

INTRAMOLECULAR EXCIMER FLUORESCENCE OF DI(9-(10-PHENYL)-ANTHRYL METHYL) ETHERS WITH VARIOUS CHAIN LENGTHS

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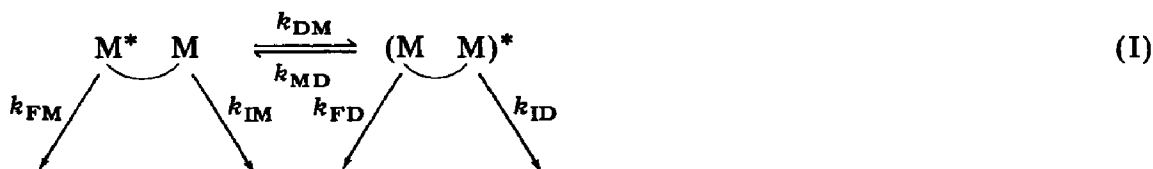
Summary

A study was carried out on the intramolecular excimer formation properties of bis(9-(10-phenyl)anthryl methyl) ether (DPAE) and bis(9-(10-phenyl)anthryl methoxy)methane (DPAA) using spectral data and time-dependent fluorescence intensities at different temperatures and wavelengths. No deviations from Förster's scheme were observed. For DPAE there is a clear solvent viscosity dependence of the excimer formation. An intramolecular interaction in the ground state conformation of DPAE and DPAA is observed. This interaction induces deviations in the properties of the bichromophoric local excited state with respect to the model compound 9-(10-phenyl)anthryl dimethyl ether. The striking differences in the excimer properties of DPAE and DPAA are explained in terms of different excimer geometries.

1. Introduction

The observation of intramolecular excimer emission from diphenyl and triphenyl alkanes in dilute solutions [1] has given rise to extensive investigations of the photophysics of non-conjugated bichromophoric and polychromophoric systems with pendent aromatic chromophores [2 - 7]. Spectral data for a large variety of bichromophoric systems with different chain lengths and natures are also available [8 - 33]. In most of the studies on bichromophoric systems kinetic and thermodynamic parameters were obtained from stationary data. However, quantitative data derived from direct lifetime measurements as a function of temperature are scarce [9, 26, 27, 33]. For a few bichromophores the monomolecular equivalent of the following kinetic scheme of excimer formation proposed by Förster [28] has been tested using

the single-photon counting technique combined with stationary data [12, 27, 32 - 34]. This scheme has been found to be valid for 2,4-diphenylpentane [27], but deviations are reported for dinaphthyl compounds [4, 12, 33, 34].



where k_{DM} is the rate constant of excimer formation, k_{MD} is the rate constant of excimer dissociation, k_{FM} is the rate constant of fluorescence from the local excited (LE) state, k_{IM} is the rate constant of non-radiative decay from the LE state, k_{FD} is the rate constant of fluorescence from the excimer and k_{ID} is the rate constant of non-radiative decay from the excimer. This scheme for intramolecular excimer formation was proposed by Förster and was elaborated by Klöpffer and Johnson [6, 28 - 31].

The role of the conformational distribution in excimer formation was suggested by Goldenberg *et al.* [14]. Longworth and Bovey [34] mentioned the importance of the configurational aspects of excimer formation in bichromophoric systems. Comparison of the photophysical properties of the two diastereomers of bichromophoric polymer model molecules confirmed this suggestion [12, 18, 19, 25, 26]. The different excimer-forming properties of the diastereomers are a direct consequence of the different conformational distributions of the ground states such as has been proved for intramolecular exciplexes [35]. Extensive studies at room temperature of the spectral properties, the kinetic parameters and the intramolecular photo-reactivity of a large variety of 9-anthryl-substituted bichromophores and their 10-substituted derivatives have already shown the important role of the linking chain and/or substituent in the 10 position, but no thermodynamic data are yet available [22, 23, 36].

In this study we deal with intramolecular excimer formation in dilute alkane solutions of bis(9-(10-phenyl)anthryl methyl) ether (DPAE) and bis-9-(10-phenyl)anthryl methoxy)methane (DPAA) in comparison with 9-(10-phenyl)anthryl dimethyl ether (PAE) as a model compound (Fig. 1). Our main goal is the study of the influence of the linking chain on the spectral, kinetic and thermodynamic properties of the intramolecular complex and their mutual relations. These data will help to interpret the experimental results recently obtained in investigating one of the above bichromophores (DPAE) as a fluorescent molecule for probing molecular motions in bulk polymers [37].

