

Chain Length Dependence of Intramolecular Excimer Formation with 1,*n*-Bis(1-pyrenylcarboxy)alkanes for *n* = 1–16, 22, and 32

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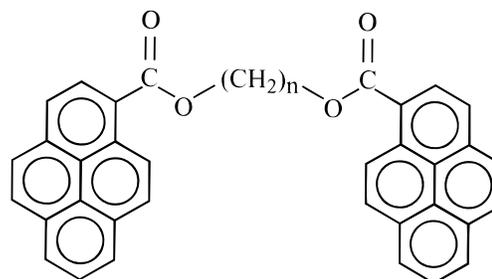
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Time-resolved and photostationary measurements in alkane solvents as a function of temperature are presented for the 1,*n*-bis(1-pyrenylcarboxy)alkanes (1PC(*n*)1PC, *n* = 1–16, 22, 32) with *n* methylene groups in the chain. For all compounds except 1PC(1)1PC intramolecular excimer fluorescence is observed. From fluorescence decay analysis and quenching data, the rate constant k_a of excimer formation in the series 1PC(*n*)1PC is determined as a function of chain length. The value of k_a , as well as that of the excimer-to-monomer fluorescence quantum yield ratio Φ'/Φ , peaks at *n* = 5 and then gradually decreases with increasing *n*. These results are in clear contrast to those obtained previously with the 1,*n*-di(1-pyrenyl)alkanes (1Py(*n*)-1Py), where Φ'/Φ reaches its maximum at *n* = 3, with a sharp minimum (no excimer formation) at *n* = 7. This difference is attributed to a reduced steric hindrance at the excimer configuration (k_a) and to dimer formation in the electronic ground state between the pyrenylcarboxy end groups in 1PC(*n*)1PC (Φ'/Φ). Both effects arise from the absence of methylene hydrogens next to the pyrenyl moieties of these molecules, which hydrogens prevent excimer formation in the case of 1Py(7)1Py.

Introduction

The influence of chain length on intramolecular excimer formation has been studied extensively with compounds in which aromatic hydrocarbons such as benzene,^{1a} naphthalene,^{1b} pyrene,^{1c} biphenyl,^{1d} anthracene,^{1e} and phenanthrene,^{1f} as well as aliphatic amines^{1g} and carbazole,^{1h} are linked by an alkane chain. Among the chains of a different molecular nature,² those containing ester groups have received a considerably smaller amount of attention.^{3,4} Intramolecular cycloaddition in the excited state was investigated with bis(anthracenylcarboxy)-alkanes linked at the 1,1'- and at the 2,2'-positions of the anthracene moieties.³ These photochemical reactions were assumed to proceed via an intramolecular excimer as the primary reaction intermediate. In the case of the bis(2-anthracenylcarboxy)alkanes, 2AC(*n*)2AC, where *n* represents the number of CH₂ groups between the carboxy units in the chain, intramolecular excimer emission was in fact detected for *n* = 2–5, but not for *n* = 7 and 9, in dichloromethane at 25 °C. Further, Nishijima et al.⁵ studied 1,*n*-di(1-pyrenylmethyl)alkanedioic esters 1PyCH₂OCO(*n*)OCOCH₂1Py with *n* = 1–4, 6, 8, 10, 14, 18, and 22.

In the present paper, data derived from time-resolved and photostationary measurements with 1,*n*-bis(1-pyrenylcarboxy)-alkanes 1PC(*n*)1PC, for *n* = 1–16, 22, and 32, are reported. In particular, the dependence of the rate constant of intramolecular excimer formation on chain length, solvent viscosity, and temperature is discussed. ¹H NMR experiments⁴ have shown that in the series 1PC(*n*)1PC ground-state dimers⁶ are formed for *n* = 3–16, with an efficiency decreasing with increasing chain length. Especially for *n* = 3–7, two different dimer configurations are detected, predominantly an asymmetric



1PC(*n*)1PC

structure, next to a symmetric one. In accordance with this observation, two intramolecular excimers are formed.⁴ The presence of these dimers, from which excimers can be formed directly by light absorption from the ground state, has to be taken into account in the analysis of time-resolved and photostationary data.^{4,7,8}

Experimental Section

Bis(1-pyrenylcarboxy)methane, 1PC(1)1PC, was made from 1-pyrenecarboxylic acid in a reaction with methylene iodide in aqueous sodium hydroxide solution (25%).⁹ The 1,*n*-bis(1-pyrenylcarboxy)alkanes 1PC(*n*)1PC with *n* = 2–16, 22, and 32, were synthesized from the corresponding α,ω -dialcohols HO(*n*)OH and 1-pyrenecarboxylic acid chloride. The dialcohols with *n* = 13, 14, 22, and 32, which were not commercially available, were prepared by reduction of the diesters with LiAlH₄. The 1-pyrenecarboxylic acid chloride was made from 1-pyrenecarboxylic acid in a reaction with thionyl chloride.¹⁰ The compounds 1PC(*n*)1PC were purified by chromatography (Al₂O₃, cyclohexane:chloroform 1:1) and subsequently recrystallized. HPLC was the last purification step. The melting points

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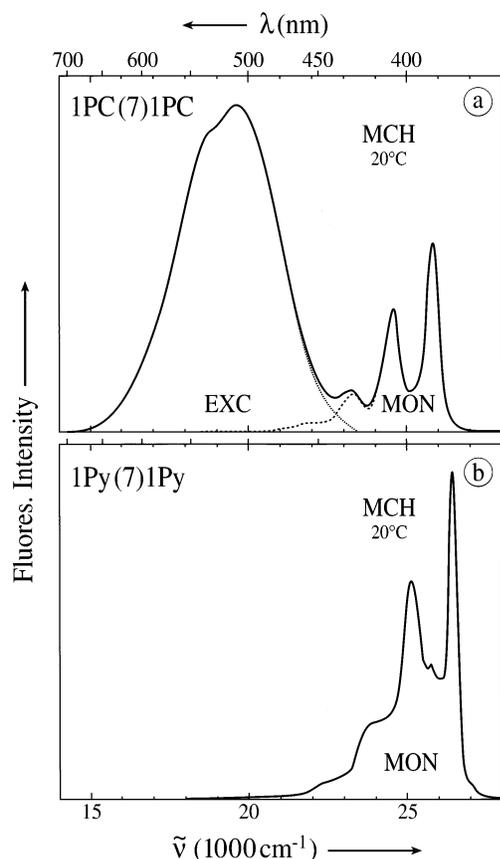


Figure 1. Fluorescence spectra in methycyclohexane (MCH) at 20 °C of (a) 1,7-bis(1-pyrenylcarboxy)heptane (IPC(7)IPC) and (b) 1,7-di(1-pyrenyl)heptane (1Py(7)1Py). In the spectrum of IPC(7)IPC the emissions from the excimer (exc) and the monomer (mon) were separated by employing the monomer fluorescence of the 1-pyrenecarboxylic acid hexyl ester (1×10^{-5} M in MCH), taken to represent the monomer fluorescence spectrum of IPC(7)IPC. With 1Py(7)1Py only monomer fluorescence is observed.

