sections.⁹ The calculations assume that the phenol behaves as an ideal gas, possibly underestimating the number density and yielding too large a cross section.

Conclusion

We have demonstrated a photoacoustic apparatus and technique capable of detecting a minimum absorptivity on the order of 4 $\times 10^{-10}$ /cm. To demonstrate this sensitivity, we recorded the 4–0 and 5–0 O–H overtone spectra of phenol in the gas phase using the vapor present over the solid at room temperature. Several modifications to the standard methods of overtone photoacoustic spectroscopy were made to achieve this level of sensitivity. Two important and simple changes are that the cell is run at an acoustic resonance with a heavy rare gas as a buffer and that baffles are added between the windows and the region near the microphone. Although the cell design described in this paper is not necessarily optimal, we believe that it offers many advantages for intracavity gas-phase photoacoustic spectroscopy because the design is simple, inexpensive, easy to maintain, may be used for a wide variety of samples, even those with limited vapor pressure, and is still extremely sensitive.

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Ground-State Dimers in Excimer-Forming Bichromophoric Molecules. NMR and Single-Photon-Counting Data. 2. Racemic and Meso Dipyrenylpentanes and Dipyrenylalkanes

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¹H NMR spectra of the racemic and meso diastereomers of 2,4-di(1-pyrenyl)pentane (1DPP) in toluene- d_8 and of the 1,*n*-di(1-pyrenyl)alkanes (1Py(*n*)1Py with n = 0-10 and 13) and 1,*n*-di(2-pyrenyl)alkanes (2Py(*n*)2Py with n = 1-10 and 14) in chloroform-*d* were measured at room temperature. The conformer distribution in both 1DPP molecules was determined from an analysis of the vicinal coupling constants between the methylene and methine protons. In *meso*-1DPP, an intramolecular sandwichlike ground-state dimer was detected, whereas in *rac*-1DPP a dimer only overlapping at the aromatic protons H9 and H10 is formed. The presence of both dimers was confirmed by time-resolved fluorescence measurements (single-photon counting (SPC)). With the dipyrenylalkanes, an analysis of the chemical shifts of the aromatic protons shows that sandwich dimers are not present. Only in the case of 1Py(3)1Py is a partial-overlap dimer detected. These findings are supported by results from SPC measurements.

Introduction

Intramolecular excimer formation has been studied with various dipyrenylalkanes,1-5 including meso and racemic dipyrenylpentanes,^{2,3} by employing photostationary and time-resolved fluorescence measurements. With 1,3-di(2-pyrenyl)propane, 2Py(3)2Py, it has been shown that the monomer and excimer fluorescence decays are double-exponential,⁴ whereas triple-exponential decays were observed in the case of 1,3-di(1-pyrenyl)propane, 1Py(3)1Py.^{1d,5} These data have been analyzed by use of a kinetic scheme consisting of two or three discrete excited states, respectively, identified as one group of rapidly (<400 ps) interconverting monomer conformers and either one or two excimers.³⁻⁵ In a different approach, the monomer fluorescence decays of 1Py(3)1Py have been interpreted by using distributions of decay times.^{5b,6} As ground-state dimers have been detected in both series of the 1,n-bis(1-pyrenylcarboxy)- and 1,n-bis(2pyrenylcarboxy)alkanes,⁷ leading to changes in the kinetic schemes and hence in the treatment of data coming from the fluorescence experiments,^{3b} the presence of dimers was also investigated for the corresponding dipyrenylalkanes. The results of these studies, comprising ¹H NMR and time-correlated single-photon-counting (SPC) measurements, are reported in this paper.

Experimental Section

 $1,6-Di(1-pyrenyl)hexane,^{8} 1Py(6)1Py$, was synthesized as follows. 6-(1-Pyrenyl)hexanoic acid (mp 200-201 °C) was made from the monoethyl ester of 1,6-hexanedioic acid chloride in a

Friedel-Crafts reaction with pyrene and subsequent reduction with hydrazine hydrate. The acid chloride of this compound was reacted with pyrene to 1-(1-pyrenoyl)-5-(1-pyrenyl)pentane (mp 172-174 °C), which was reduced (Huang-Minlon) to 1Py(6)1Py (mp 187-188 °C). The synthesis of the other compounds treated here has been described before^{1a,3b,4} or will be published elsewhere.

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Figure 1. Conformers present in (a) the racemic and (b) the meso diastereomers of 2,4-di(2-pyrenyl)pentane (2DPP) and 2,4-di(1-pyrenyl)pentane (1DPP), based on an analysis of the vicinal coupling constants in the ¹H NMR spectra. The conformer TG(=GT) (within brackets in (a)) is not detected in the racemic compounds at room temperature; see text.

The meso and racemic diastereomers of 2,4-di(1-pyrenyl)pentane were separated by HPLC. The experimental conditions for the ¹H NMR were the same as in the preceding paper.⁷ The SPC measurements (at 520 nm) were carried out with a nanosecond flash lamp (N₂, 337 nm),^{1d} with substances purified by HPLC. A monochromator was used to select the excitation wavelength.

Results and Discussion

rac- and meso-2,4-Di(2-pyrenyl)pentane. The conformer distribution in the racemic and meso diastereomers of 2,4-di(2pyrenyl)pentane, rac- and meso-2DPP, has been analyzed in detail on the basis of the vicinal coupling constants in the aliphatic chain.^{2b,3b} In the case of rac-2DPP, the conformers TT and GG (Figure 1a) are present in a mole fraction ratio of 70/30 (chloroform-d) and 78/22 (toluene-d₈) at 27 °C. With meso-2DPP in these solvents, the predominant conformer is TG(=GT). In addition, at least 10% of the excimer-like ground-state dimer TT and smaller percentages of the other three conformers, except $\bar{G}\bar{G}$, were detected (Figure 1b).^{3b} Using these data, a connection between the conformer population and the chemical shifts can be made. This can then be used as a basis for the interpretation of chemical shift data of molecules for which the conformers cannot be determined directly from the vicinal coupling constants, as with 1Py(3)1Py and the other dipyrenylalkanes, to the treated below.

The changes in chemical shift for the aromatic protons H3–H7 of *rac*- and *meso*-2DPP in toluene- d_8 at 27 °C, as compared to 2-isopropylpyrene (2IPy),^{3b} $\Delta \delta = \delta$ (2DPP) – δ (2IPy), are depicted in Figure 2, with clearly different results for the two diastereomers. As possible through-bond interactions from one pyrenyl group on the other via the connecting chain will be identical for the two compounds, the differences in the chemical shift patterns must be brought about by ring-current effects,⁷ reflecting the different conformer populations.

In rac-2DPP, the two pyrenyls can only exert a ring-current effect on each other in conformer TT, as the separation between these groups in the second conformer GG is too large (Figure 1a). The $\Delta\delta$ values for rac-2DPP (Figure 2a), therefore, represent the pattern for TT. In this conformer (cf. Table III in ref 3b) the proton H1 (=H3) is in the shielding cone of the other aromatic moiety, which explains the negative $\Delta\delta$ value. The positive $\Delta\delta$ values for H5-H7 are due to the fact that these protons are located in the deshielding zone.

