Photophysics of pyrene substituted oligosilanes

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Abstract. The absorption and fluorescence properties of 1-pyrenyl substituted permethyl-oligosilanes are reported. The charge transfer in 1-pyrenyltridecamethylhexasilane is explained by electron transfer from the Si–Si σ orbitals to pyrene in the excited state. Evidence is found for ground state interactions in 1,3-di(1-pyrenyl)hexamethyltrisilane, based on absorption and ¹H-NMR measurements. The fluorescence properties of 1-(1-pyrenyl), 3-(*p*-N,N-dimethylanilino)hexamethyltrisilane are compared with its carbon analogue 1-(1-pyrenyl), 3-(*p*-N,N-dimethylanilino)propane. Ground state interactions are found for the silicon-bridged donor-acceptor compound.

Keywords. Pyrene substituted oligosilanes; ground state interactions; silicon-bridged compounds; exciplex; electron transfer.

1. Introduction

Polysilanes or polysilylenes are polymers which contain only silicon atoms in the backbone. Recently, polysilanes attracted a lot of scientific interest, mainly due to the unexpected chemical and spectroscopic properties of the completely sigma-bonded silicon backbone (Miller and Michl 1989). The first electronic transition of oligosilanes and polysilanes ($\text{Si}_n\text{R}_{2n+2}$) occurs at surprisingly low energies as compared to their carbon analogues. This transition shifts to higher wavelengths with increasing silicon-chain length and reaches a constant value for n between 40 and 50. The transition has been assigned as a $\sigma(\text{Si-Si}) \rightarrow \sigma^*(\text{Si-Si})$ in which the sigma electrons are delocalised along the silicon backbone. The electronic structure and spectral properties of oligo- and polysilanes more closely resemble those of conjugated π -systems such as polyacetylenes than those of the related carbon-based systems such as polyethylene. It has been proposed that the conjugation through *gauche* SiSiSiSi is smaller than that of conjugation through *trans* SiSiSiSi (Klingensmith *et al* 1986). Recently, Plitt and Michl (1992) demonstrated that *trans*-Si₄Me₁₀ shows the expected red shift relative to Si₃Me₈, but *gauche*-Si₄Me₁₀ does not, which is experimental evidence for the better conjugation in a *trans* than in a *gauche* chain.

Charge transfer fluorescence has been observed for several pentamethyldisilanyl-substituted aromatic compounds. This charge transfer was not observed for the

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Figure 1. Structures and abbreviations of the compounds studied.

trimethylsilyl substituted aromatic compounds. Shizuka assigned the charge transfer fluorescence to a state produced by electron transfer from the aromatic ring to the $3d\pi$ orbitals of the disilane (Shizuka *et al* 1981, 1985). However, Sakurai *et al* (1990) proposed electron transfer from the Si–Si sigma bond to the aromatic moiety in the excited state. Orthogonal intramolecular charge transfer was suggested in which the Si–Si sigma bond lies in the plane of the aromatic ring and thus orthogonal to the π orbitals. We reported already that P6 (see figure 1) showed charge transfer fluorescence although P1, P2 and P3 showed only fluorescence from the locally excited state (Declercq *et al* 1991). We concluded that electron transfer in P6 occurred from the hexasilane chain to pyrene in the excited state, which supports the mechanism proposed by Sakurai *et al* (1990). In this paper, the charge transfer of P6 is studied in greater detail and additional evidence on the proposed mechanism is given. P3P and P6P (figure 1) were synthesised in order to study the excimer formation between two pyrene groups linked by a silane chain. P3D and P6D (figure 1) were synthesised in order to study the possibility of through bond interaction, mediated by a silicon chain, between a donor (N,N-dimethylaniline) and an acceptor (pyrene).

2. 1-Pyrenylsubstituted oligosilanes: P1, P2, P3 and P6

2.1 Absorption properties

The absorption spectrum of P1, is comparable to that of 1-methylpyrene. The maximum of the ^1La -transition is situated at 344 nm. Introduction of a disilanyl group (P2) results in a bathochromic shift towards 349 nm. The higher homologues P3 and P6 show a maximum at 350 and 351 nm respectively. Going from P1 towards P6, a gradual decrease of the absorption vibrational fine structure and the molar extinction coefficient at the maximum is observed (see table 1 and figure 2).

