Comparison between SiMe2 and CMe2 spacers as sigma-bridge for photoinduced charge transfer

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Comparison between SiMe₂ and CMe₂ Spacers as σ-Bridges for Photoinduced Charge Transfer


Contribution from the Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands, Radiation Chemistry Department, IRD, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands, and Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

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Abstract: The potential of dimethylsilylene and isopropylidene σ-spacers as bridges for photoinduced charge transfer (CT) in 4-cyano-4-(dimethylamino)- and 4-cyano-4-methoxy-substituted diphenylmethylsilanes and 2,2'-diphenylpropanes was studied. Fluorescence solvatochromism and time-resolved microwave conductivity measurements show that upon photoexcitation a charge separated state (D*σA**) is populated in all compounds. Excited state dipole moments for a given donor-acceptor combination are, irrespective of the bridge, equal. The CT states of the silanes are however lying at lower energies, implying that the presence of silicon thermodynamically facilitates the CT process. Cyclic voltammetry data of model compounds show that this is a consequence of the lowering of the acceptor reduction potential by the silicon bridge. It was however inferred from radiative decay rates that the electronic coupling between the CT and locally excited states as well as the coupling between the ground and CT state is larger for the carbon-bridged compounds. As shown by both solution and solid state electronic spectra and radiative decay rates, the photophysics of the DOA compounds are dominated by intensity borrowing of the CT transitions from transitions localized in the DO and σA chromophores.

Introduction

Oligosilylenes, linear or cyclic σ-bonded silicon compounds, have received considerable attention owing to their unusual electronic and photophysical properties. They exhibit intense σ→σ* electronic transitions in the near-UV region,1–5 intermolecular charge transfer (CT) complexes involving permethylated oligosilanes have been reported,6,7 and in photoexcited arylsilanes intramolecular CT emission originating from a 1(σ,π*) charge transfer state has been observed.8–12 Furthermore, rapid electron transfer between chromophores connected

1 Department of Physical Organic Chemistry, Utrecht University.
2 Laboratory of Organic Chemistry, University of Amsterdam.
3 Radiation Chemistry Department, IRD, Delft University of Technology.
4 Department of Crystal and Structural Chemistry, Utrecht University.
5 Abstract published in Advance ACS Abstracts, August 1, 1996.
In the present study the potential of the SiMe₂ spacer as a bridge for photoinduced CT is further elaborated and its properties are compared to those of the CMe₂ bridge. To this end we investigated the photophysical and electrochemical properties of 4-donor–4’-acceptor substituted diphenylmethyldisilanes and 2,2-diphenylpropanes and related compounds (Chart 1). It is shown that the charge transporting properties of the two bridges are strongly related to the interaction of these bridges with the donor and acceptor moieties, which can be traced back to the behavior of trimethylsilyl and tert-butyl groups as substituents. In addition, the electronic coupling between involved photophysical states is evaluated. Besides providing insight into the charge transporting capability of monoatomic bridges the present study also contributes to the understanding of photoinduced charge separation processes.

Results

Synthesis. Donor–acceptor substituted silanes 1Si and 2Si were prepared starting from 4-bromophenyl)chlorodimethylsilane (11), obtained by reaction of dichlorodimethylsilane and 4-bromophenyllithium (Scheme 1, reaction 1). Compound 11 was reacted with either 4-(dimethylamino)phenyllithium or 4-methoxyphenyllithium to give 12Si and 13Si, respectively. In this reaction, the use of phenyllithium instead of Grignard reagents gives significantly improved yields. Finally, bromides 12Si and 13Si were converted into the corresponding cyano derivatives 1S1 and 2Si with copper(I) cyanide in DMF (reaction 9). The syntheses of monosubstituted silanes 3Si–8Si and bissubstituted silanes 9Si and 10Si have been reported previously.

4-Methoxy-substituted 2,2-diphenylpropanes 4C and 13C were synthesized by Friedel–Crafts alkylation of anisole with a 2-phenyl-2-propanol in the presence of either phosphoric acid or methanesulfonic acid (reaction 3). Preparation of 4C was conducted with phosphoric acid in 31% yield; however, use of methanesulfonic acid as applied in the synthesis of 13C gave improved results (yield 63%).

Neither a protic acid nor an aluminium chloride mediated Friedel–Crafts route was accessible for (dimethylamino)-diphenylpropanes. Therefore the synthetic pathway started with nitration of 2,2-diphenylpropane with nitronium tetrafluoro-borate to give 2-(4-nitrophenyl)-2-phenylpropane (14) (reaction 4); the bisnitro-substituted compound 15 was also obtained using this method. Bromination of 14 afforded 16, while bromination of 2,2-diphenylpropane gave 17 (reaction 5). Compounds 14, 15, and 16 were reduced to the corresponding amines 18, 19, and 20, respectively. Reduction of 14 and 15 was executed with hydrogen with palladium as catalyst. Bromide 16 was reduced with hydrazine in the presence of a ruthenium catalyst in order to circumvent dehalogenation of the bromophenyl ring. Subsequently amines 18, 19, and 20 were methyalted to their quaternary ammonium salts, which were subsequently cleaved by use of ethanolamine (reaction 7). 2-(4-Bromophenyl)-2-phenylpropane (21) was obtained by reaction of the diazonium salt of amine 20 with hypophosphorous acid (H₃PO₃) (8). Finally, the 4-bromo-substituted diphenylpropanes 12C, 13C, 17, and 21, as well as 4-bromo-tert-butylbenzene, were converted into the corresponding cyano derivatives 1C, 2C, 10C, 5C, and 8C, respectively, using copper(I) cyanide in DMF. tert-Butylanisole (7C) was prepared by methylation of 4-tert-butylenol with iodomethane in the presence of potassium carbonate.

Substituent Effects. In Table 1 UV absorption maxima and intensities of monosubstituted trimethylsilylbenzenes, tert-butylbenzenes, diphenylmethyldisilanes, and 2,2-diphenylpropanes are collected. Inspection of the data reveals that the spectra of 3–10Si and 3–10C are all related to the spectra of N,N-dimethylaniline, anisole, or benzonitrile. The effect of 4-positioned tert-butyl (tBu) and trimethylsilyl (TMS) substituents on the energy levels and electronic spectra of N,N-dimethylaniline and anisole has been discussed previously by Alt and Bock. They pointed out that these substituents do

not affect the SHOMO (HOMO-1) and LUMO owing to their nodal character at the 1 and 4 positions (Figure 2). The HOMO energies of \(N,N\)-dimethylaniline and anisole are slightly raised by the inductively donating tBu substituent. The TMS group is inductively donating as well, but this effect is opposed by its mesomeric electron accepting behavior,\(^{19,37,42}\) so that the net perturbation of the HOMO should be small. These substituent effects are more or less in line with cyclic voltammetry data, which reveal that 6C has a comparable oxidation potential as \(N,N\)-dimethylaniline, whereas the potential of 6Si is somewhat more positive (Table 2). The latter observation suggests that the electron accepting effect of the TMS group is somewhat stronger than the electron donating effect. In contrast, the oxidation potential of anisole seems to be hardly affected by the TMS substituent, whereas for 7C the potential is reduced by some 0.2 V. However, owing to the irreversible nature of the electrode process electrochemical oxidation potentials of anisoles do not adequately reflect their ionization potentials.\(^{40}\)

The \(1\ell_a\) bands of anilines and anisoles correspond predominantly to a HOMO-LUMO transition. Consequently, they are not shifted significantly by tBu and TMS substitution,\(^{37}\) as the orbital amplitudes are either not (LUMO) or only slightly (HOMO) affected by substitution. The tBu group, being an inductive donor, raises both the HOMO and SLUMO, in about equal amounts.\(^{41}\) The \(1\ell_b\) bands of 6C and 7C, which are predominantly based on promotion of an electron from the dimethylamino group.\(^{37}\) The shift of the \(1\ell_a\) band is more pronounced for 7Si than for 6Si because the CT character of the transition is larger for the stronger donating dimethylamino group.