(in °C) of the IPC(*n*)IPC are (*n* = 1–6) 235, 174.4, 145.9, 166.5, 120.6, 154.0; (*n* = 7–12) 115.0, 150.5, 107.7, 130.8, 119.3, 124.2; (*n* = 13–16, 22, 32): 108.8, 125.5, 106.6, 127.3, 129.2, 132.8. Note that the melting points of IPC(*n*)IPC show an alternating effect as a function of *n*, similar to what has been observed for the *n*-alkanes and, especially, for the dicarboxylic acids.¹¹ The 1-pyrenecarboxylic acid methyl ester, IPC(1), and hexyl ester, IPC(6), were made from 1-pyrenecarboxylic acid and methanol or *n*-hexanol, respectively. The melting points are: 86.6 °C (IPC(1)) and 67.2 °C (IPC(6)). The solvents methycyclohexane (MCH) and *n*-hexadecane were chromatographed over SiO₂/Al₂O₃. Liquid-paraffin (Merck) was likewise chromatographed over SiO₂/Al₂O₃ in a 1:1 mixture with *n*-hexane, which was subsequently removed under a high vacuum. For the pure liquid-paraffin a viscosity of 125 cP at 20 °C was found. The solutions, having a concentration of 1×10^{-5} M or lower, were degassed by the freeze–pump–thaw technique (6 cycles). The fluorescence spectra were obtained by using a quantum-corrected FICA 55, Perkin-Elmer MPF-44E or Shimadzu 5000PC fluorimeter. Fluorescence quantum yields were determined relative to a solution of quinine sulfate in 1.0 N H₂SO₄ ($\Phi = 0.546$ at 25 °C)¹² of equal optical density at the excitation wavelength. The fluorescence decay times were measured by employing time-correlated single-photon counting (SPC). The nanosecond SPC experiments were made with a

TABLE 1: Data from Fluorescence Spectra of the 1,*n*-Bis(1-pyrenylcarboxy)alkanes IPC(*n*)IPC in Methycyclohexane at 20 °C

IPC(<i>n</i>)IPC	$h\nu_c^{\max,a}$ (1000 cm ⁻¹)	$\Delta(1/2)^b$ (1000 cm ⁻¹)	Φ'/Φ^c	E_a^d (kJ/mol)
1			0.00	
2	19.2	3.39	2.75	15.3
3	19.2	2.92	3.90	15.3
4	19.5	2.73	4.08	15.1
5	19.7	2.84	7.91	15.6
6	19.8	2.87	5.70	15.3
7	19.8	2.97	5.54	16.3
8	19.7	2.93	4.42	15.1
9	19.7	2.93	4.23	16.7
10	19.7	2.89	3.66	16.5
11	19.7	2.85	3.27	16.3
12	19.7	2.79	2.99	16.3
13	19.6	2.75	2.65	15.3
14	19.6	2.70	2.37	14.6
15	19.6	2.66	2.18	14.6
16	19.6	2.69	1.98	16.5
22	19.5	2.71	1.10	15.0
32	19.5	2.73	0.66	15.2
IPC(1) ^e	19.5	2.68		12.4

^a Excimer emission band maximum. ^b Width at half-maximum of the excimer emission band. ^c Excimer-to-monomer fluorescence quantum yield ratio. ^d Apparent activation energy of excimer formation, obtained from an Arrhenius plot of the excimer-to-monomer fluorescence intensity ratio I'/I in the low-temperature limit (LTL), see text. The activation energy for free diffusion in methycyclohexane: $E(T/\eta) = 12.6$ kJ/mol. ^e Data on intermolecular excimer formation with the model compound 1-pyrenecarboxylic acid methyl ester, IPC(1), at 3×10^{-3} M.

system described previously.¹³ The analysis of the decays was carried out by using modulating functions, extended by global analysis.^{14,15}

Results and Discussion

Excimer and Monomer Fluorescence. The dipyrenylcarboxyalkanes IPC(*n*)IPC with *n* = 2–16, 22, and 32 all undergo intramolecular excimer formation, in a variety of solvents.⁴ In Figure 1a, as an example, the fluorescence spectrum of IPC(7)IPC in MCH at 20 °C is depicted, consisting of an intramolecular excimer emission band (maximum at 19 800 cm⁻¹) next to the structured monomer fluorescence, which is strongly quenched (see data for I_0/I in Table 2, below). With the corresponding 1,7-di(1-pyrenyl)heptane (1Py(7)1Py), in clear contrast, excimer formation does not occur,^{1c,16–19} as shown in Figure 1b. For IPC(1)IPC, as the only exception in the present series, excimer emission could not be detected. The related di(1-pyrenyl)methane 1Py(1)1Py likewise does not show excimer fluorescence.^{17,18}

The excimer-to-monomer fluorescence quantum yield ratio Φ'/Φ of the series IPC(*n*)IPC was determined for *n* = 2–16, 22, 32, in MCH at 20 °C (Figure 2a and Table 1). Two aspects of these results are worth noting. First, the largest value for Φ'/Φ is found for *n* = 5, different from what has been observed previously for the 1,*n*-di(1-pyrenyl)alkanes (1Py(*n*)1Py), see Figure 2b, and other diarylalkanes, for which excimer formation and emission invariably reached its maximum for *n* = 3: the Hirayama rule.¹ Deviations from this rule have also been observed with the ester compounds 1PyCH₂OCO(*n*)OCOCH₂-1Py, where the most efficient excimer formation occurs for *n* = 2.⁵ Second, in the series 1Py(*n*)1Py, excimer fluorescence is relatively weak around *n* = 7 (see Figure 1b), a minimum that is not observed in the Φ'/Φ plot for IPC(*n*)IPC. The differences in Φ'/Φ are attributed to the presence of the carboxy groups in

TABLE 2: Spectroscopic Data on Intramolecular Excimer Formation with the 1,*n*-Bis(1-pyrenylcarboxy)alkanes 1PC(*n*)1PC in Methylcyclohexane (rate constants and decay times refer to 20 °C)

1PC(<i>n</i>)1PC	k_a^a (10^8 s $^{-1}$)	τ^b (ns)	$\tau_0(n)^c$ (ns)	E_a^d (kJ/mol)	k_a^e (10^{11} s $^{-1}$)	I_0/I^f	$k_a(s)^g$ (10^8 s $^{-1}$)	$k_a(s)/k_a^h$	α^i
1			8.4			1.00			
2	3.50	2.3	11.4	14.6	1.6	5.28	3.75	1.07	0.05
3	3.36	2.4	13.0	16.5	3.0	8.11	5.47	1.63	0.34
4	3.84	2.2	14.2	15.1	1.9	9.12	5.72	1.49	0.29
5	5.42	1.6	14.8	14.5	2.1	13.7	8.58	1.58	0.34
6	3.85	2.3	15.3	15.3	2.0	8.37	4.82	1.25	0.18
7	3.96	2.2	15.5	15.3	2.1	8.13	4.60	1.16	0.12
8	3.17	2.6	15.7	16.0	2.3	6.76	3.67	1.16	0.12
9	3.04	2.7	15.8	15.8	2.0	6.29	3.35	1.23	0.08
10	2.82	2.9	15.9	15.6	1.7	5.85	3.05	1.10	0.06
11	2.35	3.4	15.9	15.4	1.4	5.42	2.78	1.08	0.13
12	2.24	3.5	15.9	15.3	1.2	5.09	2.57	1.15	0.10
13	2.03	3.8	15.9	14.6	0.8	4.56	2.24	1.08	0.07
14	1.87	4.0	15.9	14.4	0.7	4.23	2.03	1.10	0.06
15	1.69	4.3	15.9	14.3	0.6	3.75	1.73	1.09	0.02
16	1.59	4.5	15.9	15.0	0.8	3.70	1.70	1.02	0.05
22	1.20	5.5	15.9	13.7	0.3	3.13	1.34	1.07	0.07
32	0.81	7.0	15.9			2.56	1.0	1.12	
1PC(1) ^j		15.9		12.4					

^a Excimer formation rate constant from decay times τ (eq 3). ^b Monomer fluorescence decay time (single-exponential, LTL limit), see text. ^c Corrected lifetime of model compound 1PC(1), see text. ^d Activation energy of excimer formation obtained from Arrhenius plot of k_a (eq 2). The activation energy for free diffusion in methylcyclohexane is $E(T/\eta) = 12.6$ kJ/mol. ^e Preexponential factor in Arrhenius expression of k_a . ^f See eqs 5 and 6. ^g Excimer formation rate constant derived from I_0/I (eq 6). ^h See eq 7. ⁱ Percentage of excitation light absorbed by the ground state dimer D, see Scheme 1 and eq 7. ^j The model compound 1-pyrenecarboxylic acid methyl ester. Data on intermolecular excimer formation are listed for this molecule.