2. Experimental details

The synthesis of DPAE and PAE is described in ref. 38.

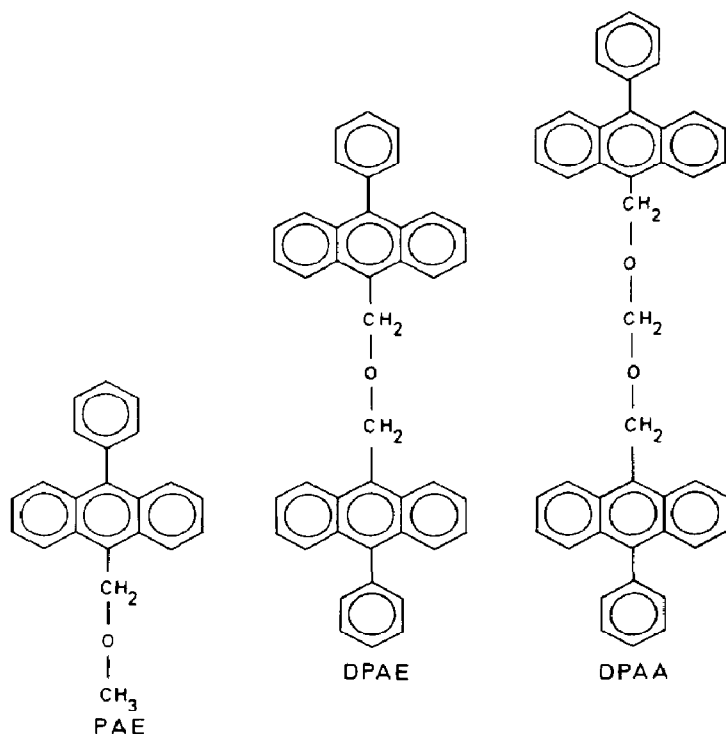


Fig. 1. Structures of PAE, DPAE and DPAA.

2.1. Synthesis of bis(9-(10-phenyl)anthryl methoxy)methane

9-(10-phenyl)anthraldehyde was synthesized according to ref. 39.

9-(10-phenyl)anthryl methanol was obtained from the reduction of the aldehyde with LiAlH_4 in dry diethyl ether.

DPAA was obtained by coupling the alcohol in excess with diiodomethane and NaH following a modified Williamson synthesis [40]. The reaction was carried out in a dry nitrogen atmosphere. 0.01 mol of the alcohol was added to 0.009 mol of sodium hydride in dry tetrahydrofuran. After refluxing for 1 day, 0.001 mol of CH_2I_2 in dry tetrahydrofuran was added slowly. After neutralization of the excess alcoholate with water, the solution was dried and evaporated. Further purification was carried out on silica with toluene followed by purification using high pressure liquid chromatography (60:40 hexane:dichloromethane mixture as eluent). (Nuclear magnetic resonance data: $\delta = 8.44 - 8.52$ ppm, doublet, 4 H; $\delta = 7.5$ ppm, multiplet, 22 H; $\delta = 5.8$ ppm, singlet, 4 H; $\delta = 5.16$ ppm, singlet, 2 H; M^+ = 580, exact mass, 580.240 217.)

2.2. Solvent purification

Dodecane (C_{12}) of Spectro grade purity was obtained from Aldrich.

Hexadecane (C_{16}) and methylcyclohexane (MCH) were passed through a column containing layers of activated silica and carbon black. The MCH was further dried with sodium and distilled.

The solvents showed no absorption at wavelengths longer than 260 nm after purification.

2.3. Instrumentation

Absorption spectra were recorded on a Perkin-Elmer 124 double-beam spectrophotometer. Fluorescence spectra were obtained from a Spex Fluorolog and a Fica 55 spectrofluorometer. The time-dependent intensities of fluorescence were obtained from a single-photon counting apparatus consisting of Ortec and Canberra modules and an optical system supplied by Applied Photophysics. Deconvolution was carried out using a non-linear least-squares method [41].

