

INTRAMOLECULAR MONOMER AND EXCIMER FLUORESCENCE WITH DIPYRENYLPROPANES: DOUBLE-EXPONENTIAL *VERSUS* TRIPLE-EXPONENTIAL DECAYS[†]

KLAAS A. ZACHARIASSE, REINHARD BUSSE, GERT DUVENECK and WOLFGANG KÜHNLE

Abteilung Spektroskopie, Max-Planck-Institut für biophysikalische Chemie, Am Fassberg, D-3400 Göttingen (F.R.G.)

(Received September 12, 1984)

Summary

The fluorescence decays of 1,3-di(1-pyrenyl)propane undergoing intramolecular excimer formation can be fitted to a sum of three exponentials, whereas only two exponentials are needed for 1,3-di(2-pyrenyl)propane. It is concluded, from an analysis of the decay parameters, that one monomer and two excimers are involved in the excimer formation for 1,3-di(1-pyrenyl)propane, in contrast with that for 1,3-di(2-pyrenyl)propane where only one excimer and one monomer are needed in the kinetic scheme. Kinetic and thermodynamic data are presented for both molecules. The significance of the various cases (double and higher) of multi-exponential decay is discussed.

1. Introduction

Intramolecular excimer formation with diarylpropanes $M(\text{CH}_2)_3M$ has received considerable attention. The first studies were reported by Hirayama [1] on 1,3-diphenylpropane and by Chandross and Dempster [2] on the dinaphthylpropanes. Later, investigations were carried out on 1,3-di(1-pyrenyl)propane (1Py(3)1Py) [3 - 5], 1,3-di(4-biphenyl)propane [4], 1,3-di(2-anthryl)propane [6] and the 1,3-di(*m*-phenanthryl)propanes with $m = 1, 2, 3$ and 9 [7, 8]. With 1,3-di(9-anthryl)propane intramolecular excimer formation was not detected, as was concluded from the observation that the (single-exponential) fluorescence lifetime of this compound is equal to that of 9-methylantracene [9]. A photochemical reaction was found to

[†]Paper presented at the Xth IUPAC Symposium on Photochemistry, Interlaken, Switzerland, July 22 - 27, 1984.

occur with this compound, however [9, 10]. The reason for the absence of excimer formation may be sought in a prohibitive steric hindrance exerted by the hydrogen atoms at the 1 and 8 positions of the anthryl moieties, preventing the formation of a sandwich-like excimer structure.

The fluorescence decay behaviour of the various diarylpropanes has been discussed from various points of view, especially with regard to the number of exponentials observed in the decays and the relative magnitude of their amplitudes [11 - 14]. Triple-exponential decay was detected for 1Py(3)1Py over a wide range of temperatures and solvents [5], whereas deviations from double-exponential decay were not reported for the other diarylpropanes mentioned above. However, polymer chemists and physicists have come to believe that the effect of the presence of different chain conformers will be seen in intramolecular excimer formation with diarylpropanes, and they expect this to lead to multi-exponential fluorescence decays for these compounds [12].

In other words, it has been argued that the kinetic scheme applicable to intermolecular excimer formation (see scheme (I) below), comprising one excited state monomer and one excimer, is unable to describe intramolecular excimer formation with diarylpropanes. Reports on the observation of multi-exponential decay, attributed to the influence of different chain conformers, have been published for a number of systems: for intramolecular exciplex formation with *n*-phenyl-1-*N,N*-dimethylaminoalkanes [13] and for polymer systems [11, 14].

It is the purpose of this paper to present fluorescence decay time data obtained with 1Py(3)1Py [5] and 1,3-di(2-pyrenyl)propane (2Py(3)2Py) [15] and to discuss the kinetic schemes that operate in the two cases. This will then lead to a general consideration of the question whether chain conformers (*i.e.* kinetically distinguishable excited state monomers) do in general play a role in intramolecular excimer formation with diarylpropanes. The case of diarylalkanes with polymethylene chains other than trimethylene [3] and of systems with different end groups will be discussed elsewhere [16].

2. Experimental details

The fluorescence decay times were determined using the method of time-correlated single-photon counting as described before [5]. Details of the data processing and of the synthesis of the compounds can be found in the literature [3 - 5, 7] or will be presented elsewhere [15, 16]. The concentration of the dipyrenylpropanes was lower than 1×10^{-5} M. The quantum-corrected fluorescence spectra were obtained employing a Hitachi-(Perkin-Elmer) MPF-44E spectrofluorometer. The excited state absorption spectra were measured using an excimer laser (Lambda-Physik EMG 500; 248 nm (KrF)).

3. Kinetic schemes

In this section the significance of the observation of double-exponential *versus* triple-exponential decays of the monomer and excimer fluorescence will be discussed.

3.1. Double-exponential decay

The kinetically most simple case that can be encountered in the study of intermolecular or intramolecular excimer formation is represented by



where one monomer ${}^1M^*$ in the excited singlet state interacts with one excimer D. In this scheme ${}^1M^*$ can also represent the locally excited monomer ${}^1M^*(CH_2)_3M$ in the case of intramolecular excimer formation. Under these conditions k_a is the first-order rate constant of intramolecular excimer formation, while k_d is the rate constant for thermal dissociation of the excimer to the excited state monomer. τ_0 and τ_0' stand for the monomer lifetime and the excimer lifetime respectively. In the intermolecular case k_a is replaced by $k_a[M]$, where k_a is then a second-order rate constant. Scheme (I) has been shown to describe intermolecular excimer formation correctly [17] in the time and/or viscosity domain where the time dependence of the rate constant k_a can be neglected [18].

Scheme (I) leads to the following coupled differential equations when the various intramolecular pathways for the formation and reaction of ${}^1M^*$ and D are taken into account (the quantities in square brackets represent the concentrations):

$$\frac{d[{}^1M^*]}{dt} = - \left(k_a + \frac{1}{\tau_0} \right) [{}^1M^*] + k_d[D] + I_0 \quad (1)$$

$$\frac{d[D]}{dt} = k_a[{}^1M^*] - \left(k_d + \frac{1}{\tau_0'} \right) [D] \quad (2)$$

Here I_0 (einsteins $l^{-1} s^{-1}$) represents the intensity of the light exciting M.

