

## Short Communication

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### Restricted internal rotation of an intramolecular exciplex in polymeric matrices

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#### 1. Introduction

Farid *et al.* [1] have shown that, in contrast with intermolecular exciplex formation in polymeric matrices, non-conjugated bichromophoric systems of the D—(CH<sub>2</sub>)<sub>n</sub>—A type (D ≡ donor, A ≡ acceptor) fail to form intramolecular exciplexes when dissolved in polymers. This effect allows further insight into the time required for the folding process and the internal rotation around the carbon—carbon single bonds in the methylene bridge of the open electronically excited D—(CH<sub>2</sub>)<sub>n</sub>—A molecule to form the favoured sandwich-structured exciplex.

In this work we report on the photophysical behaviour at room temperature of 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane (see structural formula in Fig. 1), the most thoroughly investigated model compound for intramolecular exciplex formation [2 - 6], in methyl methacrylate (MMA) and in polymethyl methacrylate (PMMA).

#### 2. Experimental

The MMA (Merck, Darmstadt) was washed several times with aqueous sodium hydroxide to remove the inhibitor. Drying and purification were achieved by column chromatography on neutral aluminium oxide and by final distillation.

Solutions of approximately 10<sup>-4</sup> M 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane in MMA with a trace of dibenzoyl peroxide were carefully degassed in four freeze-pump-thaw cycles at 10<sup>-5</sup> Torr and were sealed in Pyrex tubes of 2 cm diameter. Thermal polymerization was carried out in the dark at 40 °C for 2 days. The plastic sample was easily machined and polished to a 1 cm<sup>2</sup> square of 4 cm length. A blank PMMA sample was prepared in the same manner.

The absolute fluorescence spectra, the fluorescence quantum yields as well as the decay times were measured at room temperature using a recording spectrofluorimeter and a fluorimeter relying on the pulse-sampling

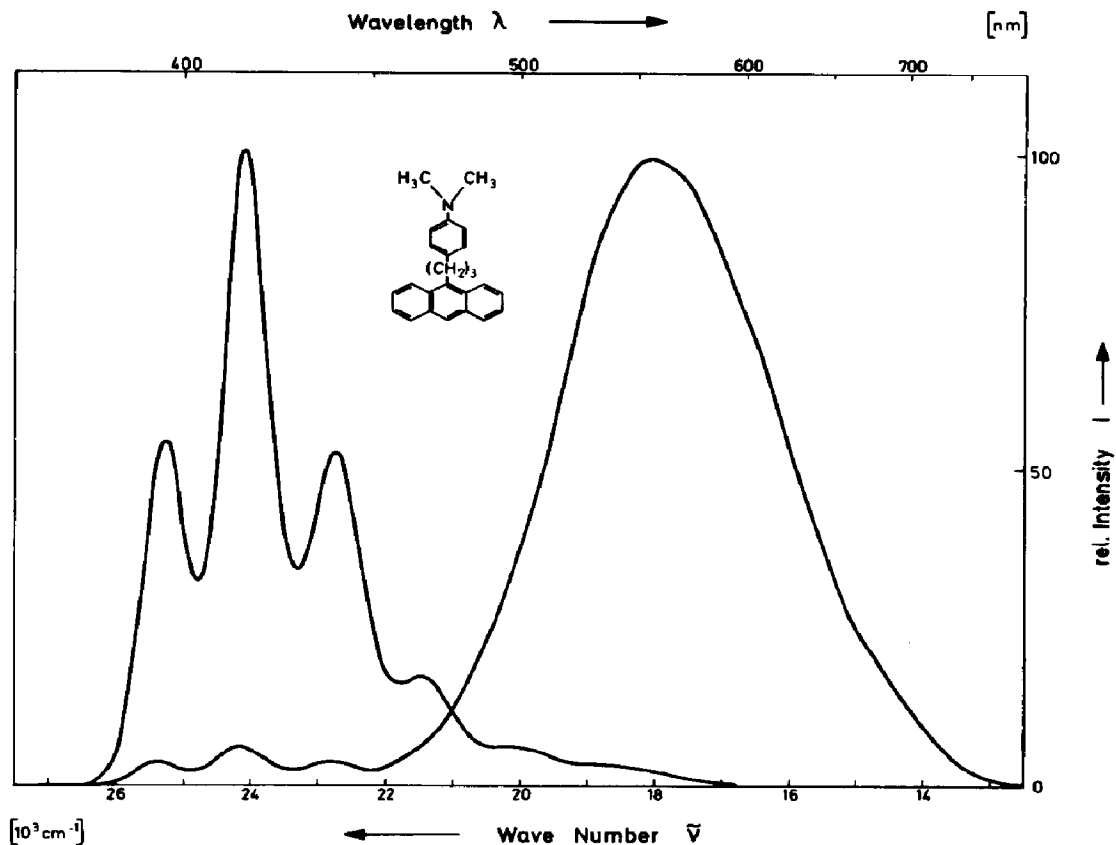


Fig. 1. Absolute fluorescence spectra of 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane in oxygen-free PMMA (left) and oxygen-free MMA (right).

method. Details about the instrumentation built at this laboratory and about the measurement techniques have been published earlier [7, 8]. For the determination of the fluorescence quantum yields according to the method of Parker and Rees [9], quinine bisulphate in 0.1 N H<sub>2</sub>SO<sub>4</sub> was used as a reference standard, assuming a fluorescence quantum yield of 0.55 [10]. Refractive indices of 1.414 for MMA and 1.491 for PMMA were taken into account for calculation of the fluorescence quantum yields. For polarization studies two UV polarizing filters (Polacoat, Cincinatti, Ohio) were used in two positions perpendicular to each other on the side of excitation.