3. Experimental results

Absorption and fluorescence spectra were obtained in dilute solutions (10^{-6} M) of PAE, DPAE and DPAA in MCH, C_{12} , C_{16} and acetonitrile. The 1L_a absorption of DPAE shifts 5 nm to longer wavelengths and the 1B_b band splits up on the hypsochromic side. The vibrational pattern of the 1L_a band is different from that of PAE (Fig. 2). This effect is less pronounced for DPAA under the same experimental conditions. No dependence of solvent polarity or viscosity on the absorption spectra was observed. The value of the intrinsic rate constant of fluorescence k_{FM}^0 calculated from the 1L_a absorption for the LE state is the same ($5.3 \times 10^7 \text{ s}^{-1}$) for each chromophore as the value for PAE. This value corresponds to k_{FM}^0 obtained from the quantum yield of fluorescence Φ_{FM} and the lifetime τ_M of the LE state at low temperatures.

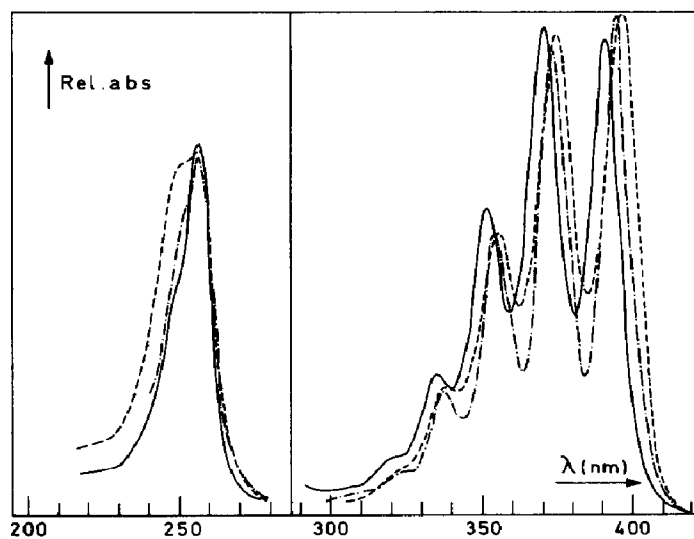


Fig. 2. Absorption spectra of PAE (—), DPAE (---) and DPAA (- · -) in MCH (10^{-6} M) at 293 K.

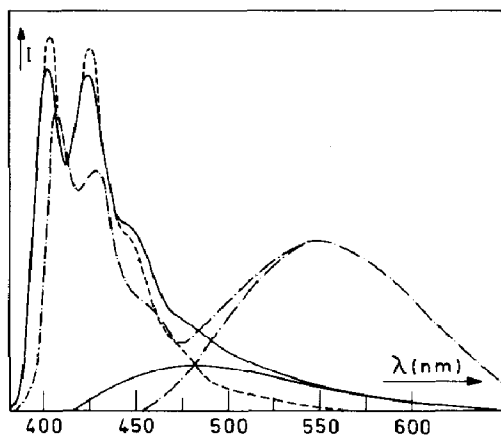


Fig. 3. Corrected emission spectra of PAE (---), DPAE (- · -) and DPAA (—) in MCH (10^{-6} M) at 293 K ($\lambda_{\text{exc}} = 375$ nm) showing the excimer emission.

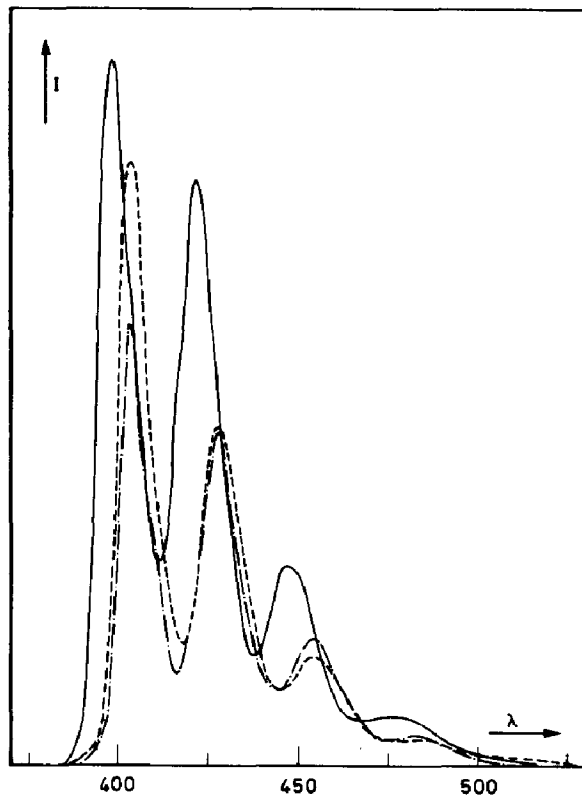


Fig. 4. Corrected emission spectra of PAE (—), DPAE (---) and DPAA (- · -) in a 3:1 MCH:IP matrix at 77 K ($\lambda_{\text{exc}} = 375$ nm).

