Ground- and Excited-State Interaction in Di-1-pyrenyl-Substituted Oligosilanes

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Abstract: Excimer formation is reported for 1,2-di(1-pyrenyl)tetramethyldisilane (P2P), 1,3-di(1-pyrenyl)hexamethyltrisilane (P3P), and 1,4-di(1-pyrenyl)octamethyltetrasilane (P4P), while 1,6-di(1-pyrenyl)dodecamethylhexasilane (P6P) shows a $\sigma(\text{Si–Si}) \rightarrow \pi^*$ charge-transfer fluorescence. The ^{1}H-NMR spectra of the bichromophores were measured and compared with the reference compounds 1-(trimethylsilyl)pyrene (P1), 1-pyrenylpentamethyldisilane (P2), 1-pyrenylheptamethyltrisilane (P3), and 1-pyrenyltridecamethylhexasilane (P6). A strong shielding is observed for the aromatic protons of the bichromophoric compounds, which suggests that a fraction of the molecules are present in a conformation in which the two pyrene groups interact intramolecularly. These large shielding effects were not observed for the carbon analogues where the dimethylsilane unit is replaced by a CH_2 group. The shielding of the aromatic protons of P3P in solution increases going from $CDCl_3$ to deuterated cyclohexane, which can be explained by a better solvation of the pyrenyl moiety by chloroform. The tendency for the two pyrene groups to come together decreases going from P3P to P4P and P6P. Additional structural information concerning the conformation of the bichromophores in which the two pyrene groups interact could be gained using ^{1}H NMR. Two different ground-state conformations in which the two pyrene moieties interact are proposed for P3P and P4P. In the first conformation, the two pyrene groups adopt a symmetrical sandwich structure, while in the second, an asymmetrical, not completely overlapping structure is proposed. A symmetrical conformation in which the two pyrene groups are not parallel while the two H_{10} atoms point to each other is proposed for P2P. These suggestions were confirmed by time-resolved fluorescence measurements of the excimer emission and by the differences in the absorption spectra of the bichromophores and their reference compounds.

Introduction

The intramolecular excimer formation in bichromophoric molecules linked by a short flexible chain has been studied extensively.[1] The efficiency of excimer formation depends on the length as well as on the chemical nature of the chain. Intramolecular excimer fluorescence has been studied for systems where the two pyrene groups are separated by a saturated hydrocarbon chain,[2-5] by a diethyl ether link,[3,6,7] by a peptide chain,[8-10] or by a fluorocarbon chain[11] or are capping the ends of a polymeric chain.[12-14] The excimer fluorescence is an efficient tool to probe the dynamics and the flexibility of the chain linking both chromophores. In a previous paper, we reported excimer fluorescence for 1,3-di(1-pyrenyl)hexamethyltrisilane (P3P).[15] In this paper, the excimer formation of 1,2-di(1-pyrenyl)tetramethyldisilane (P2P), 1,4-di(1-pyrenyl)octamethyltetrasilane (P4P), and P3P are reported. The latter compound is studied in more detail and compared with its alkane analogue 1,3-di(1-pyrenyl)propane (P3′P). The structures of these compounds, together with the respective reference 1-pyrenylmethylsilane compounds P1, P2, P3, and P6, are presented in Figure 1.

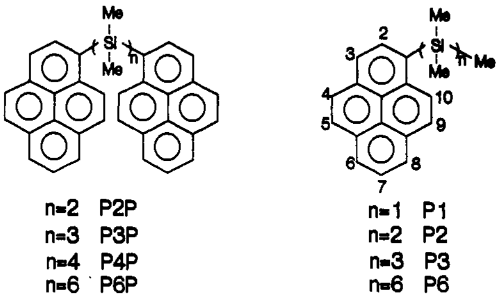

Figure 1. Representations of the compounds studied and their corresponding abbreviations.

Excimers are defined as complexes which are formed in the excited state,[16] this in contrast with EDA complexes and ground-state aggregates. However, ground-state interaction has been observed in several excimer-forming species. Rochlitz reported intermolecular ground-state interaction for pyrene and 3-methylpyrene;[17] Reynders et al. reported that in solution a fraction of the chain conformers of *meso*-2,4-di(1-pyrenyl)pentane[18] and bis[(pyrenylcarbonyl)oxy]alkanes[19] show ground-state interac-

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tions. On the basis of single photon timing measurements, Andriessen et al. found that at room temperature about 9% of *meso*-bis[1-(2-pyrenyl)ethyl] ether in isooctane adopts an excimer geometry in the ground state.[7] Ground-state interactions can be detected by absorption properties, NMR, and time-resolved fluorescence measurements. In this paper, ground- and excited-state interactions in P2P, P3P, P4P, and P6P will be studied.

Experimental Section

A. Synthesis. The general procedure consisted of substitution of a chlorine in the corresponding dichlorooligosilane by a pyrenyl group through reaction with pyrenyllithium:

$$2\mathrm{PyrLi} + \mathrm{Cl(SiMe_2)}_n\mathrm{Cl} \rightarrow \mathrm{Pyr(SiMe_2)}_n\mathrm{Pyr} + 2\mathrm{LiCl}$$

Pyrenyllithium could be synthesized in two ways: using 1-bromopyrene and phenyllithium or using 1-bromopyrene and 2 equiv of *tert*-butyllithium. The reactions with *tert*-butyllithium generally resulted in higher yields and easier purification. The dichlorosilanes were synthesized using literature procedures and were distilled over CaH_2 before use. *All reactions* were carried out under argon, using oven-dried glassware. Tetrahydrofuran was dried over sodium under argon and distilled just before use. Anhydrous diethyl ether was purchased from Aldrich and transferred to the reaction flask under argon.