For the predominant conformer TG(=GT) in *meso*-2DPP, ring-current effects are not to be expected; see Figure 1b. This



Figure 2. Differences in chemical shift $\Delta\delta$ (in ppm) of the aromatic protons, with respect to the model substance 2-isopropylpyrene (2IPy), of *rac*- and *meso*-2,4-di(2-pyrenyl)pentane (*rac*- and *meso*-2DPP) in chloroform-d at 27 °C ($\Delta\delta = \delta(2DPP) - \delta(2IPy)$). See text. The aromatic protons H2-H7 are indicated as circles, in a side-on view of the pyrene moiety.

is also the case for GG and $G\overline{G}(=\overline{G}G)$. The experimentally observed changes in chemical shift (Figure 2b) must therefore come from TT, next to a small contribution from the minor^{3b} component $T\bar{G}(=\bar{G}T)$. In the excimer-like ground-state dimer TT the two pyrenyls will exert a shielding on all aromatic H atoms. The relative magnitude of this effect on the different protons depends on the specific configuration of the two pyrenvls in the dimer. For example, identical shieldings occur for all protons in a parallel sandwich, as has been discussed⁷ for [4.4](2,7) pyrenophane and for the 1,n-bis(2-pyrenylcarboxy)alkanes, 2PC(n)-2PC, with n > 8. On the other hand, a shielding diminishing from H3 toward H7 (Figure 2b) points to a dimer in which the interplanar distance between the pyrenyls increases from H3 toward H7. Such a wedge-shaped dimer structure is in fact to be expected in a dipyrenylpentane, considering the values of the van der Waals radii (0.35 nm)⁹ of the pyrenyls as compared to the distance requirements set by the alkane chain in the TT conformer of meso-2DPP.

rac- and meso-2,4-Di(1-pyrenyl)pentane. The ¹H NMR spectra of *rac-* and *meso-1DPP* in toluene- d_8 at 24 °C are analyzed in a manner similar to that used for *rac-* and *meso-2DPP* (aliphatic protons)^{3b} and 1Py(3)1Py (aromatic protons); see below. The coupling constants and chemical shifts are listed in Table I, where also the data for the model substance 1-isopropylpyrene (11Py) can be found. The conformer populations are determined according to the same procedure employed with the 2,4-di(2-pyrenyl)pentanes, considering first only one, then two, and, when necessary, more than two conformers at a time.^{3b} In this procedure the calculated data of Table II are used.¹⁰

rac-1DPP. In the NMR spectrum of *rac-1DPP*,^{2a} in contrast to *rac-2DPP*,^{3b} no split s is observed for the central peak of the methylene triplet. Moreover, a line-form analysis shows that a broadening of this peak has not occurred. From s = 0, it then follows that $\Delta J = 0$; i.e., ${}^{3}J_{AX} = {}^{3}J_{AX'}$ (Table I).^{3b,11a,12} Only

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⁽¹⁰⁾ Contrary to the statement in Table VI of ref 3b, the methylene protons in the conformer pairs such as TG(=GT) in *meso*-2DPP are not equivalent; i.e., the ring-current effects exerted in TG are not canceled by GT; see ref 11a. Therefore, the expected ring-current effects given for $\Delta\delta(CH_2)$ in that table are in error. This is corrected in the present Table II. The conclusions presented in ref 3b are not affected.

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liffe, L. H. High Resolution Nuclear Magnetic Resonance Spectrosrgamon: Oxford, 1967; Vol. 1.

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TABLE I: Chemical Shifts, δ (in ppm), and Vicinal Coupling Constants, J (in Hz), for the Racemic and Meso Diastereomers of 2.4-Di(1-pyrenyl)pentane (rac- and meso-1DPP) and for 1-Isopropylpyrene (1IPy) in Toluene-d₈ at 24 °C

	• ·	•		
substance	rac-1DPP	1 IP y	meso-1DPP	
δ(CH ₂)	2.398		2.469/2.108	
δ(CH)	3.626	3.829	3.847	
$\delta(CH_1)$	1.375	1.379	1.423	
³ J _{сн-сн}	6.90	6.90	6.79	
split s ^a	0.0			
3 J . v b	7.55			
3 J b	7.55			
³ <i>J</i> ² , ²			7.57	
³ / ₄ , ⁶			7.01	
2 J d			-13.7	
$\delta(H2)$	7.874	7.813	7.857	
δ(H3)	8.020	7.946	8.013	
δ(H4)	7.867	7.809	7.810	
δ(H5)	7.827	7.783	7.780	
δ(H6)	7.887	7.930	7.910	
δ(H7)	7.655	7.758	7.742	
δ(H8)	7.458	7.910	7.877	
δ(H9)	6.839	7.888	7.755	
$\delta(H10)$	7.130 ^e	8.168	8.000	
³ J ₂₃	8.05	7.97	7.99	
${}^{3}J_{45}^{25}$	9.07	9.06	9.0	
${}^{3}J_{67}^{3}$	7.63	7.60	7.63	
${}^{3}J_{9,10}^{3}$	9.34	9.32	9.3	
${}^{4}J_{68}$	1.1	1.1	1.0	

^aSee text and refs 3b and 11a. ^bVicinal coupling constant between a methine proton (A) and a methylene proton (X or X') in rac-1DPP. "Vicinal coupling constant between a methine proton (A) and a methylene proton (M or X) in *meso*-1DPP. ${}^{d}J_{gem}$ is the geminal coupling constant between the methylene protons. e The lines attributed to H9 and H10 are unusually broad (line width 7.2 Hz). This phenomenon will be treated in a separate publication.

for TG(=GT), in a single-conformer approach, are the calculated coupling constants ${}^{3}J_{AX}$ and ${}^{3}J_{AX'}$ (7.5 Hz, Table II) close to the experimental value of 7.55 Hz (Table I). However, this conformer would lead to a positive $\Delta \delta$ (= δ (rac-1DPP) - δ (1IPy)) for CH and a negative $\Delta \delta$ for CH₃ (see Table III of ref 3b), contrary to observation: $\Delta\delta(CH) = -0.203$ ppm and $\Delta\delta(CH_3) = -0.004$ ppm (Table I). In an analysis with two conformers, only pairs from the set TT, GG, and TG(=GT) can be considered, as the other members of the total conformer population (Table II) would lead to a lowering of the mean value $\langle J \rangle$ of ${}^{3}J_{AX}$ and ${}^{3}J_{AX'}$. An appreciable participation of TG(=GT) can be excluded, however, as $\delta(CH_3)$ does not show the then expected upfield shift; see above. Therefore, only TT and GG remain. From ${}^{3}J_{AX} = {}^{3}J_{AX'}$ (Table I), it can be deduced^{3b,11a} that their mole fraction is equal to $50/50.^{13}$ For rac-1DPP in chloroform-d the same result has been obtained.2a

meso-1DPP. From a comparison of the experimental coupling constants ${}^{3}J_{AM} = 7.57$ Hz and ${}^{3}J_{AX} = 7.01$ Hz of meso-1DPP in toluene- d_8 (Table I) with the calculated couplings for the six different staggered conformers (Table II), it follows immediately that these data cannot be explained with only one conformer. This also applies to TG(=GT), the conformer with couplings approaching the experimental data.14

Allowing two conformers and taking the data from Table II, it is seen that, e.g., the pair $TG(=GT) + T\overline{G}(=\overline{G}T)$ in a mole fraction ratio 9/1 would approximately reproduce the experimentally determined coupling ${}^{3}J_{AX}$. However, this pair would lead to an overall shielding for the methine proton (Table II),