The emission spectra of the LE state of DPAE and DPAA deviate in the same way as the absorption spectra and no relative deviations in Stokes shift are observed (Fig. 3). Even at 77 K in a 3:1 MCH:isopentane (IP) matrix the LE states of PAE, DPAE and DPAA show differences in the emission spectra but no excimer emission is detected indicating that rotation is required for excimer formation (Fig. 4). In MCH solution a new unstructured bathochromic fluorescence appears above 153 K for DPAE and above 173 K for DPAA. The intensity of this excimer emission increases until 348 K with an isoemissive point at 500 nm for DPAE. Above 348 K both the excimer and the LE state emission decrease with the loss of the isoemissive point. The fluorescence spectra of DPAA show an isoemissive point near 470 nm at all temperatures. At higher temperature ($T \geq 320$ K) the decrease of the excimer emission of DPAA is compensated by an increase of the LE state emission.

The most striking difference between the excimer emission of DPAE and that of DPAA is the spectral distribution of the intramolecular excimer which can be described by the wavelength λ_{max} of the maximum excimer emission and the full width at half-height (FWHH) (Table 1). The DPAE excimer emission shows only a slight hypsochromic shift and broadening of

TABLE 1

Spectral, thermodynamic and kinetic properties of bis(9-(10-phenyl)anthryl methyl) ether and bis(9-(10-phenyl)anthryl methoxy)methane compared with those of 1,5-di(9-anthryl)pentane (A-5-A) [23]

	DPAE	DPAA	A-5-A
λ_{\max} (nm)	545	480	510 ^a
FWHH (cm^{-1})	3500	4600	—
φ_{FM}	0.21	0.69	0.31
φ_{FD}	0.34	0.21	0.16
E_{DM} (kJ mol^{-1})	14 ^b 15 ^c	15 ^b 14 ^c	
E_{MD} (kJ mol^{-1})	—	36 ^b 33 ^c	
ΔH (kJ mol^{-1})	—	-21 ^b -19 ^b	
ΔS ($\text{J mol}^{-1} \text{K}^{-1}$)	—	-54 ^c	
E_{R} (kJ mol^{-1})	—	23 ^c	
E_{D} (kJ mol^{-1})	7 ^c	— ^d	
k_{FD} (s^{-1})	14×10^6 ^c	7×10^6 ^c	7×10^6 ^c
k_{DM} (s^{-1})	4×10^8 ^c	2×10^8 ^c	1×10^8 ^c
k_{MD} (s^{-1})	— ^c	4×10^7 ^c	1×10^7 ^c
k_{D} (s^{-1})	30×10^6 ^c	8×10^6 ^c	9×10^6 ^c

Room temperature; solvent, MCH.

^aThis value was erroneously reported as 490 in ref. 23.

^bObtained from the Stevens-Ban plot.

^cObtained from single-photon counting data.

^d k_{D} of DPAA is small at all temperatures and despite the large experimental error has little dependence on temperature.

the FWHH with increasing temperature (545 nm and 3500 cm^{-1} at 293 K and 530 nm and 4600 cm^{-1} at 495 K (C_{16})). In contrast with DPAE, the λ_{\max} (480 nm) and FWHH (4600 cm^{-1}) of DPAA shift from 495 nm at 253 K to 475 nm at 293 K (MCH). In this small temperature range the emissive properties of the DPAE excimer do not change at all. Finally, it is important to mention that the spectral distributions of both excimers are within the experimental error independent of solvent viscosity and polarity.

A Stevens-Ban [42] plot of both systems (Fig. 5) generates a straight line at low temperatures (MCH, C_{12}). Because of the isoemissive point, it corresponds to the activation of excimer formation E_{DM} according to scheme (I). At high temperatures, a straight line (of gradient $-\Delta H/R$) was obtained only for DPAA in MCH. The value of E_{DM} and ΔH obtained in MCH are listed in Table 1. An E_{DM} value of 22 kJ mol^{-1} was found for DPAE in C_{12} . In C_{16} , however, the low temperature region could not be reached.