The SLUMO and SHOMO of benzonitrile are insensitive to substitution, again as a consequence of nodes at the 1 and 4 positions. The tBu group raises the energy of the SLUMO, presumably as a result of (\(p-d\))\(^{\pi}\) bonding.\(^{19,37,42}\) This results in a bathochromic shift of ca. 2000 cm\(^{-1}\) for the \(1\ell_a\) transitions, which can be regarded as involving CT from the dimethylamino toward the TMS moiety. The shift of the \(1\ell_a\) band is more pronounced for 6Si than for 7Si because the CT character of the transition is larger for the stronger donating dimethylamino group.\(^{37}\)

The UV and Fluorescence Data, in Cyclohexane, of Donor or Acceptor Substituted Diphenyldimethylsilanes, 2,2-Diphenylpropanes, Trimethylsilylbenzenes, tert-Butylbenzenes, and Benzenes

### Table 1

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<th>(\nu_{\ell_a}^a)</th>
<th>(\nu_{\ell_b}^a)</th>
<th>(\epsilon_{\ell_a}^b)</th>
<th>(\epsilon_{\ell_b}^b)</th>
<th>Fluorescence</th>
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<td>33.3</td>
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<tr>
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<td>19.9</td>
</tr>
<tr>
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<td>33.3</td>
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<td>34.1/33.3</td>
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<td>(\text{C}_6\text{H}_5\text{NMe}_2)</td>
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</tr>
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<tr>
<td>(\text{C}_6\text{H}_5\text{CN})</td>
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<td>12.0</td>
<td>37.0/36.2(^d)</td>
<td>0.62</td>
<td>34.6/33.9</td>
</tr>
</tbody>
</table>

\(^a\) Units 10\(^6\) cm\(^{-1}\), \(^b\) Units 10\(^3\) M\(^{-1}\) cm\(^{-1}\), \(^c\) Fluorescence quantum yield. \(^d\) Main vibrational components; the \(\epsilon_{\text{max}}\) value refers to the most intensive component given in italics.

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Oxidation potentials of donor substituted diphenyldimethylsilanes 3Si and 4Si and 2,2-diphenylpropanes 3C and 4C all are slightly more positive than those of analogously substituted (trimethylsilyl)- and tert-butylbenzenes. Replacement of a methyl group of the SiMe₃ and CMe₃ groups by a phenyl group apparently leads to a somewhat modified substituent behavior. The lowering of the cyanophenyl reduction potential by the dimethylphinosilyl substituent of 5Si is stronger than that by the TMS group of 8Si. The reduction potential of 5C, on the other hand, is higher than that of 8C. Consequently, a difference of 0.22 eV is found between the reduction potentials of 8Si and 8C.

Despite the changes in redox potentials the UV spectra of the monosubstituted diphenyldimethylsilanes and diphenylpropanes hardly differ from the corresponding (trimethylsilyl)- and tert-butylbenzenes. Generally, the positions of 1Lₐ bands are not shifted, while shifts of the 1Lₐ bands are small, ca. 600 cm⁻¹. It can thus be concluded that excitations are localized in the anilino, anisyl, and cyanophenyl moieties. The bissubstituted compounds 9Si, 9C, 10Si, and 10C display the same UV maxima as their analogues of type 3 and 5 as well. Hence, no substantial electronic interaction between two donors or acceptors across silicon and carbon can be inferred. Intensities of the 1Lₐ and 1Lₐ bands of the bissubstituted compounds are to a first approximation twice as large as those of the compounds containing only one dimethylamino or cyano group, reflecting the presence of two identical chromophores in one molecule.

Fluorescence emission maxima and quantum yields are also recorded in Table 1. For a given donor hardly any shift in emission maximum upon substitution is observed whereas distinct differences were found in the UV spectra. Consequently, the type of donor determines the emission wavelength; in the lowest singlet excited state the silicon or carbon containing substituent is not contributing. This compares favorably with the nature of the lowest lying (1Lₐ) excited state as the position of the LUMO is independent of substituents (Figure 2). This also rationalizes that for donor substituted compounds differences in fluorescence maxima between compounds containing SiMe₃ and SiMe₂C₂H₅ groups or CMe₃ and CMe₂C₂H₅ groups, respectively, are marginal. For the cyanides a small difference of some 400 cm⁻¹ between the emission maxima of the carbon and silicon based substituents is observed; the latter are situated at lower energies. Moreover, there is a clear bathochromic shift with respect to benzonitrile. Fluorescence quantum yields of the donor substituted silicon containing compounds 3Si, 4Si, 6Si, and 7Si are generally lower than or equal to the values of their analogues with carbon-based substituents. For the cyanides quantum yields of the silanes are generally higher.

Donor–Acceptor Substituted Compounds. The UV spectra (Figure 3) of the donor–acceptor substituted compounds 1Si, 2Si, 1C, and 2C are composed of the transitions appearing in reference compounds containing only a donor or acceptor chromophore (e.g. 3Si and 5Si for 1Si). It is however seen in Figure 3 that enhanced absorption occurs below 35 000 cm⁻¹, which arises from a transition involving the anilino or anisyl donor and cyanophenyl acceptor orbitals and can be designated as a CT absorption. No concentration dependence on the UV spectra was observed, implying that the CT is intramolecular in nature. The presence of discrete intramolecular CT bands

and LUMO, while the TMS group hardly affects the HOMO energy and stabilizes the LUMO. The cyclic voltammetry data show that the reduction potential of 8Si is 0.12 V lower than that of benzonitrile and 0.22 V lower than that of 8C. The 1Lₐ band, mainly associated with the HOMO-LUMO transition, is shifted by introduction of both the tBu and TMS groups. In the case of 8C this shift is caused by an increase of the HOMO energy, while in the case of 8Si the lowering of the LUMO is responsible. The shift of the benzonitrile 1Lₐ band upon substitution is small.

Figure 2. Qualitative MO diagram of donor benzenes (D = Me₂N, MeO) and benzonitrile and their 4-tert-butyl- and 4-trimethylsilyl substituted derivatives. Orbital coefficients were obtained from extended Hückel calculations (see Experimental Section).

Table 2. Cyclic Voltammetry Data of Donor or Acceptor Substituted Diphenyldimethylsilanes, 2,2-Diphenylpropanes, Trimethylsilylbenzenes, tert-Butylbenzenes, and Benzenes

<table>
<thead>
<tr>
<th>compd</th>
<th></th>
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<th>compd</th>
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<tr>
<td>1Si</td>
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<td>1C</td>
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<tr>
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</table>

α Halve-wave oxidation (Eox) and reduction potentials (Ered) are given in V relative to SCE.


(44) Difference spectroscopy revealed that the CT bands of both 1Si and 1C are situated at 34 800 cm⁻¹, while those of 2Si and 2C are difficult to determine reliably. According to the relation νCT = Eox(D) - Ered(A) + C (compare with eq 3) the CT bands of the silanes should be red shifted to the CT bands of the diphenylpropanes. This discrepancy is in line with an earlier report (ref 47) on the unreliability of determining CT maxima by difference spectroscopy.
A hypsochromic shift for the 1 L a bands of Molecules; Methuen: London, 1963; p 271.

As the intensity of the 1 L a transitions in the spectra of the donor–acceptor compounds is lower than the summation of the acceptor substituted compounds (Table 3) with respect to the 1Lb maxima of the reference compounds suggests that the local transitions mix with the CT transition via configuration interaction. A hypsochromic shift for the 1Lb bands of methoxy compounds 2Si and 2C is not revealed by the data in Table 3 because overlapping of bands obscures the actual maxima. The 1Lb bands are not involved in the CT process because of the presence of nodes at the substitution positions of the orbitals involved in these transitions.

The oxidation and reduction potentials of the donor–acceptor substituted compounds (Table 2) are generally within experimental error equal to those of the separate chromophores. The only redox potential which deviates from that of its separate chromophores is the oxidation potential of 2C. As already discussed above the oxidation potentials of the methoxy compounds are not too reliable. Ground state interactions can thus not be inferred from the cyclic voltammetry data.48

Fluorescence spectra of 1C, 2C, 1Si, and 2Si are highly dependent on the solvent polarity (Table 4). The bathochromic shift with increasing solvent polarity is typical of CT fluorescence originating from a charge separated state D+σA−. The spectra of all compounds consist of a single emission band in all solvents, excepted 1Si in acetonitrile where the CT emission is so weak that another band centered at 25 640 cm−1 becomes visible. This is probably a local emission. Time resolved fluorescence measurements showed that the two emission bands behave independently, indicating that they are related to separate photophysical phenomena.

A quantitative relationship between the CT fluorescence maxima and the solvent polarity is provided by the Lippert–Mataga equation:49

\[ \nu_{\text{CT}} = \nu_{\text{CT}(0)} - \frac{2\mu_e^2}{hc\rho^3} \Delta f \]  

(1a)

with

\[ \Delta f = \frac{\epsilon_s - 1}{2\epsilon_s + 1} - \frac{n^2 - 1}{4n^2 + 2} \]  

(1b)

where \( \nu_{\text{CT}} \) denotes the emission wavenumber, \( \nu_{\text{CT}(0)} \) the (hypothetical) gas-phase emission wavenumber, \( \mu_e \) the excited state dipole moment (the ground state dipole moment is neglected in eq 1a), \( h \) the Planck constant, \( c \) the light velocity, and \( \rho \) the Onsager radius of the solute. The solvent polarity parameter \( \Delta f \) is related to the solvent dielectric constant \( \epsilon_s \) and refractive index \( n \) (eq 1b).50 Plotting of \( \nu_{\text{CT}} \) vs \( \Delta f \) enables the calculation of the excited state dipole moment \( \mu_e \) from the slope of the linear fit, provided that the Onsager radius \( \rho \) of the solute is known.