Figure 3. Differences in chemical shift $\Delta\delta$ (in ppm) of the aromatic protons, with respect to the model substance 1-isopropylpyrene (1IPy), of rac- and meso-2,4-di(1-pyrenyl)pentane (rac- and meso-1DPP) in chloroform-d at 24 °C ($\Delta \delta = \delta (1\text{DPP}) - \delta (1\text{IPy})$). See Table I. The aromatic protons H2-H7 are indicated as circles, in a side-on view of the pyrene moiety

whereas a deshielding ($\Delta \delta = 0.013$ ppm) is in fact observed; see Table I. This deshielding can be attributed to the ground-state dimer TT, in which a strong shift to higher ppm values occurs for the CH group (Table II). Taking another combination with TT, the pair TG(=GT) + TT would result in a value between 7.5 and 12.5 Hz for ${}^{3}J_{AM}$ (Table II). The observed ${}^{3}J_{AM}$ of 7.57 Hz would then practically exclude a participation of TT. However, an increase in ${}^{3}J_{AM}$ caused by TT can be compensated by the presence of GG. In such a case, the mole fraction difference between TT and GG equals 5.6%, determined from the experimental difference $\Delta J = 0.56$ Hz as compared to the calculated value of 10.0 Hz (Table II). As the three conformers TG(=GT), TT, and GG have a value of 7.5 Hz for $\langle J \rangle$, clearly larger than the observed value of 7.29 Hz, they cannot be the only ones. Hence, some admixture of $T\bar{G}(=\bar{G}T)$ and $G\bar{G}(=\bar{G}G)$ is necessary.¹⁵ The resulting conformer population in *meso*-1DPP, with TG(=GT) as the major conformer, next to TT, GG, $T\bar{G}(=\bar{G}T)$, and $G\bar{G}(=\bar{G}G)$, is similar to what has been observed with meso-2DPP (Figure 1b) and is in accord with calculations of the conformer energies for meso-2,4-diphenylpentane.3b,16 It should be pointed out in this connection that the ¹H NMR spectrum of meso-1DPP¹⁷ reveals that this substance contains around 15% of an impurity, cis- and trans-2,4-di(1-pyrenyl)pentene-2, in about equal amounts.¹⁸ This impurity could not be removed by HPLC. Such a pentene elimination product has also been encountered with meso-2,4-di(N-carbazolyl)pentane.¹⁹ For this reason, time-resolved monomer fluorescence measurements of meso-1DPP can be complicated by the presence of these pentenes.²⁰

⁽¹²⁾ $s = (J_{gem}^2 + \Delta J^2)^{1/2} - |J_{gem}|$, where J_{gem} is the geminal coupling constant ${}^2J_{XX'}$ between the methylene protons X and X' and $\Delta J = |{}^3J_{AX} - {}^3J_{AX'}|$; see ref 13. (13) When in *rac*-1DPP the two conformers TT and GG with mole fractions X_1 and X_2 are present, $\Delta J = |{}^3J_{AX} - {}^3J_{AX'}| = |X_1 - X_2|(J_1 - J_g)$, where ${}^3J_{AX}$ and ${}^3J_{AX'}$ are the vicinal couplings between the methine proton A and the methylene protons X and X'. J_1 and J_g are the trans and gauche couplings, respectively: see refs 11a and 3b. respectively; see refs 11a and 3b. (14) For meso-1DPP in chloroform-d a mole fraction of 99% for TG(=-

GT) has been reported; see ref 2a.

⁽¹⁵⁾ The conformers $T\bar{G}(=\bar{G}T)$ and $G\bar{G}(=\bar{G}G)$ are expected to be present in equal amounts, on the basis of a calculation of the relative conformer energies im *meso*-2,4-diphenylpentane; see ref 16. These calculations also show that the presence of \overline{GG} can be excluded.

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⁽¹⁷⁾ The assignment of the resonances of meso-1DPP (see Table I) and of cis- and trans-2,4-di(1-pyrenyl)pentene-2 is confirmed by analyzing a 2D-COSY NMR spectrum. The amount of the two pentenes (15%; see text) is determined by integration of their NMR resonances. An analysis of the mass spectrum of meso-1DPP (around 10% of the pentenes) supports this conclusion.

⁽¹⁸⁾ From molecular mechanics calculations (Program MMP2, Revision 6.0; Molecular Design Limited: San Leandro, CA) on 2,4-di(1-pyrenyl)-pentene-2, a dihedral angle of around 55° between the pyrenyl and the ethylenic groups was determined. In accordance with this relatively large dihedral angle, only small differences were found to exist between the fluorescence and absorption spectra of the pentenes and those of meso-1DPP, making the detection of the pentenes in these spectra difficult.

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⁽²⁰⁾ meso-1DPP undergoes a photochemical reaction under laser excitation at 298 nm. As a consequence, the amplitude of the shortest excimer decay time decreases with the duration of the excitation. Such a reaction is not obvious at an excitation wavelength of 330 nm.

TABLE II: Calculated Vicinal Coupling Constants ${}^{3}J_{AX}$, ${}^{3}J_{AX'}$, and ${}^{3}J_{AM}$ (in Hz) and Expected Ring-Current Effects, As Compared to 2-Isopropylpyrene, on the Chemical Shifts for the Various Protons of the Staggered Conformers in the Racemic and Meso Diastereomers of 2,4-Di(2-pyrenyl)pentane (*rac*- and *meso*-2DPP)^a

	rac-2	2DPP	•		т			
conformer	\overline{J}_{AX}	³ <i>J</i> _{AX'}	$^{3}J_{AM}$	³ J _{AX}	δ(CH ₃)	δ(CH)	δ(CH ₂)	$\Delta\delta(\mathrm{CH}_2)^b$
TT	12.5	2.5	12.5	2.5	(+)	++	+	++
GG	2.5	12.5	2.5	12.5	0	0	++	≈ 0
GG	2.5	2.5	2.5	2.5	(++)	0	(+)	++
TG(=GT)	7.5	7.5	7.5	7.5	(+)	-	+	+
$T\overline{G}(=\overline{G}T)$	7.5	2.5	7.5 '	2.5		-	0	≈0
$G\overline{G}(=\overline{G}G)$	2.5	7.5	2.5	7.5	-	+	+	+

^aSee Table VI in ref 3b and ref 10. ${}^{b}\Delta\delta(CH_2) = \delta(CH_2)_M - \delta(CH_2)_X$. An effect leading to lower ppm values (-) for the chemical shift is caused by a pyrenyl group positioned over a proton. A shift to higher ppm values (+) is observed when a pyrenyl group is located next to a proton (reversed ring current effect). Otherwise no effect (0) is found. A double sign (++) is used when both halves of 2DPP give a contribution. Parentheses around +/- indicate a minor effect.



Figure 4. Schematic representations of the possible rotamers in the TT conformers of (a) *rac*- and (b) *meso*-2,4-di(1-pyrenyl)pentane (*rac*- and *meso*-1DPP). *Rac*- and *meso*-2,5-di(2-pyrenyl)pentane *rac*- and *meso*-2DPP) are also depicted for comparative purposes. The rotamer T_1T_1 is favored energetically, as in T_1 the repulsion between the CH₃ group and the aromatic proton H2 is smaller than in T_2 .