Equations (1) and (2) give as solutions for the time dependence of the concentration of ${}^1M^*$ and D

$$[{}^1M^*] = A_{11} \exp(-\lambda_1 t) + A_{12} \exp(-\lambda_2 t) = \frac{i_M(t)}{k_f} \quad (3)$$

$$[D] = A_{21} \exp(-\lambda_1 t) + A_{22} \exp(-\lambda_2 t) = \frac{i_D(t)}{k_f'} \quad (4)$$

where $i_M(t)$ and $i_D(t)$ are the fluorescence intensities of the monomer and the excimer respectively and k_f and k_f' represent the radiative rate constants in each case.

The eigenvalues λ_1 and λ_2 can be obtained by solving the second-order determinant of the coefficient matrix of eqns. (1) and (2):

$$\begin{vmatrix} -\left(k_a + \frac{1}{\tau_0}\right) + \lambda & k_d \\ k_a & -\left(k_d + \frac{1}{\tau_0'}\right) + \lambda \end{vmatrix} = 0 \quad (5)$$

With the substitutions $X = k_a + 1/\tau_0$ and $Y = k_d + 1/\tau_0'$ this determinant gives rise to a quadratic equation

$$\lambda^2 - (X + Y)\lambda + XY - k_a k_d = 0 \quad (6)$$

which results after some minor algebraic manipulations in the well-known [17, 19] expression for the decay parameters λ_1 and λ_2 :

$$\lambda_{1,2} = \frac{X + Y \mp \{(Y - X)^2 + 4k_a k_d\}^{1/2}}{2} \quad (7)$$

The amplitude ratio $A = A_{12}/A_{11}$ (eqn. (3)) can be shown [17] to be equal to

$$A = \frac{X - \lambda_1}{\lambda_2 - X} \quad (8)$$

3.2. Triple-exponential decay

Similarly, for three instead of two kinetically interacting species in the excited state [5], the fluorescence decays (monomer $i_M(t)$ and excimer $i_D(t)$) consist of three exponentials. Under these conditions four kinetic schemes are possible *a priori* [5]:





Schemes (IIa) and (IIb) involve one excited state monomer ${}^1M^*$ and two kinetically distinguishable excimers D_1 and D_2 ; in schemes (IIc) and (IIId) two kinetically different monomeric species ${}^1M_1^*$ and ${}^1M_2^*$ (different chain conformers) and one excimer D appear [5, 20]. By taking scheme (IIa) as an example (see below) we obtain in a manner completely analogous to the situation with two excited state species (as treated in Section 3.1)

$$\frac{d[{}^1M^*]}{dt} = -\left\{k_a(1) + k_a(2) + \frac{1}{\tau_0}\right\}[{}^1M^*] + k_d(1)[D_1] + k_d(2)[D_2] \tag{9}$$

$$\frac{d[D_1]}{dt} = k_a(1)[{}^1M^*] - \left\{k_d(1) + \frac{1}{\tau_0'(1)}\right\}[D_1] + 0[D_2] \tag{10}$$

$$\frac{d[D_2]}{dt} = k_a(2)[{}^1M^*] + 0[D_1] - \left\{k_d(2) + \frac{1}{\tau_0'(2)}\right\}[D_2] \tag{11}$$

with

$$[{}^1M^*] = A_{11} \exp(-\lambda_1 t) + A_{12} \exp(-\lambda_2 t) + A_{13} \exp(-\lambda_3 t) = \frac{i_M(t)}{k_f} \tag{12}$$

$$[D_1] = A_{21} \exp(-\lambda_1 t) + A_{22} \exp(-\lambda_2 t) + A_{23} \exp(-\lambda_3 t) = \frac{i_{D_1}(t)}{k_f'(1)} \tag{13}$$

$$[D_2] = A_{31} \exp(-\lambda_1 t) + A_{32} \exp(-\lambda_2 t) + A_{33} \exp(-\lambda_3 t) = \frac{i_{D_2}(t)}{k_f'(2)} \tag{14}$$

as the solutions for the time dependence of the concentrations of ${}^1M^*$, D_1 and D_2 after flash excitation. The set of three differential equations (eqns. (9) - (11)) gives rise, with the substitutions $X = k_a(1) + k_a(2) + 1/\tau_0$, $Y = k_d(1) + 1/\tau_0'(1)$ and $Z = k_d(2) + 1/\tau_0'(2)$, to a determinant of order three

$$\begin{vmatrix}
 -X + \lambda & k_d(1) & k_d(2) \\
 k_a(1) & -Y + \lambda & 0 \\
 k_a(2) & 0 & -Z + \lambda
 \end{vmatrix} = 0 \tag{15}$$

which leads to the cubic equation [21]

$$\lambda^3 + p\lambda^2 + q\lambda + r = 0 \tag{16}$$

with

$$p = -(X + Y + Z)$$

$$q = XY + XZ + YZ - k_a(2)k_d(2) - k_a(1)k_d(1)$$

and

$$r = XYZ - k_a(2)k_d(2)Y - k_a(1)k_d(1)Z$$

The eigenvalues λ and the corresponding normalized eigenvectors (the amplitudes A_{ij}) can then be determined either analytically [22] or by utilizing a computer library program [16, 23].

3.3. Significance of multi-exponential decay

We shall outline here the information that can be obtained from the observation of double-, triple- or higher than triple-exponential decay in the study of excimer or exciplex formation.

3.3.1. Double-exponential decay

This can signify that two excited state species, a monomer and an excimer, are present. However, scheme (I) is the correct kinetic scheme only when identical values are obtained for λ_1 and λ_2 in the analysis of the monomer as well as the excimer fluorescence decays. In addition, the sum of the amplitudes in the excimer or exciplex decays must be equal to zero (eqn. (4) at $t = 0$), indicating that the excimer is not present before excitation. This last condition of course implies that the excimer and monomer emissions can be separated by choosing appropriate wavelengths for their observation. This can present problems, especially in the case of weak excimer or exciplex emissions, leading to a non-zero sum of the excimer amplitudes, even when scheme (I) is applicable [7].

3.3.2. Triple-exponential decay

This indicates the presence of at least three excited state species. Only when the three decay parameters λ_i have identical values for the monomer and the excimer decays is one of the various possibilities as described in Section 3.2 (schemes (IIa) - (IIId)) applicable. Again, the sums of the amplitudes of the excimer decays must be equal to zero, provided that they can be separated in the fluorescence spectrum (see above). Otherwise none of the schemes (IIa) - (IIId) can fit the data. When the three decay parameters λ_i observed for the monomer and excimer are not identical, more than three excited state species are present [16].