The solvatochromic relationships are shown in Figure 4, and parameters of these relationships are given in Table 4. For all compounds a satisfactory linear relationship is found. However, the solvatochromic behavior of 2C is more appropriately described by two relationships, one for solvents of low polarity and one for solvents of high polarity, suggesting that as a function of solvent polarity different emitting species are present. This can be rationalized by taking the driving force \( \Delta G^0 \) for photoinduced CT processes into account, which is given by:51

\[ \Delta G^0 = E_{\text{ox}}(D) - E_{\text{red}}(A) - E_{00} + C \]  

(2a)

with

Table 4. Fluorescence Emission Maxima ($\nu_{CT}$) and Quantum Yields ($\Phi_{\text{ct}}$) of Dimethyldisilylene- and Isopropylidene-Bridged Donor–Acceptor Compounds in Various Solvents and Results of Solvatochromic Fits

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<tr>
<th>solvent</th>
<th>$\Delta f$</th>
<th>$\nu_{CT}$</th>
<th>$\Phi_{\text{ct}}$</th>
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<tr>
<td>THF</td>
<td>0.308</td>
<td>19.77</td>
<td>0.07</td>
<td>26.21</td>
<td>0.04</td>
<td>21.65</td>
<td>0.44</td>
<td>27.78</td>
<td>0.26</td>
<td></td>
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<tr>
<td>butyronitrile</td>
<td>0.376</td>
<td>17.67</td>
<td>$d$</td>
<td>24.36</td>
<td>$d$</td>
<td>19.42</td>
<td>$d$</td>
<td>26.39</td>
<td>$d$</td>
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<tr>
<td>acetonitrile</td>
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<td>16.67$^c$</td>
<td>0.0015</td>
<td>23.27</td>
<td>0.13</td>
<td>18.28</td>
<td>0.03</td>
<td>25.00</td>
<td>0.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-2\alpha^3 / \hbar c \rho^3$</td>
<td>36.51</td>
<td>30.78</td>
<td>37.18</td>
<td>26.50</td>
<td>30.78</td>
<td>37.18</td>
<td>26.50</td>
<td>30.78</td>
<td>37.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_{\text{em}}$</td>
<td>31.03</td>
<td>35.61</td>
<td>33.03</td>
<td>35.84$^c$</td>
<td>34.79$^c$</td>
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<td></td>
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<tr>
<td>corr coeff</td>
<td>0.983</td>
<td>0.995</td>
<td></td>
<td>0.989</td>
<td>0.995$^c$</td>
<td>0.975</td>
<td>0.995$^c$</td>
<td>0.975</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

* Units $10^3 \text{ cm}^{-1}$. $^b$ Not used in solvatochromic fit. $^c$ Excitation wavenumber 35 090 cm$^{-1}$. $^d$ Not determined because of solvent absorption at 37 740 cm$^{-1}$. Excitation wavenumber 33 330 cm$^{-1}$ for 1Si and 1C and 35 090 cm$^{-1}$ for 2Si and 2C, respectively. $^e$ Another band observed at 28 640 cm$^{-1}$. $^f$ Polar solvents. $^g$ Nonpolar solvents.

Table 5. Thermodynamic Data for Photoinduced Charge Transfer in Donor–Acceptor Compounds

<table>
<thead>
<tr>
<th>compd</th>
<th>$E_{\text{vis}}$ (eV)</th>
<th>$\Delta G^0$ (eV)</th>
<th>$K_1$ (eV)</th>
<th>$K_2$ (eV)</th>
<th>$E_{\text{vis}}$ (eV)</th>
<th>$\Delta G^0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Si</td>
<td>3.71</td>
<td>$-0.69$</td>
<td>0.09</td>
<td>0.53</td>
<td>0.7</td>
<td>$-0.52$</td>
</tr>
<tr>
<td>1C</td>
<td>3.76</td>
<td>$-0.55$</td>
<td>0.09</td>
<td>0.53</td>
<td>0.7</td>
<td>$-0.49$</td>
</tr>
<tr>
<td>2Si</td>
<td>4.19</td>
<td>$-0.13$</td>
<td>0.09</td>
<td>0.53</td>
<td>2.4</td>
<td>$+0.04$</td>
</tr>
<tr>
<td>2C</td>
<td>4.25</td>
<td>$+0.02$</td>
<td>0.09</td>
<td>0.53</td>
<td>4.4</td>
<td>$+0.08$</td>
</tr>
</tbody>
</table>

* Zero—zero transition energy, taken as the onset of the UV spectrum.

 diphenylpropanes ($R_{DA} = 4.9 \text{ Å}$). The effective radii $r_{DA}^+$ and $r_{DA}^-$ were estimated from the molecular volumes $V_n$ of 1Si (392 Å$^3$) and 1C (364 Å$^3$) in their crystal structures by $r_{DA}^+ = r_{DA}^- = (3V_n/4\pi)^{1/3}$, giving 4.5 Å for 1Si and 2Si and 4.4 Å for 1C and 2C. $K_1$ and $K_5$ values obtained with these parameters are collected in Table 5.

Equation 2c implies that upon going to a less polar solvent $\Delta G^0$ becomes more positive; at a certain medium polarity CT is thermodynamically not allowed anymore. The dielectric constants at which $\Delta G^0$ is zero, $e_s(0)$, and the driving force in cyclohexane ($e_s = 2.015$), is present. The effective radii at which $\Delta G^0$ are given in Table 5. These data show that in the dimethylamino compounds 1Si and 1C photoinduced CT is feasible even in cyclohexane, the most nonpolar solvent. In contrast, CT is forbidden for 2C in solvents with $e_s < 4.4$. This result corresponds nicely to the data shown in Figure 4, which reveal that in diethyl ether ($e_s = 4.2$) and solvents of lower polarity another emitting species is present than in high-polarity solvents. Since the emission in the low-polarity solvents is still moderately solvatochromic, it is anticipated that a partially charge separated state $D^{+\sigma}A^{-\sigma}$ is present. The $e_s(0)$ value for 2Si, 2.4, indicates that this is also the case for this compound in cyclohexane. Indeed the emission maximum for 2Si in cyclohexane deviates from the solvatochromic fit and coincides with the emission maxima of its separate chromophores 4Si and 5Si.

Excited state dipole moments $\mu_e$ were obtained from the slopes of the solvatochromic fits (eq 1a). Radii $\rho$ were estimated by $\rho = (3V_n/4\pi r_{DA}^3)^{1/3}$, giving 4.5 Å for the diphenyldimethylsilanes and 4.4 Å for the diphenypropanes (vide supra). With these values excited state dipole moments of 18.2 (1Si), 17.7 (1C), 16.7 (2Si), 15.0 (2C, polar solvents), and 11.1 D (2C, nonpolar solvents), respectively, were obtained. The $\mu_e$ obtained for 2C in polar solvents seems to be rather small in comparison with the excited state dipole moment of the other compounds, but inspection of Figure 4 reveals that is caused by a somewhat

![Figure 4. Fluorescence solvatochromism of donor–acceptor substituted compounds 1Si (open circles), 1C (filled circles), 2Si (open squares), and 2C (filled squares).](image-url)

\[ C = -\frac{e^2}{\epsilon R_{DA}} - \left(\frac{e^2}{2}\right)\left(\frac{1}{r_{DA}^+} + \frac{1}{r_{DA}^-}\right) - \left(\frac{1}{35.9} - \frac{1}{\epsilon_s}\right) \] (2b)

In these equations $E_{\text{vis}}$ represents the zero—zero excitation energy, $e$ the elementary charge, $R_{DA}$ the donor–acceptor center-to-center distance, and $r_{DA}^+$ and $r_{DA}^-$ the effective radii of the radical cations and anions, respectively. $E_{\text{vis}}(D)$ is the oxidation potential of the donor and $E_{\text{vis}}(A)$ the reduction potential of the acceptor as measured in acetonitrile ($e_s = 35.9$); the term $C$ corrects for the solvent effect by taking into account the Coulombic attraction energy between radical cations and anions and a solvation free energy term. Equations 2a and 2b can be conveniently combined to

\[ \Delta G^0 = \Delta G_{\text{em}}^0 - K_1 + K_2/\epsilon_s \] (2c)

in which $\Delta G_{\text{em}}^0 = E_{\text{vis}}(D) - E_{\text{vis}}(A) - E_{\text{em}}^0$ (e$e$ being infinitely large) and $K_1$ and $K_2$ constants are determined by the type of bridge via $R_{DA}$, $r_{DA}^+$, and $r_{DA}^-$. $R_{DA}$ was taken as the distance between the centers of the aromatic rings in the crystal structure of 1Si for the silanes ($R_{DA} = 5.4 \text{ Å}$) and 1C for the...
deviating emission maximum in butyronitrile. With the exception of the value for 2C in nonpolar solvents, the dipole moments correspond to a unit charge separation over 3.1–3.8 Å. Since the distance between the centers of the anilino or anisyl and cyanophenyl moieties is estimated from X-ray structures to be 5.4 Å for the silanes and 4.9 Å for the carbon compounds, 63–70% of an elementary charge is transferred over the donor–acceptor distance. Although this suggests at first sight that full CT does not take place, obtained μ_e values are very sensitive to the magnitude of ρ. In view of the uncertainty in both ρ and the donor–acceptor distance it is therefore difficult to decide whether full or partial CT occurs.