The weak ^1Lb transition ($\epsilon < 1000$), detected at 375 nm for P1 and P2 could not be observed for P3 and P6, due to overlap of the ^1La transition. The increased absorbance around 250–270 nm for P6 as compared to P1, is due to the absorbance of the hexasilane chain, tetradecamethylhexasilane has an absorption maximum around 260 nm (Gilman *et al* 1964). The effect of the silicon chain on the absorption spectra

Table 1. Absorption properties of pyrene, P1, P2, P3 and P6 in *iso*-octane.

Compound	$\lambda_{\max}^1\text{La}(\text{nm})$	$\epsilon^1\text{La}(\text{L mol}^{-1} \text{cm}^{-1})$
Pyrene	334	54,300
P1	344	50,600
P2	349	43,500
P3	350	38,600
P6	351	27,170

Figure 2. Absorption spectra of P1 (—) and P6 (····) in *iso*-octane at room temperature.

of pyrene is remarkable if we compare this with the carbon analogues of the compounds mentioned above: 1-methylpyrene and 1-ethylpyrene have an absorption maximum of the ^1La transition at 342.4 and 342.6 nm, respectively (Reynders 1988). It can be concluded that although the electronic transition is still recognizable as perturbed pyrene $\pi \rightarrow \pi^*$ transition, there is an interaction in the ground state between a saturated silicon system and pyrene.

2.2 Fluorescence properties

The fluorescence maxima of P1, P2 and P3 are situated around 390 nm, and they are not dependent on solvent polarity. The fluorescence decay, recorded by means of the 'single photon timing' technique, could be analysed as monoexponential decay. This fluorescence can be attributed to a $\pi^* \rightarrow \pi$ pyrene fluorescence. The respective fluorescence quantum yields, Φ_f , together with their fluorescence decay times, are given in table 2.

Table 2. Quantum yields and fluorescence decay times in iso-octane at 25°C.

Compound	Φ_f	$\tau(\text{ns})$	$k_f(10^6 \text{ s}^{-1})$	Φ_{isc}
Pyrene			2.2	
P1	0.80	324	2.5	0.19
P2	0.75	282	2.7	0.25
P3	0.74	230	3.2	0.26
P6	0.47	76.4	6.1	—

The fluorescence rate constants can be calculated using the fluorescence quantum yield and the fluorescence decay time. k_f increases on going from pyrene towards P3. The fluorescence of pyrene occurs from the ^1Lb state. The increase of k_f could be due to a contribution of the ^1La state in the lowest excited state, which increases the transition probability. It has already been suggested that Φ_{isc} is very small for planar polycyclic aromatic compounds such as pyrene (Wilkinson 1975), so that Φ_{isc} can be calculated using $(1 - \Phi_f)$. Going from P1 towards P2 results in an increase of Φ_{isc} by a factor 1.5, probably due to the introduction of a second heavy silicon atom. However, introduction of a third silicon atom in the silane chain does not affect Φ_{isc} that much. The same value of Φ_{isc} within experimental error was obtained using Laser Induced Photoacoustic Spectroscopy (LIOAS) (Van Haver *et al* 1992).

In contrast with P1, P2 and P3, the fluorescence of P6 is dependent on the solvent polarity (Declercq *et al* 1991). A change from iso-octane to ethylacetate as solvent results in a bathochromic shift of the fluorescence maximum from 390 to 476 nm and a decrease of the fluorescence quantum yield from 0.47 to 0.05 (figure 3). The fluorescence decay in iso-octane could be analysed as a monoexponential function, which indicates that the charge transfer state is produced very rapidly. The fluorescence rate constant k_f of P6 in iso-octane is much larger than the k_f of P1, P2 and P3 (table 2), which indicates that the fluorescence from the charge transfer state is faster than from the locally excited state. Using the Lippert–Mataga formalism (Von Lippert 1957; Beens *et al* 1967), the dipole moment of the excited state can be calculated as 21D, assuming 6 Å for the solvent cavity radius ρ . This indicates that in the excited state, a very polar species is produced, in which the charges are separated over more than 4 Å. This polar species is attributed to a charge transfer state, which is produced by electron transfer from the hexasilane chain towards pyrene in the excited state. The fact that no electron transfer is observed for P1, P2 and P3 can be explained based on the change of free energy for electron transfer. The ΔG_{et}^0 values can be calculated using the redox potentials of the respective permethylated silane chain and of pyrene, the excitation energy and the Coulombic stabilisation energy. If the redox potentials are measured in acetonitrile, the Coulombic attraction energy can be neglected. If it is assumed that the oligosilane chain acts as a donor, $E_{(\text{A/A}^-)}^\circ + h\nu_{0,0}$ equals 1.18 eV, and $E_{(\text{D}^+/ \text{D})}^\circ$ of Si_2Me_6 , Si_3Me_8 and $\text{Si}_6\text{Me}_{14}$ equals 1.880, 1.520 and 1.075 eV, respectively (Boberski and Allred 1975). It can then be worked out that ΔG_{et}^0 will be negative for P6 and positive for P1, P2 and P3. Thus, electron transfer is possible from the hexasilane chain towards pyrene in the excited state due to the lower redox potential of the hexasilane chain.