The time-dependent fluorescence intensities $I_{\text{M}}(t)$ and $I_{\text{D}}(t)$ of the local excited state and the excimer respectively were recorded at 405 nm and 530 nm respectively using the single-photon counting technique. The $I_{\text{M}}(t)$

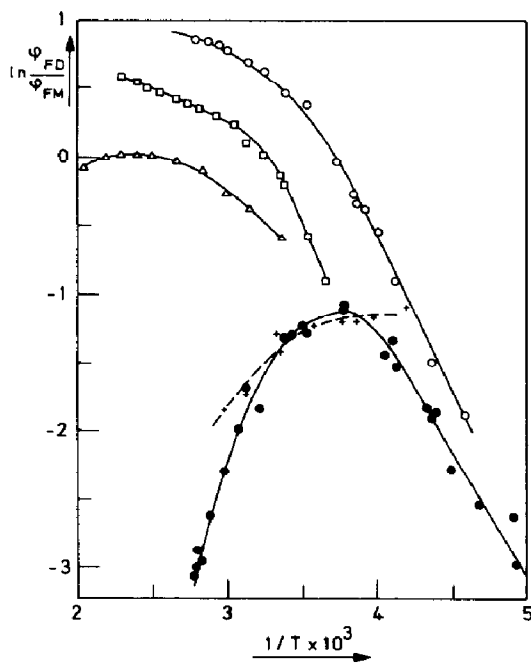


Fig. 5. Stevens-Ban plots of DPAE in MCH (\circ), C_{12} (\square) and C_{16} (\triangle) and of DPAA in MCH (\bullet) and CH_3CH ($+$).

of DPAE can be analysed in all solvents (MCH, C_{12} , C_{16}) and at all temperatures as a monoexponential decay with a lifetime shorter than PAE under identical experimental circumstances. The $I_D(t)$ of DPAE can always be fitted to a difference of two exponentials with a rise corresponding to the decay parameter of $I_M(t)$.

The time-dependent intensities at 405 nm of DPAA and MCH can be fitted to a monoexponential decay below 222 K. Above 222 K a second longer-lived component with the same decay parameter as one of those in $I_D(t)$ appears. Its contribution increases with increasing temperature, reflecting the return of the excimer to the LE state according to scheme (I).

The lifetimes of DPAE and DPAA in a 3:1 MCH:IP matrix (6.5 ns and 7.9 ns respectively) are not in agreement with the lifetime of PAE (8.5 ns) under the same experimental conditions. This is again an indication of an interaction between the chromophores in the ground state. The lifetime of PAE is independent of temperature below 250 K, and if we assume that this is also the case for the LE states of DPAE and DPAA we can use the lifetimes at 77 K as model lifetimes. Above 250 K the short-lived component of DPAA and DPAA is much shorter than the PAE lifetime and the choice of a model lifetime in calculating the thermodynamic and kinetic parameters is not so critical.

By using the two decay parameters in $I_M(t)$, the model lifetime and the ratio of the contribution of the fast decaying component to the contribution of the slower decaying component (A factor) (Tables 2 - 5), we can calculate all the kinetic parameters according to scheme (I) [6, 28 - 31]. The tempera-

TABLE 2

Single-photon counting data for 9-(10-phenyl)-anthryl dimethyl ether analysed at 402 nm

T (K)	τ (ns)	<i>Solvent</i>
77	8.5	MCH-IP
191	8.8	MCH
208	8.6	MCH
231	8.6	MCH
251	8.8	MCH
291	8.5	MCH
296	8.5	C ₁₆
322	7.9	MCH
328	7.6	C ₁₂
349	7.5	C ₁₂
351	7.0	MCH
373	6.0	C ₁₂
416	6.1	C ₁₂
473	4.9	C ₁₆

TABLE 3

Single-photon counting data for bis(9-(10-phenyl)anthryl methyl) ether at 545 nm

<i>C₁₆ solvent</i>		<i>MCH solvent</i>	
T (K)	τ_E (ns)	T (K)	τ_E (ns)
296	31.6	294	32.0
298	30.3	304	27.6
316	26.5	319	26.7
335	22.4	328	22.9
352	19.5	335	21.9
390	16.0	345	20.4
433	10.5	357	19.3

τ_E , real lifetime.

ture dependences of the rate constants k_{DM} , k_{MD} and k_D of DPAAE and DPAA are plotted in Figs. 6 and 7, and the values of E_{DM} , E_{MD} , E_D , ΔH and ΔS obtained in MCH are listed in Table 1. E_{DM} for DPAAE increases from 14 kJ mol⁻¹ in MCH to 19 kJ mol⁻¹ in C₁₂ and to 25 kJ mol⁻¹ in C₁₆. This viscosity effect is in line with the results obtained with other bichromophores [9, 31]. Because of the lack of excimer return to the LE state of DPAAE, it is not possible to determine the ΔH and ΔS values for the DPAAE excimer.

