeit in constrained analogs (section 4.1.1).

As many types of localized excited state structures have been found in this work, a simplified introduction to these structures is given here to help the reader from becoming disoriented later in the results section. Green emission can result from many different classes of minima. A class of minima which includes many different structures is that of the trigonal bipyramidal (TBP) rehybridization minima. This class can be broken up into two types of structures which both have

pre-dimethylsilylene extrusion character and are shown in Figure 4.4. The TBP rehybridization minima result from excitation localization and can exist in longer chains. TBP rehybridization minima were first located by Fogarty,¹²⁵ but as calculated emission energies were approximately $12\,000\text{ cm}^{-1}$, considerable doubt was associated with the structures as this is not even close to the experimental emission maximum, $20\,000\text{ cm}^{-1}$. This chapter will show that better methods yield similar structures, but with emission energies which correlate better with experiment.

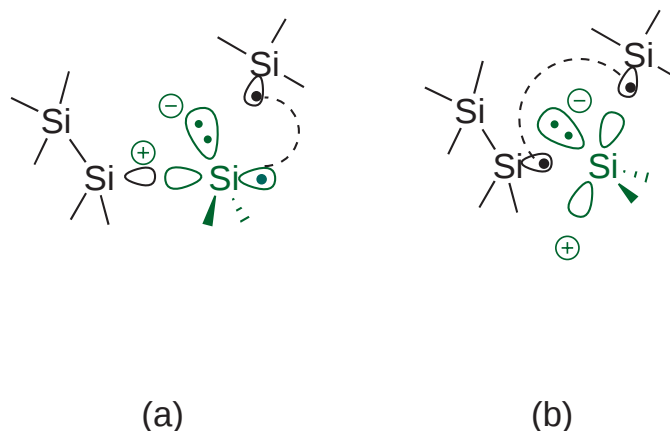


Figure 4.4: Trigonal bipyramidal (TBP) rehybridization minima. Green denotes a silylenic fragment which shares a Si 3p orbital either with a terminal (a) or an internal (b) Si atom. Dashed lines indicate singlet coupling.

Another important class of green emitters is described by structures with small SiSiSi valence angles (the opposite of the blue emitting Si-Si bond stretch minima), and wide SiSiC valence angles (Figure 4.5). There are additional ways in which the small SiSiSi valence angle minima are the opposite of the blue-emitting Si-Si bond stretch minima. The latter have wide SiSiSi valence angles. The green-emitting minima have heavy $\sigma\sigma^*$ and $\sigma\pi^*$ mixing. The LUMO is now localized on the stretched SiSi bond, as opposed to the LUMO in the case of the blue emitting Si-Si bond stretch minima. The HOMO in the structures with small Si-Si-Si valence angles is delocalized over the Si backbone, as opposed to in the blue-emitting Si-Si bond stretch minima where it is localized on one Si-Si bond. The small SiSiSi valence angle minima can also exist in longer chains. The small SiSiSi valence angle minimum was first found by Teramae and Michl in tetrasilane.¹²⁶

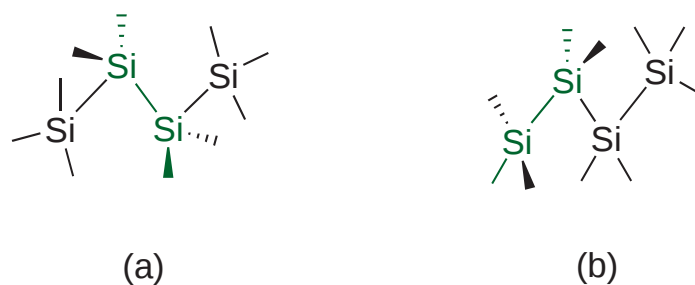


Figure 4.5: SiSiSi small angle minima. Green denotes the Si-Si and Si-C atoms on which the LUMO is localized in the : internal (a) and terminal (b) structures.

Additional structures that emit in or near the green spectral region have been found in this work and will be discussed. These include the diffuse Si-Si bond stretch minima, the Si-C bond stretch minima, and more extremely localized polarization minimum structures, which are analogous to **2e**. A few of the isomers are schematically shown in Figure 4.6. For a truly localized exciton there should be no size or length dependence, as the part of the molecule which is not involved in the excitation should also be of little importance to the chromophoric unit.

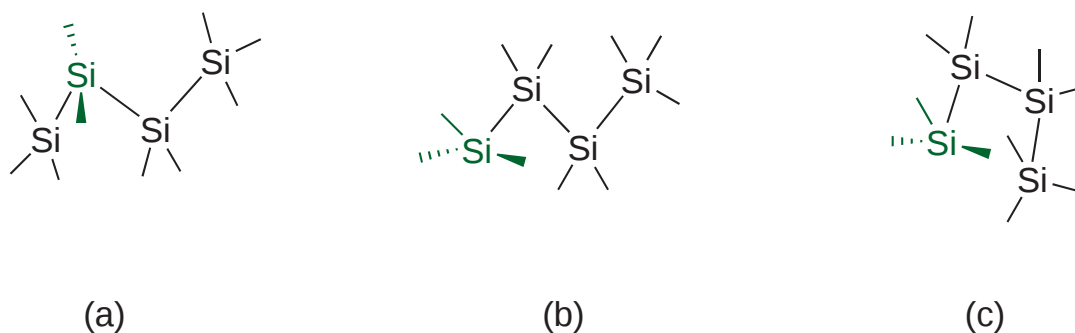


Figure 4.6: Polarization minima. Green denotes the Si atom that has an additional nonbonding orbital. Minima can exist with internal (a) and terminal (b) and (c) localization.

4.2 Computational Methods

Photochemistry and the exploration of excited state surfaces challenges many methods. Re-hybridization minima presented here require methods that do not induce artificial charge transfer. This is accomplished by using ab initio methods such as RICC2 or RIADC(2), described in Computational Methods section of Chapter 2. If TDDFT is used, long range corrected functionals, or

at least those which include an amount of HF exchange which is as large as possible are recommended.¹⁶⁸ Various functionals used in TDDFT calculations were tested. Vibrational analysis was performed with Turbomole version 6.2.

MSCASPT2 methods (see the Computational Methods section of Chapter 3) were used as well. The ANO-L basis set¹⁸¹ for the following atoms: Si:ANO-L[5S4P2D], C:ANO-L[3S2P1D], H:ANO-L[2S1P]. The ANO-L' basis set refers to a slightly larger basis set: Si:ANO-L[5S4P2D], C:ANO-L[4S3P2D], H:ANO-L[2S1P]. An active space of 6 electrons and 10 orbitals was chosen. Improved virtual orbitals as described the MOLCAS program were utilized in defining the active space. Unless otherwise noted, nine states were diagonalized in the MSCASPT2 procedure.

In order to explore the excited state (S_1) potential energy surface for decamethyltetrasilane, excited state stochastic searches were performed. A Fortran 90 program was written to selectively kick Si,C and H various distances. Approximately 100 optimizations were carried out with each functional and the SVP basis set.

Table 4.3: Excited state stochastic search parameters.

Atom	bond percent change	kick distance
Si	50	1.175
C	40	0.756
H	30	0.330

4.3 Results

4.3.1 Relaxed Excited State Tetrasilane Geometries

Excited state (S_1) relaxed geometries were found with various methods (denoted in the tables) for the permethylated tetrasilane minima. The minima are named similarly to their counterparts in shorter silanes (Chapter 2). For **4**, these include the C-Si bond stretch minimum **4b**, the diffuse Si-Si bond stretch minimum **4c**, the terminal Si polarization minima **4e1** and **4e2**, the internal Si polarization minimum **4f**, the wide SiSiSi angle minimum **4g** and the small SiSiSi valence angle minima **4h1** and **4h2**. A large group of new minima were located for **4**, these are given the new

names: **4i** and **4j**. These minima correspond to TBP rehybridization minima and will be discussed later in this section. The Si-Si bond stretch minima **4a1** and **4a2** are believed to be responsible for blue emission and are the main subject of Chapter 3.

4.3.1.1 Localized Bond Stretch Minima

The C-Si bond stretch minimum **4b** was found to have a small SiSiSiSi dihedral angle (34.3°), cf. Figure 4.7 and Table 4.4. A single Si-C bond on a terminal Si atom was greatly elongated (2.336 Å). The adjacent Si-Si bond length (2.822 Å) was also longer than the ground state equilibrium value. This structure was only found with the B3LYP functional, and other conformations (with differing dihedral angles) were not found.

The B3LYP/TZVP method located a diffuse Si-Si bond stretch minimum **4c**. This structure has a transoid dihedral angle (164.8°) and a large Si-Si bond length at 2.990 Å. There is a characteristic flattening (decrease) of the SiSiC valence angles (Figure 4.7 and Table 4.5) associated with the terminal Si-Si bond (which is elongated) and Si-C bonds. Only one conformation was found, as gauche starting points reorganized to a different minimum (**4i**).

Table 4.4: Optimized S_1 TDDFT (B3LYP/SVP) geometry for the C-Si bond stretch minimum **4b**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ CSiC /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
4b	34.3	114.9	109.9	106.9	111.1	2.375	1.918	1.904
		114.1	108.8	104.5	109.2	2.379	1.916	1.905
			109.0	108.3	111.8	2.822	1.919	1.901
			107.7	100.3	160.1		1.936	1.936
				92.9	98.0			1.913
				91.9	95.1			2.336
				108.0				
				108.3				

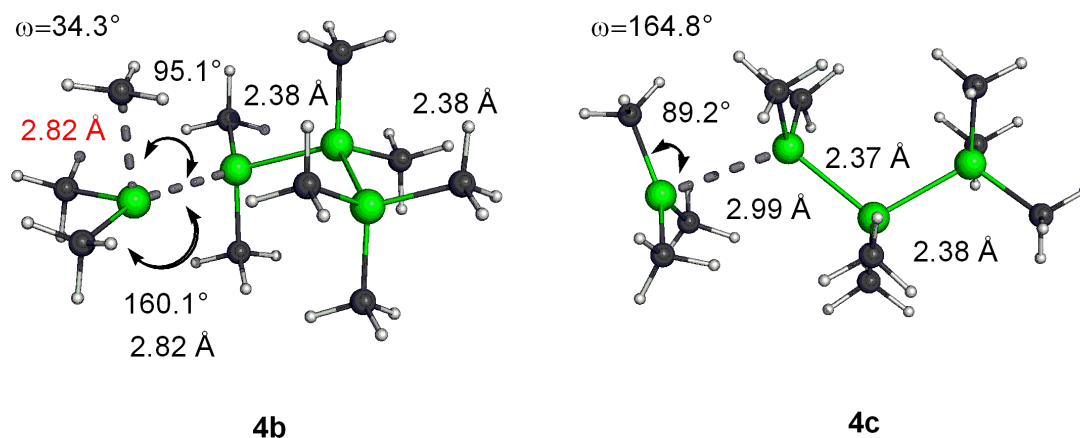


Figure 4.7: Geometries (BHLYP/SVP) for the C-Si bond stretch minimum **4b** and the diffuse Si-Si bond stretch minimum **4c**. The Si-Si bond lengths and the elongated C-Si bond length (red) are indicated (Å), and selected valence angles as well as the all-Si dihedral angle (ω) are shown in degrees.

Table 4.5: Optimized S_1 TDDFT (BHLYP/TZVP) geometry for the minimum **4c**.

Structure	ω_{SiSiSiSi} /deg	$\angle \text{SiSiSi}$ /deg	$\angle \text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle \text{CSiC}$ /deg	$\angle \text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
4c	164.8	121.2	110.5	107.8	91.8	2.990	1.903	1.853
		110.4	111.7	109.0	90.7	2.369	1.904	1.858
			108.7	123.7	89.2	2.380	1.897	1.875
			110.7	108.4	110.4		1.897	1.895
				108.8	110.2			1.892
				108.1	110.9			1.893
				115.6				
				120.7				

4.3.1.2 Polarization Minima

Two minima were located for the terminal Si polarization minimum, **4e**: a transoid conformer **4e1** and a gauche conformer **4e2** (Figure 4.8). According to the PBE0/SVP method, both minima have a large CSiC angle located on the terminal Si atom (165.8° and 166.0° , respectively). The two Si-C bonds which are elongated are also on this terminal Si atom and have narrow SiSiC valence

angles. The terminal Si-Si bond also is elongated (2.517 Å according to the PBE0/SVP method for **4e1**) compared to the other Si-Si bonds. The Si-Si bond stretching is even more pronounced according to the ab initio RIADC(2)/TZVP method for the **4e1** minimum (2.731 Å (Table 4.6). The internal Si polarization minimum **4f** was found to have a very similar expanded CSiC valence angle on an internal Si using both the BHLYP/SVP and PBE0/SVP methods. This minimum also has a transoid dihedral angle (Table 4.7).