$$\Delta G_{\text{et}}^0 = E_{(\text{D}^+/ \text{D})}^\circ - E_{(\text{A/A}^-)}^\circ - h\nu_{0,0} - e^2/(4\pi\epsilon_0\epsilon_r r).$$

Figure 3. Fluorescence spectra of P6 in *iso*-octane (—) and ethylacetate (---).

The fluorescence spectrum in benzene does not change upon cooling the solution from 10°C to a rigid matrix at -3.3°C , beneath the melting point of benzene. This suggests that no rotation is necessary to have intramolecular charge transfer in P6, which has been proposed by Sakurai (Sakurai *et al* 1990) for the phenyldisilanes.

3. Bipyrenyl-substituted oligosilanes: P3P and P6P

The absorption spectrum in *iso*-octane of P3P clearly differs from that of its reference compound P3, which is an indication that the two pyrene groups interact in the ground state. However, almost no differences in the absorption spectra of P6 and P6P can be observed (figure 4).

The ^1H -NMR spectra of P3P and P6P were analysed and compared with those of their reference compounds. A strong shielding is observed for the aromatic signals of P3P, compared with P3, which indicates that the two pyrene groups exert ring current effects in the ground state (figure 5). These effects are much smaller for P6P compared with P6, suggesting that the average distance between the two pyrene groups is larger in the latter bichromophore.

The large shielding effects in P3P were not observed for the related carbon compound 1,3-(di-1-pyrenyl)-propane, which is an indication that the two pyrene groups in the silicon system have a much larger tendency to come together in the ground state than in the carbon-based system. It should be emphasized that the Si-Si bond length is $2.35\text{\AA}$, a value much larger than the $\text{CH}_2\text{-CH}_2$ bond, so that the methyl groups on the silicon atoms do not hinder the rotation of the silicon chain.

Figure 4. Absorption spectra of P3P, P3, P6P and P6 in iso-octane.

Figure 5. $\Delta\delta = \delta(\text{P3P}) - \delta(\text{P6})$ and $\Delta\delta = \delta(\text{P6P}) - \delta(\text{P6})$ for the pyrene protons of the silicon compounds (■) and for the related carbon compounds (●) in CDCl_3 .

One can conclude that the hexamethyltrisilane chain is more flexible than the propane chain. Welsh and Johnson (1990) calculated the energy barrier for the rotation of a Si–Si bond in all-*trans* poly(dimethylsilane). The maximum energy barrier was located at the *cis* conformation, $2.75 \text{ kcal.mol}^{-1}$ higher in energy than the *trans*, which is indeed in sharp contrast with the relatively high barriers ($> 6 \text{ kcal.mol}^{-1}$) in the case of *n*-alkanes.

The emission spectrum of P3P is dominated by a broad, solvent-independent fluorescence band, which can be assigned to excimer fluorescence (Declercq *et al* 1991). However, the fluorescence of P6P is dependent on the solvent polarity, and can consequently not be described as an excimer fluorescence. The fluorescence maximum depends on the solvent polarity, in the same way as for P6, so that the excited state of P6P can also be explained as a $\sigma(\text{Si-Si}) \rightarrow \pi^*$ charge transfer state.