3.3.3. Higher than triple-exponential decay

This signifies either that more than three excited state species are present or that an altogether different kinetic scheme applies, for which the time dependence of the concentrations of the various excited state species cannot be described as a sum of exponentials.

4. Results and discussion

4.1. Spectra and decay times

The fluorescence spectra (Fig. 1) of 1Py(3)1Py and 2Py(3)2Py in methylcyclohexane (MCH) at 25 °C both consist of a strong unstructured excimer emission with a maximum around 20 000 cm^{-1} and a relatively weak residual monomer emission (Table 1). At first sight, from the similarity of these spectra it would be expected that the two dipyrrenylpropanes would show the same behaviour when the fluorescence response functions $i_M(t)$ and $i_D(t)$ of the monomer and excimer are studied as a function of time after flash excitation. Surprisingly, however, this is not the case (Figs. 2 and 3). With 1Py(3)1Py the fluorescence decay functions can only be fitted with three exponentials having the same values for the decay parameters λ_1 , λ_2 and λ_3 for the excimer and the monomer within the limits of experimental accuracy [5, 16] (Fig. 2 and eqns. (12) - (14)). This is observed, as stated above, to be the case over an extended temperature range and for various solvents. Further, the values of the three decay parameters λ_1 , λ_2 and λ_3 have been found to remain unchanged when experiments are carried out at different wavelengths over the entire excimer fluorescence band. This has been

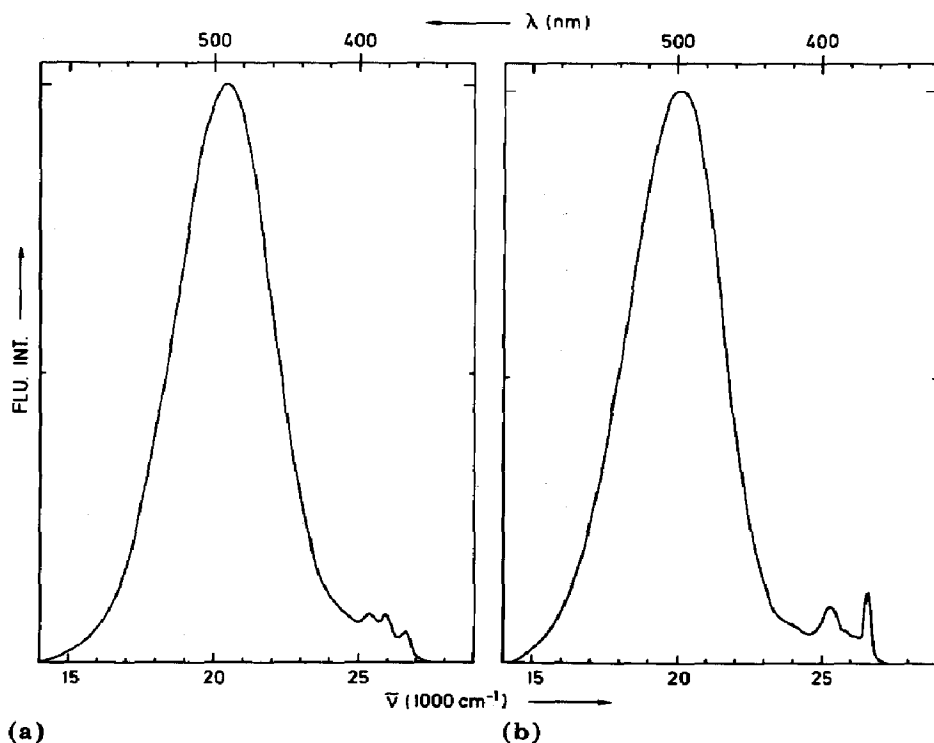


Fig. 1. Fluorescence spectra of (a) 2Py(3)2Py and (b) 1Py(3)1Py in MCH at 25 °C. Both spectra consist of a broad emission band with a maximum around 500 nm in addition to a relatively weak structured monomer emission band. The similarity of the spectra should be noted.