1-(Trimethylsilyl)pyrene (P1). 1-Bromopyrene[20] (1.19 g, 4.2 mmol) and 50 mL of a tetrahydrofuran/diethyl ether (1/1) mixture were cooled in a liquid air/diethyl ether bath. Then 5.3 mL (8.9 mmol) of a 1.68 M solution of *tert*-butyllithium in pentane was slowly added over 15 min to the cooled solution. The solution was stirred for 2 h at a temperature lower than –40 °C. Then 0.51 g (4.7 mmol) Me_3SiCl was added to the red solution, which was stirred overnight. After workup, 1.1 g of a light brown solid was obtained. After flash chromatography with hexane and two recrystallizations in ethanol, 0.9 g (79%) of product was obtained: mp = 109–110 °C; ^{1}H NMR δ (ppm) 0.63 (s, 9H); 8.0–8.4 (m, 9H); *m/e* 274 ($M^{\bullet+}$).

1-(Pentamethyldisilanyl)pyrene (P2). Pyrenyllithium was synthesized in the same way as P1 using 1.5 g (5.4 mmol) of 1-bromopyrene and 6.4 mL (10.7 mmol) of a 1.68 M *tert*-butyllithium solution. To the cooled solution, 1.3 mL (6.5 mmol) of 1,2-dichlorotetramethyldisilane[21] was added slowly. The solution was allowed to come to room temperature and was stirred overnight. Then 3.3 mL (9 mmol) of a 2.73 M solution of methylmagnesium bromide in diethyl ether was slowly added. The solution was stirred for 4 h and refluxed for another hour. After workup and flash chromatography with hexane, 1.23 g (70%) of product was recovered: mp = 101–102 °C; ^{1}H NMR δ (ppm) 0.09 (s, 9H), 0.61 (s, 6H), 8.0–8.3 (m, 9H); *m/e* 332 ($M^{\bullet+}$).

1-(Heptamethyltrisilanyl)pyrene (P3) was synthesized in the same way as P2, using 1,3-dichlorohexamethyltrisilane.[22] Yield: 32%. The product was purified by flash chromatography with hexane: ^{1}H NMR δ (ppm) 0.00 (s, 9H), 0.20 (s, 6H), 0.74 (s, 6H), 8.0–8.3 (m, 9H); mp = 53.5–54.5 °C; *m/e* 390 ($M^{\bullet+}$).

1-(Tridecamethylhexasilanyl)pyrene (P6) was synthesized in the same way as P2, using 1,6-dichlorododecamethylhexasilane.[23] The product was purified by flash chromatography with hexane: yield 7%; ^{1}H NMR δ (ppm) 0 (s, 9H), 0.04 (s, 6H), 0.06 (s, 6H), 0.09 (s, 6H), 0.21 (s, 6H), 0.68 (s, 6H), 8.0–8.3 (m, 9H); *m/e* 564 ($M^{\bullet+}$).

1,2-Di(1-pyrenyl)tetramethyldisilane (P2P). 1-Bromopyrene (2 g, 7.1 mmol) and 30 mL of benzene (distilled over sodium) were placed in an oven-dried centrifuge tube. Then 3.8 mL (7.6 mmol) of a 2 M phenyllithium solution in cyclohexane was slowly added at room temperature and stirred for 5 h. The red color disappeared, while a yellow precipitate was formed. After centrifugation, the solvent was removed under argon and 30 mL of tetrahydrofuran and 0.46 mL (2.45 mmol) of 1,2-dichlorotetramethyldisilane were slowly added. The mixture was stirred for 5 h. After workup, 0.152 g (25%) of solid was recovered. The solid was purified using flash chromatography with toluene and recrystallization in toluene/ethanol: mp = 210.5–212 °C; ^{1}H NMR δ (ppm) 0.66 (s, 12H), 7.6–8.2 (m, 18H); MS CI *m/e* 519 ($MH^{\bullet+}$).

1,3-Di(1-pyrenyl)hexamethyltrisilane (P3P) was synthesized in the same way as P2P, using 1,3-dichlorohexamethyltrisilane.[22] The product (0.2 g, 75%) obtained was purified by flash chromatography with 5% ethyl acetate in hexane and by recrystallization in hexane: mp = 110.5–112.5 °C; ^{1}H NMR δ (ppm) 0.43 (s, 12H), 0.43 (s, 6H), 0.55 (s, 12H), 7.6–8.1 (m, 18H); *m/e* 576 ($M^{\bullet+}$).

1,4-Di(1-pyrenyl)octamethyltetrasilane (P4P). 1-Pyrenyllithium was synthesized in the same way as P1, using 3.85 mmol of 1-bromopyrene and 4.11 mL (7.7 mmol) of a 1.87 M *tert*-butyllithium solution. 1,4-Dichlorooctamethyltetrasilane[24,25] (0.487 g, 1.6 mmol) was added to the cooled solution. The mixture was stirred at room temperature for 3 h and refluxed for 15 min. After workup, purification by flash chromatography (3% ethyl acetate in hexane), and recrystallization in hexane, 0.175 g (17%) was recovered: mp = 191.5–193 °C; ^{1}H NMR δ (ppm) 0.0 (s, 12H), 0.57 (s, 12H), 8.0–8.2 (m, 18H); *m/e* 634 ($M^{\bullet+}$),

1,6-Di(1-pyrenyl)dodecamethylhexasilane (P6P) was synthesized in the same way as P2P, using 1,6-dichlorododecamethylhexasilane. The product was purified by flash chromatography (5% toluene in hexane) and by recrystallization in hexane: yield 5%; mp = 177–178 °C; ^{1}H NMR δ (ppm) –0.06 (s, 12H), 0.16 (s, 12H), 0.67 (s, 12H), 8.0–8.2 (m, 18H); *m/e* 750.3 ($M^{\bullet+}$).