Chemical Shifts of rac- and meso-1DPP. The chemical shift differences $\Delta\delta$ for rac- and meso-1DPP, as compared to 1IPy, are presented in Figure 3, showing considerably different pictures. For rac-1DPP, a strong shielding ($-\Delta\delta > 1.0$ ppm) is observed for H9 and H10, whereas a smaller shielding is found for H8-H6 and a deshielding occurs for H2-H5. With meso-1DPP, the absolute $\Delta\delta$ values are much smaller than for rac-1DPP. Nevertheless, for H9 and H10 a considerable shielding is observed.

In the discussion of these data it should be recalled that the number of possible conformers for the 2,4-di(1-pyrenyl)pentanes is 4 times as large as that for the 2,4-di(2-pyrenyl)pentanes.^{2a} This is the case, as for each pyrenyl group two orientations are possible (Figure 4a,c), leading to three or four different rotamers. This means that with rac- and meso-1DPP six sets of four rotamers have to be taken into account. In conformer GG of rac-1DPP (Figure 1a), the pyrenyls are too far apart to undergo ring-current effects (see Table III of ref 3b). Therefore, the large shielding on H9 and H10 (Figure 3a) is attributed to one of the three possible rotamers of the TT conformer (T_1T_1 in Figure 4a). In this partial-overlap conformer T_1T_1 , the two pyrenyls only overlap at the protons H9 and H10, without forming a sandwichlike ground-state dimer. The smaller shielding of H8 and H7 means that these protons are approaching the deshielding cone, which is responsible for the positive $\Delta \delta$ values for H2-H5 (Figure 3). It has been suggested^{3b} that the configuration of rac-1DPP in which the pyrene moieties overlap at the protons H10-H7, is structurally related to the asymmetric, relatively short-lived (73 ns, n-hexadecane)^{5a} excimer of 1Py(3)1Py. In rac-1DPP this is the by far predominant excimer, as is seen from the amplitude ratio 103.5/2.8 of the decay times τ_2 (64.2 ns) and τ_1 (146 ns) in Figure 5b, below.

In meso-1DPP, neither the major conformer TG(=GT) nor GG and $G\bar{G}(=\bar{G}G)$ give rise to ring-current effects, which are only to be expected (Figure 1b) for TT and $T\bar{G}(=\bar{G}T)$.^{3b} In TT, three different rotamers have again to be envisaged: T_1T_1 , $T_1T_2(=T_2T_1)$, and T_2T_2 ; see Figure 4c. The rotamers T_1T_1 and T_2T_2 are fully overlapping dimers, leading to a shielding for all aromatic protons as discussed with meso-2DPP, whereas in $T_1T_2(=T_2T_1)$ the pyrenyls only overlap at one aromatic ring. In the conformer $T\bar{G}$ (= $\bar{G}T$) the same relative orientations of the pyrenyl groups are present as in TT of *rac*-1DPP (Figure 4a), although the methyl groups take up different positions. The shielding of H9 and H10, therefore, is attributed to $T\bar{G}(=\bar{G}T)$. As a result, the superposition of the contributions from the three rotamers in each of the two conformers TT and $T\bar{G}(=\bar{G}T)$ leads to the $\Delta\delta$ pattern observed for meso-1DPP (Figure 3b).

SPC Measurements. meso- and rac-1DPP. The presence of excimer-like ground-state dimers can be tested by measuring the ratio of the negative and positive amplitudes in excimer fluorescence decays.⁷ The time-resolved (SPC) excimer fluorescence response functions of meso- and rac-1DPP in toluene at 25 °C are shown in Figure 5.²¹ The ratio of the negative amplitude $A(-) = A_{23}$ and the sum of the two positive amplitudes $A(+) = A_{21} + A_{22}$, R = -A(-)/A(+), in the triple-exponential representations of the excimer fluorescence intensity $i_D(t)$

$$i_{\rm D}(t) = A_{21}e^{-t/\tau_1} + A_{22}e^{-t/\tau_2} + A_{23}e^{-t/\tau_3} \tag{1}$$

of both compounds (eq 1), clearly is smaller than unity: R = 0.82for *meso*-1DPP and R = 0.46 for *rac*-1DPP.²² A similar observation has been made with *meso*-2DPP (R = 0.90), whereas with *rac*-2DPP a value of R close to unity (R = 0.98) was found.^{3b} It was then concluded that excimer formation with *meso*-2DPP, in contrast to *rac*-2DPP, can take place directly²³ by light absorption in the excimer-like conformer TT, present to at least 10% (see above). The observation that R = 0.82 for *meso*-1DPP

⁽²¹⁾ It should be noted that the longest time (τ_1) in the excimer fluorescence decay of *rac*-1DPP in toluene at 25 °C (Figure 5b) cannot be determined with high precision, due to the unfavorably large value of the ratio $A_{22}\tau_2/A_{21}\tau_1$. The monomer fluorescence decay of *rac*-1DPP can only be fitted with four exponentials.

⁽²²⁾ The value of the excimer amplitude ratio R = -A(-)/A(+) remains unchanged, when the excimer fluorescence response functions depicted in Figure 5 are fitted with four exponentials in a global analysis (ref 3) together with the corresponding monomer decays (see ref 21). In the excimer decays, the shortest subnanosecond time τ_a is not resolved under the time resolution of the experiment. SPC experiments with *meso*- and *rac*-1DPP in toluene at 25 °C, using a picosecond laser instead of a nanosecond flash lamp as the excitation source (same time per channel), result in similar values for the amplitude ratio R.

⁽²³⁾ The observation that the amplitude ratio R = -A(-)/A(+) is smaller than unity, when other factors influencing R (see ref 7) can be excluded, does not necessarily mean that excimers are formed instantaneously after light absorption by a ground-state dimer. It can also indicate that excimer formation takes place from conformers in which a change in the relative configuration of the pyrenyl groups occurs within the time resolution of the SPC experiment. This cannot be decided from the data presented here. Experiments with improved time resolution are in progress to investigate this particular problem.

	δ(H1)	δ(H4) ^a	δ(H5)	δ(H6) ^a	δ(H7)	$\delta(\alpha$ -CH ₂)	$\delta(\beta$ -CH ₂)	$\delta(\gamma$ -CH ₂)
2Py(n)2Py, n =								
1	8.123	8.009	8.052	8.162	7.978	4.891		
2	8.084	8.022	8.063	8.175	7.989	3.612		
3	8.040	8.026	8.052	8.158	7.972	3.200	2.446	
4	8.003	7.980	8.037	8.153	7.975	3.140	2.001	
5	8.007	7.975	8.017	8.149	7.969	3.071	1.950	1.59
6	7.988	8.003	8.039	8.152	7.965	3.055	1.882	1.53
7	7.983	7.992	8.026	8.144	7.962	3.042	1.853	1.48
8	7.989	8.009	8.036	8.146	7.961	3.036	1.848	Ь
9	7.989	8.010	8.034	8.144	7.958	3.032	1.837	Ь
10	7.993	8.016	8.038	8.146	7.960	3.035	1.837	Ь
14	7.998	8.019	8.041	8.146	7.959	3.039	1.840	Ь
2EtPv	8.011	8.016	8.039	8.141	7.954	3.089	(1.464)	