Excited state dipole moments are thus virtually independent of the bridge and are determined by the donor–acceptor combination only. For a given donor–acceptor combination the almost parallel solvatochromic plots show that the energies of the CT states of the silicon-bridged compounds are a systematic amount lower than those of their carbon-bridged counterparts. This is understood by considering the solvent dependence of the CT state energies E_CT, given by

\[ E_{CT} = E_{ox}(D) - E_{red}(A) + C' - \mu_e^2 \frac{\epsilon_2 - 1}{\rho^2} \frac{\epsilon_3 - 1}{2\epsilon_3 + 1} \tag{3} \]

Taking μ_e, ρ, and the Coulomb term C’ equal for a given donor–acceptor pair, differences in E_CT appear to be determined only by differences in oxidation and reduction potentials. This applies nicely to the dimethylsilylene- and isopropylidene-bridged donor–acceptor compounds. The difference in E_{ox}(D) – E_{red}(A) for the pair 1Si and 1C is 0.19 eV; for 2Si and 2C the value is 0.21 eV (Table 2). The emission wavenumber of 1Si is on average 0.23 eV (1820 cm⁻¹) lower than that of 1C, while the emission energy difference between 2Si and 2C is on average 0.22 eV (1740 cm⁻¹) in the polar solvents. Consequently, a dimethylsilylene bridge provides an energetically more favorable pathway for CT to occur than an isopropylidene bridge by relatively lowering the CT state by some 0.2 eV. Full CT probably occurs for instance in 2Si in ethereal solvents, whereas only partial CT is observed in its analogue 2C in these solvents. As was seen above the 0.2-eV difference is predominantly caused by a lowering of the cyanophenyl acceptor reduction potential by the dimethylsilylene bridge.

Time-Resolved Microwave Conductivity Studies. The nature of the excited state of 1Si and 1C was further elucidated using the flash-photolysis time-resolved microwave conductivity (TRMC) technique. The formation of dipolar excited states upon pulsed laser photoexcitation (flash-photolysis) leads to an increase in the high-frequency dielectric loss of a solution. Using the TRMC technique this increase is monitored by time-resolved measurement of the change in microwave conductivity Δσ which is related to the difference in dipole moment of the excited state μ_e and ground state μ_g according to:

\[ Δσ = (\epsilon_2 + 2)N(\mu_e^2 - \mu_g^2)F_{ωθ}27k_BTΩ \tag{4} \]


Figure 5. Time-resolved microwave conductivity transients of 1Si (top) and 1C (bottom) in benzene. Apart from the measured signals the singlet and triplet components of the fits to the experimental data are shown.

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\[ Δσ = (\epsilon_2 + 2)N(\mu_e^2 - \mu_g^2)F_{ωθ}27k_BTΩ \tag{4} \]

with N being the solute concentration, k_b the Boltzmann constant, T the temperature, and F_{ωθ} a factor containing the applied microwave frequency ω and the dipole relaxation time Θ: \( F_{ωθ} = (ω/Ω)^2[1 + (ω/Ω)^2] \). The dipole relaxation time Θ,

values of \( \Theta \) together with PM3 calculated ground state dipole moments of 5.0 (1SI) and 4.1 D (1C) results in estimates of the excited state dipole moments within the range 16 D < \( \mu_\text{exc} < 25 \) D and 15 D < \( \mu_\text{exc} < 23 \) D for 1SI and 1C, respectively. The actual dipole moments would be expected to lie close to the means of these extremes, i.e. 20.5 and 19 D. The values of 18.2 and 17.7 D determined from solvatochromic shifts are seen to be in reasonably good agreement with these estimates from the TRMC experiment.

Radiative Decay Rates and Internstate Electronic Couplings. Fluorescence quantum yields of the donor–acceptor compounds display a general trend of maximizing at medium solvent polarity (Table 4). Often a monotonous decrease with increasing medium polarity is found for donor–acceptor systems. The trend in quantum yields found here has been explained previously by the occurrence of intersystem crossing to locally excited triplet states in nonpolar solvents. Fluorescence lifetimes \( \tau_\text{fl} \) of 1SI and 1C, presented in Table 6, follow a similar trend to the quantum yields: they reach a maximum of 18.2 and 17.7 D determined from solvatochromic shifts are seen to be in reasonably good agreement with these estimates from the TRMC results.

Most remarkably the fluorescence lifetime of 1C is longer in polar media, while in less polar solvents such as diethyl ether and benzene it is shorter. In cyclohexane the lifetime of 1C is again longer. Intuitively it is expected that, since the CT state of 1SI is systematically situated at lower energies, charge recombination in 1SI is faster and hence its fluorescence lifetimes will be shorter. The situation becomes more clear when the radiative decay rates, defined by \( k_\text{rad} = \Phi_{\text{fl}}/\tau_\text{fl} \), are taken into consideration (Table 6); in a given solvent the decay of the CT state of 1C is faster than that of 1SI. The still remaining marked solvent dependence of the radiative rates of both compounds strongly suggests that locally excited (LE) states are involved in the decay process, via intensity borrowing.\(^{(59)}\) The involvement of LE states can qualitatively be understood by the fact that owing to the small donor–acceptor separation and hence small excited state dipole moments the solvent stabilization on the CT states of 1SI and 1C is relatively small (eq 3). The CT states are thus lying close to the LE states, promoting their mutual electronic coupling.

When LE states are involved in the radiative decay process the decay rate depends, in addition to the electronic coupling between the ground and CT state \( \nu \), on the coupling between the LE and CT state \( \nu^* \) and the transition dipole moment \( \mu_\text{exc} \) of the local excitation of energy \( E_{\text{LE}} \).\(^{(60)}\)

\[
\text{(5)}
\]
\[
k_\text{rad} = \frac{64\pi^4 n^3}{3h} \left( |\langle V \mu_\text{exc} \rangle^2 v_{\text{CT}}^2 + 2V^* \langle \Delta \mu \cdot \mu_\text{LE} \rangle v_{\text{CT}}^2 (E_{\text{LE}} - v_{\text{CT}}) + \langle V^* \mu_\text{LE} \rangle^2 v_{\text{CT}}^2 (E_{\text{LE}} - v_{\text{CT}})^2 \right)
\]

In eq 5 \( \Delta \mu = \mu_\text{exc} - \mu_\text{le} \) and the couplings between states are defined by \( V = \langle D^+ \alpha^+ \alpha | H | D \alpha^+ \alpha \rangle \) and \( V^* = \langle D^+ \alpha^+ \alpha | H | D^+ \alpha \rangle \). When the mixing of the CT state with the LE state dominates the decay process only the last term of eq 5 has to be taken into account, leading to

\[
\text{(6)}
\]
\[
k_\text{rad} = \frac{64\pi^4 n^3}{3h} V^* \mu_\text{LE} \nu_{\text{CT}} (E_{\text{LE}} - v_{\text{CT}})^2
\]