1,3-Di(1-pyrenyl)propane (P3′P) (Molecular Probes) was used as received.

B. Instrumentation. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 6 UV/vis spectrophotometer. Corrected fluorescence spectra were measured using a SLM-Aminco 8000C spectrophotometer. The absorbance at the excitation wavelength (350 nm) was 0.1 or less. The samples used for fluorescence were thoroughly degassed by several freeze–pump–thaw cycles. The single photon timing technique (SPT) was used to collect fluorescence decay curves at various emission wavelengths. The experimental setup has been described elsewhere.[26] The reference convolution method was used to correct for the wavelength dependence of the instrument response function.[27] For each sample, several decays were recorded at a set of different emission wavelengths and time increments. These decays were subsequently analyzed globally.[28] The samples used in the SPT experiments were purified by HPLC. Isooctane was commercial UV spectral grade and was used without further purification.

The ^{1}H-NMR spectra were measured on a 400-MHz Bruker AMX400. The spectral bandwidth, the time domain, and the number of scans of the 1D spectra were 4630 Hz, 32K, and 32, respectively. Sixteen scans were taken for the 2D spectra, with the spectral bandwidth of F_1 and F_2 equal to 280 Hz and the time domain of F_1 and F_2 equal to 512 and 256 W, respectively. The concentrations of the NMR samples were below 8×10^{-3} M, preventing intermolecular interactions between the two pyrene groups.

Experimental details of the X-ray analysis of P3P will be published elsewhere.[29]

Results and Discussion

Absorption and Fluorescence Properties. The absorption spectra of P3P and its reference compound 1-pyrenylheptamethyltrisilane (P3) in isooctane are presented in Figure 2. The absorption spectrum of P3P is clearly different from that of P3: the absorption maximum is shifted by 2 nm, and more importantly, the vibrational fine structure of the ^1L_a-transition is broadened. The deviation of the absorption spectrum is a first indication that the two pyrenyl groups interact in the ground state. Similar conclusions can be drawn for P2P when compared with P2. However, the differences in absorption properties decrease going

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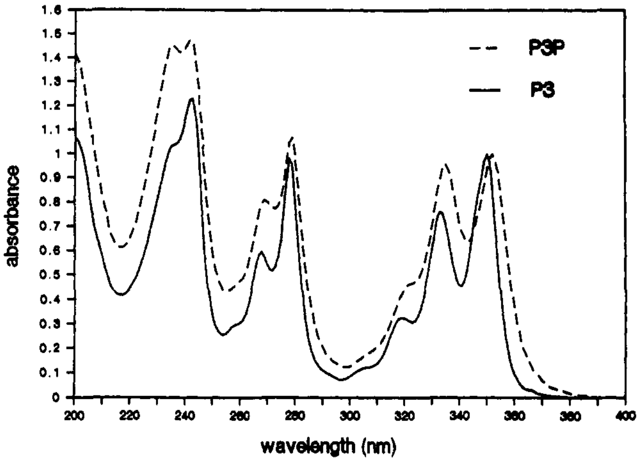

Figure 2. Absorption spectra of P3P and P3 in isooctane, normalized at the maximum of the ^1L_a-transition.

Table I. Absorption and Fluorescence Properties in Isooctane at Room Temperature

	absorption	fluorescence^a		
	λ_{max} (nm)	λ_{max} (nm)	Φ_f	FWHM (cm^{-1})
P1	344	377, 389	0.80	
P2	349	389	0.75	
P3	350	389	0.74	
P6	351	390^b	0.47^b	
P2P	353	438	0.43	3500
P3P	352	483	0.44	3960
P4P	351	488	0.54	3740
P6P	351	390^b	0.43^b	

^{a} Excitation at 350 nm. ^{b} Dependent on the solvent polarity.[15]

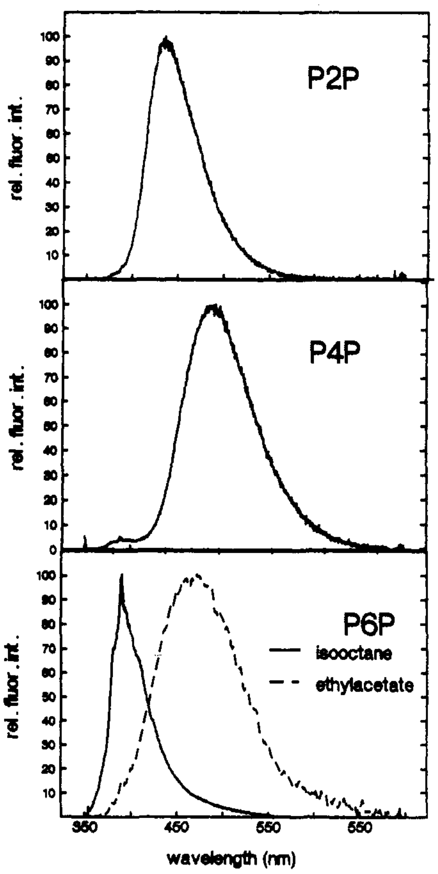

Figure 3. Fluorescence spectra of P2P and P4P in isooctane and P6P in isooctane and ethyl acetate at room temperature.