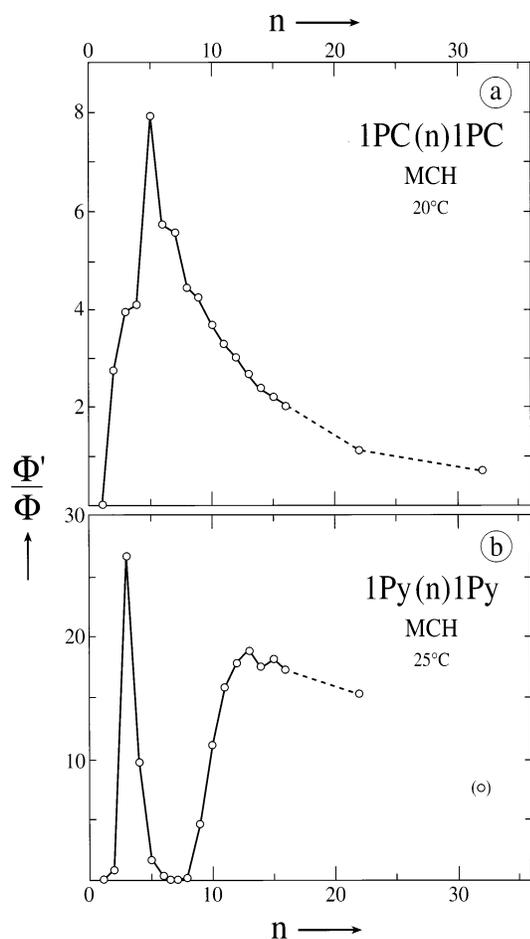


Figure 2. Excimer-to-monomer fluorescence quantum yield ratio Φ'/Φ as a function of alkane chain length n of (a) 1,*n*-bis(1-pyrenylcarboxy)alkanes (1PC(*n*)1PC) and (b) 1,*n*-di(1-pyrenyl)alkanes (1Py(*n*)1Py) in methylcyclohexane (MCH) at 20 °C.

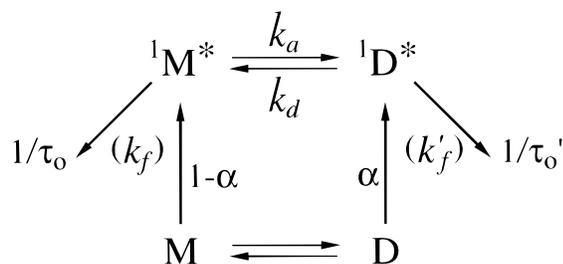
1PC(*n*)1PC, which molecules therefore do not have methylene hydrogens next to their excimer-forming end groups. These H atoms are assumed to be responsible, by way of intrachain H/H-

repulsion, for the sharp decrease of the ratio Φ'/Φ for the di-(1-pyrenyl)alkanes around 1Py(7)1Py,^{1c,16} see Figure 2b, a chain cyclization problem analogous to the well-known minimum in the yield of chemical ring-closure reactions with 10-membered rings.²⁰ For $n > 12$, the predominant chain control of the excimer formation is clearly reduced. With 1PC(*n*)1PC (Figure 2a) such an influence of the chain hydrogens is much less obvious.

The energies $h\nu_c^{\max}$ of the maximum and the width at half-maximum $\Delta(1/2)$ of the excimer emission band of 1PC(*n*)1PC for $n = 2-16, 22$, and 32, in MCH at 20 °C are listed in Table 1. With increasing chain length, starting from $n = 6$ and 7, both parameters gradually become equal to those observed for the intermolecular excimer of the model substance 1PC(1), showing again that the conformational strain coming from the chain is released when n becomes larger. For $n = 5-16$, $h\nu_c^{\max}$ is slightly blue-shifted relative to that of the intermolecular excimer of 1PC(1). A similar, although more pronounced, blue-shift has previously been observed with 1Py(*n*)1Py for n between 6 and 11, which was also attributed to intrachain H/H-repulsion.^{1c,15} The excimer half-width $\Delta(1/2)$ of 1PC(*n*)1PC is larger than that of 1PC(1), especially for $n = 2$. This increase is caused by the presence of two structurally different intramolecular excimers.⁴

Chain Length Dependence of Φ'/Φ and Excimer Structure. The pronounced chain length dependence of the excimer formation kinetics (Φ'/Φ) observed with 1Py(*n*)1Py (Figure 2b) originates from the conformational requirements for the chain to reach the specific sandwich structure of the two pyrenyl end groups that ensures a sufficiently large intramolecular orbital overlap in the excimer. This process is hindered by the hydrogens of the methylene group attached to the pyrene moiety. An example for the precise steric requirements dictated by the excimer structure is the absence of excimer formation with 9,10-diphenylanthracene, due to the mutual repulsion of the strongly twisted phenyl groups.^{21,22} In the case of 1PC(*n*)1PC, the fact that the carboxy group does not contain hydrogens enables the chain to minimize the repulsive intrachain H/H-interactions.

SCHEME 1



Excimer Kinetics and Ground-State Dimers. Φ'/Φ and I'/I . Excimer formation involving one excited-state monomer $^1M^*$ and one excimer $^1D^*$, is described by Scheme 1, which also incorporates the occurrence of a ground-state dimer D, absorbing a fraction α of the excitation light.^{4,7} This scheme refers here to an intramolecular process, M^* standing for a bichromophoric system $M^* - M$, and $^1D^*$ representing the intramolecular excimer $^1(MM)^*$. In Scheme 1, k_a and k_d are the first-order rate constants of intramolecular excimer formation and dissociation, respectively. τ_o (monomer) and τ_o' (excimer) are the fluorescence lifetimes. The radiative rate constants k_f (monomer) and k_f' (excimer) are also indicated. Scheme 1, formally analogous to that applicable to intermolecular excimer formation, has been shown to correctly describe the intramolecular excimer formation and dissociation for a number of chained molecules, such as 1,3-di(2-pyrenyl)propane and 1Py(*n*)1Py with $n > 13$.^{15,16,18,23} When the presence of ground-

state dimers D is not taken into account, the fluorescence quantum yield ratio Φ'/Φ (or the intensity ratio I'/I) is given by eq 1:²¹

$$\frac{\Phi'}{\Phi} = \frac{k_f' [^1D^*]}{k_f [^1M^*]} = \frac{k_f' k_a}{k_f (k_d + 1/\tau_o')} \approx \frac{I'}{I} \quad (1)$$

A simplified kinetic situation is realized when the excimer dissociation reaction can be neglected with respect to the reciprocal excimer lifetime, i.e., when $k_d \ll 1/\tau_o'$.^{1d,21} Under these low-temperature-limit (LTL) conditions, the equation for Φ'/Φ (or I'/I) reduces to eq 2:

$$\frac{\Phi'}{\Phi} (\text{LTL}) = \frac{k_f'}{k_f} k_a \tau_o' \quad (2)$$

For the complete Scheme 1, the following expressions eqs 1a and 2a are obtained.

$$\frac{\Phi'}{\Phi} = \frac{k_f' [^1D^*]}{k_f [^1M^*]} = \frac{k_f' k_a + \alpha \cdot 1/\tau_o'}{k_f k_d + (1 - \alpha) \cdot \tau_o'} \approx \frac{I'}{I} \quad (1a)$$

$$\frac{\Phi'}{\Phi} (\text{LTL}) = \frac{k_f' k_a + \alpha \cdot 1/\tau_o'}{k_f (1 - \alpha) \cdot \tau_o'} \quad (2a)$$

Arrhenius Plots of I'/I , Φ'/Φ as a Function of Chain Length. Stevens–Ban plots of $\ln(I'/I)$ against the reciprocal absolute temperature are presented in Figure 3 for 1PC(2)1PC, 1PC(5)1PC, and 1PC(16)1PC in the solvents MCH, *n*-hexa-