 $a^{3}J_{45} = 9.04$ Hz, ${}^{3}J_{67} = 7.65 \pm 0.03$ Hz, independent of chain length. ^bCannot be determined due to line congestion. ^c Methyl group.

similarly supports the conclusion deduced from its NMR spectrum discussed above, that a preformed excimer (TT, see Figure 4c) is present in this compound. The shortest decay times τ_3 of both meso dipyrenylpentanes are of the same order of magnitude: 2.5 ns (meso-1DPP, Figure 5a) and 2.0 ns (meso-2DPP).^{3b} From this similarity it is concluded that the same conformers are operating in the excimer formation process of both meso compounds (Figure 1b). With rac-1DPP (Figure 5b), however, the shortest decay time ($\tau_3 = 1.0$ ns) has a considerably smaller value than that observed with rac-2DPP ($\tau_3 = 16.8$ ns, ref 3b), indicating that excimer formation is more rapid with rac-1DPP than with rac-2DPP, in spite of the fact that both compounds have identical alkane chains. The difference has been attributed^{3b} to the presence of rotamers (Figure 4a) in the case of rac-1DPP. This then means that the partial-overlap rotamer T_1T_1 (see above) acts as an excimer precursor, from which an excimer can be formed within the time resolution of the nanosecond SPC experiments (<400 ps),²³ resulting in a value R = 0.46. Support for this conclusion comes from the observation that the excimer-to-monomer fluorescence intensity ratio I'/I of rac-1DPP, as well as that of meso-1DPP, is a function of excitation wavelength.²⁴ This wavelength dependence reflects the absorption spectrum of the ground-state dimer, similar to what has been observed with 1,3bis(2-pyrenylcarboxy)propane, 2PC(3)2PC.

Conclusion: Meso and Racemic Dipyrenylpentanes. For meso-1DPP a ground-state dimer (TT) is detected in toluene at 24 °C, by an analysis of vicinal coupling constants together with chemical shifts. This conclusion, similar to what has been found for meso-2DPP,^{3b} is supported by the results of SPC experiments. The pattern of the chemical shift differences $\Delta \delta$ of meso-1DPP is more complex than that of meso-2DPP, due to the presence of rotamers in the former molecule. With the conformer TT of rac-1DPP, an interaction between the pyrenyl groups in the ground state only occurs in the rotamer T_1T_1 , in which the pyrenyls partially overlap at H9 and H10. Such a configuration is not possible for rac-2DPP (Figure 4b). It is of interest that, besides the sandwich dimers found in the case of meso-1DPP, meso-2DPP^{3b} and the bis(pyrenylcarboxy)alkanes PC(n)PC,⁷ also this partial-overlap conformer T_1T_1 opens up a rapid²⁴ way to excimer formation, faster than the processes involving bond rotations in the alkane chain

NMR Spectra of 2Py(3)2Py and 1Py(3)1Py. In the ¹H NMR spectrum of 2Py(3)2Py (Figure 6a) an AB₂ spectrum is encountered around 8 ppm, as in the case of pyrene,^{25,26} which can be assigned to the aromatic protons H6/H8 (=B₂) and H7 (=A) by computer simulation (Table III). The other lines form an AB subspectrum (H4/H5) and a singlet (H1). The aliphatic protons,



Figure 5. Excimer fluorescence response functions (at 520 nm) of (a) *meso*-2,4-di(1-pyrenyl)pentane (*meso*-1DPP) and (b) *rac*-2,4-di(1-pyrenyl)pentane (*rac*-1DPP) in toluene at 25 °C. The values for the decay times τ_i and their preexponential factors A_{2i} are given; see eq 1. The ratio R = -A(-)/A(+), see text, equals 0.82 for *meso*-1DPP and 0.46 for *rac*-1DPP.

 α -CH₂ (3.200 ppm, triplet) and β -CH₂ (2.446 ppm, quintet), of the (A₂)₂X₂ type^{11a} do not show any sign of frozen-in chain conformers. The same conclusion applies to the alkane chains in the other compounds treated in this paper.

The ¹H NMR spectrum of 1Py(3)1Py is depicted in Figure 6b. Next to the resonances of the α -CH₂ (3.530 ppm) and the β -CH₂ (2.470 ppm) groups (see Table IV), three AB subspectra and one ABX subspectrum are present around 8 ppm. Similar to what

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Figure 6. ¹H NMR spectra of (a) 1,3-di(2-pyrenyl)propane (2Py(3)2Py) and (b) 1,3-di(1-pyrenyl)propane (1Py(3)1Py) in chloroform-d at 24 °C. The subspectrum of the aromatic protons is presented as an insert on an extended scale.



Figure 7. Chemical shifts δ (in ppm) of the aromatic protons of a series of 1,*n*-di(2-pyrenyl)alkanes (2Py(*n*)2Py with n = 1-10 and 14) in chloroform-*d* at 24 °C, as a function of the number of methylene groups (*n*) in the alkane chain. The data for 2-ethylpyrene (2EtPy) are also given. See Table III.

was found for 1OcPy,⁷ the protons neighboring the substitution position have undergone the largest shifts as compared to pyrene: H10 is the doublet at 8.2 ppm, whereas H2 is shifted upfield (doublet around 7.9 ppm). The assignment of these H atoms is based on the value of their vicinal coupling constants (Table IV), which are larger for H9/H10 than for H2/H3.^{7,26} Using these values, the coupling partners H9 and H3 can also be found. The remaining subspectrum AB consists of two line pairs for H4 and H5.^{7,27} The resonances in the ABX spectrum come from H6/ H7/H8. They are assigned by computer simulation, resulting in the same value for ${}^{3}J_{67}$ as found with 2Py(3)2Py (Table III).

Dipyrenylalkanes: 2Py(n)2Py and 1Py(n)1Py. The chemical shifts and vicinal coupling constants derived from the ¹H NMR spectra of the dipyrenylalkanes 2Py(n)2Py and 1Py(n)1Py are listed in Tables III and IV. The chemical shift differences $\Delta\delta$ for the aromatic protons of these compounds with respect to the model substances $2Py(14)2Py^{28}$ and 1OcPy, respectively, generally are considerably smaller than those obtained for the 1,*n*-bis(2-pyrenylcarboxy)- and 1,*n*-bis(1-pyrenylcarboxy)alkanes, 2PC-(*n*)2PC and 1PC(n)1PC.⁷



Figure 8. Differences in chemical shift $\Delta\delta$ (in ppm), with respect to the model substance 1,14-di(2-pyrenyl)tetradecane (2Py(14)2Py; see text), for (a) di(2-pyrenyl)methane (2Py(1)2Py), (b) 1,3-di(2-pyrenyl)propane (2Py(3)2Py) and 1,4-di(2-pyrenyl)butane (2Py(4)2Py), and (c) 1,8-di-(2-pyrenyl)octane (2Py(8)2Py), in chloroform-d at 24 °C. The aromatic protons H3-H7 are indicated as circles, in a side-on view of the pyrene moiety.



Figure 9. Schematic representations of two configurations of 1,2-di(2-pyrenyl)methane (2Py(1)2Py); see text. The aromatic protons H3-H6 are indicated with solid circles.