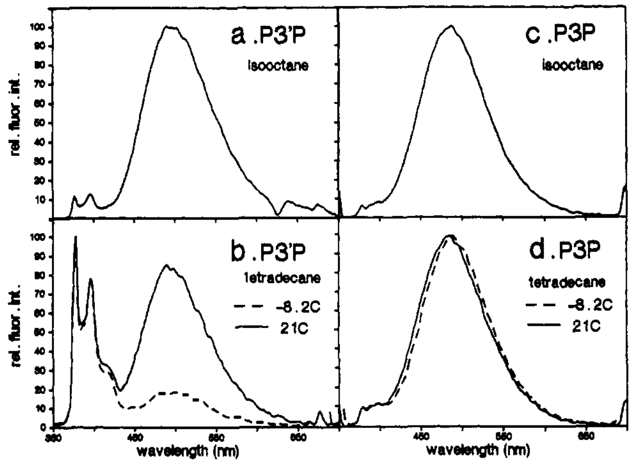

Figure 4. Fluorescence spectra of P3P and P3P' in isooctane (at 21 °C) and in *n*-tetradecane (at 21 and −8.2 °C).

from P2P toward P6P (Table I): the absorption spectra of P6P and P6 in isooctane at room temperature can be superimposed.

The fluorescence at room temperature of P2P, P3P, and P4P in isooctane is dominated by a broad band with a maximum at 438, 483, and 488 nm, respectively (Figures 3 and 4c). The contribution of the locally excited pyrenyl fluorescence is either weak (P3P and P4P) or absent (P2P). The broad fluorescence band can be attributed to intramolecular excimer fluorescence. The fluorescence of P6P (Figure 3) depends on the solvent polarity and consequently cannot be described as an excimer fluorescence. In analogy with the reference compound P6,[15] the excited state can be described as a charge-transfer state originating from electron transfer from the hexasilane chain toward pyrene in the excited state. The ratio of the locally excited state fluorescence to the excimer fluorescence for P2P, P3P, and P4P is very small. However, it is known that this ratio in the corresponding alkyl compounds (where the dimethylsilane group is replaced by a CH_2 group) is strongly dependent on the chain length.[2] For instance, 1,2-di(1-pyrenyl)ethane shows almost no excimer fluorescence.[2] This is in strong contrast with P2P, which shows no locally excited state fluorescence.

It is further known that the intramolecular excimer formation of the alkyl compounds is dependent on the solvent viscosity:[30] increasing the viscosity of a solution of 1,3-di(1-pyrenyl)propane (P3'P), when going from isooctane (η = 0.504 cP[31]) to tetradecane (η = 2.18 cP[32a]), results in an increase of the ratio of the locally excited state fluorescence to the excimer fluorescence (Figure 4). Cooling of the solution to −8 °C, below the melting point of tetradecane (mp = 5.8 °C), results in a drastic decrease of the excimer fluorescence. However, increasing the solvent viscosity does not affect the locally excited state/excimer emission ratio for P3P. Even cooling of the tetradecane solution below its melting point does not result in an increase of the monomer fluorescence; only a small bathochromic shift of the emission from 484 to 489 nm is observed (Figure 4).

^{1}H NMR Study. It has been shown that ^{1}H NMR is an efficient tool to detect ground-state interactions between aromatic compounds.[17-19] These interactions are detected as a ring-current effect on the chemical shifts of the H atoms of the pyrenyl groups.

A. Analysis of ^{1}H NMR. Using NOEDIFF spectra, the aromatic protons which are close in space to the dimethylsilane group in the 1-position (H2 and H10) can be identified. It is known that the vicinal coupling constant, ^3J, between H2 and H3

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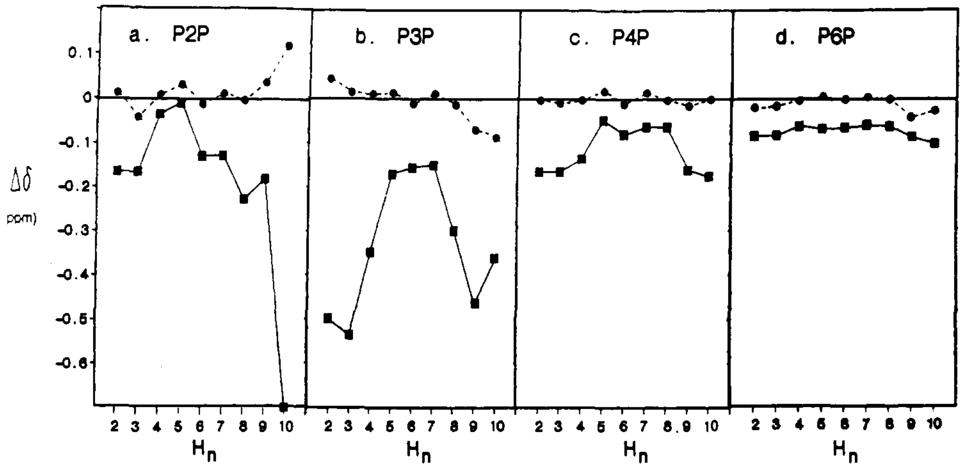

Figure 5. Differences in chemical shift, Δδ (in ppm), of the aromatic protons, with respect to the reference compound P6 (■), together with Δδ for the respective carbon compounds (•).[19]

(9 Hz) is larger than between H9 and H10 (7.5 Hz), since the 9,10 bond has more double-bond character than the 1,2 bond.[33] In this manner, the specific identification of the doublets corresponding to H2 and H10, and their coupling partners H3 and H9, can be made. H7 appears as a triplet, so that the corresponding coupling partners H6 and H8 can be identified. The two remaining doublets with a vicinal coupling constant of 9 Hz can be attributed to H4 and H5. The specific identification of the two doublets corresponding to respectively H4 and H5 can be made using the COSY long-range technique. This technique was also useful for the specific identification of the signals belonging to H6 and H8.