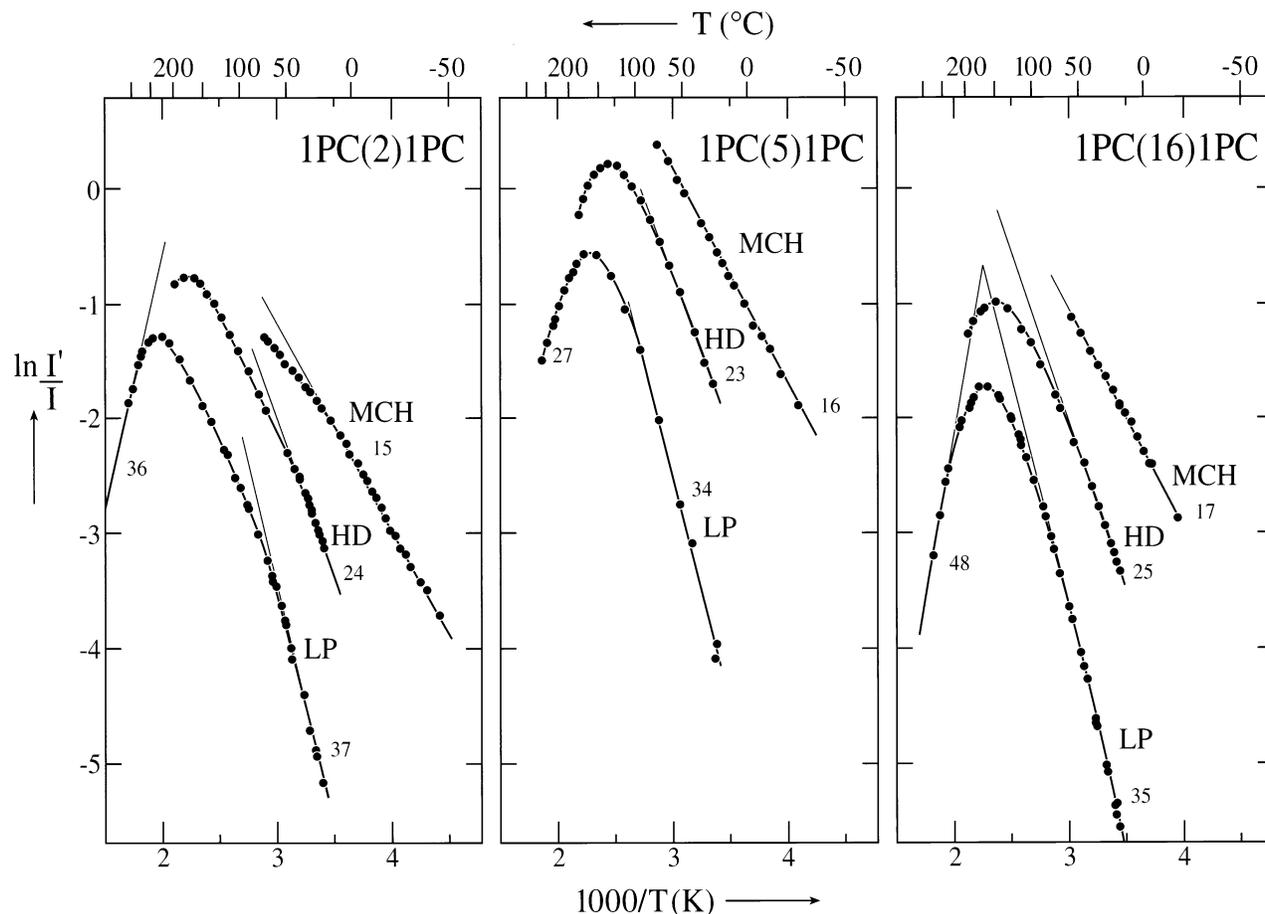


Figure 3. Stevens–Ban plots of the excimer-to-monomer fluorescence intensity ratio, $\ln(I'/I)$ versus the reciprocal absolute temperature, for 1PC(2)1PC, 1PC(5)1PC, and 1PC(16)1PC in methylcyclohexane (MCH), *n*-hexadecane (HD) and liquid-paraffin (LP). The numbers (in kJ/mol) at the slopes represent the activation energies E_a of excimer formation (negative slope) and the excimer formation enthalpy $-\Delta H$ (positive slope).

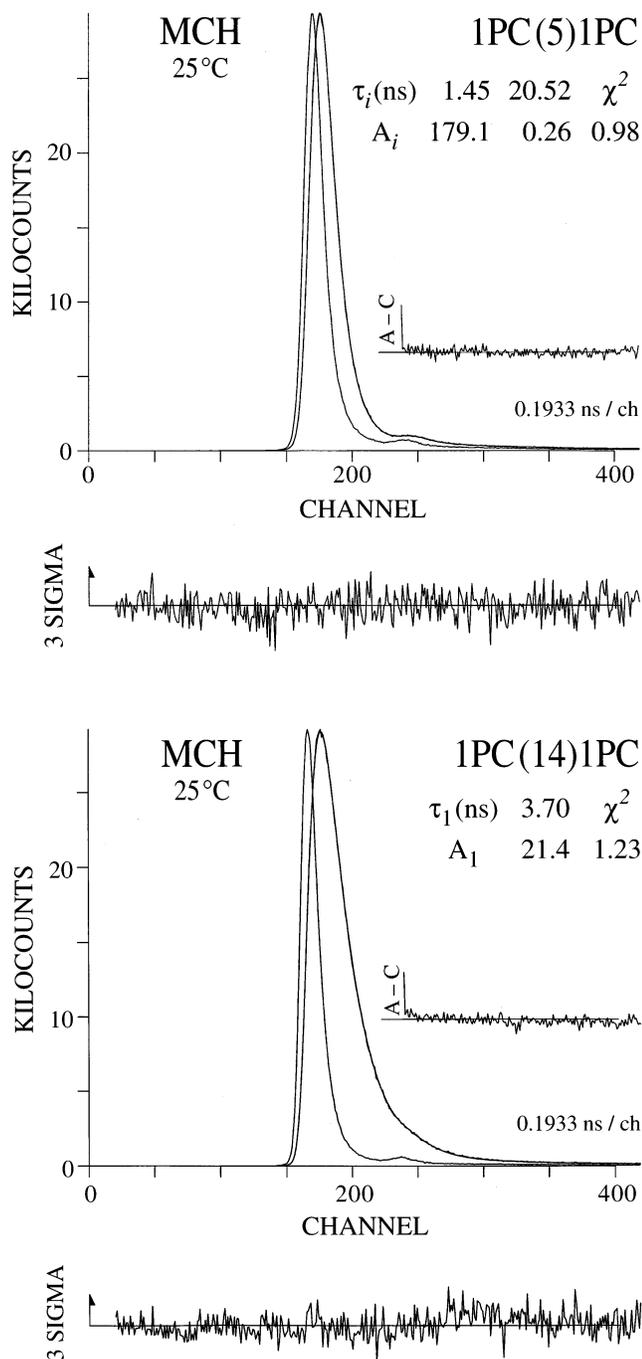


Figure 4. Monomer fluorescence (at 386 nm) decay curves of IPC(5)1PC and IPC(14)1PC in methylcyclohexane (MCH) at 25 °C. The decays were obtained by using nanosecond flash lamp excitation at 337 nm, with 0.1933 ns/channel. The decay times (τ_2 , τ_1) and their preexponential factors A_i are given. The time τ_2 is listed first (IPC(5)1PC). The weighted deviations, expressed as 3σ (expected deviations), the autocorrelation functions A-C, and the values for χ^2 are also indicated.

decane, and liquid-paraffin. The excimer-to-monomer intensity ratio (I'/I) reaches its maximum at temperatures around 150 °C. At each temperature for each of the three molecules, the value of I'/I decreases from MCH to liquid-paraffin, i.e., with increasing solvent viscosity.^{24,25} This observation reflects the viscosity influence on the rate constants of intramolecular excimer formation (k_a) and dissociation (k_d), see eq 1.