4. Donor-acceptor substituted oligosilanes: P3D and P6D

The differences in the absorption spectra of P3D and its reference compound P3 in *iso*-octane indicate interactions in the ground state. P6D and P6, however, show similar absorption spectra (figure 6). The fluorescence of P6D is dependent on the solvent polarity. The dependence of the fluorescence maximum on the solvent polarity term $f - 1/2f = (\epsilon - 1)/(2\epsilon - 1) - (n^2 - 1)/2(2n^2 + 1)$ is the same as for P6, so that the dipole moment of the excited state of P6D should be approximately the same as for P6 (figure 7). However, the Stokes shifts of P6D are systematically larger than those of P6, suggesting an additional interaction of the N,N-dimethylaniline group with the $\sigma(\text{Si-Si}) \rightarrow \pi^*$ charge transfer state. N,N-dimethylaniline is a better donor than tridecamethylhexasilane, so that electron transfer could occur from N,N-dimethylaniline towards pyrene by mediation of the hexasilane chain.

P3D also shows a solvent-dependent fluorescence spectrum. Using the Lippert–Mataga formalism (Von Lippert 1957; Beens *et al* 1967)-, the dipole moment of the

Figure 6. Absorption spectra of P3D, P3, P6D and P6 in iso-octane.

Figure 7. Fluorescence maxima of P6D, P6 and P3D in function of the solvent polarity term $f - \frac{1}{2}f'$.

Table 3. Comparison of the absorption and fluorescence properties of P3D and P3'D.

	P3D	P3D
¹ La absorption maximum	351 nm	342 nm
Maximum exciplex fluorescence	467 nm	477 nm
μ_{exciplex}	14.3D	12.2D
Φ_f	0.012	0.247
τ_1	0.57 ns	3.73 ns
τ_2	3.12 ns	88.1 ns
A_1/A_2 (exciplex region)	-0.64	-1

excited state of P3D is 14.3D, a value which is comparable with 12.2D of the related carbon compound 1-(1-pyrenyl, 3-(*p*-N,N-dimethylanilinopropane)) (P3'D) (Imbayashi *et al* 1988). The photophysical properties of P3D and its carbon analogue P3'D are compared in table 3.

It is immediately clear that the fluorescence quantum yield is much smaller for P3D than for its carbon analogue. The fluorescence decay in the exciplex region could be fitted to a difference of two exponentials, with two decay times which are much smaller than the ones of the carbon system. This could suggest that exciplex formation in P3D is much faster than in P3'D. In contrast with P3'D, the ratio of the negative pre-exponential factor to the positive pre-exponential factor (A_1/A_2 in table 3) deviates from -1, which suggests that the Birks kinetic scheme is not applicable to exciplex formation in P3D (Reynders *et al* 1990) and that there is

interaction in the ground state between the donor and the acceptor. Further, the differences in the absorption spectra of P3D and P3 and the differences in the excitation spectra of P3D, measured in the locally excited state wavelength region and in the exciplex region, give additional evidence for the interaction between the donor and the acceptor. It is important to note that the fluorescence spectrum of P3D in benzene does not change upon cooling from room temperature to -3.3°C , below the melting point of benzene. Further, X-ray analysis showed that the trisilane chain is not folded but in an extended conformation so that the pyrene and N,N-dimethylaniline can not interact through space. The fact that the fluorescence is the same in solution as in a rigid matrix indicates that the trisilane chain does not need to rotate to ensure exciplex emission, which suggests that through-bond effects might be important in the interaction between pyrene and N,N-dimethylaniline.

5. Conclusions

Delocalised sigma systems can act as donors in the fluorescence quenching of aromatic compounds, provided that the ionisation potential of the sigma system is low enough: electron transfer is observed from the hexasilane chain towards pyrene in the excited state in P6. However, no electron transfer occurs in P3, due to the higher ionisation potential of the trisilane chain, a shorter delocalised system than the hexasilane chain. It has been shown that the two pyrene groups in P3P tend to come together in the ground state, which is not observed in the carbon analogue where the dimethylsilane groups are replaced by CH_2 groups. This suggests that a hexamethyltrisilane chain is more flexible than a carbon chain. The fluorescence of P3P is characterised as excimer fluorescence and P6P shows a $\sigma(\text{Si-Si}) \rightarrow \pi^*$ charge transfer, such as with P6. P3D shows exciplex fluorescence and it is proposed that the observed interactions between pyrene and N,N-dimethylaniline could be mediated through the trisilane chain.

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