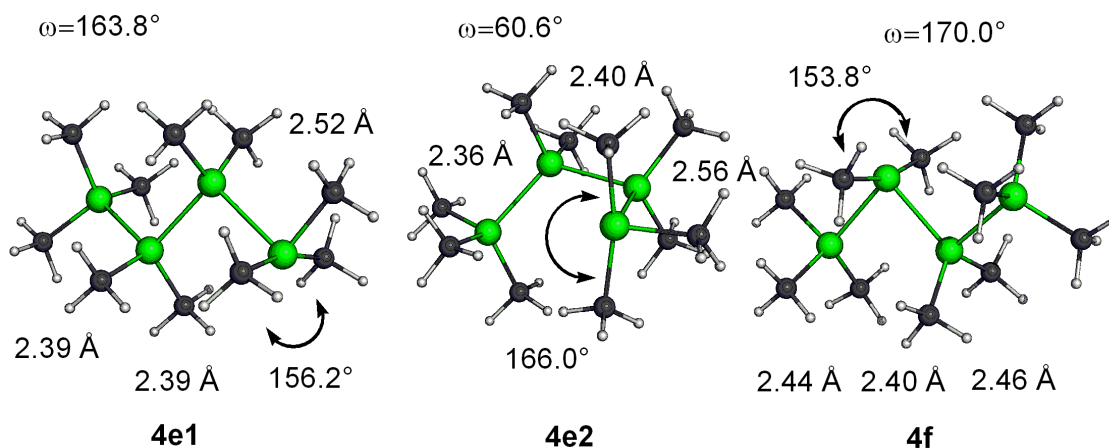


Figure 4.8: Geometries (BHLYP/SVP) for the transoid polarization minimum **4e1**, the gauche polarization minimum **4e2** and **4f**. The Si-Si bond lengths are indicated (Å), and selected valence angles and the all-Si dihedral angle (ω) are shown in degrees.

4.3.1.3 SiSiSi Valence Angle Distortion Minima

The wide SiSiSi valence angle minimum **4g** was only found to exist in the anti conformation (Figure 4.9 and Table 4.8). This structure has an extremely large SiSiSi valence angle (164.5°) according to the PBE0/SVP method. This angle is slightly smaller than that found for **3g** (168.7°), but that valence angle was found with the PBE0/TZVP method. For **4g** two Si-Si bonds are elongated at 2.449 and 2.460 Å. These and additional parameters are given for **4g** in Table 4.8.

Teramae and Michl found a narrow SiSiSi valence angle minimum, **4h2** with a CASSCF approach.¹²⁶ In this work, both TDDFT and RIADC(2) methods were also able to find this minimum. An additional isomer of this structure, where the structural distortions are concentrated

Table 4.6: Optimized S₁ TDDFT and ab initio geometries for the polarization minimum **4e**.

Structure	ω_{SiSiSiSi} /deg	$\angle \text{SiSiSi}$ /deg	$\angle \text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle \text{CSiC}$ /deg	$\angle \text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
4e1 PBE0/SVP	163.8	103.6 95.7	109.3	110.5	109.6	2.393	1.887	1.886
			114.4	109.0	111.9	2.388	1.882	1.886
			110.6	109.4	106.3	2.517	1.886	1.893
			113.8	94.4	91.7		1.886	1.934
				165.8	94.7			2.014
				94.1	96.4			2.015
				110.3 109.2				
4e1 RIADC(2)/TZVP	169.6	105.0 101.9	109.9	109.9	108.8	2.368	1.898	1.895
			111.8	109.2	110.8	2.352	1.897	1.896
			114.0	109.3	109.7	2.731	1.896	1.896
			114.2	96.0	110.0		1.897	1.907
				167.4	86.0			1.953
				96.0	86.2			1.953
				109.2 108.9				
4e2 PBE0/SVP	60.6	100.9 116.1	110.6	108.5	94.9	2.560	1.886	2.005
			112.3	108.2	92.0	2.399	1.884	1.928
			109.7	166.0	95.4	2.363	1.889	2.003
			101.1	108.2	106.0		1.908	1.895
				111.5	111.7			1.888
				109.1	110.0			1.884
				94.4 94.7				

on the terminal Si-Si bond and its methyl groups, has also been located (Figure 4.10 and Table 4.9). This minimum, **4h1**, was found with the TDDFT BHLYP/SVP method. Optimization of this structure with RIADC(2) located a dimethylsilylene funnel. The narrow SiSiSi valence angle minimum **4h1** has two small SiSiSi valence angles, one at 95.0°, and the other at 75.7°, according to the BHLYP/SVP method. The narrow SiSiSi valence angle minimum **4h2** has two more equally contracted SiSiSi valence angles (90.4 and 88.4°, when optimized with the BHLYP/SVP method). The **4h2** minimum found with the BP86/SVP method interestingly has very similar SiSiSi valence angles (92.2 and 91.0°). This result is in contrast to the results for the **3h** structures (section 2.3.3.3), where the neglect of HF exchange in the optimization method correlated with

Table 4.7: Optimized S₁ TDDFT geometries for the internal polarization minimum **4f**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ CSiC /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
4f BHLYP/SVP	169.9	97.9 88.9	118.9	108.3	104.5	2.415	1.889	1.892
			115.7	165.9	110.9	2.439	1.888	1.880
			94.8	109.0	112.7	2.486	2.021	1.878
			96.6	107.8	118.2		2.021	1.884
				108.5	99.3			1.894
				108.9	113.2			1.882
				108.7				
				110.8				
4f PBE0/SVP	170.0	95.4 87.3	121.0	108.5	103.8	2.438	1.892	1.895
			117.5	165.8	109.3	2.396	1.891	1.881
			95.2	109.6	112.8	2.463	2.041	1.879
			97.6	107.3	118.9		2.041	1.892
				107.7	99.1			1.904
				108.2	114.5			1.890
				109.3				
				111.6				

Table 4.8: Optimized S₁ TDDFT (PBE0/SVP) geometry for the **4g** wide SiSiSi valence angle minimum .

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ CSiC /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
4g	180.0	164.5	95.0	121.3	105.2	2.449	1.976	1.896
		123.9	95.0	107.8	105.2	2.460	1.976	1.896
			103.0	108.7	120.4	2.369	1.907	1.899
			103.0	107.9	113.8		1.907	1.900
				108.7	109.2			1.895
				107.9	109.2			1.895
				108.1				
				108.6				

large SiSiSi valence angles (around 100°).

4.3.1.4 TBP Rehybridization Minima

The trigonal bipyramidal (TBP) rehybridization minima found were of two types. The first type, **4i**, has large SiSiC valence angles which are defined by the terminal Si-Si bond and the internal Si-C bonds (see Figure 4.11). The second type, **4j**, has large SiSiC angles which are defined by the

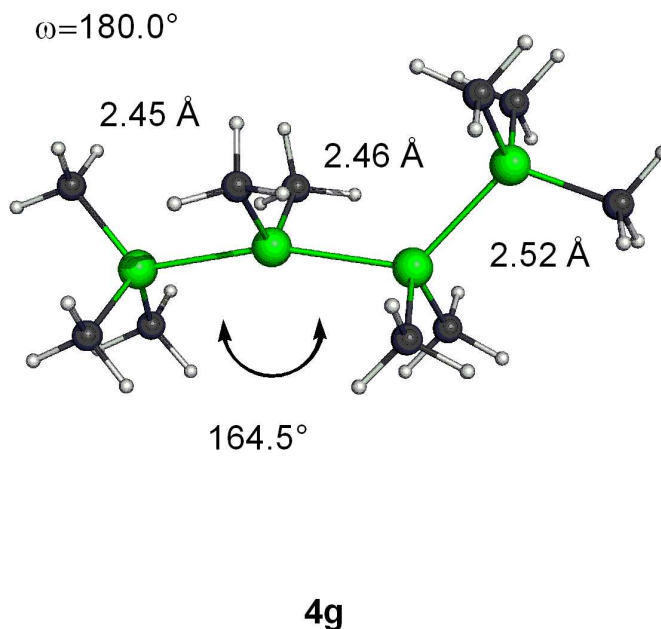


Figure 4.9: Geometries (BHLYP/SVP) for the wide SiSiSi valence angle minimum **4g**. The Si-Si bond lengths are indicated (Å), and selected valence angles and the all-Si dihedral angle (ω) are shown in degrees.

internal Si-Si and Si-C bonds (Figure 4.12). For the TBP rehybridization minima **4i**, the central Si-Si bond is the longest (Table 4.10). The TBP rehybridization minima **4j** can have either a terminal or the central Si-Si bond as the longest, ranging from 2.590 Å (**4j3**) to 2.610 Å (**4j3**) according to the BHLYP/SVP method (Table 4.11). The TBP rehybridization minimum **4i1** gave the longest Si-Si bond of the BHLYP/SVP structures at 2.643 Å (Table 4.10).

Relatively few of the various tetrasilane minima were found with the RIADC(2)/SVP method (Table 4.12), which in most cases located S_0 - S_1 funnels (type **Fa** and **Fh**, Chapter 2). Three minima were located with the RIADC(2) method: **4e1**, **4h2** and **4i1**. For **4h2**, the RIADC(2) method yielded smaller SiSiSi valence angles (78.2° as opposed to 88.4°) and slightly more twisted SiSiSiSi dihedral angles (163.8 vs. 168.8°) than the BHLYP/SVP method. It is interesting to note that the trisilane analog **3h** could not be located with the RIADC(2) method, which instead gave the funnel

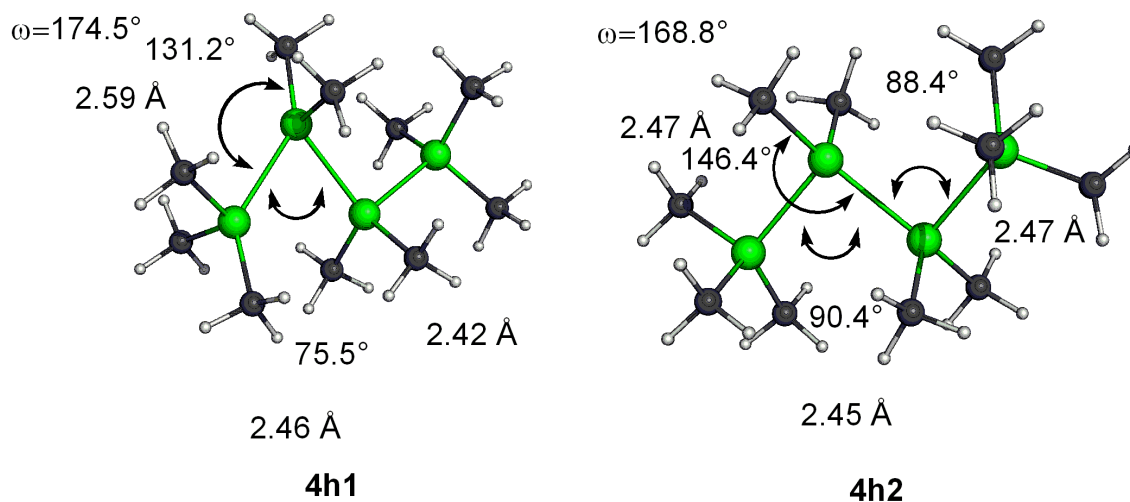


Figure 4.10: Geometries (BHLYP/SVP) for the terminal small SiSiSi valence angle minimum **4h1** and the internal small SiSiSi valence angle minimum **4h2**. The Si-Si bond lengths are indicated (Å), and selected valence angles and the all-Si dihedral angle (ω) are shown in degrees.