Finally, DPAA shows no reaction after light excitation. Castellan *et al.* [38] ascribed the absence of an intramolecular reaction of DPAAE to the bulky phenyl groups.

TABLE 4

Single-photon counting data for bis(9-(10-phenyl)anthryl methyl) ether at 405 nm

<i>MCH solvent</i>		<i>C₁₂ solvent</i>		<i>C₁₆ solvent</i>	
<i>T</i> (K)	τ_M (ns)	<i>T</i> (K)	τ_M (ns)	<i>T</i> (K)	τ_M (ns)
215	5.3	273	4.3	293	3.3
225	4.9	289	3.3	298	3.0
232	4.3	299	2.6	316	1.5
245	3.7	315	2.4	334	1.4
263	2.3	322	2.3	335	1.7
293	1.8	326	2.2	342	1.2
294	1.7	397	1.5	352	1.0
324	1.2	345	1.3	363	0.8
358	0.7	383	1.1	373	0.7
				393	0.3
				413	0.9
				433	0.5

TABLE 5

Single-photon counting data for bis(9-(10-phenyl)anthryl methoxy)methane in methyl cyclohexane at 405 nm

<i>T</i> (K)	λ_2^{-1} (ns)	λ_1^{-1} (ns)	<i>A factor</i>
176	8.0	—	—
179	7.9	—	—
191	7.9	—	—
196	7.6	—	—
198	7.7	—	—
212	7.4	—	—
223	7.1	—	—
234	6.5	—	—
248	5.4	77.9	115.01
267	4.6	68.4	40.25
276	4.0	61.2	25.19
296	2.9	41.7	11.01
307	2.5	34.9	6.95
311	2.4	32.2	5.57
335	1.6	20.8	2.46
340	1.4	18.8	1.99
350	1.3	16.9	1.64
361	1.2	14.7	1.35

λ_2^{-1} , decay parameters; *A factor*, ratio of the pre-exponential of λ_2 to the pre-exponential of λ_1 .

4. Discussion

The experimental data give no indication of a deviation from the classic kinetic scheme using modified model lifetimes. There is full compatibility

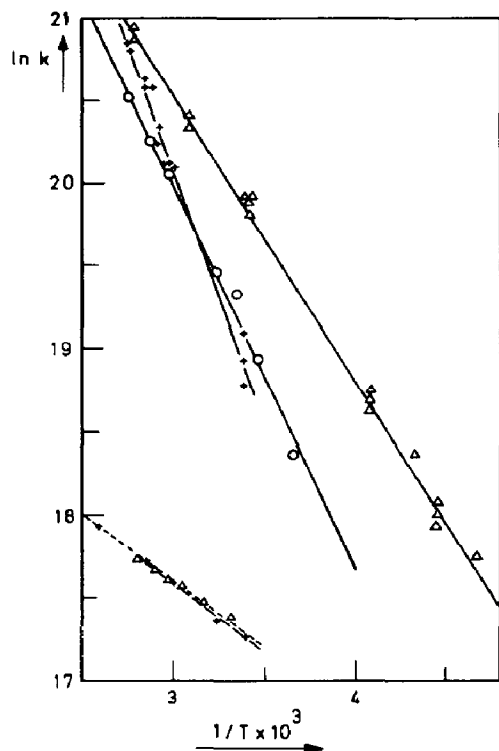


Fig. 6. Temperature dependence of k_{DM} (—) and k_D (---) for DPAAE in MCH (Δ), C_{12} (\circ) and C_{16} (+).