B. Chemical Shifts. The chemical shifts of the aromatic region of the bichromophoric compounds and their respective reference compounds are represented in Table II. The NMR spectra of the aromatic region of P2, P3, and P6 are nearly identical. The progressive deshielding of the aromatic protons going from pyrene to P1 and P2 suggests an electron-attracting inductive effect of a trimethylsilane group or a Si–Si bond. The larger δ values for H10, relative to the other aromatic protons, is due to the steric interaction between the neighboring groups, the van der Waals or peri effect, which has also been observed for other 1-substituted pyrene derivatives.[34] The differences between the chemical shifts for the corresponding aromatic protons of the disubstituted oligosilanes and the reference compound P6, $\Delta\delta = \delta(\mathrm{P}x\mathrm{P}) - \delta(\mathrm{P6})$ (with x = the number of silicon atoms in the chain), are depicted graphically in Figure 5. Since the δ values of the aromatic region of P2, P3, and P6 are nearly identical, similar Δδ patterns are found when using P2 or P3 as a reference. For comparison, the respective Δδ values for the respective alkane analogues are also shown in the same figure.[18] Negative Δδ values, signifying large shielding effects, are found for all the aromatic protons. These effects are much larger than those found in the respective alkane analogues. This suggests interactions in the ground state, in which ring-current effects of the two pyrenyl groups influence each other, resulting in the shielding. The fraction of molecules which show the intramolecular ground-state interactions seems to be larger for the silicon compounds than for the carbon compounds. The shielding effects are smaller for P4P and especially for P6P, suggesting a smaller tendency for the two pyrene moieties to come together in the ground state or a larger average distance between the two pyrene groups.

C. Relative Orientation of the Two Pyrene Groups in the Conformation Which Shows Intramolecular Ground-State Interactions. All the aromatic protons of P2P have negative Δδ values. Nevertheless, the values of H4 and H5 approach 0 and a large negative value is found for H10. A symmetrical structure is proposed in which the two pyrene groups are not parallel relative to each other, in such a way that the interplanar distance between the two planes is largest at H4 and H5 and smallest at H10 (Figure 6). Using space-filling models, it can be seen that the two H10 atoms make contact resulting in the large deviation for the Δδ value of H10. Since the distance between H4 and H5 is large, the Δδ values for these two atoms approaches 0.

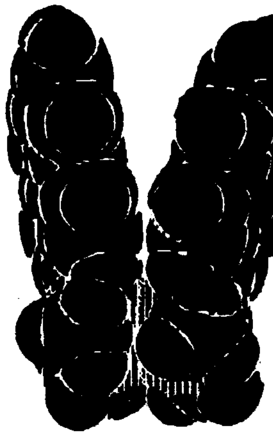

Figure 6. Proposed ground-state conformation for P2P in which the two pyrene groups interact intramolecularly.

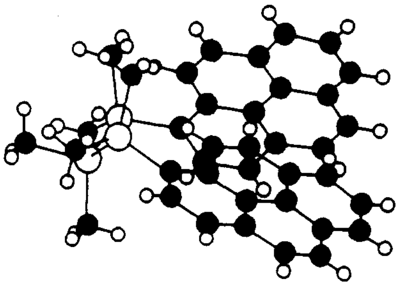

Figure 7. Proposed ground-state conformation for P3P in which the two pyrene groups interact intramolecularly: asymmetrical structure.

The Δδ pattern for P3P has a symmetrical structure with the largest negative values for H2, H3 and H9, H10, H5, H6, and H7 are less shielded than the other protons. Such a pattern can be explained if a not completely overlapping asymmetrical structure is assumed (see Figure 7). H9, H10, H2, and H3 are located above the plane of the other pyrene, resulting in the large negative Δδ values for these protons. However, the other aromatic protons still have relatively large −Δδ values, which can not be explained by this conformation alone. It has already been suggested by Reynders et al.[18] that the aromatic protons of symmetrical sandwich structures should show shieldings of

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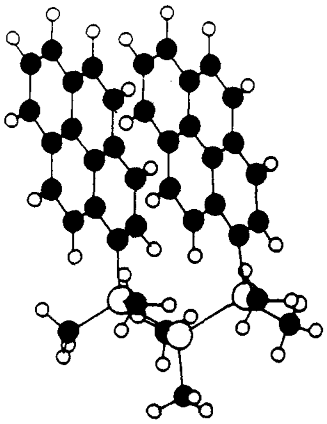

Figure 8. Proposed ground-state conformation for P3P in which the two pyrene groups interact intramolecularly: symmetrical structure.

identical magnitude, on the basis of the structure and NMR data of the [*n*,*n*]pyrenophanes.[28,35] This indicates that there is a second conformation possible which adopts a symmetrical sandwich geometry, resulting in a shift of the pattern of the first structure to larger $-\Delta\delta$ values (Figure 8). The silicon backbones of the two proposed structures have the same conformation, with the two pyrene groups in a gauche conformation relative to the silicon chain. The two structures differ only in the relative orientation of the pyrene moieties. In the symmetrical one, the H10 atoms of both pyrene groups are located between the methyl substituents on the silicon to which pyrene is attached and a methyl group on the silicon in the center of the chain. In the asymmetrical structure, the H10 atom of the first pyrene group is located near the silicon atom in the middle of the chain, while the H10 atom of the second pyrene moiety is located between the two methyl groups of the silicon atom to which it is attached.