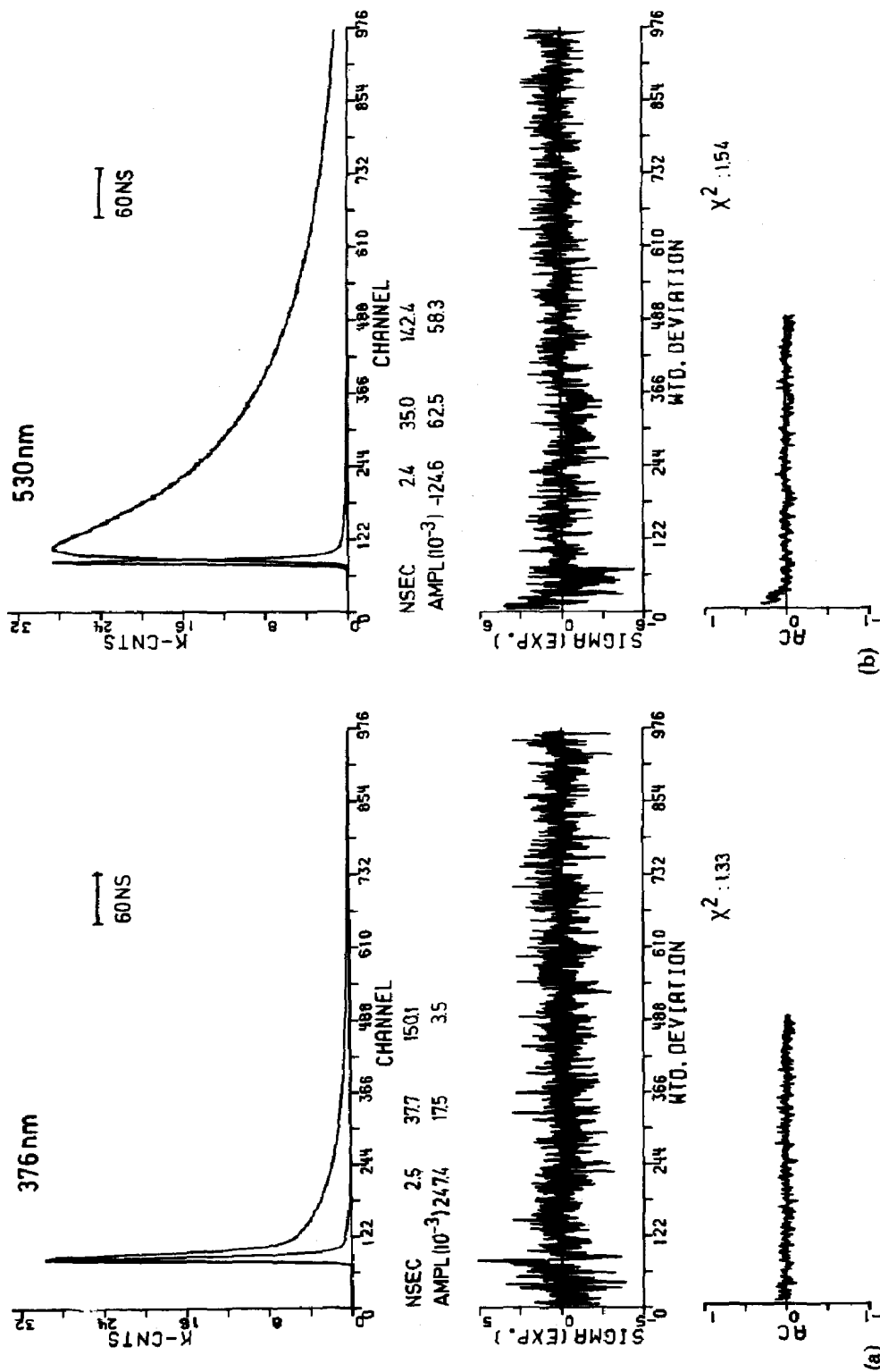


Fig. 2. Fluorescence decay curves of (a) the monomer (376 nm) and (b) the excimer (530 nm) of 1Py(3)1Py in *n*-heptane at 61 °C. The decay curves have been fitted to three exponentials. Fits with two exponentials do not lead to acceptable results (see ref. 5, Figs. 2 and 5). The reciprocal decay parameters $1/\lambda_1$, $1/\lambda_2$ and $1/\lambda_3$ (see text) have similar values for the excimer as well as for the monomer (see ref. 5). The weighted deviations in units of σ (expected deviation), the autocorrelation function AC and the value for χ^2 are also indicated.

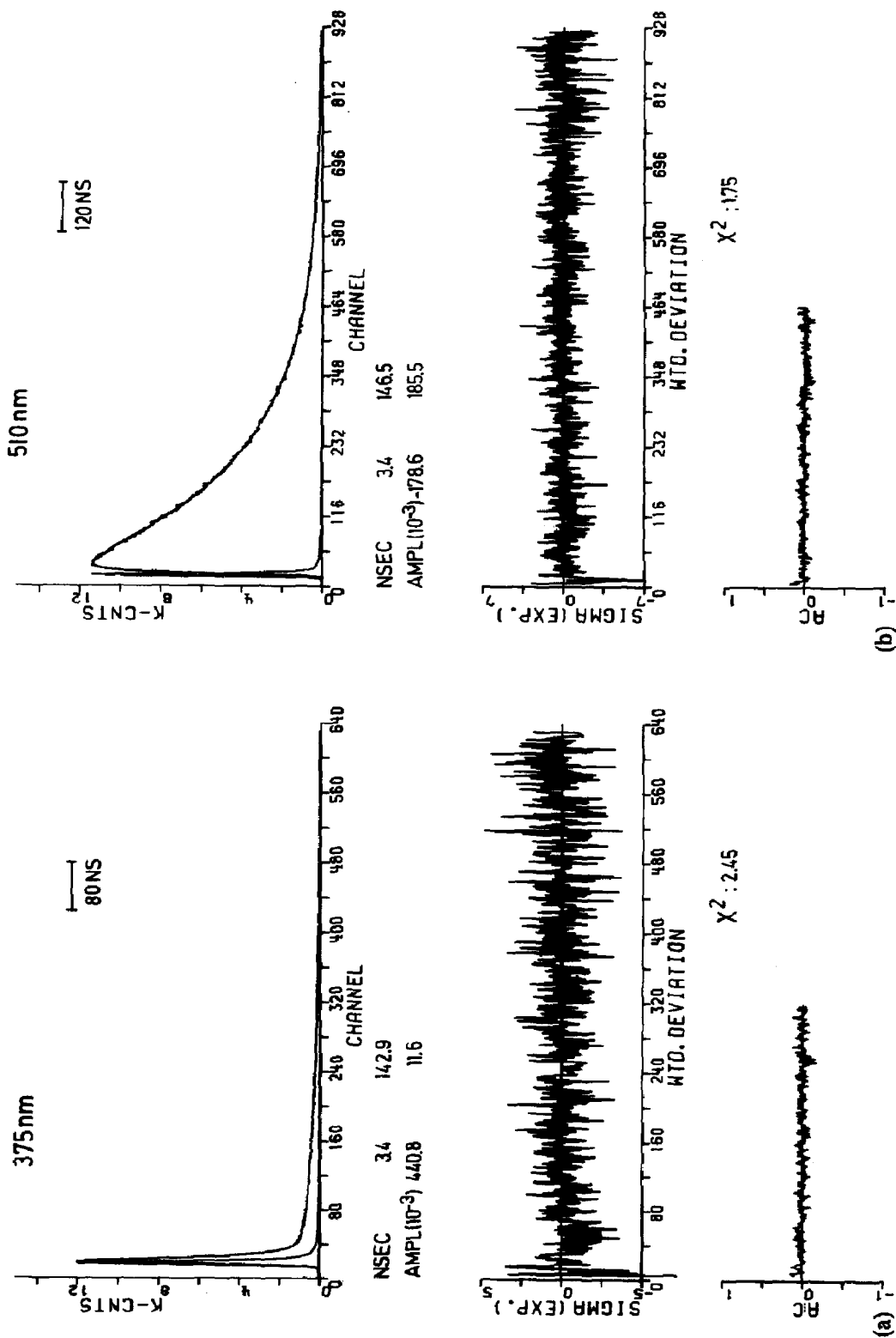


Fig. 3. Fluorescence decay curves of (a) the monomer (375 nm) and (b) the excimer (510 nm) of 2Py(3)2Py in MCH at 61 °C. The decay curves can be fitted to a sum (monomer) or a difference (excimer) of two exponentials. The reciprocal parameters $1/\lambda_1$ and $1/\lambda_2$ (see text) have similar values for the excimer as well as for the monomer. The weighted deviations in units of σ (expected deviation), the autocorrelation function AC and the value for χ^2 are also indicated.