This relationship predicts a linear relationship between \( k_\text{rad}n^3 \) and \( v_{\text{CT}}^2 (E_{\text{LE}} - v_{\text{CT}})^2 \). Taking \( E_{\text{LE}} = 37 \ 300 \ \text{cm}^{-1} \) for 1SI and \( E_{\text{LE}} = 39 \ 100 \ \text{cm}^{-1} \) for 1C (the maxima of the \( \lambda_{\text{max}} \) bands, the nearest lying bands for which mixing with the CT state is symmetry allowed) indeed linear relations are found between these quantities (Figure 6). The linear fit for 1SI is excellent, whereas that for 1C is somewhat less satisfactory. Nevertheless, the coupling between the CT and LE states in both 1SI and 1C is convincingly demonstrated. The coupling parameter \( V^* \) can be obtained from the slope of the fits, provided that \( \mu_\text{LE} \) is known. This transition dipole moment is obtained using

\[
\text{(7)}
\]
\[
|\mu_{\text{LE}}|^2 = \frac{3 \hbar^2 f_{\text{LE}}}{8 \pi^2 m_\text{e} \omega_{\text{LE}}}
\]

with \( \omega_{\text{LE}} \) the absorption frequency (s\(^{-1}\)) and \( 3 \hbar^2 / 8 \pi^2 m_\text{e} = 7.095 \times 10^{14} \ \text{m}^2 \text{~s}^{-1} \text{~C}^2 \). The oscillator strength of the local excitation \( f_{\text{le}} \) is given by

\[
\text{(8)}
\]
\[
f_{\text{LE}} = (4.32 \times 10^{-9}) \nu_{\text{max}} \Delta \nu_{1/2}
\]

where \( \Delta \nu_{1/2} \) is the band width at half height in cm\(^{-1}\). The values of interest for 1SI are \( \Delta \nu_{1/2} = 2890 \ \text{cm}^{-1} \), \( f_{\text{LE}} = 0.35 \), and \( \mu_{\text{LE}} = 4.4 \ \text{D} \). For 1C they are \( \Delta \nu_{1/2} = 3540 \ \text{cm}^{-1} \), \( f_{\text{LE}} = 0.29 \), and \( \mu_{\text{LE}} = 4.0 \ \text{D} \). It follows that \( V^* = 2190 \ \text{cm}^{-1} \) for 1SI and \( V^* = 4080 \ \text{cm}^{-1} \) for 1C. The CT state of 1C is thus stronger coupled to the LE state than is the case for 1SI.

According to eq 6 the fits in Figure 6 should have an intercept of zero. This applies for 1SI but not for 1C. Consequently, lower order terms in eq 5 including \( V \) should be taken into consideration to describe the behavior of 1C, whereas they can be neglected for 1SI. It can thus be concluded that the electronic coupling between the CT and ground state \( V \) is larger for the carbon compound as well.\(^{(63)}\)

**Table 6.** Solvent Dependence of Fluorescence Lifetimes and Radiative Decay Rates

<table>
<thead>
<tr>
<th>solvent</th>
<th>( \tau_{\text{fl}} )</th>
<th>( k_{\text{rad}} )</th>
<th>( g^\ast )</th>
<th>( \tau_{\text{fl}} )</th>
<th>( k_{\text{rad}} )</th>
<th>( g^\ast )</th>
</tr>
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<tbody>
<tr>
<td>cyclohexane</td>
<td>1.7</td>
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<td>78.6</td>
<td>0.19</td>
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<td>benzene</td>
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<td>6.7</td>
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<td>21.4</td>
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<tr>
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<td>28.5</td>
<td>0.077</td>
</tr>
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<td>ethyl acetate</td>
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<td>0.016</td>
<td>34.0</td>
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<tr>
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<td>0.83</td>
<td>0.011</td>
<td>5.0</td>
<td>6.0</td>
<td>0.038</td>
</tr>
</tbody>
</table>

\(^\ast\) Units ns. \(^\ast\) Units \( 10^6 \) s\(^{-1}\). \(^\ast\) Lifetime obtained with TRMC experiment.

---

The foregoing analysis is valid on the conditions that the degree of admixture of the LE state into the CT state \( g^* \), given by

\[
g^* = \frac{[V^*/(E_{LE} - \nu_{CT})]^2}{(9)}
\]

is small: \( g^* < 0.1 \) and \( V^* \approx E_{LE} - \nu_{CT} \). These conditions are fulfilled quite well with the exception of 1C in cyclohexane \( (g^* = 0.19, \text{Table 6}) \). It must however be realized that the obtained \( V^* \) values are strongly associated with the magnitude of the local excitation transition dipole moment \( \mu_{LE} \), as the product \( V^*/\mu_{LE} \) is obtained from the slopes of the fits. It has been shown\(^{62} \) that application of \( \mu_{LE} \) of only the first local transition often leads to an underestimated value. The effective magnitude of \( \mu_{LE} \), which incorporates contributions of several local excitations, may be a factor of 3 to 4 larger. The consequence is that \( V^* \) (and hence \( g^* \)) is the same factor smaller, and in retrospect the applied analysis is justified.

The \( g^* \) data show that the admixture of the LE into the CT state decreases with increasing solvent polarity. The consequence is that CT state lifetimes are short in nonpolar solvents because decay \textit{via} the short lived LE state is prominent. The shorter lifetimes of 1C in nonpolar media are related to the larger extent of mixing of the CT and LE states in this compound. In polar solvents the lifetimes are more an intrinsic property of the CT states themselves. In these solvents the lifetimes of 1Si are shorter since its CT state is situated at lower energies. Furthermore the small \( g^* \) value in all solvents indicates that CT state dipole moments are hardly affected by the admixture of LE states, and can be considered to be virtually independent of the solvent polarity.

Solid State Structures and Properties of 1Si and 1C. The molecular structures of 1Si\(^{62} \) and 1C have been determined by single-crystal X-ray diffraction (Figure 7, Tables 7–9). Both compounds crystallize in the same space group (Pnma), are located on a crystallographic mirror plane, and possess similar structures. In both compounds the geometry around the bridging nitrogen atoms is nearly planar, indicating that these nitrogen atoms. The electron density is essentially tetrahedral, with bond angles ranging from 107.00(6)° to 112.11(8)° in 1Si and from 107.7(2)° to 111.2(2)° in 1C (Table 9). The geometry around the dimethylamino nitrogen atoms is nearly planar, indicating that these nitrogen atoms are to a large extent sp\(^2 \) hybridized. In 1C the sum of bond angles around N(2) is 356.3(4)°, and the C(13)–N(2)–C(12)–C(11) dihedral angle is 12.7(5)°. In the silane the corresponding parameters are 347.09(18)° and 10.8(2)°. The sp\(^2 \) hybridization of nitrogen atoms, allowing maximal overlap between their lone pairs and the benzene π-systems, is usual for \( N,N \)-diminelines.\(^{64} \)

Interestingly, an increased quinoid character of the ground state of the (dimethylamino)phenyl group in 1Si can be distinguished. This quinoid contribution can be expressed by a parameter \( Q \), which is in this case

\[
Q = 1/2(d_{10-10} + d_{11-12}) - d_{10-11}
\]

where \( d \) denotes the distance between the indicated carbon atoms. \( Q \) is zero for \( D_{6h} \) benzene, and 0.138 for a perfect quinoid structure with a single bond length of 1.455 Å and a double bond length of 1.317 Å.\(^{65} \) For the (dimethylamino)-phenyl ring in 1Si \( Q \) is 0.018(2) Å, while it is 0.000(5) Å in 1C. The latter result is somewhat surprising, since a small quinoid contribution is expected to be present in diminelines. We attribute the apparent absence of quinoid contributions in 1C to the unexpected short C(9)–C(10) distance of 1.383(3) Å. Even though the increased quinoid character in 1Si is indicative of a (ground state) CT interaction between the dimethylamino group and the silicon bridge, reflecting the latter’s electron accepting properties. The presence of the CT interaction in 1Si is also manifested by the shorter N(2)–C(12) distance (1.377(2) Å in 1Si, 1.393(5) Å in 1C) and the larger difference between the M–C(9) bond length (1.8576(19) Å in

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Q = 1/2(d_{10-10} + d_{11-12}) - d_{10-11}
\]

where \( d \) denotes the distance between the indicated carbon atoms. \( Q \) is zero for \( D_{6h} \) benzene, and 0.138 for a perfect quinoid structure with a single bond length of 1.455 Å and a double bond length of 1.317 Å.\(^{65} \) For the (dimethylamino)-phenyl ring in 1Si \( Q \) is 0.018(2) Å, while it is 0.000(5) Å in 1C. The latter result is somewhat surprising, since a small quinoid contribution is expected to be present in diminelines. We attribute the apparent absence of quinoid contributions in 1C to the unexpected short C(9)–C(10) distance of 1.383(3) Å. Even though the increased quinoid character in 1Si is indicative of a (ground state) CT interaction between the dimethylamino group and the silicon bridge, reflecting the latter’s electron accepting properties. The presence of the CT interaction in 1Si is also manifested by the shorter N(2)–C(12) distance (1.377(2) Å in 1Si, 1.393(5) Å in 1C) and the larger difference between the M–C(9) bond length (1.8576(19) Å in