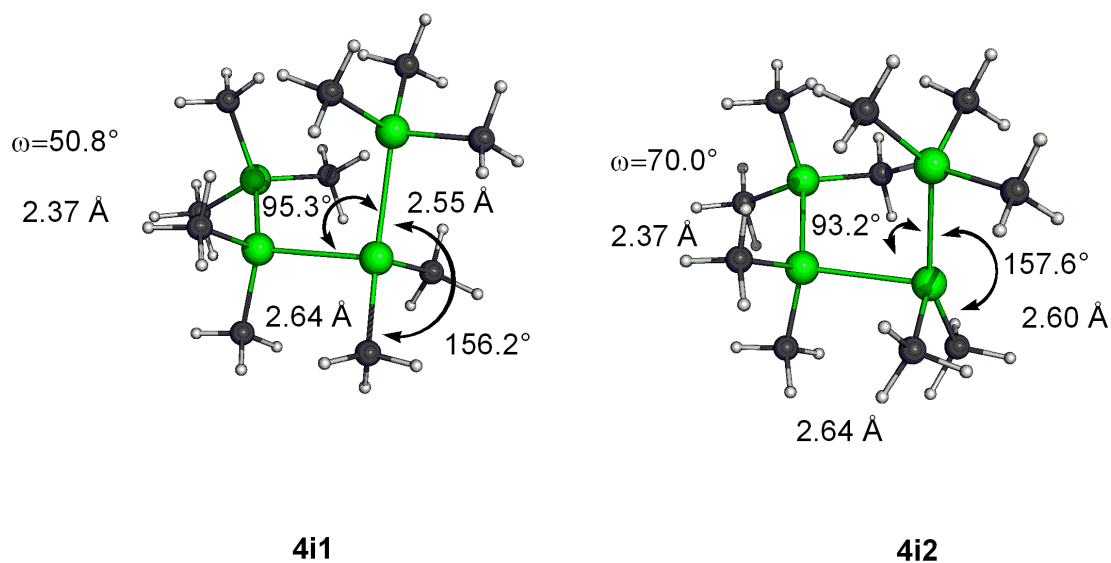


Figure 4.11: Geometries (BHLYP/SVP) for the TBP rehybridization minima **4i1** and **4i1**. Si-Si bond lengths are indicated (Å), and selected valence angles and the all-Si dihedral angle (ω) are shown in degrees.

Table 4.9: Optimized S₁ TDDFT geometries for the narrow SiSiSi valence angle minima **4h**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ CSiC /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
4h1 BHLYP/SVP	174.5	95.0 75.5	115.7	109.9	113.0	2.420	1.888	1.884
			123.1	99.9	109.9	2.455	1.898	1.883
			131.2	108.3	106.7	2.588	1.937	1.892
			100.6	103.4	94.1		1.905	1.906
				106.5	137.8			1.910
				107.9	104.0			1.891
				110.1 108.7				
4h2 BHLYP/SVP	168.8	90.4 88.4	146.4	101.1	103.6	2.469	1.938	1.890
			104.7	101.4	117.9	2.448	1.902	1.881
			143.9	109.4	107.8	2.468	1.932	1.882
			105.5	108.2	116.1		1.903	1.879
				108.4	102.1			1.894
				110.3	111.1			1.882
				108.1 109.8				
4h2 BP86/SVP	171.3	92.2 91.0	147.4	101.1	104.6	2.501	1.972	1.910
			104.6	101.3	116.2	2.448	1.925	1.898
			144.8	109.3	108.0	2.489	1.967	1.900
			105.8	108.3	114.3		1.926	1.899
				108.5	103.4			1.914
				110.1	111.8			1.900
				108.3 110.1				

3Fh, as discussed in Chapter 2. The BHLYP/SVP method gave a slightly larger Si-Si bond length (2.643 Å) and a smaller SiSiSiSi dihedral angle (48.4°) for the TBP rehybridization minimum **4i1**.

The minima **4i** and **4j** were also obtained with the BHLYP/TZVP method to check for basis set effects. The larger TZVP basis set yielded slightly longer Si-Si bond lengths, *e.g.*, **4i** has an elongated Si-Si bond at 2.658 Å when the TZVP basis set is used (Table 4.13), slightly different from the SVP result (2.638 Å). The SiSiSiSi valence angles differ at most by 3° (Table 4.14).

4.3.2 Natural Bond Orbital Analysis

NHO analysis (CIS/6-311G(d,p)) was carried out for the tetrasilane TBP rehybridization minima, **4i** and **4j**. The results for **4i1** are summarized in Figure 4.13.

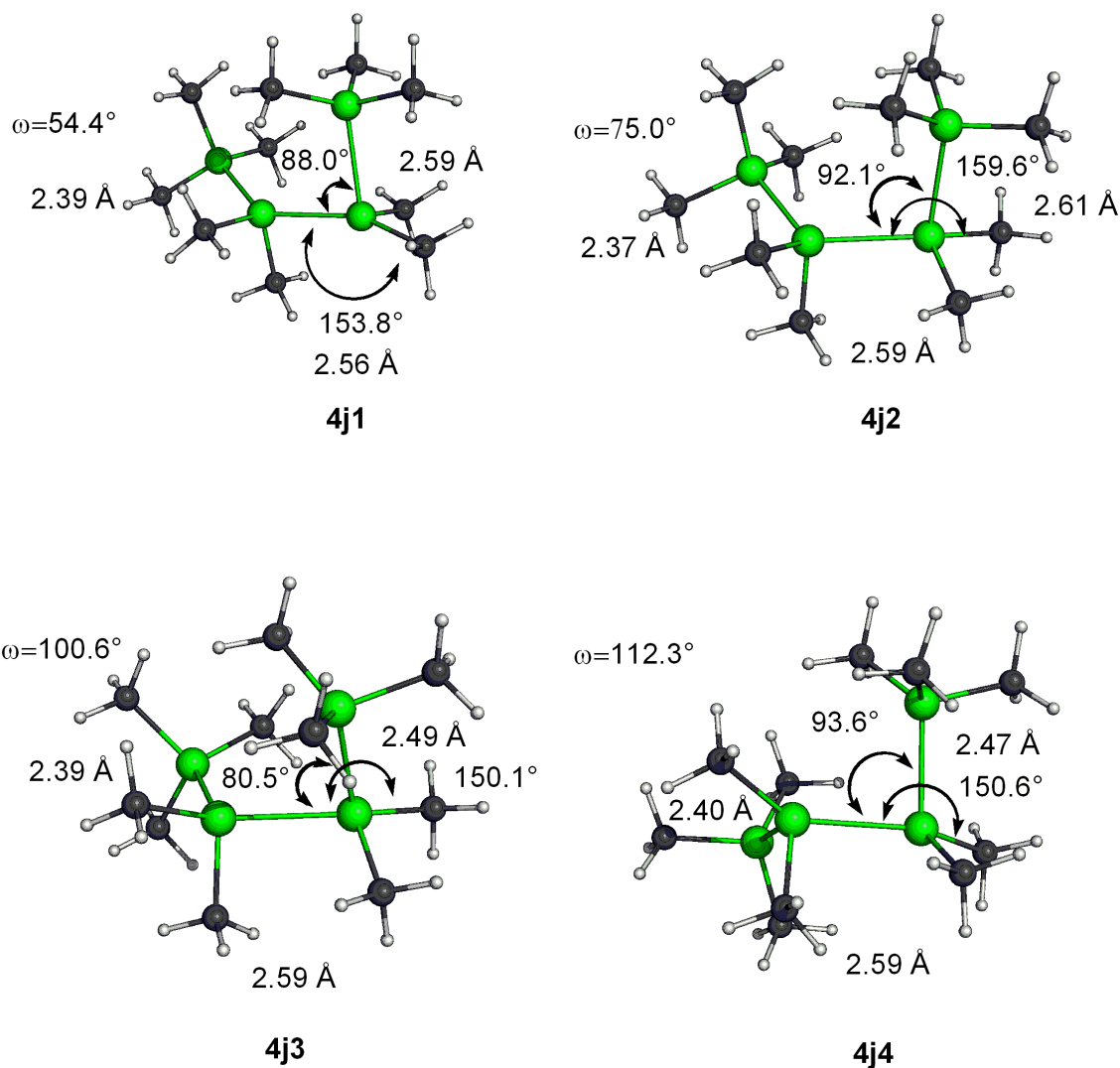


Figure 4.12: Geometries (BHLYP/SVP) for rehybridization minima **4j1-4j4**. The Si-Si bond lengths are indicated (Å), and selected valence angles and the all-Si dihedral angle (ω) are shown in degrees.

NHO analysis of **4i1** shows rehybridization of the NHOs of an internal Si atom into a Si 3p orbital of low occupation (0.5 electrons) which points to an internal Si atom, and an $sp^{1.5}$ orbital with high occupation of approximately 1.4 electrons (Figure 4.13). The opposite internal Si atom also has rehybridized orbitals which follow a similar pattern, but to a lesser extent. For this minimum the covalent resonance structure no longer is the main contributor to the S_1 density

Table 4.10: Optimized S₁ TDDFT (BHLYP/SVP) geometries for the TBP rehybridization minima **4i**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ C _i Si _i Si _t /deg	$\angle$ C _i Si _i C _i /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
4i1	50.8	95.3 113.9	106.5	99.4	97.7	134.6	2.552	1.905	1.918
			95.5	156.2	109.6	109.1	2.643	1.948	1.896
			103.5	114.5		92.7	2.371	1.877	1.910
			103.1	111.5		112.7		1.886	1.877
						105.7			1.891
						109.2			1.881
4i2	70.0	107.2 93.2	102.4	112.3	108.3	109.9	2.374	1.887	1.880
			110.2	115.6	98.3	105.5	2.638	1.878	1.890
			96.4	97.9		111.5	2.600	1.910	1.876
			100.3	157.6		94.7		1.945	1.907
						105.9			1.897
						136.0			1.917

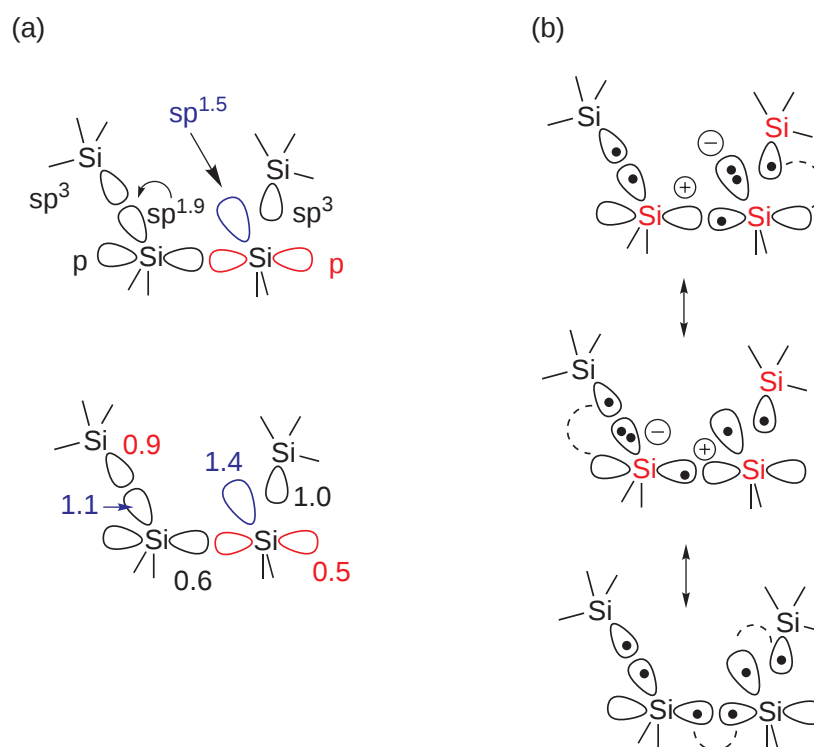
**Figure 4.13:** NHO analysis (CIS/6-311G(d,p)) for the S₁ density of **4i1**. Hybridization of Si NHOs and their occupancies are shown (a), as well as major contributing natural resonance structures. Dashed lines indicate singlet spin coupling and Si atoms denoted in red color indicate 3-center 2-electron bonding in the resonance structures.