TABLE 1

Data obtained from the fluorescence spectra of 1,3-di(1-pyrenyl)propane and 1,3-di(2-pyrenyl)propane in methylcyclohexane at 25 °C

	$h\nu_c(\text{max})^a$ ($\times 10^3 \text{ cm}^{-1}$)	$\Delta_{1/2}^b$ ($\times 10^3 \text{ cm}^{-1}$)	ϕ'/ϕ^c	ϕ_0/ϕ^d
1Py(3)1Py	20.1	3.83	21	24
2Py(3)2Py	20.55	3.98	31	34

^a Excimer emission maximum.

^b Width at half-maximum of the excimer emission band.

^c Excimer-to-monomer fluorescence quantum yield ratio.

^d Ratio of the fluorescence quantum yield ϕ_0 of *n*-ethylpyrene to the residual monomer fluorescence quantum yield ϕ of *n*Py(3)*n*Py.

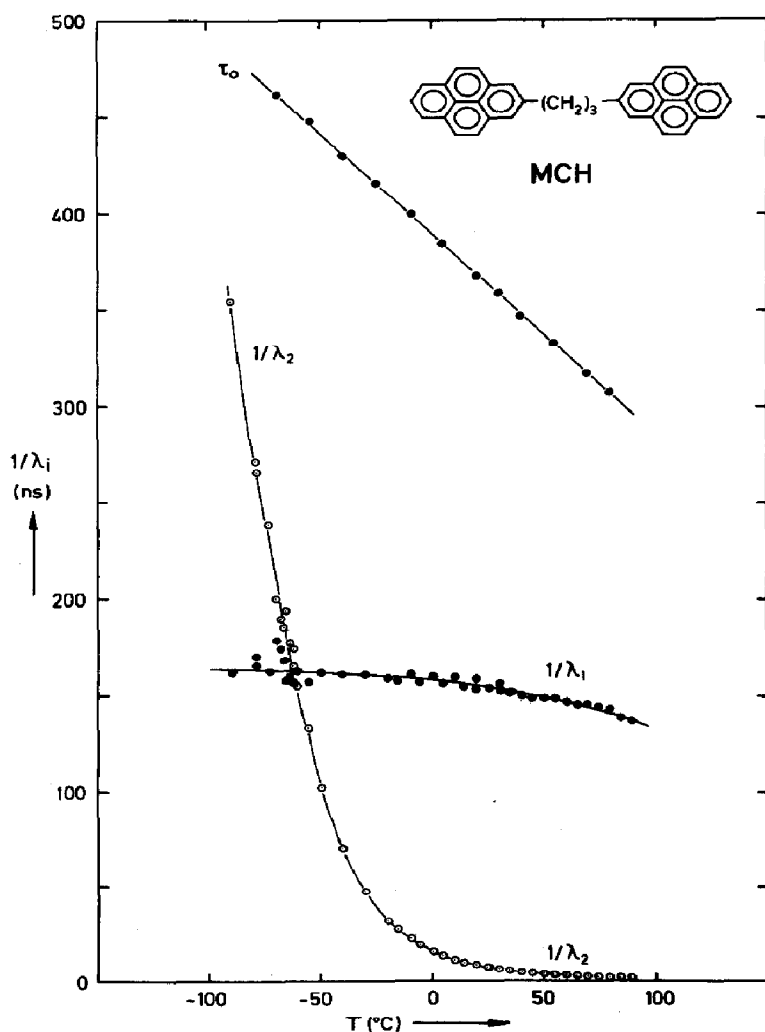


Fig. 4. Plot of the reciprocal decay parameters $1/\lambda_1$ and $1/\lambda_2$ of the excimer fluorescence decay (510 nm) of 2Py(3)2Py in MCH as a function of temperature. The lifetime τ_0 of the monomer model compound 2-ethylpyrene is also presented. The curves for $1/\lambda_1$ and $1/\lambda_2$ cross at -62 °C (see text).

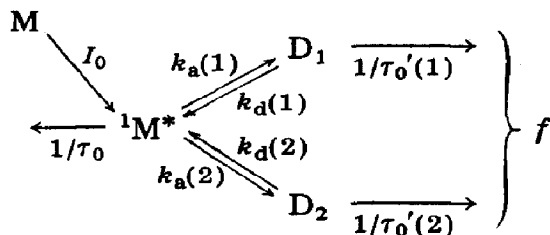
done in pentane where the monomer emission is even more strongly reduced than in MCH (see Fig. 1) owing to the low solvent viscosity [16].

In contrast, two exponentials suffice to fit the monomer and excimer decay curves of 2Py(3)2Py, again with the same values of λ_1 and λ_2 for both emissions (Fig. 3). This double-exponential decay is found over the whole temperature range in MCH (from -90 to $+90$ °C) (Fig. 4) [15]. It is important that double-exponential decay is observed over such an extended temperature range, as this excludes the possibility that at a certain temperature (*e.g.* at 60 °C in MCH as in the present case (see Fig. 3)) double-exponential decay is observed as a limiting situation of the more general case of, for example, triple-exponential decay. Such a situation has been found to occur with 1Py(3)1Py, where the triple-exponential decay is reduced to double-exponential decay in the low temperature region owing to the fact that k_d (the thermal back reaction) becomes negligible with respect to $1/\tau_0'$ [5, 16].

4.2. Triple-exponential decay (1,3-di(1-pyrenyl)propane)

It can now be concluded from the results presented in Section 4.1 that three and only three kinetically distinguishable excited state species show their presence in intramolecular excimer formation with 1Py(3)1Py, whereas only two excited state species are involved in the case of 2Py(3)2Py (Section 3.3). This signifies that with 2Py(3)2Py scheme (I) can be utilized (see below), whereas for 1Py(3)1Py one of the four subschemes (IIa) - (II d) is applicable. Which of these subschemes is correct for 1Py(3)1Py can be found by fitting the experimentally determined decay parameters and the monomer and excimer amplitude ratios with the corresponding parameters that can be calculated from the various subschemes (II) [16]. It then appears [16] that the experimental data can only be fitted within subscheme (IIa) (DMD).