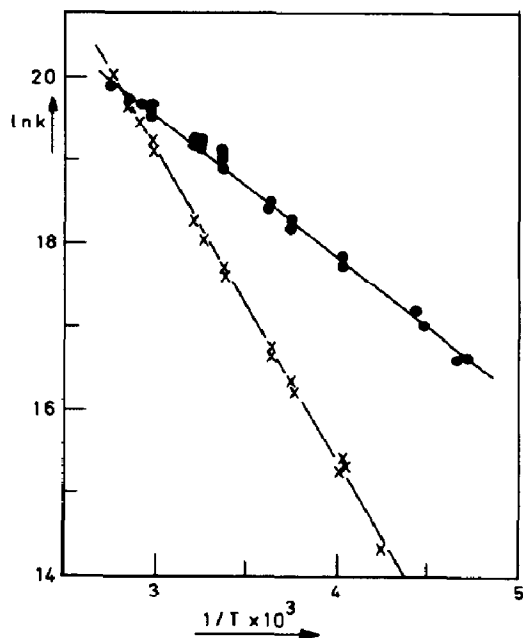


Fig. 7. Temperature dependence of k_{DM} (\bullet) and k_{MD} (\times) for DPAA in MCH.

between the thermodynamic parameters obtained from the Stevens-Ban [42] plot and the single-photon counting data. The return of the DPAA excimer is also clearly indicated in the $I_M(t)$ curves. However, PAE is not a perfect model system for DPAAE and DPAA.

The absorption spectra, the emission spectra and the lifetimes at 77 K in a 3:1 MCH:IP matrix clearly show an intramolecular interchromophore interaction in the ground state conformation of DPAAE and DPAA. The bathochromic shifts of the 1L_a bands of DPAAE and DPAA could be interpreted in terms of intramolecular exciton interaction of the participating transition dipole moments M_i .

If the tt conformation of DPAAE in solution is assumed to be the most populated in the ground state [14, 19, 43] the interchromophoric distance R can be calculated.

The dipole strength $D = M^2$ can be obtained from the oscillator strength f of the 1L_a transition of PAE using the equation

$$f = 4.315 \times 10^{-9} \int E(\nu) d\nu = \frac{8\pi^2 mc}{3h\nu} D \quad (1)$$

where $\int E(\nu) d\nu$ is the integrated absorption intensity. The exciton splitting

energy V emerging from the interaction of two identical transition dipole moments M_i can be evaluated as follows [44 - 46]:

$$V = \frac{M_1 \cdot M_2}{R^3} - 3 \frac{(M_1 \cdot R)(M_2 \cdot R)}{R^5} = \frac{D}{R^3} (\cos \theta - 3 \cos^2 \varphi) \quad (2)$$

where R is the interchromophoric distance, φ is the angle between M_i and R and θ is the angle between M_1 and M_2 . Using $R = 7.2 \text{ \AA}$, $fE(\nu) d\nu = 0.17$, $D = 11.9 \text{ debye}^2$, $\theta = 70^\circ, 110^\circ$, and $\varphi = 35^\circ, 145^\circ$, we obtain a stabilization and destabilization energy of 381 cm^{-1} resulting in the appearance of two new bands (388 nm and 394 nm) originating from the 0-0 transition of PAE at 391 nm. The relative contribution of the bathochromic and hypsochromic bands I_b and I_h can be estimated from molecular models using the equation

$$\frac{I_b}{I_h} = \frac{1 - \cos \theta}{1 + \cos \theta} \approx 2 \quad (3)$$

where θ is the angle between M_1 and M_2 .

The absorption of DPAA is dominated by the bathochromic band. The real conformation of tt DPAA should show an even better elongation of the 1L_a transition dipoles than can be derived from molecular models.

Since there is no difference between the k_{FM} of PAE with respect to the bichromophoric systems, the exciton interaction affects only the non-radiative decay processes of the LE state (k_{IM}).

The most stable chain conformation of DPAA in solution is probably tg^+g^+t or $g^+g^+g^+g^+$ [43]. In these conformations the mutual orientation of the chromophores is analogous to DPAA but the interchromophoric distance is somewhat larger, leading to smaller deviations in the absorption spectrum. In MCH, DPAA and DPAA require a similar activation energy for excimer formation. If we consider the suggested ground state conformations of DPAA and DPAA (Fig. 8), both systems need two rotations to reach the excimers g^+g^- and $g^-g^-g^+g^+$ or $g^+g^-g^+g^-$ respectively (Fig. 9). Compared with DPAA, the excimer of DPAA is characterized by a smaller FWHH, a more bathochromic λ_{max} , a weaker temperature dependence of the spectral distribution, larger