1,n-Di(2-pyrenyl)alkanes. The chemical shifts of the 1,n-di-(2-pyrenyl)alkanes, 2Py(n)2Py, with n = 1-10 and 14, and of

⁽²⁷⁾ For the specific assignment of H4 and H5, see the preceding paper (ref 7).

⁽²⁸⁾ In analogy with the findings for the 1-alkylpyrenes (Table IV), where it is seen that the chemical shifts of the aromatic protons have not yet reached their limiting values for 1-ethylpyrene (1EtPy), is is concluded that 2-ethylpyrene (2EtPy) likewise will not be the optimal model compound for the series 2Py(n)2Py. Therefore, in the absence of other 2-alkylpyrenes, 2Py(14)2Py is adopted; see Figure 7.

TABLE IV: Chemical Shifts δ (in ppm) and Vicinal Coupling Constants J (in Hz) of 1,n-Di(1-pyrenyl)alkanes (1Py(n)1Py), the Model Compound 1-Octylpyrene (1OcPy), 1-Ethylpyrene (1EtPy), and Pyrene in Chloroform-d at 24 °C; Data for 1Py(3)1Py and 1OcPy in Toluene-d₈ and in Octane-d₁₈

	δ(H2)	δ(H3)	δ(H4)	δ(H5)	δ(H6)	δ(H7)	δ(H8)	δ(H9)	δ(H10)	${}^{3}J_{23}$	${}^{3}J_{45}$	${}^{3}J_{67} = {}^{3}J_{78}$	³ J _{9,10}	$\delta(\alpha$ -CH ₂)	$\delta(\beta$ -CH ₂)	$\delta(\gamma - CH_2)$
$\overline{1Py(n)Py, n} =$																
0	8.156	8.363	8.220	8.182	8.255	8.037	8.255	7.665	7.885	7.77	9.0	7.63	9.22			
1	7.657	8.050	8.056	8.047	8.205	8.018	8.189	8.102	8.371	7.86	9.1	7.65	9.27	5.476		
2	7.877	8.059	8.031	8.031	8.14	7.987	8.14	8.128	8.398	7.84	а	7.65	9.27	3.877		
3	7.907	8.114	8.031	8.013	8.14	7.988	8.13	8.023	8.192	7.81	9.07	7.65	9.30	3.530	2.470	
4	7.862	8.089	8.019	8.019	8.14	7.989	8.14	8.076	8.277	7.79	а	7.63	9.27	3.427	2.071	
5	7.836	8.073	8.020	8.020	8.15	7.986	8.15	8.072	8.264	7.78	а	7.64	9.28	3.364	1.958	1.67
6	7.841	8.083	8.018	8.004	8.15	7.978	8.14	8.050	8.250	7.78	8.97	7.65	9.30	3.336	1.883	1.56
7	7.850	8.090	8.016	8.000	8.15	7.981	8.15	8.073	8.265	7.77	9.04	7.66	9.27	3.326	1.865	1.55
8	7.853	8.094	8.023	8.004	8.144	7.976	8.144	8.077	8.269	7.78	9.03	7.6	9.28	3.322	1.849	Ь
9	7.854	8.094	8.021	8.001	8.141	7.971	8.141	8.079	8.271	7.78	9.05	7.6	9:29	3.320	1.844	b
10	7.857	8.095	8.019	8.000	8.143	7.972	8.143	8.084	8.273	7.80	9.0	7.68	9.30	3.321	1.85	b
13	7.859	8.097	8.021	8.000	8.145	7.970	8.143	8.087	8.275	7.80	9.0	7.69	9.29	3.324	1.85	b
1OcPy	7.860	8.098	8.023	7.996	8.150	7.971	8.140	8.090	8.276	7.79	9.01	7.65	9.30	3.336	1.853	1.49
1 EtPy	7.896	8.126	8.034	8.011	8.163	7.985	8.156	8.110	8.301	7.82	9.02	7.63	9.28	3.372	(1.527) ^c	
pyrene	8.005	8.182	8.075	8.075	8.182	8.005	8.182	8.075	8.075	7.62	8.97 ^d	7.62	8.97 ^d			
1Py(3)1Py																
toluene	7.681	7.904	7.813	7.776	7.894	7.739	7.887	7.799	8.055	7.80	8.97	7.65	9.26	3.290	2.292	
octane	7.822	8.000	7.911	7.897	8.026	7.849	8.000	7.896	8.119	7.81	8.96	7.63	9.29	3.499	2.488	
1OcPy																
toluene	7.699	7.903	7.809	7.772	7.910	7.751	7.903	7.887	8.171	7.76	8.98	7.64	9.28	3.182	1.786	1.40
octane	7.768	7.978	7.901	7.884	8.025	7.848	8.021	7.978	8.212	7.80	8.98	7.65	9.29	3.318	1.882	1.51

^aCannot be determined due to chemical equivalence. ^bCannot be determined due to line congestion. ^cMethyl group. ^dFrom ¹³C-H satellite spectrum (1,3,6,8-tetradeuteriopyrene in carbon disulfide); see ref 26c. The coupling cannot be determined directly due to chemical equivalence.

2-ethylpyrene, 2EtPy, are depicted in Figure 7. The absolute values of $\Delta \delta = \delta(2Py(n)2Py) - \delta(2Py(14)2Py)$ do not exceed 0.04 ppm, except for the deshielding of H1 with n = 1 and 2 (Table III), and decrease with chain length.

Di(2-pyrenyl)methane. The $\Delta\delta$ pattern observed for 2Py(1)2Py (Figure 8a), showing a minimum for H4, can be explained by two counteracting effects. First, a mutual deshielding is exerted by the two pyrenyl groups in a V-shaped conformer (Figure 9a), affecting all protons down to H7. Such a downfield shift also operates in 2-phenylpyrene.⁷ Superimposed on this effect, an upfield shift occurs in a second conformer (Figure 9b), in which the planes of the pyrenyls are perpendicular to each other. This brings the protons H3–H6 into the shielding cones of the pyrenyls,¹¹ the maximum effect being expected for H4. A similar conformer structure has previously been deduced for diphenylmethane.^{7,29} It cannot be excluded, however, that through-bond effects, acting in this case through the single methylene group, will have some influence on H3.

2Py(n)2Py with n = 2-10 and 14. For the compounds with longer chains, the downfield shift of H1 rapidly diminishes with chain length, having practically disappeared for n = 4 (Table III and Figure 7). The shielding observed especially for H4 with n = 4-7, see Figure 7b, is attributed to a conformer with the two pyrenyls in a mutually perpendicular orientation, similar to the one already described with 2Py(1)2Py.

1,*n*-Di(1-pyrenyl)alkanes. The data for the chemical shifts of the aromatic protons of the 1,*n*-di(1-pyrenyl)alkanes, 1Py(n)1Py, with n = 0-10 and 13, can be divided into three sets, on the basis of their chain-length dependence: (a) H2 and H3, (b) H4-H8, and (c) H9 and H10 (Table IV). The chemical shifts of H3, H8, and H10, as representatives of each group, are depicted in Figure 10. The molecules with the shortest chains, n = 0 and 1, will be discussed first.