### Table 7. Crystallographic Data for 1Si and 1C

<table>
<thead>
<tr>
<th></th>
<th>1Si</th>
<th>1C</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C(<em>{17})H(</em>{20})N(_{2})Si</td>
<td>C(<em>{18})H(</em>{20})N(_{2})</td>
</tr>
<tr>
<td>mol wt</td>
<td>280.44</td>
<td>264.37</td>
</tr>
<tr>
<td>cryst system</td>
<td>orthorhombic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>space group</td>
<td>Pnma (No. 62)</td>
<td>Pnma (No. 62)</td>
</tr>
<tr>
<td>a, Å</td>
<td>11.7053(5)</td>
<td>11.4551(12)</td>
</tr>
<tr>
<td>b, Å</td>
<td>9.7903(10)</td>
<td>9.6451(12)</td>
</tr>
<tr>
<td>c, Å</td>
<td>13.6840(14)</td>
<td>13.1648(13)</td>
</tr>
<tr>
<td>V, Å(^3)</td>
<td>1568.2(2)</td>
<td>1454.5(3)</td>
</tr>
<tr>
<td>D(_{2o}), g·cm(^{-3})</td>
<td>1.188</td>
<td>1.207</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>F(000)</td>
<td>600</td>
<td>568</td>
</tr>
<tr>
<td>μ[Mo Kα], cm(^{-1})</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>crystal size, mm</td>
<td>0.5 × 0.4 × 0.4</td>
<td>0.4 × 0.2 × 0.2</td>
</tr>
<tr>
<td>T, K</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>final R(^e) &amp; wR(^2)</td>
<td>0.042 [1582F(_o) &gt; 4σ(F(_o))] &amp; 0.066 [799F(_o) &gt; 4σ(F(_o))]</td>
<td>0.098 &amp; 0.138</td>
</tr>
<tr>
<td>goodness of fit</td>
<td>1.06</td>
<td>0.99</td>
</tr>
</tbody>
</table>

\( R = \sum||F_o||-|F_c||/\sum|F_o| \), \( \text{wR}^2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2} \).
**Table 8.** Bond Lengths (Å) in 1Si and 1C with esd’s in Parentheses

<table>
<thead>
<tr>
<th>Bond</th>
<th>1Si</th>
<th>1C</th>
<th>Bond</th>
<th>1Si</th>
<th>1C</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)–C(7)</td>
<td>1.122(3)</td>
<td>1.140(6)</td>
<td>C(4)–C(5)</td>
<td>1.396(3)</td>
<td>1.400(6)</td>
</tr>
<tr>
<td>N(2)–C(12)</td>
<td>1.377(2)</td>
<td>1.393(5)</td>
<td>C(4)–C(7)</td>
<td>1.462(3)</td>
<td>1.453(6)</td>
</tr>
<tr>
<td>N(2)–C(13)</td>
<td>1.448(2)</td>
<td>1.448(4)</td>
<td>C(5)–C(6)</td>
<td>1.384(3)</td>
<td>1.380(7)</td>
</tr>
<tr>
<td>C(1)–C(2)</td>
<td>1.402(3)</td>
<td>1.391(6)</td>
<td>C(8)–M</td>
<td>1.861(19)</td>
<td>1.541(4)</td>
</tr>
<tr>
<td>C(1)–C(6)</td>
<td>1.398(3)</td>
<td>1.407(6)</td>
<td>C(9)–C(10)</td>
<td>1.397(13)</td>
<td>1.383(3)</td>
</tr>
<tr>
<td>C(1)–M</td>
<td>1.887(2)</td>
<td>1.542(5)</td>
<td>C(9)–M</td>
<td>1.857(16)</td>
<td>1.531(6)</td>
</tr>
<tr>
<td>C(2)–C(3)</td>
<td>1.379(3)</td>
<td>1.387(6)</td>
<td>C(10)–C(11)</td>
<td>1.385(19)</td>
<td>1.390(4)</td>
</tr>
<tr>
<td>C(3)–C(4)</td>
<td>1.393(3)</td>
<td>1.381(6)</td>
<td>C(11)–C(12)</td>
<td>1.405(16)</td>
<td>1.397(3)</td>
</tr>
</tbody>
</table>

* M: Si(1) in 1Si, C(14) in 1C.

1Si, 1.531(6) Å in 1C and the M–C(1) bond length (1.8872–(18) Å in 1Si, 1.542(5) Å in 1C). Thus, the difference between these bond lengths is 0.030(3) Å for 1Si and 0.011(8) for 1C. Quinoid contributions in the cyanophenyl moieties of 1Si (Q = 0.016(7) Å) and 1C (Q = 0.011(14) Å) are of similar magnitude.

The most remarkable feature in the X-ray structures is the orthogonality of the donor and acceptor chromophores, with the cyanophenyl moieties lying in the plane bisecting the (dimethylamino)phenyl groups. Concerning 1Si this geometry differs markedly from the X-ray structure of dimethylbis-(tetraethialfulvanelyl)silane, which possesses a butterfly conformation (see Figure 9) with an angle of 88.92° between the normals to the tetraethialfulvanelyl planes. Other 2,2-diphenylpropanes in which the phenyl groups are arranged orthogonally are known, but scarce. It would be expected that attractive forces between the donor and acceptor moieties force 1Si and 1C in particular into a spatial arrangement in which a through-space donor–acceptor interaction is possible. Apparently these forces are weak. It is not so that the orthogonal geometry around the bridging atoms prevents steric repulsions between the methyl carbon atoms and phenyl protons positioned ortho to the bridge. A close contact of 2.57(3) Å between C(8)a and H(10) is found in the structure of 1C. This distance, which is 0.33 Å less than the sum of contact radii of carbon and hydrogen (2.90 Å), has also been reported to be present in another conformation of the 2,2-diphenylpropane skeleton.

The steric crowding leads to a nonequivalence of the C(1)–C(9) bond and an intermolecular through-space ground state interaction. Although an NMR study on 4-substituted diphenyldimethylsilanes and 2,2-diphenylpropanes provided evidence that substituent effects extend beyond the bridging atoms, this transmission of substituent effects, indicative of a ground state interaction, is operative via σ-orbitals (bond polarization mechanism), which prevents an interaction with orbitals of π-symmetry. An intramolecular through-space donor–acceptor interaction in the solid state structures of 1Si and 1C is however feasible. All π-type orbitals of the cyanophenyl moiety are antisymmetric with respect to the crystallographic mirror plane, and can overlap with (dimethylamino)phenyl orbitals such as the SHOMO and the LUMO (Figure 2) which are antisymmetric with respect to this plane as well. In particular p-type AO’s of atom C(2), which is nearest to the dimethylamino ring, are involved. The overlap must however be very small, suggesting once more that intensity borrowing contributes significantly to the CT transitions.

**Discussion and Conclusions**

The apparently conflicting situation has arisen that the electronic interactions of the bridge with the donor and acceptor orbitals are orthogonals to each other.
evaluate the intrinsic ability of silicon, as compared to carbon, other hand, the electronic coupling of the CT state with both bridge, which can be traced back to a lowering of the twist (propeller) and butterfly forms. Especially in the coupling of the CT state with both the LE and the ground state, which is primarily associated to its smaller size. The photodynamics charge transfer is more favorable for the SiMe₂ bridge, i.e. mononatomically bridged diphenyls, are the twist (propeller) and butterfly forms. Especially in the latter conformation spatial overlap between p atomic orbitals on phenyl carbon atoms adjacent to the bridge is possible (Figure 9). Since the C–C bond length is shorter than the Si–C bond length (Table 8), the spatial overlap is larger for the carbon-bridged compounds, which explains the stronger inter-state couplings. This way of reasoning is supported by the supposed larger rate of intersystem crossing via exciton coupling in the diphenylpropanes. Another contemplation which suggests the involvement of a through-space mechanism is that, even when in solution the orthogonality of the donors and acceptors exists, the geometry of excited states can be quite different.

In summary, the nature of the mononatogenic bridges under investigation has a profound effect on the CT process. Thermodynamically charge transfer is more favorable for the SiMe₂ bridge, which can be traced back to a lowering of the cyanophenyl reduction potential by the silicon bridge. On the other hand, the electronic coupling of the CT state with both the LE state and the ground state is larger for the CMe₂ bridge, which is primarily associated to its smaller size. The photo-physics of SI Si and 1C, in which the donor–acceptor distance is very short, are dominated by intensity borrowing, which has been demonstrated by both the solution and solid state electronic spectra and the radiative decay behavior.

Furthermore, we have shown that an intramolecular CT absorption occurs in a donor–acceptor substituted monosilane, while other workers could not detect such an absorption.23,24 The CT absorption is however likely to be based on a through-space interaction, by which it is unfortunately not possible to evaluate the intrinsic ability of silicon, as compared to carbon, to transmit electronic effects.