In order to be able to discuss some of the results obtained with this procedure, scheme (IIa) will be presented in some detail:



The rate constants in this scheme DMD have a meaning analogous to those in scheme (I) (Section 3.1). In the present scheme, (1) and (2) refer to the two excimers D_1 and D_2 respectively. Seven rate constants play a role in the DMD mechanism: $k_a(1)$, $k_a(2)$, $k_d(1)$, $k_d(2)$, $1/\tau_0'(1)$, $1/\tau_0'(2)$ and $1/\tau_0$, the last three being in fact reciprocal decay times. The fluorescence lifetime τ_0 of the model compound (1-methylpyrene at 5×10^{-7} M) can be measured separately, so that six rate constants have still to be determined.

However, a further complication arises when the experimental data obtained with 1Py(3)1Py are fitted to the kinetics of scheme (IIa). In the fluorescence spectrum of 1Py(3)1Py (Fig. 1(b)) the emission bands of the two excimers cannot be separated (Section 4.1). Therefore, when the fluorescence response function of this multiple excimer emission band is measured (at 530 nm where the monomer emission can be neglected) the sum $i_{\text{DMD}}(t)$ of the fluorescence intensities of the two excimers D_1 and D_2 is necessarily observed with

$$i_{\text{DMD}}(t) = k_f'(1)[D_1] + k_f'(2)[D_2] \quad (17)$$

As not the absolute values of the amplitudes but only their ratios can be used in the procedure outlined here, the following expression can be defined, in analogy with eqns. (13) and (14):

$$\frac{i_{\text{DMD}}(t)}{k_f'(1)} = (A_{21} + fA_{31}) \exp(-\lambda_1 t) + (A_{22} + fA_{32}) \exp(-\lambda_2 t) + (A_{23} + fA_{33}) \exp(-\lambda_3 t) \quad (18)$$

where $f (= k_f'(2)/k_f'(1))$ is the ratio of the radiative rate constants k_f' of the two excimers. Scheme (IIa) therefore confronts us with seven unknowns: $k_a(1)$, $k_a(2)$, $k_d(1)$, $k_d(2)$, $1/\tau_0'(1)$, $1/\tau_0'(2)$ and the ratio f .

We shall now address the question how to obtain these seven unknowns from the experimental data. From the analysis of the triple-exponential monomer and excimer fluorescence decay curves six independent quantities can be deduced: the three decay parameters λ_1 , λ_2 and λ_3 , two monomer amplitude ratios A_{11}/A_{13} and A_{12}/A_{13} and one excimer amplitude ratio (eqn. (18)). Only one independent excimer amplitude ratio can be utilized as the sum of the excimer amplitudes is equal to zero (see eqns. (13) and (14) and Section 3.3).

Evidently, these six experimental quantities do not suffice to determine the six rate constants and the ratio f appearing in scheme (IIa). The missing piece of information can be obtained from an inspection of the excimer decay parameters λ_i of 1Py(3)1Py as a function of temperature [16]. It then appears that two of the excimer decay parameters, λ_1 and λ_2 [5], become equal to the reciprocal excimer lifetimes in the low temperature limits [16] and, furthermore, that they are then essentially independent of temperature. Their difference $1/\tau_0'(1) - 1/\tau_0'(2)$ can therefore be employed as the required seventh independent piece of information. Similarly, in the case of 2Py(3)2Py for which double-exponential excimer fluorescence decays are observed (Section 4.3), one of the two decay time parameters λ_i becomes equal to the almost temperature-independent reciprocal excimer lifetime $1/\tau_0'$ at sufficiently low temperatures (below +60 °C in MCH (see Fig. 4)). It is assumed that the difference between these often already temperature-independent excimer decay times does not change with temperature. Using this procedure the values for all the rate constants in subscheme (IIa) have been obtained as a function of temperature in a variety of solvents [16]. The values for the rate constants at 61 °C and the corresponding Arrhenius activa-

tion energies in two representative solvents, *n*-heptane and *n*-hexadecane, are listed in Table 2.

TABLE 2

Rate constants, lifetimes and activation energies E_i for intramolecular excimer formation with 1,3-di(1-pyrenyl)propane in *n*-heptane and *n*-hexadecane

Parameter	<i>n</i> -heptane	<i>n</i> -hexadecane
$k_a(1)$ ($\times 10^6 \text{ s}^{-1}$)	133	67
$k_a(2)$ ($\times 10^6 \text{ s}^{-1}$)	242	101
$k_d(1)$ ($\times 10^6 \text{ s}^{-1}$)	3.0	1.4
$k_d(2)$ ($\times 10^6 \text{ s}^{-1}$)	44	17
$\tau_0'(1)$ (ns)	154	151
$\tau_0'(2)$ (ns)	76	73
$E_a(1)^a$ (kJ mol^{-1})	12	20
$E_a(2)$ (kJ mol^{-1})	22	25
$E_d(1)$ (kJ mol^{-1})	32	42
$E_d(2)$ (kJ mol^{-1})	44	46
$\Delta H(1)$ (kJ mol^{-1})	-20	-22
$\Delta H(2)$ (kJ mol^{-1})	-22	-21

The data apply to the kinetics scheme DMD (scheme (IIa) (see text)); $\tau_0 = 230 \text{ ns}$ ($5 \times 10^{-7} \text{ M}$ 1-methylpyrene in heptane at 61°C).

^a The activation energies E_{diff} for diffusion determined from the solvent viscosity η in an Arrhenius plot of T/η are 10.6 kJ mol^{-1} (*n*-heptane) and 17.5 kJ mol^{-1} (*n*-hexadecane).

4.3. Double-exponential decay (1,3-di(2-pyrenyl)propane)

The reciprocal decay time parameters $1/\lambda_1$ and $1/\lambda_2$ of 2Py(3)2Py in MCH have been plotted in Fig. 4 as a function of temperature. From these data and the amplitude ratio A_{12}/A_{11} in the monomer fluorescence decay (eqns. (7) and (8)), the rate constants k_a , k_d and $1/\tau_0'$ have been calculated [15, 17]. The values for τ_0 that are required for this calculation have been determined separately from dilute (less than $5 \times 10^{-7} \text{ M}$) solutions of 2-ethylpyrene in MCH as a function of temperature (Fig. 4). The values for the rate constants and lifetimes at 61°C are presented in Table 3, together with the Arrhenius activation energies E_i and the pre-exponential factors k_i^0 derived from the temperature dependence of the rate constants. Further, the excimer stabilization energy ($-\Delta H = E_d - E_a$) and the change ΔS in entropy associated with excimer formation have been listed.