1,1'-Bipyrene. The chemical shift differences of 1,1'-bipyrene, $\Delta \delta = \delta(1Py(0)1Py) - \delta(1OcPy)$, are shown in Figure 11a. A pronounced shielding is observed for H9 and H10, whereas positive $\Delta \delta$ values are found for H2-H8. The downfield shift for the protons H2-H8 is a consequence of a ring-current effect and, possibly, a through-bond interaction of one pyrene moiety on the other. Both influences diminish with increasing distance from the substituent group, as in 1-phenylpyrene and the hexyl ester of 1-pyrenecarboxylic acid, 1PC(6).⁷ The strong upfield shift for



Figure 10. Chemical shifts δ (in ppm) of the aromatic protons of a series of 1,*n*-di(1-pyrenyl)alkanes (1Py(*n*)1Py with n = 0-10 and 13) in chloroform-*d* at 24 °C, as a function of the number of methylene groups (*n*) in the alkane chain. The data for the model compound 1-octylpyrene (1OcPy) are also given. See Table IV.

H9 and H10, on the other hand, is attributed to a configuration of 1Py(0)1Py (see Figure 11a) in which these protons are located in the shielding zone of the other pyrenyl group, similar to what was observed with *rac*-1DPP (T_1T_1 in Figure 4a).

Di(1-pyrenyl) methane. The $\Delta\delta$ values of 1Py(1)1Py exhibit a pattern that is completely different from that of 1Py(0)1Py; see Figure 11b. For H2 and H3 a shielding is observed, whereas the other protons have positive $\Delta\delta$ values, approaching zero for H9. The negative $\Delta\delta$ values of H2 and H3 are explained by a ringcurrent effect in a configuration of 1Py(1)1Py with mutually perpendicular pyrenyl groups (Figure 11b), in which H10 is deshielded. The downfield shift found for H4–H8 is ascribed to the combined action of a ring-current effect and a through-bond interaction, as in 1Py(0)1Py.

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Figure 11. Differences in chemical shift $\Delta\delta$ (in ppm), with respect to the model substance 1-octylpyrene (1OcPy), for (a) 1,1'-bipyrene (1Py(0)1Py), (b) di(1-pyrenyl)methane (1Py(1)1Py), and (c) 1,3-di(1-pyrenyl)propane (1Py(3)1Py), in chloroform-d at 24 °C. The aromatic protons H2-H7 are indicated as circles, in a side-on view of the pyrene moiety. In each case, molecular configurations (molecular mechanics, MMP2; see text and ref 18) are depicted. For the dihedral angle between the pyrenyl moieties in 1Py(0)1Py (a), a value of 65° is determined.

1Py(n)1Py with n = 2-10 and 13. Except for n = 3 and 6, for which an important shielding is observed for the protons H9 and H10 (Table IV and Figures 10 and 11c), only relatively small absolute values for $\Delta\delta$ (shieldings as well as deshieldings) are found inside this family. The upfield shift for H9 and H10 of 1Py(3)1Py and 1Py(6)1Py is attributed to a conformer in which the two pyrenyl groups mainly overlap in the region of these protons (Figure 11c). Such a partial overlap was also encountered with 1Py(0)1Py and *rac*-1DPP (T₁T₁), as discussed above.

No Ground-State Dimers with Dipyrenylalkanes. From the data presented in the two previous sections it follows that for the two series dipyrenylalkanes, 2Py(n)2Py with n = 1-10 and 14 and 1Py(n)1Py with n = 0-10 and 13, shieldings affecting all aromatic protons are not observed. It is therefore concluded that there is no evidence based on NMR data for the presence of ground-state dimers in any of these dipyrenylalkanes in chloroform-d at 24 °C. This is in contrast to what has been found for the bis(pyrenylcarboxy)alkanes (1PC(n)1PC and 2PC(n)2PC).⁷ However, conformers overlapping at H9 and H10 were detected for 1Py-(0)1Py, 1Py(3)1Py, and 1Py(6)1Py. Note that these partial-overlap conformers are only present in small concentration, as deduced from their $\Delta\delta$ values as compared to those of *rac*-1DPP; see above.

The differences in chemical shift $\Delta\delta$ of the dipyrenylalkanes 2Py(n)2Py and 1Py(n)1Py with respect to the model compounds 2Py(14)2Py and 1OcPy are attributed to two causes: on the one hand, to ring-current effects resulting in shielding or deshielding of the aromatic protons, depending on the relative orientation of the pyrenyl end groups; further, for the dipyrenylalkanes with the shortest chains (n = 0-2), through-bond interactions take place. In addition, the fact that in these short-chained compounds one pyrenyl group partly replaces the solvent surrounding the other end group can influence the chemical shifts by changing the effective solvent composition.

Solvent Dependence 1Py(3)1Py. For 1Py(3)1Py, the $\Delta\delta$ values of, e.g., H9 and H10 are approximately the same in chloroform-d, toluene- d_8 , and octane- d_{18} (Table IV), although these solvents have

different Hildebrand solubility parameters $\delta(\text{sol})$.³⁰ These results are contrary to those obtained with 1PC(5)1PC, for which the $\Delta\delta$ values in octane- d_{18} are considerably larger than in the other two solvents.⁷ This has been interpreted as meaning that in octane- d_{18} , the only solvent of the three with a $\delta(\text{sol})$ parameter not matching that of aromatic systems, dimerization of 1PC-(5)1PC is relatively enhanced. The difference in the solvent dependence of $\Delta\delta$ for 1PC(5)1PC and 1Py(3)1Py is therefore in agreement with the conclusion that sandwich dimers are formed with the PC(*n*)PC but are absent with the dipyrenylalkanes.

SPC Measurements 2Py(n)2Py and 1Py(n)1Py. The excimer fluorescence decays of 2Py(3)2Py, 2Py(14)2Py, 1Py(3)1Py, and 1Py(13)1Py in toluene at 25 °C are shown in Figure 12. With 1Py(3)1Py, under the experimental conditions (time resolution²³ and excitation wavelength) employed here, the excimer amplitude ratio R = -A(-)/A(+) has a value of 0.99, whereas with the three other compounds R is equal to unity. Using picosecond laser excitation at 330 nm similar values for R are obtained.³¹ The observation that R = 0.99 for 1Py(3)1Py could reflect the presence of a small amount of the partial-overlap conformer discussed above. The SPC data for the other dipyrenylalkanes show that ground-state dimers acting as excimer procursors are not present, supporting the conclusions deduced from the NMR spectra presented in this paper.

Occurrence and Absence of Dimerization. The tendency of aromatic molecules to form ground-state dimers is governed by their polarizabilities, which are involved in the attracting intermolecular dispersion (London) forces.³² This dependence on the

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Figure 12. Excimer fluorescence response functions (at 520 nm) of (a) 1,3-di(1-pyrenyl)propane (1Py(3)1Py), (b) 1,13-di(1-pyrenyl)tridecane (1Py(13)1Py), (c) 1,3-di(2-pyrenyl)propane (2Py(3)2Py), and (d) 1,14-di(2-pyrenyl)tetradecane (2Py(14)2Py) in toluene at 25 °C. The values for the decay times τ_i and their preexponential factors A_{2i} are given; see eq 1. The excimer amplitude ratio R = -A(-)/A(+), see text, is equal to (a) 0.99, and (b-d) 1.00.

molecular polarizability explains that ground-state dimers are detected for meso-2DPP, 3b whereas such dimers have not been reported for the meso diastereomers of the 2,4-diarylpentanes with 2-naphthyl and phenyl substituents,³³ which have smaller polar-izabilities than pyrenyl.^{34,35} That dimer formation does occur for the PC(n)PC molecules⁷ but not for the dipyrenylalkanes, although the polarizabilities of both end groups will be of comparable magnitude,³⁷ is attributed to the absence of repulsive H atoms near the pyrene moieties in the bis(pyrenylcarboxy)alkanes.