It can be seen from the Arrhenius plots of I'/I in Figure 3 that the data points of the three IPC(n)1PC molecules in MCH are located on a straight line, with a slope E_a/R (see Table 1),

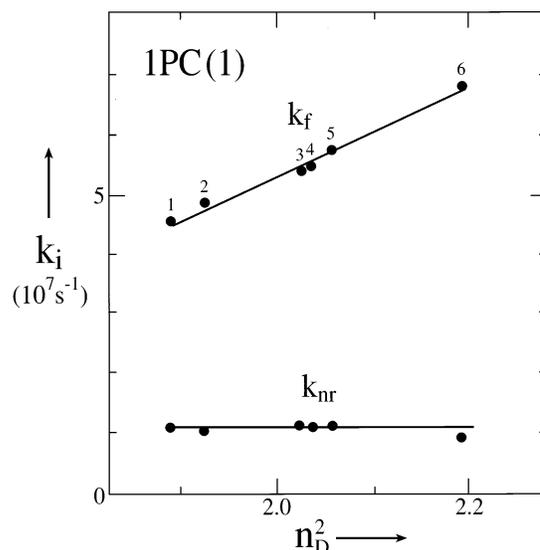


Figure 5. Radiative (k_f) and nonradiative (k_{nr}) rate constants at 20 °C for IPC(1), the methyl ester of 1-pyrenecarboxylic acid, as a function of n_D^2 (n_D is the solvent refractive index).

for temperatures lower than 25 °C ($n = 2$) and 60 °C ($n = 5$ and 16). This means that in this solvent, the LTL conditions hold for these temperature ranges ($k_d \ll 1/\tau_0'$, Scheme 1) and that the ratios I'/I and Φ'/Φ are given by eq 2. When the influence of ground-state dimers is neglected, the plot of Φ'/Φ against n for IPC(n)1PC in MCH at 20 °C in Figure 2a hence represent the relative chain length dependence of k_a (eq 2), provided that the product $k_f'/k_f \cdot \tau_0'$ remains unchanged. To circumvent these complexities, the individual rate constant k_a can be obtained directly from SPC and fluorescence quenching experiments, as will be presented in the following sections.

Determination of k_a from Decay Times. Monomer Lifetime $\tau_0(n)$ for IPC(n)1PC. The nanosecond monomer fluorescence decays for all IPC(n)1PC studied here are single exponential in MCH and n -hexadecane at room temperature, see Figure 4 for $n = 5$ and 14 at 25 °C. This is caused by the effective absence of the thermal back reaction k_d (Scheme 1), the LTL condition, as discussed in the previous section. The excimer formation rate constant k_a can then be determined from the monomer fluorescence decay time τ and the lifetime τ_0 of an appropriate model compound that does not undergo excimer formation (eq 3).²⁶ IPC(1) is used here for measuring τ_0 , in dilute solution (10^{-5} M) to avoid intermolecular excimer formation. When more than one excimer is formed, as is the case with IPC(n)1PC,⁴ the rate constant k_a under LTL conditions (eq 3), is equal to the sum of the rate constants of all the processes leading from the excited-state monomer $^1M^*$ to the different excimers:

$$k_a = 1/\tau - 1/\tau_0 \quad (3)$$

To obtain accurate rate constants k_a from the τ data (eq 3), the correct unquenched monomer lifetime $\tau_0(n)$ for each of the compounds IPC(n)1PC must be known. This is important here, as τ_0 is relatively short (for example, 15.3 ns for the model substance IPC(1) in MCH at 20 °C, Table 2), which means that the decay of $^1M^*$ ($1/\tau_0$ in Scheme 1) is an important reaction channel.²⁷ For IPC(1), as a consequence of its high fluorescence quantum yield ($\Phi = 0.85$ in MCH at 20 °C),²⁸ the lifetime τ_0 ($1/(k_f + k_{nr})$) is to a large extent determined by the radiative rate constant k_f ($5.5 \times 10^7 \text{ s}^{-1}$)²⁹ and not so much by the nonradiative rate constant k_{nr} ($1.0 \times 10^7 \text{ s}^{-1}$). The fluorescence lifetime of IPC(1) therefore strongly depends on the nature of

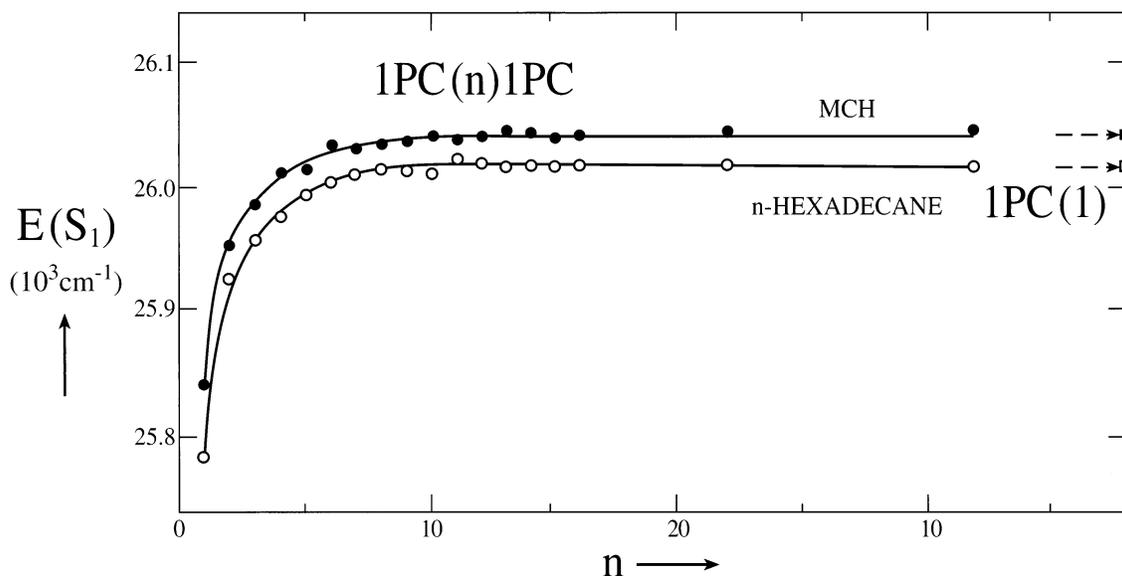


Figure 6. The energy $E(S_1)$ of the lowest-energy maximum in the absorption spectra of 1PC(*n*)1PC as a function of alkane chain length n and of 1PC(1), in methylcyclohexane (MCH) and *n*-hexadecane at 20 °C.

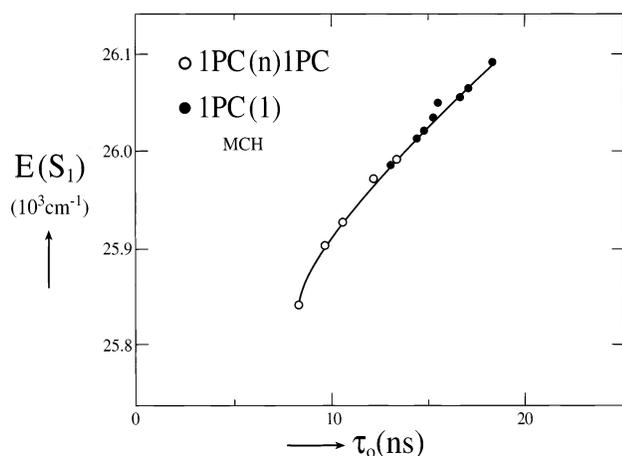


Figure 7. The energy $E(S_1)$ of the lowest-energy maximum in the absorption spectra of 1PC(*n*)1PC and 1PC(1) as a function of their (unquenched) fluorescence lifetime τ_o . The temperature is 20 °C. See text.