Table 4.11: Optimized S₁ TDDFT (BHLYP/SVP) geometries for the TBP rehybridization minima **4j**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ C _i Si _i Si _t /deg	$\angle$ C _i Si _i C _i /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
4j1	54.4	137.1 88.0	105.3	107.6	106.6	111.5	2.390	1.900	1.895
			91.9	104.0	99.7	109.5	2.558	1.918	1.893
			153.8	104.6		113.4	2.589	1.903	1.898
			99.9	102.1		109.5		1.932	1.872
						100.4			1.883
						112.2			1.868
4j2	75.0	112.5 92.1	131.0	107.4	102.9	111.3	2.365	1.925	1.895
			91.6	107.0	98.0	112.9	2.593	1.917	1.889
			159.6	97.8		109.2	2.610	1.946	1.894
			96.5	105.1		115.0		1.908	1.868
						102.1			1.878
						103.8			1.870
4j3	100.6	100.8 80.5	141.9	107.4	100.9	109.3	2.388	1.930	1.892
			93.4	109.1	100.7	116.2	2.590	1.915	1.887
			150.1	115.6		107.7	2.492	1.928	1.893
			99.7	103.0		114.4		1.901	1.880
						98.0			1.900
						115.8			1.876
4j4	112.3	83.3 93.6	150.6	112.5	100.3	114.4	2.471	1.931	1.877
			99.1	104.8	101.6	114.6	2.590	1.902	1.881
			144.3	108.8		99.8	2.403	1.928	1.899
			97.8	107.2		106.1		1.908	1.896
						114.3			1.885
						111.5			1.888

description, but has been replaced with a zwitterionic resonance structure where the lone pair occupies the sp^{1.5} orbital, leaving the empty lobe of the p orbital to form a 3-center 2-electron bond (Si atoms denoted in red color in Figure 4.13). The secondary resonance structures decrease the occupation of this lone pair orbital (to 1.4 electrons) in the NHO population analysis.

A very similar situation is encountered in the NHO analysis of the **4j1** minimum (Figure 4.14). The major difference is that for this minimum, the Si 3p orbital on the internal TBP Si atom is now directed to a terminal Si atom. This has the consequence of altering the main natural resonance structure to one which describes singlet coupling in a dimethylsilylene extrusion fashion, in preference to making a 3-center 2-electron bond (Figure 4.14). A secondary resonance structure

Table 4.12: Optimized S_1 RIADC(2)/SVP geometries for **4h2** and **4i1**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ CSiC /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
4h2	163.8	87.5 78.2	148.0	102.4	104.8	2.436	1.938	1.896
			104.7	101.9	117.2	2.452	1.907	1.888
			148.6	108.9	108.3	2.449	1.931	1.888
			104.4	106.7	119.3		1.910	1.886
				106.8	98.5			1.908
				110.6	113.3			1.888
				107.7				
				109.7				
4i1	48.4	110.8 92.5	103.6	109.9	108.8	2.361	1.882	1.886
			105.2	97.7	112.9	2.578	1.892	1.882
			107.5	108.2	105.1	2.541	1.912	1.897
			93.2	107.0	136.2		1.949	1.924
				105.8	110.4			1.902
				101.5	89.5			1.918
				113.1				
				108.3				

Table 4.13: Optimized S_1 TDDFT (BHLYP/TZVP) geometries for the TBP rehybridization minima **4i**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ C _i Si _i Si _t /deg	$\angle$ C _i Si _i C _i /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
4i1	53.4	95.4	107.3	99.0	97.3	132.6	2.543	1.910	1.921
		113.9	95.7	156.6	109.3	110.5	2.656	1.954	1.898
			104.3	114.2		93.1	2.377	1.882	1.912
			103.0	111.4		112.8		1.891	1.881
						105.8			1.894
						109.3			1.886
4i2	68.6	108.6	109.2	115.2	108.2	109.8	2.380	1.883	1.885
		94.3	102.4	112.4	98.0	111.8	2.658	1.891	1.880
			99.5	157.5		105.5	2.584	1.952	1.893
			96.9	97.9		134.5		1.913	1.920
						94.8			1.910
						107.3			1.900

does however invoke a 3-center 2-electron bond, over the two elongated Si-Si bonds. As was the case for **4i1**, the covalent resonance structure is the least weighted main contributor to the S_1 density, and likely contributes to decreasing the $sp^{1.5}$ hybridized orbital occupation from 2 to 1.4 electrons.

Table 4.14: Optimized S₁ TDDFT (BHLYP/TZVP) geometries for the TBP rehybridization minima **4j**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ C _i Si _i Si _t /deg	$\angle$ C _i Si _i C _i /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
4j1	56.6	135.5 89.4	106.4	107.9	106.5	111.4	2.394	1.903	1.898
			92.1	104.3	99.2	109.6	2.551	1.921	1.896
			99.9	102.9		113.7	2.611	1.906	1.902
			154.0	103.3		108.8		1.939	1.877
						112.1			1.872
						101.1			1.886
4j2	73.8	114.4 93.1	129.2	107.2	102.9	110.9	2.370	1.929	1.898
			91.7	107.2	97.8	113.5	2.590	1.920	1.893
			159.7	97.3		109.3	2.631	1.953	1.898
			96.5	104.3		113.8		1.911	1.873
						102.3			1.882
						104.6			1.874
4j3	98.8	103.3 82.1	140.0	107.1	101.0	109.5	2.392	1.935	1.896
			93.0	108.9	100.1	116.2	2.586	1.920	1.891
			150.6	114.1		107.8	2.507	1.936	1.897
			99.7	103.0		113.4		1.905	1.883
						98.5			1.901
						115.5			1.879
4j4	113.0	84.4 93.3	149.9	111.8	100.2	114.1	2.473	1.937	1.881
			99.5	105.6	101.4	114.5	2.582	1.906	1.886
			144.2	108.5		100.5	2.413	1.933	1.902
			98.5	107.5		105.8		1.911	1.900
						114.0			1.888
						112.0			1.891

4.3.3 Permethylated Tetrasilane Emission

For the **4h** minima, the HOMO, LUMO, transition density, and difference density are analogous to those found in the shorter chain analog, **3h**. For **4h2**, these orbitals and densities are shown in Figure 4.15. This state is of mixed $\sigma\sigma^*/\sigma\pi^*$ character.

In Chapter 2, the S₀-S₁ transition density in **3h** varied greatly for the TDDFT structures and seemed to depend on the amount of HF exchange included in the functional used in the structural optimization. No **3h** minimum was located with ab initio S₁ geometry optimization. For **4h2**, however, an ab initio minimum was located and the S₀-S₁ transition densities for the different structures varied less (Figure 4.16). This is expected as structures found with differing methods

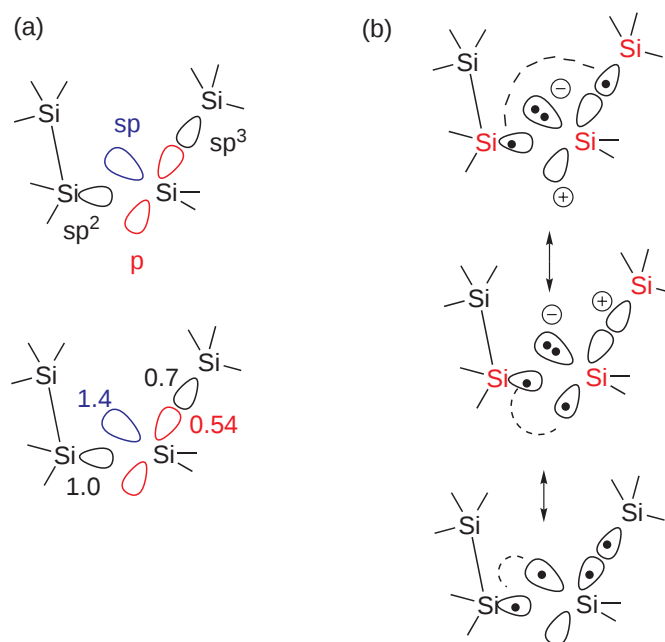


Figure 4.14: NHO analysis (CIS/6-311G(d,p)) for the S_1 density of **4j1**. Hybridization of Si NHOs and their occupancies are shown (a), as well as major contributing natural resonance structures. Dashed lines indicate singlet spin coupling and Si atoms denoted in red color indicate 3-center 2-electron bonding in the resonance structures.

were more similar for the narrow SiSiSi valence angle minimum **4h** than for the trisilane analogs.

From Figure 4.17, it is apparent that electron density is moved from between the elongated Si-Si bonds to the space created by the large SiSiC valence angle. This is apparent by inspection of the transition and difference density for the S_0 - S_1 transition.

A similar picture is presented for **4j1**. The difference is due to the relative location of the large SiSiC valence angle, which for the **4j** minima is defined by an internal Si-Si and an Si-C bond, whereas for the **4i** minima, it is defined by a terminal Si-Si and an internal Si-C bond.

In order to find an accurate method for the reproduction of the emission energies, several were tested. The MSCASPT2(6/10)/ANO-L method was used to calculate the emission energies for the the selected minima in Table 4.15. These values are larger than what is obtained with the standard B3LYP TDDFT procedure. The MSCASPT2 values are closer to those obtained with the LC'-BLYP/Def2-TZVP method (Table 4.16).

The structures obtained with the BP86/SVP method gave lower emission energies (Table

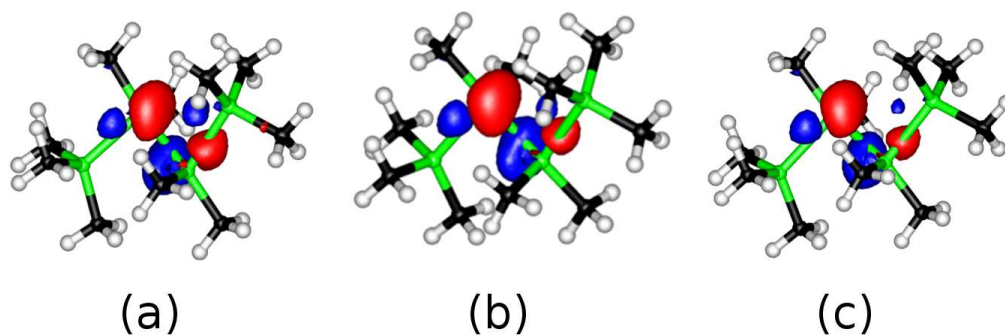
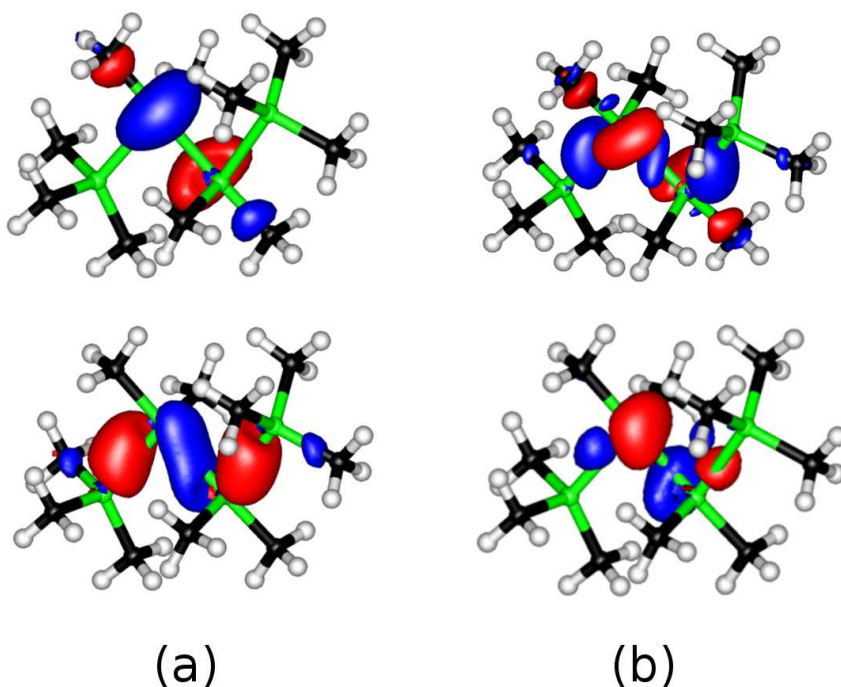


Figure 4.16: S_0 - S_1 transition densities (CIS/6-31G(d)) from RIADC(2)/SVP (a), BHLYP/SVP (b) and BP86/SVP (c) optimized **4h2** structures. Orbitals are shown with the isodensity surface values of ± 0.004 .