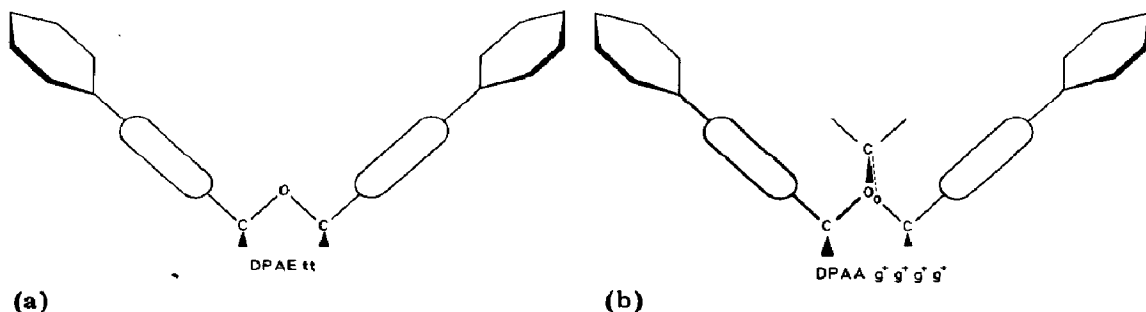


Fig. 8. Ground state conformations of (a) tt DPAA and (b) $g^+g^+g^+g^+$ DPAA.

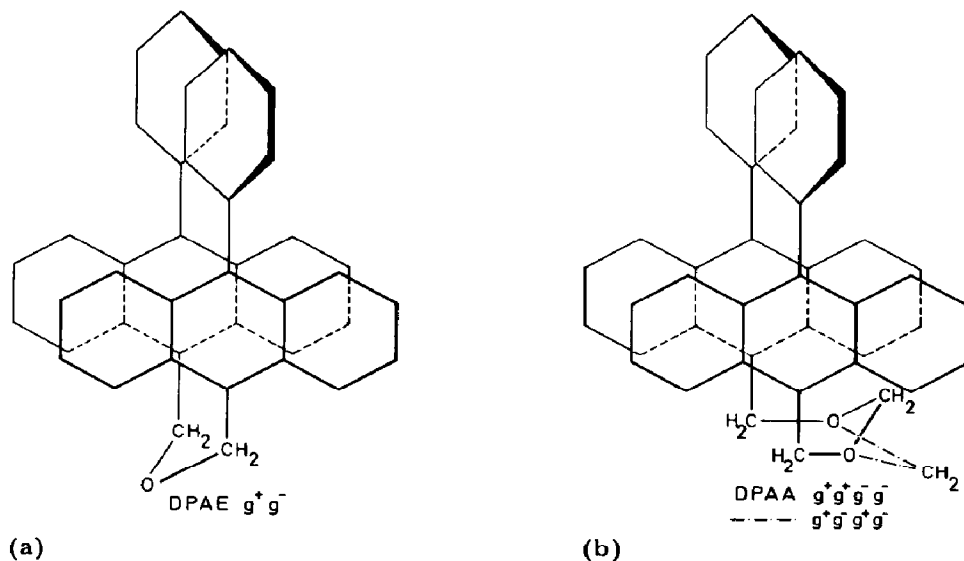


Fig. 9. Excimer conformations of (a) g^+g^- DPAAE and (b) $g^+g^+g^-g^-$ and $g^+g^-g^+g^-$ DPAA.

k_{FD} and k_{ID} and a lack of return to the LE state which is probably due to a large stabilization energy and a relatively important non-radiative decay. The ground state repulsion energy E_R of DPAA is relatively small compared with that of other $n = 3$ systems [9, 28].

A study of molecular models indicates that the g^+g^- "sandwich" excimer of DPAAE is prohibited by a strong steric hindrance of the two 10,10'-phenyl substituents. As a consequence the excimer of DPAAE is forced into a more open non-parallel overlap such as one of the staggered structures suggested by Ferguson and coworkers [46] for 1,2-di(9-anthryl)ethane whose maximum wavelength was about 550 nm. The bathochromic emission of the excimer of DPAAE might also partially result from an increased ground state repulsion. Such a repulsion between the phenyl groups is not expected for DPAA which apparently can form a coplanar excimer but at a larger interchromophoric distance [47].

The smaller value of k_{FD} of DPAA favours a higher symmetry of the excimer [48]. Finally the values of k_{FD} and k_{ID} are close to those of the analogous A-5-A [22, 23] (Table 1).

Acknowledgments

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