It should be noted that the value of $-\Delta H$ is considerably smaller than that observed for the intermolecular excimer of pyrene for which values of around 40 kJ mol^{-1} [16, 17] have been obtained. The value for ΔS determined here is of the same order of magnitude as that observed with, for example, 1,3-di(4-biphenyl)propane [4]. When the ΔS values presented here are to be compared with those observed for intermolecular excimer formation [17], the difference in the magnitude of ΔS in the two cases should be taken into account. The entities are only strictly comparable at a concentration of 1 M for the intermolecular case [24].

TABLE 3

Rate constants, lifetimes and thermodynamic data for 1,3-di(2-pyrenyl)propane in methylcyclohexane

<i>Parameter</i>	<i>Value</i>
k_a (s ⁻¹)	287.7×10^6
k_d (s ⁻¹)	7.4×10^6
k_a^0 (s ⁻¹)	5.2×10^{11}
k_d^0 (s ⁻¹)	2.1×10^{13}
τ_0 (ns)	140.8
$\tau_0'^a$ (ns)	327
E_a (kJ mol ⁻¹)	20.8
E_d (kJ mol ⁻¹)	41.3
ΔH^b (kJ mol ⁻¹)	-20.5
ΔS^c (J K ⁻¹ M ⁻¹)	-31

See text (scheme (I)).

^a Lifetime of 2-ethylpyrene (5×10^{-7} M).

^b $-\Delta H = E_d - E_a$.

^c $\Delta S = R \ln(k_a^0/k_d^0)$.

4.4. $S_1 \rightarrow S_n$ absorption spectra

The singlet-singlet excited state absorption spectrum of 2Py(3)2Py in MCH [15] consists of an absorption band with a decay time matching the 150 ns excimer decay time determined from the analysis of the single-photon counting data (Table 3 and Section 4.3). For 1Py(3)1Py, however, an absorption band with two maxima at around 475 and 500 nm is observed in the $S_1 \rightarrow S_n$ spectrum. These overlapping absorption bands display different decay times in accordance with the values obtained for $\tau_0'(1)$ and $\tau_0'(2)$ from the analysis of the fluorescence decays (Table 2 and Section 4.2).

4.5. Thermodynamic and lifetime data

The data presented in Table 2 indicate that the two excimers, identified by means of the analysis of the decay time data and independently via singlet-singlet absorption spectra, have almost identical values for the excimer stabilization energies ΔH . As the fluorescence spectrum of 1Py(3)1Py does not reveal the presence of two separate excimer emission bands (see above), this signifies that the repulsion energy δE_{rep} [17] of the Franck-Condon state reached directly after excimer emission must also have similar values for the two excimers D_1 and D_2 . The difference between these two excimers, which only becomes apparent from the decay time behaviour, is thus due to a difference in the activation energies associated with the formation of the excimers from the excited state monomers. These monomers do behave as a single group of kinetically completely identical, *i.e.* rapidly interconverting, chain conformers [13, 25] on the present time scale (larger than 0.5 ns). It should be noted that the activation barrier for the formation of excimer D_1 is almost identical with that for diffusion (E_{diff} (Table 2)) in

the particular solvent. The formation of the second excimer is associated with a higher barrier, indicating that this process is connected with (partial) rotations around the C—C bonds in the chain, in addition to the movement of the end groups through the solvent.

It is also worth noting (see Table 2) that the excimer lifetime $\tau_0'(1)$ of 1Py(3)1Py has a value similar to the τ_0' value (155 ns) of [3.3](2,7)pyrenophane [26] and that of 2Py(3)2Py (Table 3). The lifetime of the excimer D_2 is considerably shorter, resembling those of the intermolecular excimer of pyrene [17] and the intramolecular excimer of 1Py(22)1Py (52 ns at 51 °C) [16]. This is interpreted as indicating that the longer-lived excimer D_1 has a symmetric structure, as with the [3.3](2,7)pyrenophane and with 2Py(3)2Py, leading to the assumption of an asymmetric structure of the two pyrene moieties in the other excimer D_2 , as well as in 1Py(22)1Py and the intermolecular pyrene excimer [16, 17].

Likewise, for *meso*- and *racemo*-2,5-di(1-pyrenyl)pentane in MCH two excimers have been detected with lifetimes similar to those of the D_1 and D_2 of 1Py(3)1Py: 189 and 96 ns for the *meso* compound (at -10 °C); 155 and 80 ns for the *racemo* derivative (at 1 °C) [16]. It should be noted, however, that even with three exponentials the fits are not optimal in the rising part of the excimer fluorescence response curves for the *meso* compound. In addition, for both dipyrenylpentanes the sum of the excimer amplitudes is far from being equal to zero, a condition that is required when scheme (IIa) is applicable (see Section 3.3).

4.6. Identical λ values

As can be seen from Fig. 4, the lines through the data points for λ_1 and λ_2 of the excimer fluorescence response functions of 2Py(3)2Py in MCH as a function of temperature cross at around -62 °C. This observation that the values for λ_1 and λ_2 become identical at this temperature emphasizes the fact that the decay parameters λ_i cannot always be directly connected with the excimer or monomer lifetimes τ_0' and τ_0 . This follows immediately from the well-known analytical expression for λ_1 and λ_2 (eqn. (7)) derived in Section 3.1. In this equation λ_1 becomes equal to λ_2 when the expression to the power one-half is equal to zero, *i.e.* when the product $k_a k_d$ is zero and when simultaneously the equality $Y = X$ holds. This will be the case at low enough temperatures where k_d becomes almost equal to zero owing to the relatively large value of E_d (Table 2) and at that particular temperature where k_a has such a magnitude that $Y = X$, *i.e.* when $1/\tau_0' = 1/\tau_0 + k_a$. Under these conditions the monomer decay is mono-exponential with the decay parameter λ_1 , as the second exponential disappears ($A = 0$ (eqn. (8)) for $\lambda_1 = X$ when $k_d = 0$ (eqn. (7)).