The intensity of the CT absorption is too small to expect interesting second-order nonlinear optical responses for donor–acceptor substituted diphenyl(dimethyl)silanes, despite the quite large excited state dipole moments. It has indeed been recognized previously that the first hyperpolarizability of donor–acceptor substituted diphenyl(dimethyl)silanes can be described by a vector summation of the hyperpolarizabilities of the Dσ and σA chromophores. The same should be true for the donor–acceptor substituted 2,2-diphenylpropanes.

**Experimental Section**

**General.** Reactions involving organolithium reagents and/or silyl chlorides were conducted in a nitrogen atmosphere using standard Schlenk techniques. Starting materials and reagents were obtained from commercial sources and used as received. Acetone, DMF, DMSO, and methanol were stored on 4 Å or 3 Å molecular sieves prior to use. Other solvents generally were distilled before use; diethyl ether was distilled from sodium/hexane. Column chromatography was performed on Merck kieselgel 60 silica (230–400 ASTM).

NMR spectra were obtained on a Bruker AC 300 apparatus, operating at 300 MHz for 1H, 75 MHz for 13C, and 60 MHz for 31Si. Solid NMR spectra were recorded with a proton decoupled inverse gated pulse sequence; samples contained chromium(III) acetylacetonate as relaxation reagent. Infrared spectra were recorded using a Perkin Elmer 283 infrared spectrometer. Solids were measured as KBr pellets and liquids between NaCl plates. GC-MS spectra were collected on an ATI Unicam Automass System 2 quadrupole mass spectrometer. Melting points were determined using a Mettler FP5/FPS1 photoelectric apparatus. For gas chromatography a Varian 3700 chromatograph equipped with a DB5 capillary column was used. Elemental analyses were carried out at Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

Cyclic voltagmetry measurements were performed with a Heka PG 287 potentiostat/galvanostat in acetonitrile (Janssen p.A. grade, freshly distilled from calcium hydride) containing 0.1 M tetraethylammonium hexafluorophosphate (Fluka, electrochemical grade) as supporting electrolyte at scanning rates of 0.1 V/s⁻¹. Redox potentials were determined relative to Ag/0.1 M AgNO₃ in acetonitrile and were referenced to SCE by regularly measuring the oxidation potential of the FeCp/FeCp⁺ couple (EQ x vis SCE = 0.31 V V⁻¹) in this system.

Solution UV spectra were measured using a Cary 1 spectrometer in spectrophotometric grade solvents (Janssen). Solid state UV spectra were collected with a Cary 5 UV–vis–NIR spectrophotometer using a Harrick praying mantis diffuse reflectance accessory on powdered dispersions (approximately 1% w/w) in KBr. Reflectance ordinates R were transformed into Kubelka-Munk units F(R) by F(R) = (1 − R)/2R. Fluorescence spectra were obtained on a Spex Fluorolog instrument, equipped with a Spex 1680 double excitation monochromator, a Spex 1681 emission monochromator, and a Spex 1911F detector. Solvents (Janssen) generally were of spectrophotometric grade and dried on molecular sieves prior to use. Butyronitrile (Janssen, p.A.), di-n-butyl ether (Janssen, 99%), and di-n-pentyl ether (Aldrich, 99%) were distilled before use. Fluorescence emission spectra were corrected for the detector spectral response with the aid of a correction file provided by the manufacturer. Since this file does not cover the spectral range above 33300 cm⁻¹, fluorescence maxima in this region are uncorrected. Fluorescence quantum yields were determined relative to naphthalene (Φₑ = 0.23) at an excitation wavelength of 265 nm. Solutions were degassed by purging with argon during 15 min. Fluorescence lifetimes were determined using a Lumonix EX700 XeCl excimer laser (308 nm)
nm, 8.4 ns (fwhm) as excitation source, monitoring the fluorescence signal at a right angle by a RCA C-31025C photodiode via a Zeiss M2Q II monochromator. The signal was fed into a Tektronix TDS 684A oscilloscope triggered by a photodiode that detects the laser pulse. Samples (A < 0.2 at 308 nm) were degassed by purging with argon. A description of the equipment and experimental details of the flash photolysis TRMC technique can be found elsewhere. 3,5,36

Extended Hückel (EH) calculations were performed with the CACAO program 37,38 on M378 optimized (precise option) geometries. Silicon δ orbital parameters, not implemented in CACAO, were taken from the Forticon8 program.39 Other parameters used in both programs are identical. All calculations were run on a 486/33 MHz personal computer.

X-ray Structure Determinations. Details of the structure determination of 4SI have been reported elsewhere;26 pertinent data have been included in Table 7. A colorless crystal of IC suitable for X-ray diffraction was glued to the tip of a Lindemann-glass capillary and transferred into the cold-nitrogen stream of an Enraf-Nonius CAD-4 T diffractometer on rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of 25 well-centered reflections (SET41) in the range 11.40° < θ < 14.05°. The unit-cell parameters were checked for the presence of higher lattice symmetry.82 Crystal data and some details on data collection are presented in Table 7. Reflection data were collected in o scan mode with scan angle Δω = 0.50 + 0.35 tan θ°. Intensity data of 3869 reflections were collected in the range 1.55° < θ < 27.50°, 1768 of which are independent. Data were corrected for Lp effects and for a linear decay of 6% of the three periodically measured reference reflections (2 2 2, 2 2 0, 2 0 2) during 10 h of X-ray exposure.30 The crystal structure was solved by automated direct methods (SHELXL83). Refinement on F2 was carried out by full-matrix least-squares techniques (SHELXL-93 84). All calculations were performed on a DECstation 5000 cluster.

Syntheses. The preparation of the compounds 3SI, 4SI, 5SI, 6SI, 7SI, and 8SI has been reported previously.29 The preparation and characterization of synthetic intermediates 13SI, 2-(4-bromophenyl)-2-propanol, 13C, 14, 15, 16, 17, 18, 19, 20, 12C, and 21 is described in the supporting information. 4-tert-Butyl-N,N-dimethylsilanilic (6C) was purchased from Aldrich and used as received.

(4-Bromophenyl)(4-dimethylamino)phenyl)dimethylsilane (12SI). A solution of 4-bromo-N,N-dimethylsilanilic (6.7 g, 35.3 mmol) in 50 mL of diethyl ether was added dropwise to finely cut lithium pieces (0.68 g, 27.7 mmol) in 20 mL of diethyl ether. The mixture was stirred overnight at room temperature. The solution was filtered over quartz wool into a dropping funnel and added to a solution of 11 (8.01 g, purity 85%, 27.3 mmol) in 20 mL of diethyl ether, after which the mixture was refluxed overnight. Water (25 mL) was added cautiously, and the layers were separated. Subsequently the organic layer was washed with 3 × 25 mL of a 10% ammonium chloride solution, dried on magnesium sulfate, and filtered. After concentration under reduced pressure a purple liquid was obtained, which solidified on standing. 12SI (7.32 g, 21.9 mmol, 80%) was obtained in the form of white crystals after flash chromatography (silica, chloroform) and recrystallization from pentane. Mp 58 °C. 1H NMR (CDCl3): δ 7.50 and 7.41 (AA′BB′, 2H, Ar-H), 2.99 (s, 6H, NMe), 0.53 (s, 6H, SiMe). 13C NMR (CDCl3): δ 151.2, 138.4, 135.8, 135.3, 130.8, 123.7, 122.2, 112.0 (all aromatic C), 40.2 (NMe2), −2.2 (SiMe). 29Si NMR (CDCl3): δ −8.4. IR (KBr): 2815 (NMe2), 1250, 835 (SiMe2). 1115 (Si-Ar) cm−1.

(4-Cyanophenyl)(4-dimethylamino)phenyl)dimethylsilane (15SI). In a nitrogen atmosphere, a mixture of 12SI (2.52 g, 7.54 mmol), copper(I) cyanide (0.82 g, 9.15 mmol), and 5 mL of DMF was refluxed for 5 h. The cooled brownish mixture was then poured into 100 mL of 25% ammonium. After passing air through this suspension for 3.5 h under vigorous stirring, it was extracted with 3 × 30 mL of chloroform. The combined organic layers were concentrated to a volume of ca. 10 mL, and 75 mL of hexane was added. This solution was washed with water (3 × 50 mL), dried on magnesium sulfate, filtered, and evaporated under reduced pressure. The resulting brownish solid was purified by flash chromatography (eluent chloroform) and recrystallization from methanol. Yield 1.58 g (56.3 mmol, 75%) of block shaped crystals with a greenish glance. Mp 128 °C. Anal. Calc. for C19H18N2Si: C, 71.87; H, 7.19; N, 9.99. Found: C, 71.62; H, 7.25; N, 9.95. Si, 9.88. 1H NMR (CDCl3): δ 7.66 and 7.61 (AA′BB′, 2H, Ar-H), 7.42 and 6.79 (AA′XX, 2H, Ar-H), 3.01 (s, 6H, NMe), 0.58 (s, 6H, SiMe). 13C NMR (CDCl3): δ 151.4, 146.7, 135.3, 134.6, 130.9, 121.0, 112.4, 112.0 (all aromatic C), 119.2 (CN), 40.1 (NMe2), −2.4 (SiMe). 29Si NMR (CDCl3): δ −7.9. IR (KBr): 2800 (NMe2), 2300 (CN), 1260, 835–800 (SiMe2), 1115 (Si-Ar) cm−1.