Vicinal Coupling Constants. The vicinal coupling constants ${}^{3}J_{23}$ in the series 1Py(n)1Py with n = 0-10 and 13 (Table IV) are independent of chain length, except for the compounds with n = 1 and 2, for which a value different from that of 1OcPy is observed. For the other coupling constants, ${}^{3}J_{45}$, ${}^{3}J_{67}$, and ${}^{3}J_{9,10}$, a chain-length dependence is not observed, except for ${}^{3}J_{9,10}$ of 1Py(0)1Py (Table IV). In the series 2Py(n)2Py with n = 1-10and 14, the coupling constants ${}^{3}J_{45}$ and ${}^{3}J_{67}$ likewise are independent of chain length. This means that the pyrenyl groups in the dipyrenylalkanes only exert a through-bond interaction on each other for n < 3, not extending further than the bond between the atoms C2 and C3 of pyrene.

Conclusion

For rac- and meso-1DPP in toluene- d_8 the conformer population is determined from the vicinal coupling constants, using ringcurrent effects on the chemical shifts as secondary evidence. These conformer populations are found to be similar to those previously

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 A.; Kirillovich, V. A.; Vereshchagin, A. N. Izv. Akad. Nauk SSSR, Ser. (35) The values for the mean molecular polarizabilities (in 10⁻²⁴ cm³; see

ref 34) are 9.9 (benzene), 16.6 (naphthalene), and 28.2 (pyrene). The approximate expression derived (ref 32) for the dispersion interaction energy between two identical molecules is $E = -3\alpha^2 I/4R^6$, where α is the mean molecular polarizability, I is the ionization potential, and R is the intermo-Indicating point a billion of the indication potentials (ref 36) of 9.24 eV (benzene),
8.15 eV (naphthalene), and 7.43 eV (pyrene), it follows that the relative interaction energies are 1.0 (benzene), 2.5 (naphthalene), and 6.5 (pyrene). (36) (a) Levin, R. D.; Lias, S. G. Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.) 1982, No. 71. (b) Simonsick, Jr., W. J.; Hites, R. A. Anal.

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⁽³⁷⁾ It is to be expected that the mean molecular polarizability of a pyrenylcarboxy group will be approximately the same as that of pyrene, in view of the literature values (in 10^{-24} cm³) for the methyl ester of benzoic acid (9.8; ref 34c) and benzene (9.9; ref 34a).

obtained for *rac*- and *meso*-2DPP. In *meso*-1DPP and *meso*-2DPP the excimer-like ground-state dimer (TT) leads to a value smaller than unity for the excimer amplitude ratio R = -A(-)/A(+) in time-resolved fluorescence measurements. With both racemic, 2,4-dipyrenylpentanes, sandwich dimers are not observed. However, in *rac*-1DPP, contrary to *rac*-2DPP, a conformer partially overlapping at the protons H9 and H10 is present. This partial-overlap dimer undergoes rapid excimer formation, leading again to a value smaller than unity for the ratio R.

From an analysis of the NMR spectra, completely overlapping ground-state dimers are not detected in the two series of dipyrenylalkanes, 2Py(n)2Py and 1Py(n)1Py. This is in contrast to what has been observed with the bis(pyrenylcarboxy)alkanes 2PC(n)2PC and 1PC(n)1PC as well as with the *meso*-2,4-dipyrenylpentanes. Instead, a conformer is detected in which the pyrenyls only overlap at the edges, as in rac-1DPP. This is the case with 1Py(0)1Py, 1Py(3)1Py, and 1Py(6)1Py, in which the partial overlap occurs at H9 and H10. In time-resolved fluorescence measurements with 2Py(3)2Py, 2Py(14)2Py, 1Py-(3)1Py, and 1Py(13)1Py, it is seen that the excimer amplitudes practically sum to zero, confirming the conclusions based on the NMR experiments.

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Correlation-Consistent Valence Bond Method with Purely Local Orbitals. Application to H_2 , Li_2 , FH, F_2 , and Collinear H_3 and Li_3

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We propose a general method for constructing ab initio valence bond wave functions. The emphasis is put on building compact wave functions designed to be as close as possible to the concept of chemical bonding schemes. This is achieved through the use of strictly local fragment orbitals, leading to nonorthogonal configuration interaction. A set of rules is proposed for selecting the configuration list such that correlation consistency is enforced over the potential surface. The compactness of the wave function is ensured by correlating only the electrons occupying active orbitals, defined as the orbitals directly involved in bond breaking or bond making. The method is applied to the dissociation of H₂, Li₂, FH, and F₂, and to the collinear exchange reactions $X + X_2 \rightarrow X_2 + X$ (X = H, Li). The dimensions of the corresponding valence bond CIs are respectively 6, 12, 31, and 24 symmetry-adapted configurations for the dimers, and 26 and 60 for the trimers. All calculated equilibrium bond lengths, dissociation energies, and reaction barriers are found to agree, within 0.02 Å and 3 kcal/mol, with best reference calculations in the same basis set. The method appears to be well suited for the calculation of diabatic curve crossing diagrams as introduced by Shaik and Pross.

The valence bond (VB) theory of electronic structure has recently regained acceptance in the world of chemistry,¹⁻³ from both the qualitative and quantitative points of view. On the qualitative side, the discussion of molecular structure and reactivity in terms of atomic properties has been developed by Goddard et al.⁴ More recently, the study of chemical reactions by VB diagrams has been introduced by Shaik and Pross.² Such diagrams have already been widely used and proved to be helpful for understanding and predicting the size of the reaction barriers in reactions like S_N2 substitution³ or radical exchange,⁵ and have also been used to understand electron delocalization in π systems.^{5,6} This model

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considers the energy barrier of a reaction as a consequence of the avoided crossing of two VB diabatic curves: one representing the bonding scheme of the reactants, the other that of the products (see the following paper for more details). Shaik and Pross^{2,3} have shown that it is possible to relate the energetic behavior of these VB structures to simple thermodynamic quantities, and, by means of simple approximations, to order the size of the energy barrier in some families of reactions. These applications of the VB diagrams are still qualitative in nature, and to our knowledge no quantitative calculations have yet been performed to confirm or falsify their validity. It is thus essential to develop a reliable computational method of the VB type, which on the one hand provides energies of adiabatic states with good accuracy and on the other hand allows one to follow the energetic behavior of the various VB structures involved in the qualitative theory of curve crossing VB diagrams.

On the quantitative side, ab initio VB methods have become practical for generating potential energy surfaces and are referred to as generalized valence bond (GVB),⁷ resonating GVB (R-GVB),⁸ spin-coupled valence bond (SCVB)⁹ and so on. They provide wave functions having nearly the quality of multiconfigurational SCF (e.g., CASSCF¹⁰), with the extra advantage of compactness. As with CASSCF, quantitative accuracy further requires extensive configuration interaction (CI). Such calcula-

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