4.7. Other diarylpropanes

For the other diarylpropanes mentioned in Section 1, double-exponential decay is observed for 1,3-di(4-biphenyl)propane [4], 1,3-di(1-naphthyl)propane [16] and the 1,3-di(*m*-phenanthryl)propanes with $m = 1$,

2, 3 and 9 [7, 16]. Triple-exponential decay was detected with 1Py(3)1Py, as discussed in Section 4.2, and in addition for 1,3-di(2-naphthyl)propane [16] and 1,3-di(4-pyrenyl)propane [16]. An inspection of the molecular structure of these compounds reveals that triple-exponential decay is only observed for those diarylpropanes with a structure less symmetrical than that of the corresponding molecules for which double-exponential decay is observed. It is important to point out in this connection that the one dinaphthylpropane undergoing a photochemical reaction, the 1,3-di(1-naphthyl)propane [2, 27], only shows double-exponential decay for the excimer and the monomer [16]. This finding excludes the possibility that multi-exponential decay in general will be due to the presence of photochemically produced fluorescent species. The double-exponential decays observed with the 1-(*m*-pyrenyl)-3-(*N,N*-dimethylanilino)propanes, with *m* = 1, 2 and 4 and the multi-exponential decay detected with other systems such as 1,3-di(*N*-carbazolyl)propane will be discussed elsewhere [16].

5. Conclusion

It has been concluded that in intramolecular excimer formation with the dipyrenylpropanes 1Py(3)1Py and 2Py(3)2Py, the different conformers of the propane chain do not show up as kinetically distinguishable monomers $^1M^*$. Although the two excimers identified in the case of 1Py(3)1Py have different fluorescence lifetimes, they appear to have almost identical fluorescence emission bands and stabilization energies. From the difference in lifetimes and from a comparison with the excimer decay times of other systems, it is concluded that one of the excimers has a symmetric structure as with the [3.3](2,7)pyrenophane and with 2Py(3)2Py. The other (shorter-lived) excimer is assumed to be asymmetric with respect to the relative orientation of the two pyrene moieties. From the difference in the activation barriers for the formation of the two excimers, information on the chain rotation and the coupling of the different parts of the diarylpropanes to the solvent can be deduced [16].

Acknowledgments

Stimulating discussions with Dr. A. Maçanita are gratefully acknowledged. Thanks are also due to Dr. K.-H. Grellmann for the use of the excimer laser (Deutsche Forschungsgemeinschaft, Sonderforschungsbereich 93 "Photochemie mit Lasern").

References

- 1 F. Hirayama, *J. Chem. Phys.*, **42** (1965) 3163.
- 2 E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92** (1970) 3586.

- 3 K. A. Zachariasse and W. Kühnle, *Z. Phys. Chem. (Frankfurt am Main)*, **101** (1976) 267.
- 4 K. A. Zachariasse, W. Kühnle and A. Weller, *Chem. Phys. Lett.*, **59** (1978) 375.
- 5 K. A. Zachariasse, G. Duveneck and R. Busse, *J. Am. Chem. Soc.*, **106** (1984) 1045.
- 6 F. C. De Schryver, J. Huybrechts, N. Boens, J. C. Dederen, M. Irie and K. A. Zachariasse, in B. Pullmann and N. Goldblum (eds.), *Excited States in Organic Chemistry and Biochemistry*, Reidel, Dordrecht, 1977, p. 313.
- 7 K. A. Zachariasse, R. Busse, U. Schrader and W. Kühnle, *Chem. Phys. Lett.*, **89** (1982) 303.
- 8 R. Busse, W. Kühnle and K. A. Zachariasse, to be published.
- 9 A. Castellan, J.-P. Desvergne and H. Bouas-Laurent, *Chem. Phys. Lett.*, **76** (1980) 390.
- 10 H. Bouas-Laurent, A. Castellan and J.-P. Desvergne, *Pure Appl. Chem.*, **52** (1980) 2633.
- 11 F. C. De Schryver, K. Demeyer, M. Van der Auweraer and E. Quanten, in H. Morawetz and I. Z. Steinberg (eds.), *Luminescence from Biological and Synthetic Macromolecules*, *Ann. N. Y. Acad. Sci.*, **366** (1981) 93.
A. J. Roberts, D. V. O'Connor and D. Phillips, in H. Morawetz and I. Z. Steinberg (eds.), *Luminescence from Biological and Synthetic Macromolecules*, *Ann. N. Y. Acad. Sci.*, **366** (1981) 109.
- 12 H. Itagaki, K. Horie and I. Mita, *Macromolecules*, **16** (1983) 1395, and references cited therein.
- 13 M. Van der Auweraer, A. Gilbert and F. C. De Schryver, *J. Am. Chem. Soc.*, **102** (1980) 4007.
- 14 D. Phillips and K. J. Roberts (eds.), *Photophysics of Synthetic Polymers*, Science Reviews, Northwood, Middlesex, 1982.
- 15 K. A. Zachariasse, G. Duveneck and W. Kühnle, submitted to *Chem. Phys. Lett.*
- 16 K. A. Zachariasse, R. Busse, G. Duveneck, A. Maçanita and W. Kühnle, to be published.
- 17 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, London, 1970, Chapter 7.
- 18 E. Heumann, *Z. Naturforsch.*, **36a** (1981) 1323.
- 19 A. Weller, *Z. Phys. Chem. (Frankfurt am Main)*, **15** (1958) 438.
- 20 M. Goldenberg, J. Emert and H. Morawetz, *J. Am. Chem. Soc.*, **100** (1978) 7171.
- 21 I. N. Bronstein and K. A. Semendjajew, *Taschenbuch der Mathematik*, Deutsch, Thun, 1981.
- 22 K. A. Zachariasse, R. Busse and A. Maçanita, to be published.
- 23 Eigensystem Subroutine Package (Eispack), 1975.
B. S. Garbow and J. J. Dongarra, *Eispack Path Chart*, 1974.
- 24 Th. Förster and H.-P. Seidel, *Z. Phys. Chem. (Frankfurt am Main)*, **45** (1965) 58.
- 25 R. M. Levy, M. Karplus and J. A. McCommon, *Chem. Phys. Lett.*, **65** (1979) 4.
- 26 R. Busse, F. Diederich, G. Duveneck, H. A. Staab and K. A. Zachariasse, to be published.
- 27 E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92** (1970) 703.