The aromatic protons of P4P and P6P still show negative $\Delta\delta$ values. A symmetrical $\Delta\delta$ pattern is found, where the protons H2, H3, H9, and H10 show somewhat larger shieldings, similar to those found for P3P. This suggests that two conformations are present in which the two pyrene groups interact intramolecularly in the ground state, similar to those proposed for P3P. However, the $-\Delta\delta$ values are much smaller, indicating that a smaller fraction of molecules show intramolecular ground-state interactions or that the average distance between the two pyrenyl groups which interact intramolecularly is larger. The shielding of the aromatic protons of P6P is very small, suggesting that almost no molecules are present in the ground state which allow intramolecular interaction between the two pyrene groups. This supports the information obtained from the absorption spectra of P6P and P6.

D. Solvent Dependence of the Intramolecular Ground-State Interaction in P3P. The NMR spectrum of P3P was also taken in deuterated cyclohexane. In Figure 9, $\Delta\delta = \delta(\text{P3P}) - \delta(\text{P3})$ in chloroform-*d* and cyclohexane-d_{12} are compared. Although the $\Delta\delta$ pattern for the pyrenyl protons is similar in the two solvents, the $\Delta\delta$ values in cyclohexane-d_{12} are always more negative than in chloroform-*d*, which suggests that the shielding and thus the intramolecular interaction are more pronounced in cyclohexane. This can be explained by comparing the Hildebrand parameters of both solvents.[4,18,19,32] The Hildebrand solubility parameters, δ_H(solvent), of chloroform and cyclohexane are 9.3 and 8.2 (cal/cm^3)$^{1/2}$, respectively; δ_H(solvent) of polycyclic aromatic compounds (such as naphthalene, anthracene, and phenanthrene) is situated around 9.9 (cal/cm^3)$^{1/2}$. Thus, the δ_H(solvent) parameter of chloroform is closer to the value of aromatic compounds than cyclohexane. A better solvation of the pyrene groups can be expected in chloroform and, hence, a greater tendency of the two pyrene groups to come together intramolecularly in chloroform than in cyclohexane.

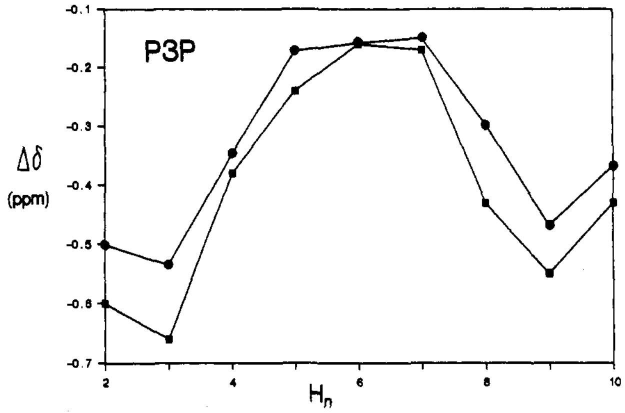

Figure 9. Differences in chemical shift, $\Delta\delta$ (in ppm), of the aromatic protons of P3P, with respect to *P*3: $\Delta\delta = \delta(\text{P3P}) - \delta(\text{P3})$ in $CDCl_3$ (•) and in C_6D_{12} (■).

Table II. Chemical Shift δ (in ppm) of P*x*P and the Reference Compounds in Deuterated Chloroform

	δ (H2)	δ (H3)	δ (H4)	δ (H5)	δ (H6)	δ (H7)	δ (H8)	δ (H9)	δ (H10)
pyrene[15]	8.000	8.182	8.075	8.075	8.182	8.005	8.182	8.075	8.075
P1	8.195	8.145	8.079	8.045	8.170	8.000	8.200	8.120	8.370
P2	8.210	8.210	8.140	8.110	8.260	8.065	8.240	8.170	8.320
P3	8.205	8.205	8.135	8.110	8.260	8.065	8.240	8.165	8.335
P6	8.205	8.205	8.140	8.110	8.255	8.065	8.240	8.160	8.330
P2P	8.040	8.040	8.100	8.100	8.125	7.935	8.010	7.980	7.630
P3P	7.705	7.670	7.790	7.940	8.100	7.915	7.940	7.695	7.970
P4P	8.040	8.040	8.000	8.060	8.175	8.000	8.175	8.000	8.155
P6P	8.120	8.120	8.075	8.040	8.190	8.000	8.175	8.075	8.230

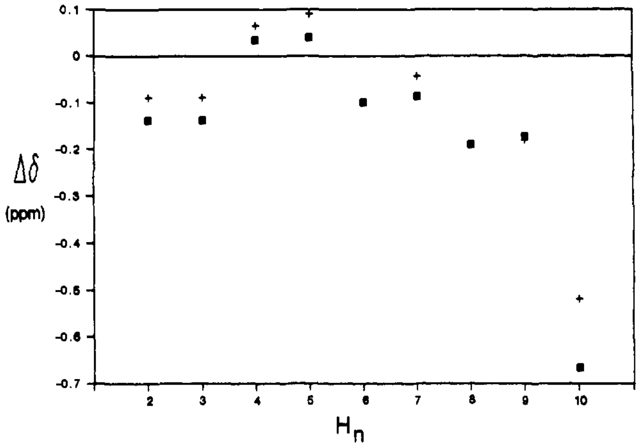

Figure 10. Differences in chemical shift, $\Delta\delta$ (in ppm), of the aromatic protons of P2P, with respect to P2: $\Delta\delta = \delta(\text{P2P}) - \delta(\text{P2})$ in CD_2Cl_2 at 20 °C (■)and at -50 °C (+).