the solvent, as k_f increases proportional to $n_D^{2,21}$ whereas k_{nr} does not depend on n_D , see Figure 5. Besides the fluorescence lifetime τ_o , also the energy $E(S_1)$ of the first band in the absorption spectrum of the compounds 1PC(*n*)1PC decreases with increasing refractive index n_D of the solvent.^{2c,30} The influence of n_D on the unquenched monomer lifetime of 1PC(*n*)1PC leads to a dependence of this lifetime $\tau_o(n)$ on chain length, due to the presence of the second pyrenylcarboxy group which modifies the overall polarizability (n_D) of the medium around the excited 1PC moiety. The magnitude of this effect depends on the relative distance between the two end groups, which distance increases with increasing chain length n . The same phenomenon is reflected by the chain-length-dependent difference in the energy $E(S_1)$ of the first absorption band maximum of 1PC(*n*)1PC and that of 1PC(1), see Figure 6. The $\tau_o(n)$ value for each molecule 1PC(*n*)1PC can now be calculated from a correlation of the energy of its first absorption band maximum, which is a measure of the effective polarizability (n_D) of the medium, with the corresponding value for τ_o of 1PC(1) at that refractive index (Figure 7). The validity of this procedure was verified by a comparison of the decay time τ and the energy $E(S_1)$ of 1PC(*n*)1PC compounds under condi-

tions, such as in liquid-paraffin at -10 °C, where excimer formation has stopped completely ($k_a = 0$, see eq 3). The decay time τ has then become identical to the monomer lifetime τ_o , see Figure 7.

k_a as a Function of Chain Length. In accordance with the prevailing LTL conditions (eq 3), the rate constant of excimer formation k_a for 1PC(*n*)1PC in MCH and *n*-hexadecane at 20 °C can be obtained from the decay times τ and $\tau_o(n)$. The data for k_a , τ , and $\tau_o(n)$ are listed in Tables 2 and 3. The dependence of k_a in MCH on the chain length n is depicted in Figure 8, showing, as to be expected (eq 2), a plot similar as presented for Φ'/Φ in Figure 2a. This means that the product $k'_f/k_f \cdot \tau'_o$ indeed does not strongly depend on n , see eq 2. In MCH, the rate constant k_a reaches its maximum for $n = 5$. From there, k_a decreases with increasing chain length, initially (until $n = 9$) alternating with n . For $n = 2-4$, the value of k_a increases toward that of $n = 5$. In *n*-hexadecane, the dependence of k_a on n is comparable with that observed in MCH, with smaller rate constants, due to the larger solvent viscosity, as discussed above. The explanation for the chain length dependence of k_a follows the same reasoning as that given above for Φ'/Φ . The increase in k_a from $n = 2$ to $n = 5$ is caused by the release of the steric hindrance exerted by the hydrogens of the methylene chain on the excimer formation. The alternating pattern of k_a for n between 5 and 8 (Figure 8) is likewise due to chain cyclization problems.²⁰ For $n > 8$, however, the monotonic decrease of k_a with larger n arises from the increase in the end-to-end distances, a phenomenon similar to reducing the effective concentration in intermolecular excimer formation.

Influence of Viscosity. The influence of solvent viscosity η on intramolecular excimer formation can be deduced from a comparison of the rate constant k_a in MCH and *n*-hexadecane. The ratio $k_a(\text{MCH})/k_a(\text{HXD})$, see Tables 2 and 3, for 1PC(*n*)-1PC gradually increases from 3.1 ($n = 5$) to a value between 3.9 and 4.1 for $n > 12$. For a diffusion-controlled reaction governed by the Stokes–Einstein relation $k \approx \eta^{-1}$, $k_a(\text{MCH})/k_a(\text{HXD}) = \eta(\text{HXD})/\eta(\text{MCH})$ at 20 °C should be equal to 4.27, see ref 24. This shows that excimer formation with 1PC(*n*)1PC has not yet reached full viscosity control even for $n = 32$. The conclusion that chain dynamics exerts an appreciable influence on the excimer dynamics of 1PC(*n*)1PC is also reached from the chain length dependence of the activation energy of excimer

TABLE 3: Spectroscopic Data on Intramolecular Excimer Formation with the 1,*n*-Bis(1-pyrenylcarboxy)alkanes 1PC(*n*)1PC in *n*-Hexadecane (rate constants and decay times refer to 20 °C)

1PC(<i>n</i>)1PC	k_a^a (10^8 s^{-1})	τ^b (ns)	$\tau_0(n)^c$ (ns)	E_a^d (kJ/mol)	k_a^e (10^{11} s^{-1})	I_0/I^f	$k_a(s)$ (10^8 s^{-1})	$k_a(s)/k_a^h$	α^i
1									
2	0.96	5.2	10.4	24.6	2.3	2.08	1.04	1.08	0.04
3	1.15	5.0	11.5	25.1	3.4	3.04	1.77	1.54	0.23
4	1.18	5.1	12.5	22.4	1.2	2.80	1.44	1.22	0.12
5	1.75	4.0	13.0	21.1	1.0	4.43	2.64	1.51	0.26
6	1.13	5.4	14.0	22.7	1.2	3.04	1.46	1.29	0.15
7	1.07	5.7	14.4	23.0	1.3	3.00	1.39	1.30	0.15
8	0.87	6.4	14.5	22.9	1.1	2.52	1.05	1.21	0.10
9	0.82	6.7	14.7	23.3	1.2	2.43	0.97	1.18	0.09
10	0.75	7.0	14.7	22.7	0.8	2.22	0.83	1.11	0.05
11	0.64	7.6	14.7	22.5	0.6	2.18	0.80	1.24	0.11
12	0.61	7.8	14.7	22.5	0.6	2.04	0.71	1.16	0.07
13	0.52	8.3	14.7	22.6	0.5	1.97	0.66	1.27	0.10
14	0.47	8.7	14.7	22.6	0.5	1.85	0.58	1.23	0.09
15	0.43	9.0	14.7	22.7	0.5	1.72	0.49	1.14	0.05
16	0.41	9.2	14.7	22.2	0.4	1.62	0.42	1.02	0.01
22	0.29	10.3	14.7	21.8	0.2	1.47	0.32	1.10	0.03
32	0.21	11.2	14.7	20.6	0.1				
1PC(1) ^j		14.7		17.3					

^a Excimer formation rate constant from decay times τ (eq 3). ^b Monomer fluorescence decay time (single-exponential, LTL limit), see text. ^c Corrected lifetime of model compound IPC(1), see text. ^d Activation energy of excimer formation obtained from Arrhenius plot of k_a (eq 2). The activation energy for free diffusion in *n*-hexadecane is $E(T/\eta) = 17.5$ kJ/mol. ^e Preexponential factor in Arrhenius expression of k_a . ^f See eqs 5 and 6. ^g Excimer formation rate constant derived from I_0/I (eq 6). ^h See eq 7. ⁱ Percentage of excitation light absorbed by the ground state dimer D, see Scheme 1 and eq 7. ^j The model compound 1-pyrenecarboxylic acid methyl ester. Data on intermolecular excimer formation are listed for this molecule.

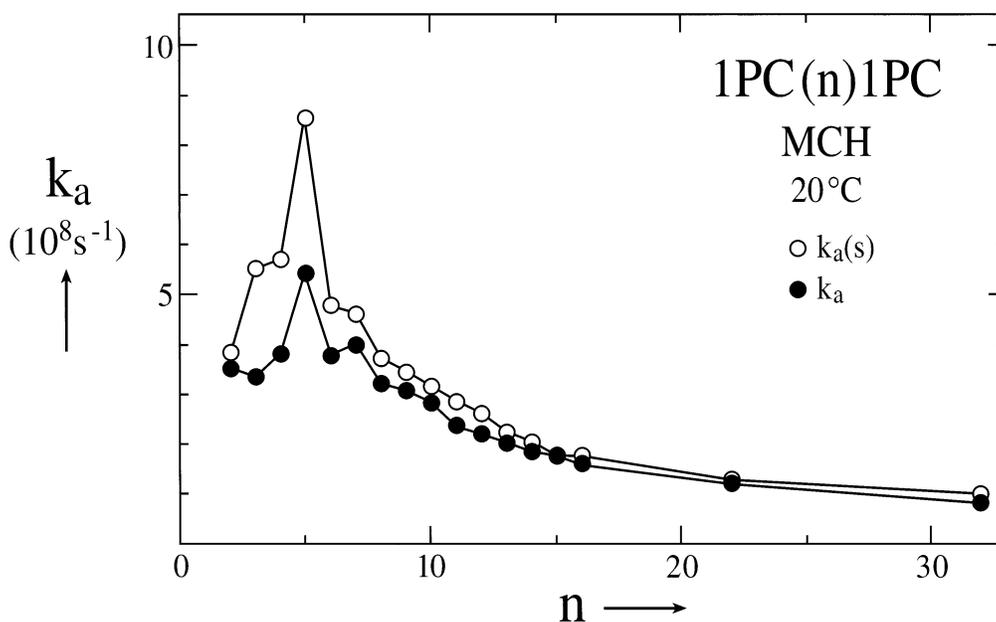


Figure 8. The excimer formation rate constant k_a , determined from fluorescence decay times, and $k_a(s)$, determined from monomer fluorescence quenching experiments, see text, both as a function of alkane chain length n , for a series of 1PC(*n*)1PC with $n = 2-16, 22, 32$, in methylcyclohexane (MCH) at 20 °C.