(4-Cyanophenyl)(4-methoxyphenyl)dimethylsilane (25SI). This compound was prepared as described for its dimethylamino analogue 15SI. It was purified by column chromatography (eluent chloroform) and obtained as white crystals upon trituration with methanol. Yield 76%. Mp 41 °C. Anal. Calc. for C21H18N2SiO: C, 71.87; H, 6.41; N, 5.24; Si, 10.50. Found: C, 70.21; H, 6.50; N, 5.11; Si, 10.15. 1H NMR (CDCl3): δ 7.60 (AA′BB′, 4H, Ar-H), 7.42 and 6.94 (AA′XX, 2H, Ar-H), 3.83 (s, 3H, OMe), 0.56 (s, 6H, SiMe). 13C NMR (CDCl3): δ 160.9, 145.9, 135.6, 134.6, 131.0, 127.2, 113.9, 112.6 (all aromatic C), 119.0 (CN), 55.1 (OMe), −2.5 (SiMe). 29Si NMR (CDCl3): δ −7.4. IR (KBr): 2800, 1250, 1030 (Ar-O-Me), 2255 (CN), 1255, 840–800 (SiMe2), 1115 (Si-Ar) cm−1.

2-(4-Methoxyphenyl)-2-phenylpropane (4C). In a 1-necked flask 2-phenylpropanol (3.78 g, 27.7 mmol) and 85% phosphoric acid (3 mL, 43.8 mmol) were mixed. To the white suspension was added anisole (3.00 g, 27.7 mmol) and the mixture was stirred overnight at 90 °C. After addition of 25 mL of diethyl ether the solution was washed three times with 15 mL of water, dried on magnesium sulfate, and filtered. The diethyl ether was removed in a rotary evaporator and the mixture was kugelrohr distilled, collecting the fraction boiling in the
Comparison between SiMe2 and CMe2 Spacers as σ-Bridges

15-329′-81.31; H, 6.78; N, 5.49; O, 6.45. 1 H NMR (CDCl3): δ 2220 (CN) cm−1, 127.5, 110.2 (all aromatic C), 118.6 (CN), 43.9 (H, 5.71; N, 11.31. 1 H NMR (CDCl3): δ 157.2, 148.9, 136.9, 131.8, 127.6, 127.4, 112.4, 109.3 (all aromatic C), 119.2 (CN), 42.6 (CMe), 40.6 (NMe), 30.5 (CMe). IR (KBr): 2820 (NMe2), 2230 (CN) cm−1.

2-(4-Cyanophenyl)-2-(4-methoxyphenyl)propane (2C). This compound was prepared from 13C (1.8 g, 9.3 mmol) and copper(I) cyanide (0.63 g, 7.08 mmol) as described for Si. The crude product was purified by column chromatography (eluent chloroform–hexane 2:1 (v/v) to give 1.07 g (4.26 mmol, 72%) of a colorless liquid. Anal. Calcd for C17H17N: C, 85.31; H, 8.84; N, 5.85. Found: C, 85.21; H, 8.81; N, 5.79. 1H NMR (CDCl3): δ 7.36 (m, 4H, Ar-H), 7.23 (m, 1H, Ar-H), 7.21 and 6.76 (AA′XX′, 2H, Ar-H), 3.00 (s, 6H, NMe), 1.76 (s, 6H, CMe). 13C NMR (CDCl3): δ 151.3, 148.5, 138.7, 127.8, 127.4, 126.7, 125.3, 112.2 (all aromatic C), 42.0 (CMe), 40.6 (NMe), 30.8 (CMe). IR (KBr): 2830 (NMe2) cm−1.

2,2-Bis(4-(dimethylamino)phenyl)propane (9C). Bisamine 19 was methylated using the same method as employed for the methylation of 18. Yield 61% of light pink crystals after recrystallization from methanol. Mp 82 °C. Anal. Calcd for C18H24N2: C, 80.80; H, 9.28; N, 9.92. Found: C, 80.68; H, 9.22; N, 9.86. 1H NMR (CDCl3): δ 7.14 and 6.68 (AA′XX′, 2 × 4H, Ar-H), 2.95 (s, 12H, NMe2), 1.64 (s, 6H, CMe). 13C NMR (CDCl3): δ 148.5, 139.5, 127.4, 112.3 (all aromatic C), 41.1 (CMe), 40.7 (NMe), 31.0 (CMe). IR (KBr): 2810 (NMe2) cm−1.

2-(4-Cyanophenyl)-2-(4′-(dimethylamino)phenyl)propane (1C). This compound was prepared as described for Si. Purification was carried out with column chromatography (elucent chloroform) and recrystallization from methanol. Yield 0.41 g (1.55 mmol, 30%) of crystals with a greenish glance. Mp 136 °C. Anal. Calcd for C18H18N: C, 81.78; H, 7.63; N, 10.59. Found: C, 81.66; H, 7.58; N, 10.52. 1H NMR (CDCl3): δ 7.56 and 7.37 (AA′XX′, 2 × 2H, Ar-H), 7.09 and 6.71 (AA′XX′, 2 × 2H, Ar-H), 2.95 (s, 6H, NMe), 1.69 (s, 6H, CMe). 13C NMR (CDCl3): δ 157.2, 148.9, 136.9, 131.8, 127.6, 127.4, 112.4, 109.3 (all aromatic C), 119.2 (CN), 42.6 (CMe), 40.6 (NMe), 30.5 (CMe). IR (KBr): 2820 (NMe2), 2230 (CN) cm−1.

4 tert-Butylbenzoxazole (8C). This compound was synthesized from 4-bromo-tert-butylbenzene as described for the synthesis of 1Si. After distillation (boiling range 67–69 °C, 0.1 mmHg) a colorless liquid was obtained in 71% yield. 1H NMR (CDCl3): δ 7.57 and 7.46 (AA′BB′, 2 × 2H, Ar-H), 1.31 (s, 9H, CMe). 13C NMR (CDCl3): δ 156.6, 131.9, 126.2, 109.3 (all aromatic C), 119.1 (CN), 35.3 (CMe), 30.9 (CMe). IR (NaCl): 2230 (CN) cm−1.

4 tert-Butylbenzilate (7C). Potassium carbonate (27.20 g, 196.8 mmol) was added in one portion to a solution of 4-tert-butylibenophenol (9.95 g, 66.24 mmol) in 100 mL of DMSO. After the mixture was stirred for 50 min methyl iodide (5 mL, 80.3 mmol) was added dropwise, keeping the temperature at 18 °C by cooling with an ice-bath. Subsequently the mixture was stirred 1 h at 45 °C and overnight at room temperature. Since GC analysis showed the presence of some starting material another 3 mL of iodomethane (48 mmol) were added, and stirring was continued for 2 h at 50 °C. Water (500 mL) was then added and the mixture was extracted with 3 × 50 mL of methylene chloride. The combined organic layers were concentrated under diminished pressure, after which the residual yellow liquid was dissolved in 60 mL of hexane and washed with 50 mL of 5% potassium hydroxide solution and 3 × 50 mL of water. After drying on magnesium sulfate, filtering, and evaporation of the solvent the residual liquid was vacuum distilled over a vigreux column (bp 58 °C at 0.1 mmHg). Yield 7.83 g (47.77 mmol, 72%) of a colorless liquid. 1H NMR (CDCl3): δ 7.38 and 6.92 (AA′XX′, 2 × 2H, Ar-H), 3.85 (OMe), 1.38 (s, 9H, CMe). 13C NMR (CDCl3): δ 157.4, 143.4, 126.2, 113.4 (all aromatic C), 55.2 (OMe), 34.1 (CMe), 31.6 (CMe). IR (NaCl): 2820, 1250, 1040 (Ar-O-Me), 1370 (CMe) cm−1.

Acknowledgment. This work was supported in part (A.L.S.) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supporting Information Available: Preparation and characterization of synthetic intermediates (13Si, 2-(4-bromophenyl)-2-propanol, 13C, 14, 15, 16, 17, 18, 19, 20, 12C and 21) and further details of the structure determination, including atomic coordinates, bond lengths and angles and thermal parameters for 1C (Tables S1-7) (13 pages). See any current masthead page for ordering and Internet access instructions.

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