E. Temperature Dependence of the Intramolecular Ground-State Interaction in P2P. The NMR spectra of P2P and P2 in CD_2Cl_2 were recorded at 20 and at -50 °C. There was a strong broadening of the signals upon lowering the temperature, making the assignment of H6 and H8 impossible (see Table II). Since even at -50 °C the broadening of the aromatic signals was also observed for P2, the rotation of the pyrene group relative to the silane chain should be slow on the NMR time scale at this temperature. $\Delta\delta = \delta(\text{P2P}) - \delta(\text{P2})$ for the different aromatic protons was calculated and reported in Figure 10. The $\Delta\delta$ variation is similar to that in $CDCl_3$, although the shieldings are less pronounced. The Hildebrand parameter of CH_2Cl_2 (δ_H(solvent) = 9.7) is indeed larger than that in $CHCl_3$ (δ_H(solvent) = 9.3), so that a better solvation of the pyrene group can be expected. The shielding decreases slightly upon lowering the temperature, which suggests that the ring-current effects are less pronounced.

Single Photon Timing Measurements. The fluorescence decays in the excimer region were recorded for P2P, P3P, and P4P in

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[35] Staab, H. A.; Riegler, N.; Diederich, F.; Krieger, C.; Schweitzer, D. *Chem. Ber.* **1984**, *117*, 246.

Table III. Fluorescence Decay Parameters of P2P, P3P, P4P, and P3′P

	P2P[a]	P3P[a]	P4P[a]	P3′P[b]
τ_1 (ns)	0.45	2.1	1.88	8.1
τ_2 (ns)	58.7	50.0	30.73	57.9
τ_3 (ns)	–	118.2	58.13	129.8
$R(-/+)$	–0.7	–0.25	–0.8	–0.99
	(500 nm)	(555 nm)	(560 nm)	(520 nm)

[a] In isooctane. [b] 1,3-Di(1-pyrenyl)propane in toluene, see ref 17.

isooctane using the single photon timing technique. The decays were analyzed globally as a sum of exponentials:

$$i_D(t) = \sum_i A_{2i} e^{-t/\tau_i} \tag{1}$$

If there is no interaction between the two pyrene groups in the ground state, the excimer in the excited state, D*, is not produced upon direct excitation, but is produced from the locally excited state. The concentration $[D^*]_0$ at $t = 0$ is therefore equal to 0. The excimer fluorescence intensity, $i_D(t)$, is proportional to the concentration of the excimer in the excited state $[D^*]_t$. Consequently, at t = 0, $i_D(t=0)$ should be 0. On the basis of eq 1, it can be seen that this is true if the sum of the preexponentials equals 0,[18,19] or $R(-/+)$, the ratio of the negative amplitude A_{21} to the sum of the positive amplitudes $A_{22} + A_{23}$, is equal to –1.

$$i_D(t=0) = 0 \Leftrightarrow \sum_i A_{2i} = 0 \quad \text{or} \tag{2}$$

$$\Leftrightarrow R(-/+) = A_{21}/(A_{22} + A_{23}) = -1 \tag{3}$$

The decay of P2P could be fitted to a sum of two exponentials, while P3P and P4P are fitted to a sum of three exponentials. The decay times and the $R(-/+)$ values are listed in Table III. It can be concluded that $R(-/+)$ clearly deviates from –1 for these three compounds. This deviation could be due to a contribution of monomer emission to the fluorescence decay. However, the locally excited state fluorescence is almost completely quenched and the decays were recorded at the red edge of the excimer emission (see Table III). The deviation could also be due to an inadequate time resolution of the SPT experiment. This is the case when the time increment is too large, hence the number of channels containing the shortest decay time are too small. However, the decays were recorded using several time increments (0.653, 0.326, and 0.163 ns per channel for the measurements of P3P) and were subsequently analyzed globally. In addition, simulations were performed using the same number of decays and the same time increments as in the experiment with P3P. Correct decay times and $R(-/+)$ values are resolved within the experimental error.

The deviation from unity must therefore be due to a fraction of molecules in which the two pyrene groups interact intramolecularly in the ground state, which directly absorb a fraction of the excitation light: excimer formation can take place immediately by light absorption by the molecules which are already in an excimer conformation in the ground state. P3P in isooctane shows the largest deviation from unity, even though a value close to unity is found for its alkane analogue P3′P in toluene.[18] This indicates that a larger fraction of the molecules which are in a conformation where the two pyrene groups interact is present for P3P than for its alkane analogue. Similar conclusions were drawn based on the NMR data. The relative orientation of the pyrene groups which interact intramolecularly in the ground state has been discussed in the NMR study. The asymmetric structure needs a minor rotation of a Si–Si bond to obtain an excimer geometry in which the long axes of the two pyrene groups are oriented at an angle with respect to one another. The formation of this excimer together with the symmetric one could explain the triexponential character of the excimer decay of P3P. P4P shows also a triexponential decay, which is an indication that two excimers are present in the excited state. The NMR data of P4P suggest that there are two geometries possible for the intramolecular interaction, analogous to those of P3P, and the triexponential decay measured in the excimer region indicates that two excimers are present in the excited state. P2P shows a double exponential decay, indicating that only one excimer exists in the excited state, presumably in a conformation similar to the structure proposed in Figure 6.