4.18) than the BHLYP/SVP structures. The emission energies for the BP86/SVP structures ranged

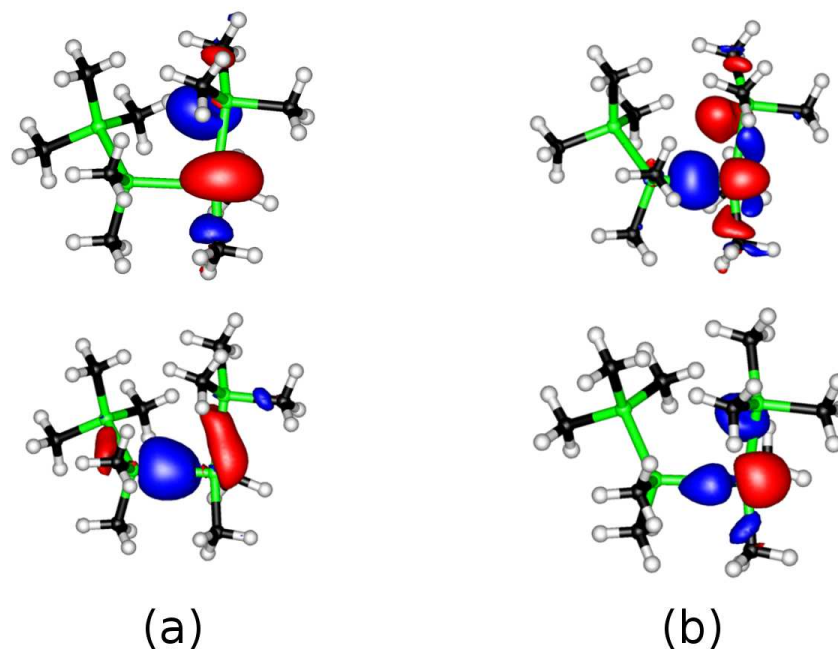


Figure 4.17: Molecular orbitals (B3LYP/Def2-TZVP) for **4i1** (a), HOMO (bottom) and LUMO (top). Densities are shown in second column (b): S_0 - S_1 transition density (CIS/6-31G(d)) (bottom), S_0 - S_1 difference density (top). Molecular orbitals are shown with the isodensity surface values of ± 0.06 , the transition density at ± 0.004 , and the difference density at ± 0.003 isodensity surface values.

Table 4.15: Vertical emission energies (MSCASPT2(6/10)/ANO-L) and S_1 dipole moments for optimized S_1 relaxed structures obtained with the BHLYP/SVP method for selected excited state minima of **4**.

Structure	$\omega_{\text{SiSiSiSiSi}}$ / deg	E_{VE} / cm^{-1}	f	S_1 Dipole Moment Debye
4i1	50.8	18 100	0.011	4.12
4j1	54.4	18 020	0.002	3.10
4i2	70.0	18 440	0.010	3.72
4j2	75.0	18 600	0.017	3.39
4j3	100.6	17 220	0.013	1.62
4j4	112.3	17 750	0.012	1.19
4h2	168.8	15 870	0.005	0.23

from $14\,870\text{ cm}^{-1}$ to $17\,750\text{ cm}^{-1}$, while the emission energies for the BHLYP/SVP structures ranged from $15\,870$ to $18\,600\text{ cm}^{-1}$. There are two BP86/SVP Λ values under 0.30. Values below this threshold indicate strong charge transfer character.⁶⁵ This is not the case for similar minima

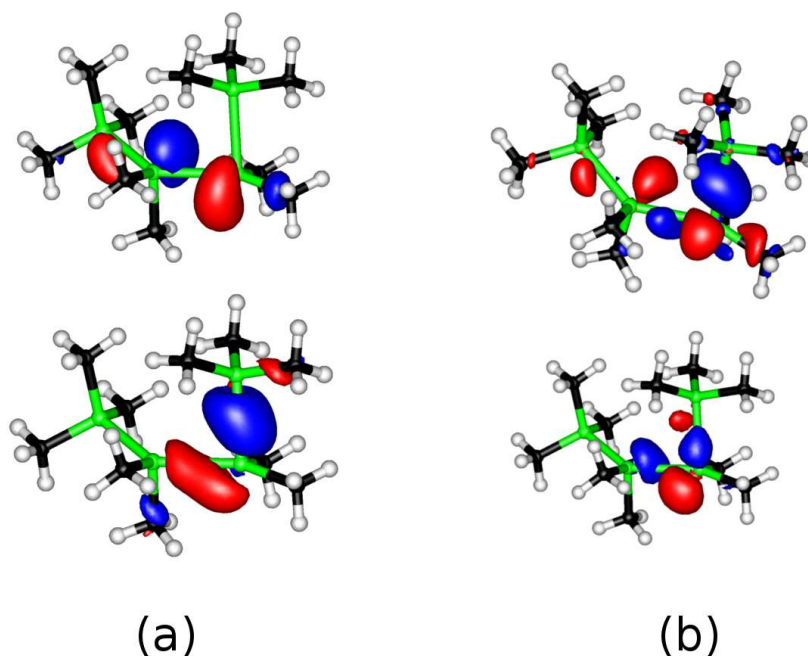


Figure 4.18: Molecular orbitals (B3LYP/Def2-TZVP) for **4j1** (BHLYP/SVP structure) (a), HOMO (bottom) and LUMO (top). Densities are shown in second column (b): S_0 - S_1 transition density (CIS/6-31G(d)) (bottom) and S_0 - S_1 difference density (top). Molecular orbitals are shown with the isodensity surface values of ± 0.06 , the transition density at ± 0.004 , and the difference density at ± 0.003 isodensity surface values.

Table 4.16: Vertical emission energies (LC'-BLYP/Def2-TZVP) and Λ parameter values for optimized S_1 structures obtained with the BHLYP/SVP method for selected excited state minima of **4**.

Structure	ω_{SiSiSiSi} / deg	E_{VE} / cm^{-1}	f	Λ
4i1	50.8	17 410	0.003	0.54
4j1	54.4	17 070	0.010	0.55
4i2	70.0	17 170	0.004	0.51
4j2	75.0	17 120	0.007	0.56
4j3	100.6	16 020	0.005	0.62
4j4	112.3	16 660	0.012	0.62
4h2	168.8	16 040	0.003	0.55

obtained with BHLYP/SVP optimization, which do not have Λ values under 0.51.

The LC'-BLYP/Def2-TZVP method was used to calculate the emission energies of several of the other localized excited state minima. Many of these structures gave low energy emissions,

Table 4.17: Vertical emission energies (LC'-BLYP/Def2-TZVP) and Λ parameter for optimized S_1 relaxed structures obtained with the BHLYP/TZVP method for selected excited state minima of **4**.

Structure	ω_{SiSiSiSi} / deg	E_{VE} / cm^{-1}	f	Λ
4i1	53.4	17 880	0.003	0.54
4j1	56.6	17 540	0.009	0.54
4i2	68.6	17 700	0.004	0.50
4j2	73.8	17 420	0.006	0.55
4j3	98.8	16 910	0.006	0.62
4j3	113.0	17 260	0.005	0.61
4h2	169.1	16 490	0.003	0.55

Table 4.18: Vertical emission energies (LC'-BLYP/Def2-TZVP) and Λ parameter values for various S_1 relaxed structures obtained with the BP86/SVP method for selected excited state minima of **4**.

Structure	ω_{SiSiSiSi} / deg	E_{VE} / cm^{-1}	f	Λ
4i1	21.1	17 320	0.001	0.26
4j1	48.6	17 750	0.004	0.43
4i2	73.5	16 020	0.001	0.29
4j2	84.6	14 130	0.003	0.50
4j3	88.9	14 870	0.003	0.47
4h2	171.3	15 870	0.002	0.53

e.g., values of 16 970, 16 190, 16 930, and 14 040 cm^{-1} were obtained for the **4b**, **4e1**, **4e2** and **4f** minima, respectively. An intermediate Λ value of 0.37 was calculated for **4e1**, the transoid conformation of the terminal Si polarization minimum. The gauche conformation **4e2** yielded a slightly higher Λ value (0.41). One minimum, the wide SiSiSi valence angle minimum **4g**, gave much larger emission energies, around 23 600 cm^{-1} . This minimum has a large Λ value (0.63) and similar emission energies are obtained with standard TDDFT calculations. The diffuse Si-Si bond stretch minimum **4c** gave similar emission energies (Table 4.19).

Table 4.19: Vertical emission energies (LC'-BLYP/Def2-TZVP) and Λ parameter values for optimized S_1 structures obtained with various methods (listed in the Opt. Method column) for selected excited state minima of **4**.

Structure	Opt. Method	E_{VE} / cm^{-1}	f	Λ
4b	B3LYP/SVP	16 970	0.004	0.48
4c	BHLYP/TZVP	23 020	0.247	0.67
4e1	PBE0/SVP	16 190	0.007	0.37
4e2	PBE0/SVP	16 930	0.005	0.41
4f	PBE0/SVP	14 040	0.012	0.38
4f	BHLYP/SVP	15 610	0.012	0.39
4g	PBE0/SVP	23 500	0.002	0.63
4g	B3LYP/SVP	23 700	0.002	0.62
4h1	BHLYP/SVP	13 360	0.002	0.59
4h2	BHLYP/SVP	16 040	0.003	0.55

4.3.4 Green Emission From Longer Permethylated Oligosilanes

4.3.4.1 Localized Geometries

To correlate the emission energies with structure in longer oligosilanes, the geometries of green excitons in heptasilane are presented. The geometries in this section have large structural distortions in one region of the molecule. This region is defined by the name of the minimum energy structure. As can be seen from the tables, the optimized geometry of the remaining part of the molecule is very similar to that of the ground state. For **7b**, the terminal Si-Si bond on the opposite side of the molecule where the elongated Si-C bond is located is calculated to be 2.38 Å, which is exactly what the B3LYP/SVP method gives for the terminal bond length in the ground state equilibrium structure. The **7b** minimum (Table 4.20) can be compared to the ground state equilibrium all transoid structure **7G** in Table 4.21. This trend is followed for other geometrical parameters such as dihedral and valence angles as well.

4.3.4.2 Localized Chromophores

As mentioned in the preceding section, large geometrical distortions in the green excitons are localized on one part of the molecule, the chromophore. Because the chromophore is the same

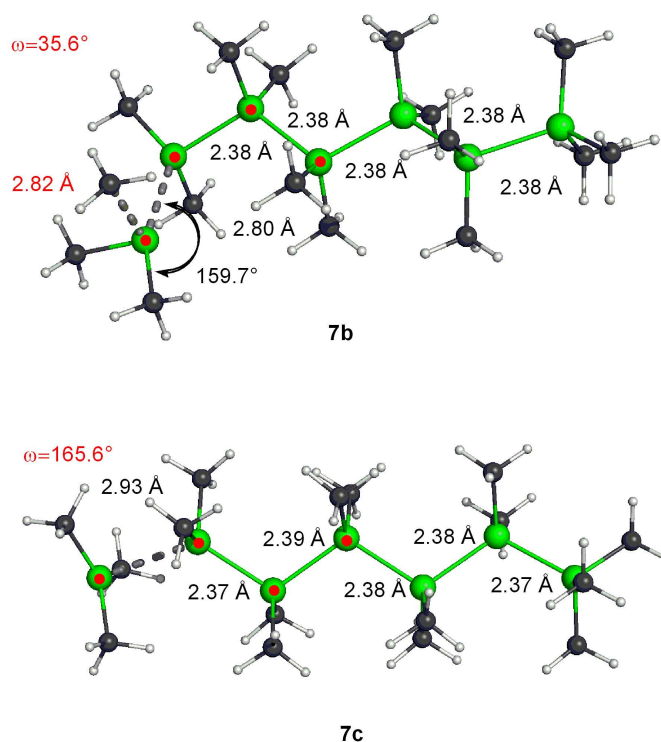


Figure 4.19: Geometries (BHLYP/SVP) for the C-Si bond stretch minimum **7b** (B3LYP/SVP) and the diffuse Si-Si bond stretch minimum **7c** (BHLYP/TZVP). The Si-Si bond lengths are indicated (Å), and selected valence angles and the all-Si dihedral angle (ω) are shown in degrees.