formation E_a (Tables 1–3). E_a remains larger than the activation energy of free diffusion $E(T/\eta)$ in MCH and *n*-hexadecane. For the barrier-free intermolecular excimer formation with IPC(1) in these solvents, on the contrary, similar values for E_a and $E(T/\eta)$ are found (Tables 2 and 3).

Determination of $k_a(s)$ from I_0/I . Alternatively, the rate constant of excimer formation can be obtained from photostationary measurements of the fluorescence intensity ratio I_0/I , which describes the fluorescence quenching of the monomer fluorescence intensity (I) with respect to that (I_0) of an unquenched model substance. I_0/I , as well as the related quantum yield ratio Φ_0/Φ , is given by the extended Stern–Volmer equation (eq 4).³¹ The fraction of the excitation light that is absorbed by the preformed dimer D, see Scheme 1, is again

represented by α .

$$\frac{I_0}{I} - 1 = \frac{\tau_0}{\tau_0'} \frac{k_a + \alpha/\tau_0}{k_a + (1 - \alpha)/\tau_0'} = \frac{\Phi_0}{\Phi} - 1 \quad (4)$$

This expression simplifies under LTL conditions ($k_d \ll \tau_0'$) to the well-known Stern–Volmer equation,³² which is valid for irreversible reactions.

$$\frac{I_0}{I} - 1 = \frac{k_a \tau_0 + \alpha}{1 - \alpha} = \frac{\Phi_0}{\Phi} - 1 \quad (5)$$

When the presence of ground-state dimers D is not taken into account in the analysis of I_0/I , an apparent rate constant $k_a(s)$ is

obtained, see eq 6. This excimer formation rate constant $k_a(s)$ was determined for IPC(*n*)IPC in MCH and *n*-hexadecane at 20 °C from the I_o/I data by employing eq 6. IPC(1) was taken as the model compound for measuring I_o and the corrected $\tau_o(n)$ values were used (see above). The results are presented in Tables 2 and 3 and for MCH in Figure 8.

$$\frac{I_o}{I} - 1 = k_a(s)\tau_o = \frac{\Phi_o}{\Phi} - 1 \quad (6)$$

Comparison of k_a and $k_a(s)$. It is seen from Figure 8 and Table 2 that the dependence of $k_a(s)$ on the chain length *n* of IPC(*n*)IPC in MCH is similar to that of k_a , but $k_a(s)$ is larger for all *n*. Both rate constants have their maximum for *n* = 5, decreasing smoothly with chain length for *n* > 7. Also the ratio $k_a(s)/k_a$ reaches its largest value for *n* = 5, see Tables 2 and 3:

$$k_a(s) = \frac{k_a + \alpha/\tau_o}{1 - \alpha} \quad (7)$$

The difference between $k_a(s)$ and k_a is attributed to a specific interaction between the pyrenylcarboxy end groups of IPC(*n*)-IPC. This interaction leads to the formation of an excimer-like ground-state dimer, which absorbs a fraction α of the excitation light, see eq 7, which is derived by combining eqs 5 and 6. Such dimers have been detected by the pronounced ring current effect in the ^1H NMR spectra of IPC(*n*)IPC, which is caused by the close proximity of these end groups.⁴ From a comparison of k_a and $k_a(s)$, information can therefore be obtained on the presence of ground-state dimers and their kinetic influence on the intramolecular excimer formation with IPC(*n*)IPC,^{4,6} see eqs 4–7. From the α data in Tables 2 and 3 it appears that dimer formation is especially important for *n* = 3–8, in MCH and *n*-hexadecane.

Chemical Ring-Closure Reactions and Excimer Formation with IPC(*n*)IPC and IPy(*n*)IPy. When the chain length dependence of intramolecular excimer formation with the dipyrenylalkanes IPy(*n*)IPy is compared with that of a chemical ring-closure reaction resulting in cycloalkanes, it appears that the relation $N = n + 3$ holds for the number *n* of the methylene groups in IPy(*n*)IPy and the number of carbon atoms *N* in the cycloalkane reaction products.¹⁶ This conclusion is based on the following observations. The most efficient excimer formation occurs for *n* = 3, whereas cyclohexane ($N = 6$) has the smallest ring strain of the cycloalkanes.^{20,33} Further, excimer formation does not occur with IPy(7)IPy, as mentioned earlier (Figure 2b), and the ring strain has its maximum value for cyclodecane ($N = 10$).^{20d,33} The $N = n + 3$ equation can be visualized (Figure 9) by the introduction of three “phantom” atoms in the case of IPy(*n*)IPy,^{1c,16} bridging the longer effective end-to-end distance enforced by the excimer structure (3.5 Å)²¹ as compared with that of a C–C chemical bond (1.5 Å).³⁴

When comparing excimer formation of IPC(*n*)IPC with the chemical ring-closure reactions, the dynamic role of the carboxy groups must be discussed. The rotational barriers of the Py–COO and Py(CO)–O bonds are considerably higher than that of the PyCOO–CH₂ bond, based on data for aromatic and aliphatic esters.^{35,36} The carboxy group is therefore considered to be an integral part of the IPC unit, from the dynamic point of view, which leads to the conclusion that the relation $N = n + 3$ will also hold for IPC(*n*)IPC. Support for this conclusion is derived from the fact that excimer formation is not observed for IPy(1)IPy and also not for IPC(1)IPC (Table 1).

A plot of $\log k_a$ of IPC(*n*)IPC versus $\log(n + 2)$, or $\log(N - 1)$, is presented in Figure 10. The data points for *n* > 4 ($N >$

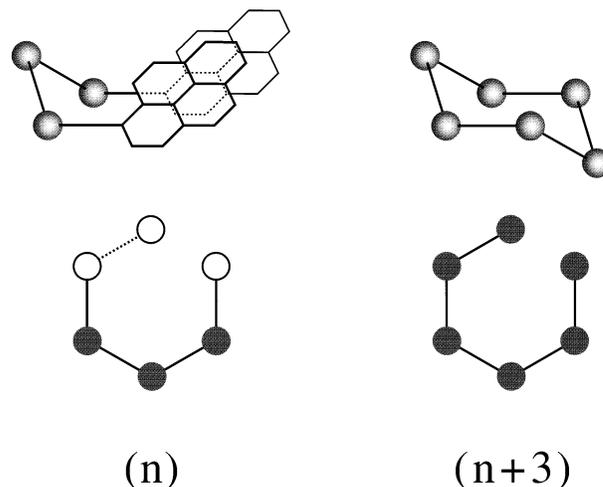


Figure 9. The number (*n*) of the methylene groups in IPC(3)IPC and IPy(3)IPy, as compared with that (*N*) of the carbon atoms in cyclohexane: $N = n + 3$. In the former case, three “phantom” atoms (open spheres) are drawn, see text.