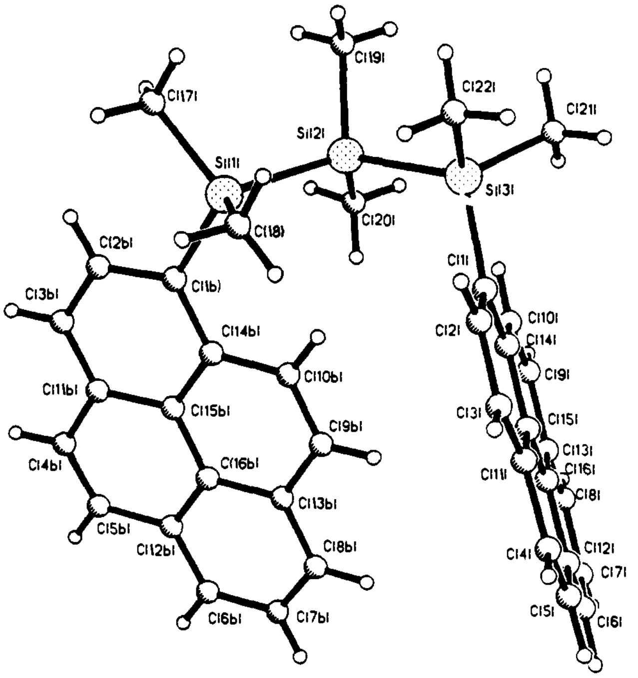

Figure 11. X-ray structure of P3P.

Crystal Structure of P3P. The structure of P3P in the solid state could be determined using X-ray analysis, as shown in Figure 11. It is immediately clear that the silane chain is folded in such a way that the two pyrene groups are close in space, with the two planes oriented perpendicular to each other. For example, the distance between C(15) and the hydrogen atom on C(9b) is only 2.65 Å. It is also noteworthy that the conformation around Si(1) and Si(2) is nearly eclipsed. In this regard, the torsional angle between C(18) and Si(3) around the Si(1) and Si(2) bond is 6.4°. The conformation of the second pyrene group (on Si(3)) relative to the silicon chain is gauche. It should be noted that the Si(1)–Si(2) bond length is 2.355 Å, a value much larger than for a CH_2–CH_2 bond, allowing a practically eclipsed geometry without steric hindrance of the methyl groups C(17) and C(19). The conformation in the crystal is, however, not very different from that of an excimer geometry. A minor rotation would result in a nonsandwich excimer geometry, where the long axes of the pyrene groups are oriented perpendicular to each other. If the molecules in solution which show intramolecular interaction should have the same structure, the largest shielding should be expected for H3 and H4. However, the NMR data indicate largest shieldings for H2, H3, H9, and H10. This suggests that a conformation close to the crystal structure is not responsible for the intramolecular interactions in the ground state.

Conclusions

P2P, P3P, and P4P all undergo excimer formation in the excited state. In contrast, the excited state of P6P is characterized as a $\sigma(\text{Si–Si}) \rightarrow \pi^*$ charge-transfer state. Comparison of the absorption spectra of the bichromophoric systems with their respective reference compounds reveals that the two pyrene groups interact in the ground state. ^{1}H NMR shows ring-current effects between the two pyrene groups. The shielding of all the aromatic protons is explained by a fraction of the molecules which are in a conformation where the two pyrene groups can interact intramolecularly in the ground state. A symmetrical sandwich structure and an asymmetrical, not completely overlapping structure is proposed for the conformations of P3P, P4P, and P6P in which the two pyrene groups interact intramolecularly. The interaction between the two pyrene groups decreases going to longer silane chains such as in P4P and P6P. For P2P, a symmetrical structure is proposed in which the two pyrene planes are not parallel, with the two H10 atoms pointing to each other. The shielding of the aromatic protons and thus the intramolecular interaction in P3P is more pronounced in cyclohexane-d_{12} than in chloroform-*d*, which is explained by a better solvation of the pyrene groups by chloroform than by cyclohexane. Upon lowering the temperature, the shielding of the aromatic protons of P2P becomes smaller, which suggests that the fraction of conformations where the two pyrene groups interact intramolecularly is smaller or that the distance between the two pyrene groups becomes larger. Additional evidence for the ground-state interaction is given by the SPT results, i.e. the ratio of the negative preexponential factor to the sum of the positive factors in the multiexponential response function of time-resolved excimer fluorescence deviates from -1. The intramolecular interaction between the two pyrene groups in the ground state also provides an explanation as to why no locally excited state fluorescence appears for P3P in solutions of increased viscosity, since even in a viscous environment enough molecules are present with a conformation in the ground state where the two pyrene groups can interact, so that excimers are immediately produced upon excitation. It can be concluded that the intramolecular ground-state interaction in the ground state between the two pyrene groups is more pronounced for the silicon systems than for the analogous alkane compounds.[18]

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