Table 4.20: Optimized S_1 TDDFT (B3LYP/SVP) geometry for the C-Si bond stretch minimum **7b**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ CSiC /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
7b	169.4	109.4	107.8	108.7	111.5	2.379	1.903	1.850
	164.4	112.5	111.4	107.9	110.6	2.380	1.903	1.850
	166.7	111.6	108.4	107.4	111.5	2.384	1.913	1.850
	35.6	114.4	108.7	107.0	159.7	2.382	1.913	1.936
		112.9	110.1	104.1	98.1	2.384	1.913	1.912
			108.7	92.1	95.4	2.803	1.910	2.335
			107.9	107.6			1.917	
			111.0	107.7			1.915	
			109.7	107.7			1.920	
			108.9	100.3			1.938	
			108.4	93.1				
			108.3					

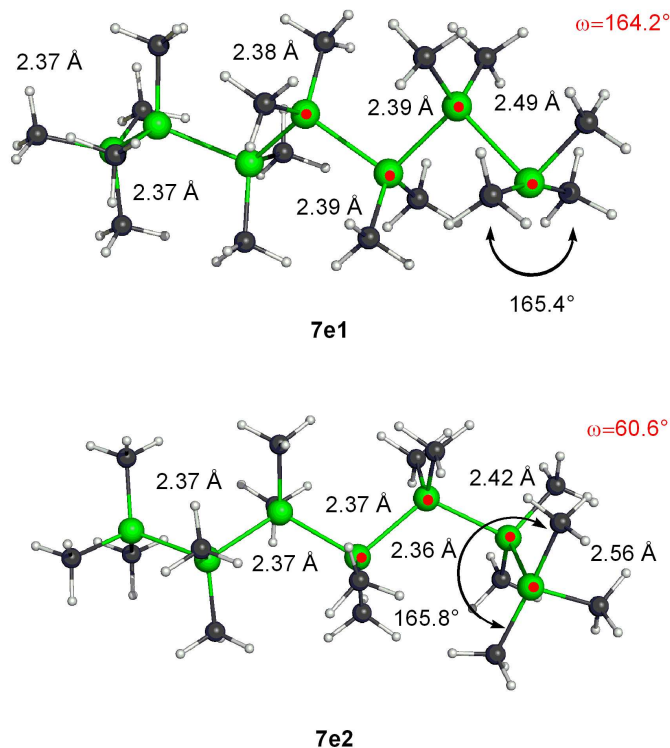


Figure 4.20: Geometries (B3LYP/SVP) for the terminal Si transoid polarization minimum **7e1** (B3LYP/SVP) and the terminal gauche polarization minimum **7e2** (B3LYP/TZVP). The Si-Si bond lengths are indicated (Å), and selected valence angles and the all-Si dihedral angle (ω) are shown in degrees.

Table 4.21: Optimized S_0 DFT (B3LYP/SVP) geometry for the minimum **7G**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ CSiC /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
7G	164.2	112.2	110.4	107.9	111.7	2.380	1.912	1.902
	164.7	111.4	108.3	107.9	109.4	2.384	1.913	1.904
	164.7	112.0	107.8	108.1	110.4	2.385	1.912	1.902
	164.2	111.4	110.9	107.9	111.7	2.385	1.912	1.902
		112.2	110.4	107.9	109.4	2.384	1.912	1.904
			108.0	108.7	110.4	2.380	1.912	1.902
			107.9	108.3			1.912	
			110.4	108.3			1.912	
			108.3	108.7			1.913	
			110.4	108.3			1.912	
			110.9	108.3				
			107.8					

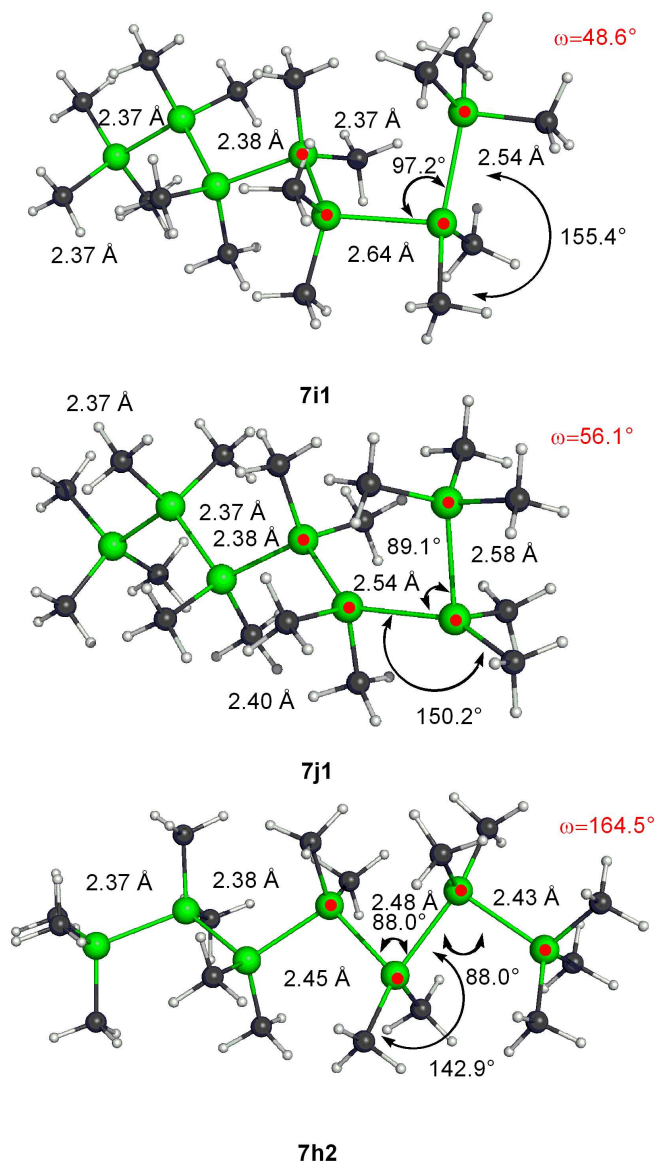


Figure 4.21: Geometries (BHLYP/SVP) for the C-Si bond stretch minimum **7b** (B3LYP/SVP) and the diffuse Si-Si bond stretch minimum **7c** (BHLYP/TZVP). The Si-Si bond lengths are indicated (Å), and selected valence angles and the all-Si dihedral angle (ω) are shown in degrees.

for analogous minima in molecules with differing chain lengths, the properties are not expected to change. This is indeed the case for the minima presented in this chapter. Emission energies and oscillator strengths vary only minutely with chain length. The S_1 dipole moment has a greater dependence on chain length for some minima, however.

For the transoid terminal Si polarization minimum **6e1**, the LUMO is localized on the ter-

Table 4.22: Optimized S₁ TDDFT (BHLYP/TZVP) geometry for the minimum **7c**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ CSiC /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
7c	165.6	122.0	108.7	108.0	92.4	2.927	1.901	1.856
	165.7	109.8	110.4	109.4	91.3	2.371	1.903	1.862
	164.7	112.1	110.2	108.1	90.6	2.388	1.896	1.879
	164.6	111.8	108.4	108.1	109.6	2.381	1.896	1.895
		112.4	107.9	107.9	110.5	2.376	1.902	1.893
			110.4	108.2	111.5	2.372	1.902	1.893
			110.0	116.5			1.902	
			108.2	120.6			1.902	
			110.3	122.7			1.903	
			108.1	108.3			1.903	
			108.2	108.7				
			110.3					

Table 4.23: Optimized S₁ TDDFT (PBE0/SVP) geometries for the minimum **7e**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ CSiC /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
7e1	164.2	96.5	113.7	108.6	96.8	2.488	1.889	2.020
	162.8	102.3	109.0	110.7	92.4	2.392	1.889	1.938
	162.4	106.1	109.1	109.9	95.0	2.391	1.881	2.020
	163.1	108.2	111.7	109.4	108.7	2.379	1.886	1.893
		110.1	112.6	109.0	109.9	2.371	1.894	1.891
			108.3	108.8	111.2	2.369	1.893	1.891
			108.3	93.8			1.897	
			111.6	94.2			1.896	
			108.1	165.4			1.900	
			111.2	108.8			1.900	
			111.5	109.4				
			108.4					
7e2	64.7	100.7	109.6	107.7	95.5	2.516	1.885	2.012
	156.6	114.7	110.9	108.4	90.6	2.424	1.888	1.935
	163.1	107.3	100.1	111.3	95.9	2.362	1.887	2.009
	163.5	109.3	112.5	109.0	109.0	2.372	1.907	1.894
		110.8	107.9	108.7	111.2	2.369	1.894	1.893
			110.3	108.6	110.2	2.367	1.896	1.892
			111.8	93.9			1.901	
			108.1	94.3			1.901	
			110.9	165.8			1.901	
			108.0	108.6			1.901	
			109.0	109.1				
			110.6					

Table 4.24: Optimized S_0 DFT geometries for the minimum **7G**.

Structure	$\omega\text{SiSiSiSi}$ /deg	$\angle\text{SiSiSi}$ /deg	$\angle\text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle\text{CSiC}$ /deg	$\angle\text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC_i /Å	SiC_t /Å
7G PBE0/SVP	163.3	111.3	110.5	108.5	111.3	2.365	1.902	1.893
	163.9	110.5	108.4	108.6	109.4	2.367	1.903	1.895
	164.0	111.2	108.0	108.9	110.1	2.367	1.902	1.893
	163.2	110.5	110.8	108.6	111.3	2.367	1.902	1.893
		111.3	110.3	108.5	109.4	2.367	1.902	1.895
			108.1	109.0	110.1	2.365	1.902	1.893
			108.1	108.5			1.902	
			110.3	108.5			1.902	
			108.4	109.0			1.903	
			110.5	108.5			1.902	
			110.8	108.5				
			108.0					
7G BHLYP/SVP	164.0	111.7	110.4	108.1	111.4	2.366	1.899	1.889
	164.3	111.0	108.4	108.1	109.5	2.370	1.899	1.891
	164.3	111.5	108.0	108.3	110.2	2.370	1.899	1.889
	164.1	111.0	110.8	108.1	111.4	2.370	1.899	1.889
		111.7	110.4	108.1	109.5	2.370	1.899	1.891
			108.1	108.8	110.2	2.366	1.899	1.889
			108.1	108.4			1.899	
			110.4	108.4			1.899	
			108.4	108.8			1.899	
			110.4	108.4			1.899	
			110.8	108.4				
			108.0					

Table 4.25: Optimized S_1 TDDFT (BHLYP/SVP) geometry for the minimum **7h2**.

Structure	$\omega\text{SiSiSiSi}$ /deg	$\angle\text{SiSiSi}$ /deg	$\angle\text{C}_i\text{Si}_i\text{Si}_i$ /deg	$\angle\text{CSiC}$ /deg	$\angle\text{Si}_i\text{Si}_t\text{C}_t$ /deg	SiSi /Å	SiC_i /Å	SiC_t /Å
7h2	164.5	92.7	103.6	102.3	105.4	2.436	1.903	1.892
	172.0	82.8	101.5	101.3	108.9	2.477	1.935	1.886
	168.6	101.1	142.9	109.8	116.7	2.451	1.904	1.885
	161.3	108.7	118.4	109.5	108.9	2.405	1.934	1.890
		110.2	114.8	108.3	111.4	2.381	1.891	1.888
			107.4	108.5	110.3	2.370	1.888	1.888
			115.8	108.6			1.892	
			106.9	109.2			1.893	
			109.1	107.7			1.897	
			110.7	108.5			1.897	
			112.4	109.1				
			106.5					

Table 4.26: Optimized S₁ TDDFT (BHLYP/SVP) geometry for the minimum **7i1**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ CSiC /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
7i1	48.6	97.2	102.7	97.5	134.4	2.544	1.951	1.919
	154.2	113.0	113.4	109.4	93.2	2.648	1.906	1.909
	165.2	106.8	104.1	111.2	108.8	2.367	1.887	1.896
	163.6	109.8	113.2	108.9	109.1	2.379	1.878	1.889
		111.0	108.2	108.4	110.4	2.373	1.890	1.888
			109.1	108.6	111.1	2.368	1.885	1.889
			111.9	102.8			1.898	
			109.5	106.9			1.896	
			110.1	106.8			1.897	
			108.0	108.6			1.897	
			109.2	109.0				
			110.7					

Table 4.27: Optimized S₁ TDDFT (BHLYP/SVP) geometry for the minimum **7j1**.