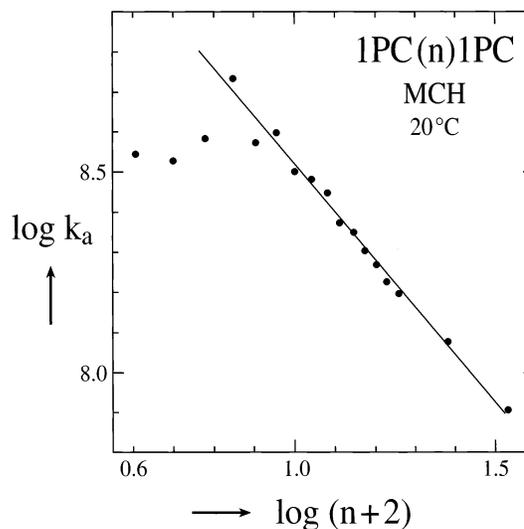


Figure 10. Double logarithmic plot of the excimer formation rate constant k_a for a series of IPC(*n*)IPC with *n* = 2–16, 22, 32, in methylcyclohexane (MCH) at 20 °C versus $\log(n + 2)$. The slope of the line through the data points for *n* > 4, obtained by a least-squares fit, is equal to -1.17 . See text.

7) fall on a straight line with a slope of -1.17 . The rate constant for the ring-closure reaction of a chain with *N* atoms for which the end-to-end distances can be described by a Gaussian distribution, depends on the number of bonds ($N - 1$) to the power $-3/2$ (eq 8):³⁷

$$k_a(G) \sim (N - 1)^{-3/2} \quad (8)$$

Slopes between -1.4 and -1.5 have been reported for end-to-end cyclization reactions involving relatively long polystyrene chains, with *N* larger than 100.^{20d,38} The smaller slope of -1.2 obtained here for IPC(*n*)IPC indicates that the end-to-end distances of the methylene chains in these molecules still deviate from a Gaussian distribution.

Activation Energies E_a and Preexponential Factors k_a^o from Decay Times τ . From the monomer fluorescence decay times τ of IPC(*n*)IPC with *n* = 2–16, 22, 32 measured as a function of temperature in MCH and *n*-hexadecane under LTL conditions (eq 3), the activation energy E_a and the preexponential factor k_a^o of the excimer formation reaction were determined.

The results are presented in Tables 2 and 3. In MCH (Table 2), E_a decreases from 17 kJ/mol for $n = 3$ down to 14 kJ/mol for $n = 22$, an energy still larger than the activation energy of free diffusion $E(T/\eta)$ for MCH of 12.6 kJ/mol, as discussed above. A minimum in E_a occurs around $n = 5$ and for $n = 2$. The preexponential factors k_a^0 gradually decrease with n , from $3.0 \times 10^{11} \text{ s}^{-1}$ for $n = 3$ to $0.3 \times 10^{11} \text{ s}^{-1}$ for $n = 22$. Also for k_a^0 a minimum for $n = 5$ and $n = 2$ is observed, corresponding to the lower E_a values.

In n -hexadecane (Table 3) the pattern of the chain length dependence of E_a is similar to that found in MCH, but with clearly larger activation energies for all n . This means that the solvent viscosity, next to the rotational barriers of the chain, plays an important role in the intramolecular excimer formation of IPC(n)IPC. E_a decreases with increasing n , from 25 kJ/mol for $n = 2$ and 3, to 21 kJ/mol for $n = 32$. The excimer activation energy for $n = 32$ in n -hexadecane is clearly larger than that for free diffusion ($E(T/\eta) = 17.5$ kJ/mol). The preexponential factors k_a^0 again decrease with n , from $3.4 \times 10^{12} \text{ s}^{-1}$ for $n = 3$ to $0.1 \times 10^{12} \text{ s}^{-1}$ for $n = 32$, with a minimum around $n = 5$. The finding that k_a^0 in n -hexadecane is a factor of 10 larger than in MCH is a consequence of the higher activation energy E_a in the former more viscous solvent.

The relatively low value for E_a and k_a^0 for IPC(5)IPC in MCH and n -hexadecane as well as the irregular chain length dependence of these parameters for n between 2 and 7, originates from the kinetic control (conformational effects) exerted by these short chains on the excimer formation process. For the longer chains, excimer formation depends more and more on their end-to-end distance, i.e., on the effective concentration as in an intermolecular process. From the fact that E_a is still larger than the activation energy $E(T/\eta)$ for free diffusion, it is concluded that the movement of the pyrenoate end groups is governed not only by solvent viscosity but also by the rotational barriers in the chain.

Conclusion

For all dipyrenylcarboxyalkanes IPC(n)IPC with $n = 1-16, 22, 32$, intramolecular excimer formation is observed in various solvents, except for IPC(1)IPC. The pattern of the excimer-to-monomer fluorescence quantum yield ratio Φ'/Φ as a function of n is strikingly different from that of the di(1-pyrenyl)alkanes 1Py(n)1Py. The maximum value for Φ'/Φ is reached for $n = 5$ instead of for $n = 3$ (the Hirayama rule) and a sharp minimum in Φ'/Φ , as found around 1Py(7)1Py, is not observed. The rate constant of excimer formation k_a , measured from single-exponential monomer fluorescence decays of IPC(n)IPC in MCH and n -hexadecane at 20 °C (LTL limit), shows a similar chain length dependence as Φ'/Φ : k_a reaches a maximum value for $n = 5$ and monotonically decreases for $n > 8$. These differences are attributed to the presence of the ether oxygen atom in the carboxy groups of IPC(n)IPC, which exerts a smaller hindrance in reaching the optimal excimer configuration (less intrachain H/H-repulsion) than the terminal CH₂ groups in 1Py(n)1Py. The excimer formation rate constant [$k_a(s)$] was also determined from I_o/I (eq 6, LTL limit). In the solvents studied, $k_a(s)$ is generally larger than k_a . These results indicate that ground-state dimers (performed excimers within the time-resolution of the nanosecond experiments) are present for IPC(n)IPC with $n = 3-16$.

The results presented here reflect a difference in the distribution function of the end-to-end distances in the electronic ground state of the two series of diarylalkanes IPC(n)IPC and 1Py(n)1Py. The chain length dependence of excimer formation

for 1Py(n)1Py is reminiscent of what was observed previously in chemical ring-closure reactions involving alkane chains, which in fact indicates that the conformation of the methylene chain in the 1Py(n)1Py compounds in the ground state is not significantly perturbed by the presence of the pyrenyl end groups and that the intrachain cyclization requirements are similar for both processes. In the case of IPC(n)IPC, the formation of ground-state dimers perturbs the distribution function of the end-to-end distances toward shorter distances, especially for IPC(5)IPC, as compared to those of the series 1Py(n)1Py. This fact explains the observed maximum in the rate constant of excimer formation of IPC(5)IPC and the occurrence of static quenching, which causes the difference between the $k_a(s)$ and k_a data. The specific dependence of the excimer formation rate constants on the molecular nature of the end groups discussed in this paper should be taken into account in general treatments of intramolecular excimer formation. With the IPC(n)IPC molecules, the dynamics of short alkane chains (n between 5 and 32) can be followed by intramolecular excimer formation, as conformational control of this process is considerably reduced by the flexible linkages (C—O bonds) near the excimer-forming chromophores. In this manner, the limits of the validity of chain dynamics models may be explored.

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(27) The correction procedure to obtain $\tau_o(n)$ is not necessary for the model compound 1-methylpyrene (1MePy) of the series 1Py(*n*)1Py, see ref 16 and Figure 2b, as $1/\tau_o$ for 1MePy ($4 \times 10^6 \text{ s}^{-1}$) is much smaller relative to $1/\tau$ (eq 3) than for 1PC(1).

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(29) The radiative rate constant k_f of $5.5 \times 10^{-7} \text{ s}^{-1}$ for 1PC(1) in MCH at 20 °C is a factor of 17 larger than the k_f value of $0.32 \times 10^{-7} \text{ s}^{-1}$ for 1-methylpyrene (ref 17), the model compound for the series 1Py(*n*)1Py. This means that for the same k'_f the ratio k'_f/k_f and hence Φ'/Φ is 17 times

larger for 1Py(*n*)1Py than for 1PC(*n*)1PC, for the same k_a , k_d , and $1/\tau'_o$ (eq 1).

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