Structure	ω SiSiSiSi /deg	$\angle$ SiSiSi /deg	$\angle$ C _i Si _i Si _i /deg	$\angle$ CSiC /deg	$\angle$ Si _i Si _t C _t /deg	SiSi /Å	SiC _i /Å	SiC _t /Å
7j1	56.1	89.1	91.1	100.8	100.0	2.577	1.925	1.884
	156.6	136.1	105.1	106.8	109.8	2.540	1.899	1.872
	165.2	115.4	105.3	107.8	112.5	2.398	1.919	1.868
	164.7	112.6	108.2	108.0	109.8	2.379	1.900	1.892
		112.5	109.4	108.0	110.5	2.372	1.903	1.890
			108.8	108.2	111.3	2.367	1.902	1.890
			108.3	109.8			1.899	
			106.9	113.8			1.900	
			110.3	110.1			1.900	
			107.8	108.2			1.900	
			108.5	108.7				
			109.6					

minal Si atom and Si-C bonds (Figure 4.22). The HOMO is localized to a much lesser extent and is partially delocalized along the Si backbone.

The HOMO and LUMO are shown for the gauche terminal Si polarization minimum **6e2** in Figure 4.23. The gauche twist localizes both the HOMO and LUMO towards the Si atom which has structurally reorganized. This minimum is extremely localized as evidenced also by the small change in emission energies with increasing chain length (Table 4.31).

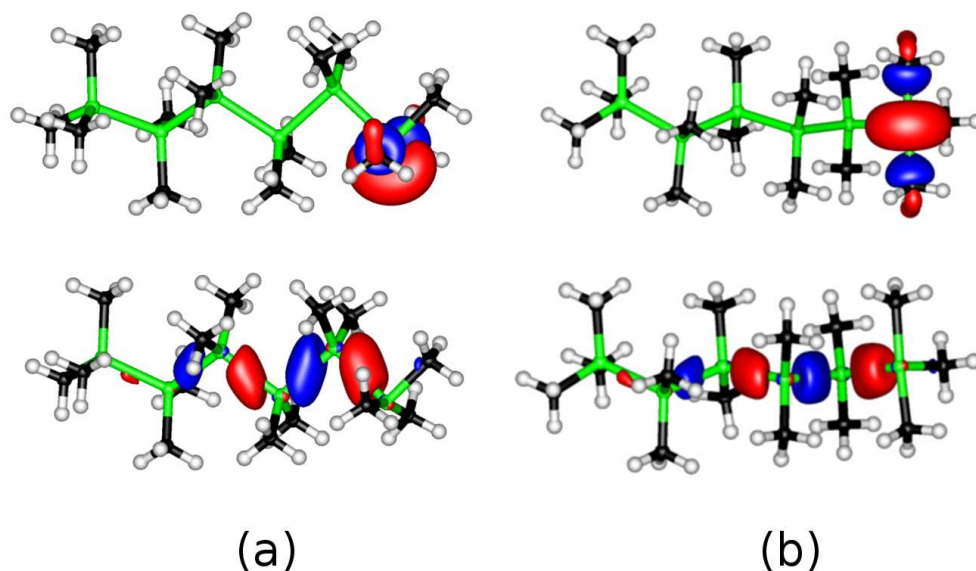


Figure 4.22: HOMO (bottom) and LUMO (top) (B3LYP/Def2-TZVP) for **6e1** (PBE0/SVP structure) . Contrasting vantage points are given, side view (a) and from underneath (b). All orbitals are shown with the isodensity surface values of ± 0.06 .

The S_0 - S_1 emission energy, oscillator strength, and S_1 dipole moment dependence on chain length of the minima are presented in the following tables.

Table 4.28: Vertical emission energies (B3LYP/Def2-TZVP) and S_1 dipole moments for optimized S_1 relaxed structures obtained with the B3LYP/SVP method for selected excited state minima of **4b-6b**.

Structure n	E_{VE} / cm^{-1}	f	S_1 Dipole Moment Debye
4	16 290	0.003	2.78
5	16 600	0.003	2.91
6	16 600	0.003	2.92

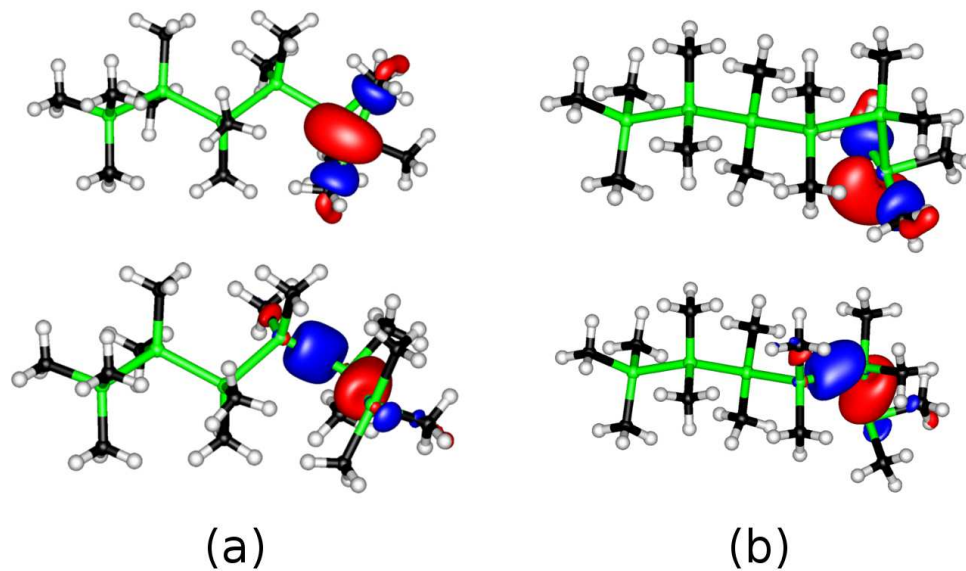


Figure 4.23: HOMO and LUMO (B3LYP/Def2-TZVP) for **6e2** (PBE0/SVP structure). All orbitals are shown with the isodensity surface values of ± 0.06 .

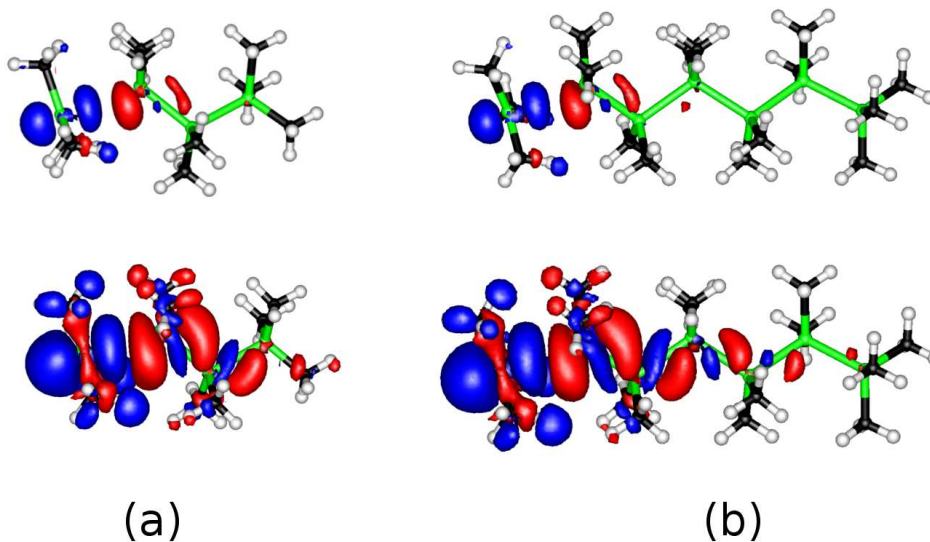


Figure 4.24: S_0 - S_1 transition densities (CIS/6-31G(d)) for **4c** (a) and **7c** (B3LYP/TZVP structures) are shown with the isodensity surface values of ± 0.004 (top) and ± 0.001 (bottom).

Table 4.29: Vertical emission energies (B3LYP/Def2-TZVP) and S_1 dipole moments for optimized S_1 relaxed structures obtained with the BHLYP/TZVP method for selected excited state minima of **4c-7c**.

Structure n	E_{VE} / cm^{-1}	f	S_1 Dipole Moment Debye
4	23 170	0.253	1.03
5	23 350	0.320	1.03
6	23 680	0.388	0.94
7	23 990	0.456	0.85

Table 4.30: Vertical emission energies (B3LYP/Def2-TZVP) and S_1 dipole moments for optimized S_1 relaxed structures obtained with the PBE0/SVP method for selected excited state minima of **4e1-10e1**.

Structure n	E_{VE} / cm^{-1}	f	S_1 Dipole Moment Debye
4	15 280	0.008	5.45
5	15 040	0.011	6.65
6	15 040	0.013	7.68
7	15 060	0.015	8.46
8	15 090	0.016	9.02
9	15 120	0.017	9.42
10	15 130	0.018	9.69
11	15 140	0.020	9.88
12	15 140	0.020	10.00

Table 4.31: Vertical emission energies (B3LYP/Def2-TZVP) and S_1 dipole moments for optimized S_1 relaxed structures obtained with the PBE0/SVP method for selected excited state minima of **4e2-9e2**.

Structure n	E_{VE} / cm^{-1}	f	S_1 Dipole Moment Debye
4	16 520	0.006	3.78
5	16 460	0.007	4.17
6	16 430	0.007	4.38
7	16 420	0.007	4.65
8	16 440	0.007	4.92
9	16 440	0.007	4.99

Table 4.32: Vertical emission energies (B3LYP/Def2-TZVP) and S_1 dipole moments for optimized S_1 relaxed structures obtained with the PBE0/SVP method for selected excited state minima of **4g-5g**.

Structure n	E_{VE} / cm^{-1}	f	S_1 Dipole Moment Debye
4	23 760	0.002	1.41
5	24 100	0.002	2.10

Table 4.33: Vertical emission energies (B3LYP/Def2-TZVP) and S_1 dipole moments for optimized S_1 relaxed structures obtained with the B3LYP/SVP method for selected excited state minima of **4h2-8h2**.

Structure n	E_{VE} / cm^{-1}	f	S_1 Dipole Moment Debye
4	16 440	0.003	0.20
5	15 340	0.002	1.21
6	15 110	0.002	2.14
7	14 940	0.003	2.79
8	14 900	0.004	3.27

Table 4.34: Vertical emission energies (B3LYP/Def2-TZVP) and S_1 dipole moments for optimized S_1 relaxed structures obtained with the PBE0/SVP method for selected excited state minima of **4i1** and **7i1**.

Structure n	E_{VE} / cm^{-1}	f	S_1 Dipole Moment Debye
4	17 460	0.003	3.61
5	17 430	0.003	4.38
6	17 400	0.003	4.95
7	17 420	0.004	5.23

Table 4.35: Vertical emission energies (B3LYP/Def2-TZVP) and S_1 dipole moments for optimized S_1 relaxed structures obtained with the PBE0/SVP method for selected excited state minima of **4j1-7j1**.

Structure n	E_{VE} / cm^{-1}	f	S_1 Dipole Moment Debye
4	17 110	0.009	3.31
5	17 300	0.015	3.95
6	17 490	0.021	4.40
7	17 580	0.027	4.82

4.4 Discussion

4.4.1 Geometries

For many minima (**4b-4h**), geometries are very similar to those found and already discussed for smaller oligosilanes. The Si-Si bond stretch minimum **4a** is believed to emit in the blue spectral region (Chapter 3). The Rydberg minimum **4d** is not calculated in this work as Rydberg states are believed to be quenched in solution.²² Proper calculations for the Rydberg states are also very expensive as basis sets augmented with diffuse functions are needed for accurate computational reproduction of these states. In tetrasilane there is an additional class of S_1 minima, the TBP rehybridization structures. There are two types of these minima: **4i** and **4j**. These structures have two highly stretched Si-Si bonds, and large rearrangements of the internal Si-C bonds. The potential energy surface is probably very flat with respect to the dihedral angle coordinate, as four minima with all-Si dihedral angles ranging from 54° to 112° (BHLYP/SVP) were located for **4j**. Basis set and functional choice also had an effect on which minimum was found when starting from a particular geometry. To better explore the S_1 potential energy surface an excited state stochastic search was carried out. While many TBP minima were found with TDDFT methods, most of these structures led to internal dimethylsilylene extrusion funnels when optimized with *ab initio* methods. This is a likely outcome, as the TBP minima have narrow SiSiSi valence angles and have an electronic structure indicative of this outcome, *e.g.*, these minima are described by natural resonance structures which directly couple the second and last silicon atoms in the S_1 state. The TBP rehybridization minima are found for twisted structures and are therefore likely candidates for the green emission from **4-c4**.

Singlet HOMO-LUMO excitation is expected to lead to bond stretching and minimization of the antibonding destabilizing interactions, but not to fully dissociate the molecule due to the combination of hole pair zwitterionic resonance structures that describe this excited state.⁶⁸ It seems there is another way in which the zwitterionic wave function can be stabilized, and that is to minimize charge separation. This can be done by rehybridization of the hybrid orbitals to

accommodate a lone pair and positive charge on the same Si atom. The resulting structure has the approximate electronic structure of singlet dimethylsilylene. This seems to be the driving force for the TBP rehybridization minima.

The electronic description of molecules with heavier group XIV elements often involves this carbene type descriptions of the resonance structures as opposed to the covalent description of the ground state bonding.¹⁸⁵ A logical extension seems plausible, *i.e.*, that the excited states of saturated systems made of lighter group XIV elements involves this description.

The C-Si bond stretch and diffuse Si-Si bond stretch minima were found for many chain lengths. This indicates that they could be responsible for the green emission. On the other hand, these minima were only found with one functional. The C-Si bond stretch minima were located only with the B3LYP functional, whereas the diffuse Si-Si bond stretch minima required the BHLYP functional. It is difficult to say whether this is significant as TDDFT is an empirical method and other, slightly different, functionals might also work. The fact that the *ab initio* methods did not find these minima does not completely rule out their existence, as these methods might simply find ways for the molecule to rearrange that lowers the energy and takes the molecule away from a given minimum. The diffuse bond stretch minima require extended Si backbone conformations, making a likely candidate for the green emission observed from **4-r2**.

The polarization minima were found with the PBE0, B3LYP, BHLYP and in one case (**4e1**) with the RIADC(2)/TZVP method. This could indicate these structures are robust and likely candidates for the green emission. Unfortunately the emission energies of these structures are a bit low, but there is a large dependence of the emission energy on the basis set used in the structural optimization (Chapter 2). Therefore these structures might be responsible for the green emission. The polarization minima can exist with multiple Si backbone conformations.

The wide SiSiSi angle minimum **4g** is also not found in longer chains ($n > 4$). The lambda values for this structure are high, indicating that TDDFT is trustworthy. This minimum might therefore only contribute to the broad green emission in the shorter chains. This structure is of extended nature so is a less likely candidate for the green emission found in **4-c4**.

The small SiSiSi valence angle minimum **4h1** also rearranges to the internal dimethylsilylene extrusion funnel when optimized with ab initio methods. The same result is realized when this structure is optimized in longer oligosilanes ($n > 4$). This indicates the **4h1** minimum is slightly less stable than the **4h2** minimum. The latter structure was found to be a minimum with the TDDFT and RIADC(2)/SVP methods and is very similar to the structure located by Teramae and Michl.¹²⁶

The structures of the minima found in this chapter can be used in the structural optimization of the corresponding radical anions. This allows ground state methods to be used in order to find out how the parent structure deals with an extra electron. Optimized structures radical anions were found to be similar to their neutral S_1 counterparts in Chapter 2. Radical anion optimizations are currently underway for the tetrasilane structures. This can provide some additional scrutiny for the non-classical minima which deviate from typical ground state tetrahedral structures of sp^3 hybridization.

4.4.2 Emission Energies

Excitation energies show some dependence the S_1 optimization basis set, typical E_{VE} increase is 600-700 cm^{-1} more for S_1 BHLYP/TZVP optimizations compared to the S_1 BHLYP/SVP optimized structures. This increase in excitation energies when a bigger basis sets used in the S_1 optimization is in the correct direction for agreement with experiment (broad emission band peaks at 20,000 cm^{-1}) but as this study aims to investigate green emission in longer silanes as well, the BHLYP/SVP method is preferred.

It seems that some artificial charge transfer character is being built into the TDDFT optimized structures, as the Λ values correlated with the amount of HF exchange included in the TDDFT optimization. The actual correlation between Λ value and emission energy is less easy to predict. Ab initio structures gave larger Λ values but lower emission energies. TDDFT structures however tended to give higher emission energies when the structure was obtained with an increasing amount of HF exchange. The low emission energies from RIADC(2) structures are more disturbing.

The SVP basis set is probably too small for accurate results, but is unavoidable for larger molecules. The small basis sets used to optimize structures can be a cause of inaccurate emission energies. Another possible inadequacy of the methods used is that multi-reference methods might be required to describe the green emission. This is the case for systems which have large bond stretching or a complicated electronic structure that requires a multideterminant description. These situations could easily fit the highly distorted emitters. While an ground to excited state transition could naturally have some charge transfer character, this is most likely not the case as the Λ values for the ab initio minima are much higher than those of the TDDFT structures obtained with pure DFT exchange.

The terminal Si polarization minimum was found with stochastic search techniques employing the B3LYP functional, but reorganized to a TBP rehybridization minimum when the BHLYP functional was used. This indicates possibly very low barriers between excited state minima. The **4g** minimum is another example. While it was found with the B3LYP and PBE0 functionals, TDDFT optimization with the BHLYP functional led to **4a2**, this time indicating small barriers between green and blue emitters. The **4g** minimum can still probably very easily rearrange to find the **Ff** type funnel, which happens to the **4g** structure when it is optimized with the RIADC(2)/SVP method.

The broad green emission band could be attributed to a superposition of emissions from many conformers found in this work. While most of the minima have calculated emission energies below 20 000 cm^{-1} , some, notably **4g** and **4c**, yielded calculated emission energies of around 23 000 cm^{-1} (LC'-BLYP/Def2-TZVP), which are located on the high energy side of the band. The S_0 - S_1 oscillator strength for the diffuse Si-Si bond stretch minimum **4c** was calculated to be very large and grows as the chain is lengthened, similar to other $\sigma\sigma^*$ states. Reasons for the difference in calculated emission energies could be many besides those mentioned already. While the scaffolding should be transparent, it could distort the framework into a geometry that is not accessed as easily by the free chain analog, and thus a shift the emission energies could be possible. The calculated minima could also not correlate with the emission peak maximum and a spectral simulation with

a plethora of structures as well as Franck-Condon factors could support this claim. Fluorescence spectrum simulation should be carried out on at least a few of the most likely structures.

The experimental finding that lowering the temperature leads to a broader emission band suggests that as temperature is decreased more conformers can contribute to the green emission. The quantum yield of the green emission also increases with a lowering temperature. The fact that the ab initio method did not find many minima indicates there are multiple deactivation routes available to the tetrasilane and rationalizes the low fluorescence quantum yields. As temperature drops, access to these funnels is limited and allows for more intense emission.

In chains longer than $n = 4$, not all the analogous minima of the tetrasilane were found. The terminal narrow SiSiSi valence angle minimum, for instance, converted into a internal narrow SiSiSi valence angle minimum upon geometry optimization, indicating a low barrier for this process and suggesting that the internal narrow SiSiSi valence angle minimum is more stable. The wide SiSiSi valence angle minimum **7g** was not found, instead optimization of this structure (where the wide SiSiSi valence angle was located over the terminal Si atoms) reorganized into the normal emitter, **7N**. While these structures were not found in the optimization of the isolated molecule, they still might exist due to solvent effects. The **7g** minimum might be more stable if the distortion is localized over internal Si atoms, as internal distortions seem to lead to minima which are stabilized to a greater extent than minima with large distortions localized on terminal Si atoms. This could be due to the fact that the transition density is naturally maximized in the center of longer chains (for all-transoid conformers), and not localized on the termini, *e.g.*, see the transition density for the normal emission, section 3.3.2.

Finally, it should be noted that some conformers (especially **4e** and longer analogs) have large S_1 dipole moments and these could lead to interesting solvent effects. Experiments with polar solvents should be undertaken.

4.5 Conclusions

The broad Franck-Condon forbidden green emission found for constrained oligosilanes is likely to result from many possible conformers. Many potential candidates have been located in this chapter, but probably more exist. Oligosilanes, being floppy, can access many degrees of freedom that will allow the molecule to distort and relax after electronic excitation. This chapter identified some of the general ways in which this is possible in longer oligosilanes.

One potential mechanism is to distort to a trigonal bipyramidal geometry on an internal Si site. This results in rehybridization from sp^3 Si hybrid orbitals to a Si 3p orbital either pointing to an internal Si or to a terminal Si, and an orbital with high s character (sp hybridized) which points towards the center of the molecule, and sp^2 hybrid orbitals which point to the methyl groups. There are six minima of this nature which have SiSiSiSi dihedral angles ranging from 50-110°. These structures give emission energies of about 18 000 cm^{-1} for permethylated tetrasilanes.

Another relaxation mechanism consists of stretching the central or terminal Si-Si bond and creating wide CSiSi angles and narrow SiSiSi angles. The centrally distorted Si-Si bond structure was located by Teramae and Michl more than a decade ago. Both this structure and newly located terminal Si-Si bond stretch isomer have emission energies around 16 000 cm^{-1} , and so possibly contribute to the low energy side of the green emission band.

A mechanism which results in an exciton and gives emission energies on the high energy side of the green emission band was also located. Here excited state relaxation of the $\sigma\sigma^*$ state leads to a large SiSiS valence angle distortion. The wide SiSiSi valence angle minimum and the diffuse Si-Si bond stretch minimum give emission energies around 23 000 cm^{-1} .

A relaxation mechanism which moves electrons to a nonbonding hypervalent site and creates a polarization minimum, similar to that found for the hexamethyldisilane, also is available to longer silanes. In longer silanes this creates huge S_1 dipole moments, and can also exist in twisted conformations. The emission energy of these structures does not change with chain length and thus is of an extremely localized nature. Fluorescence experiments in solvents of various polarity are

predicted to show a large variation in emission energy due to these conformers.

Chapter 5

Conclusions

5.1 Summary and Future Directions

To summarize, this work located many structures which could be responsible for various emissions in linear oligosilanes. From analyzing these structures some understanding of the driving forces responsible for exciton relaxation and localization has been developed. Blue emission is now (computationally) confirmed to originate from bond stretch minima. These structures minimize σ antibonding interactions. Green emission has been found to come from rehybridization minima which minimize charge separation. Calculations of these species can easily go awry in TDDFT if pure DFT functionals are used as these methods underestimate charge transfer states and thus artificial charge transfer gets built into the structure as the molecular geometry is optimized.

In this work, an effective approach for exploring the S_1 surface, the excited state stochastic search was utilized. This method appears to be an extremely efficient way to scan excited state potential energy surfaces for new minima. Different methods (functionals and basis sets) should be incorporated into the search.

New bonding patterns in the excited states of oligosilanes have been identified. These include mechanisms to minimize antibonding interactions and often lead a silicon atom to become hypervalent.

New deactivation mechanisms for oligosilanes have been identified. These mechanisms are either barrierless or have very low barriers, which hot oligosilanes can no doubt easily overcome. These involve simple bending motions of the Si and methyl substituent framework. Transient

absorption spectroscopy and nonadiabatic dynamics calculations could provide insight into the time scales involved in these processes.

With the plethora of deactivation mechanisms identified it is amazing that oligosilane fluorescence is observed at all. Reasoning for this could be that fluorescence is most likely observed in longer chains as minima resulting from delocalized excitation are located closer to the vertical starting geometries, and barriers connecting the minima to the funnel regions become larger as the chain length is increased. Large geometrical rearrangements would ensue only when the excitation becomes localized and this is not the preferred relaxation mechanism in extended conformations in longer oligosilanes. Increasing barrier heights from S_1 minima to S_0 - S_1 funnel regions was calculated for the **2Fa** and **3Fa** funnels, but more work on these barriers needs to be done. Shorter oligosilanes also have large site distortion energies and are likely to be able to overcome small barriers to minima and funnels imposed by various molecular rearrangements.

Localized emission from longer oligosilanes has been identified as possible as long as the correct conformations can be accessed. Experiments with constrained and or hindered oligosilanes in various polar solvents would a very interesting addition to the experimental background information on these states, as many are calculated to have significant S_1 dipole moments.

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