### 3. Results and discussion

The absorption spectrum of 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane in MMA from 320 to 400 nm is essentially identical with that of an equimolar mixture of 9-methylantracene and *N,N*-dimethyl-*p*-toluidine, indicating that at room temperature there is no measurable charge transfer interaction in the ground state between the anthracene acceptor and the dimethylaniline moiety as the donor. The absorption spectrum in PMMA

TABLE 1

Fluorescence quantum yields and decay times of the anthracene moiety and the intramolecular exciplex of 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane in MMA and PMMA at room temperature

	$Q_F^A$	$Q_F^E$	$Q_{F_0}^A$	$Q_{F_0}^E$	$\tau_0^A$ (ns)	$\tau_0^E$ (ns)	$\tau^E$ (ns)
MMA	0.006	0.035	0.01	0.33	—	105.7	11.2
PMMA	—	—	0.62	—	9.3	—	—

$Q_F^A$  and  $Q_{F_0}^A$ , fluorescence quantum yields of the anthracene moiety with and without oxygen respectively;  $Q_F^E$  and  $Q_{F_0}^E$ , fluorescence quantum yields of the intramolecular exciplex with and without oxygen respectively;  $\tau_0^A$ , decay time of the anthracene moiety without oxygen;  $\tau^E$  and  $\tau_0^E$ , decay times of the intramolecular exciplex with and without oxygen respectively.

agrees completely with that in MMA. The absolute fluorescence spectra of 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane in oxygen-free MMA and oxygen-free PMMA are shown in Fig. 1.

In deoxygenated MMA the intense unstructured intramolecular exciplex fluorescence is in equilibrium with little emission from the open unfolded 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane. In the polymer matrix of PMMA, however, no intramolecular exciplex emission can be detected, as has been recently found in polystyrene by Farid *et al.* [1]. While the maximum of the anthracene-like emission does not change when going from polystyrene to PMMA, the exciplex emission is shifted by 40 nm to a longer wavelength because of a solvent-induced change of the electronic structure of the exciplex [11] in the more polar PMMA.

Since the anthracene moiety exhibits a low triplet state energy of  $14\,927\text{ cm}^{-1}$  [12], intermolecular guest-to-host energy transfer in PMMA with a triplet state at approximately  $25\,000\text{ cm}^{-1}$  [13] can be ruled out at the concentration used in our experiments.

Furthermore, PMMA forms a clear glass with UV transparency until well above  $30\,000\text{ cm}^{-1}$ ; thus, the electronic levels of 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane are sufficiently low to preclude interaction with those of the polymer matrix. Finally, excitation of 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane in PMMA with polarized light showed no discernible difference in the fluorescence intensity, which indicates a random distribution of the solute in PMMA.

The intensity of the typically structured anthracene-like emission of the open 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane increases drastically when going from MMA to PMMA. In Table 1 the fluorescence quantum yields and the fluorescence decay times in MMA and PMMA at room temperature are summarized.

The increase of the fluorescence quantum yield of the anthracene moiety from MMA to oxygen-free MMA is the expected increase for *meso*-substituted anthracene derivatives [8]. The tenfold increase of the fluores-

TABLE 2

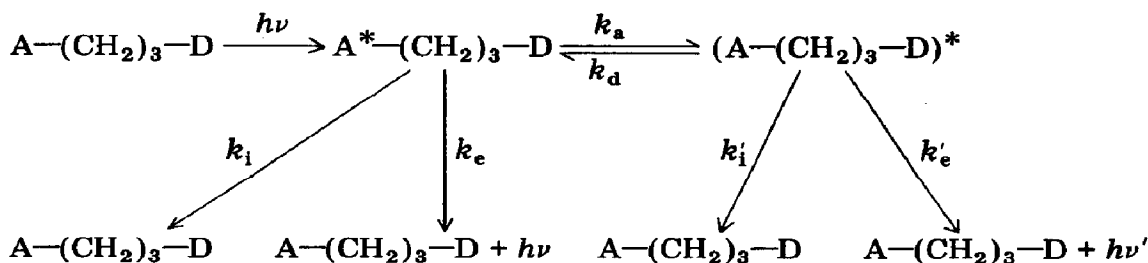
Rate constants of 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane and its intramolecular exciplex in MMA at room temperature

Rate constant	Rate constant value ( $s^{-1}$ )	
	1- <i>p</i> -Dimethylaminophenyl-3-anthryl-(9)-propane	9-Methylantracene
$k_e$	$6.67 \times 10^7$	$6.68 \times 10^7$
$k_i$	$4.09 \times 10^7$	$7.23 \times 10^7$
$(k_i)_q^a$	$1.14 \times 10^8$	$1.42 \times 10^8$
$k_a$	$1.23 \times 10^{10}$	$1.19 \times 10^{10}$
$k_d$	$8.2 \times 10^6$	$7.6 \times 10^6$
$k'_e$	$3.2 \times 10^6$	—
$k'_i$	$6.3 \times 10^6$	$6.2 \times 10^6$
$(k'_i)_q^a$	$8.9 \times 10^7$	$8.5 \times 10^7$

<sup>a</sup>Quenched by atmospheric oxygen.

cence quantum yield of the intramolecular exciplex from air-saturated MMA to degassed MMA indicates a much longer lifetime of the intramolecular exciplex. Hence, a fluorescence decay time of the exciplex more than ten times longer than that of the anthracene moiety is demonstrated by direct measurement (see Table 1).

Application of the kinetic reaction scheme of Klöpffer and Liptay [14, 15] for the rate constants of intramolecular exciplex formation and dissociation together with the experimental data from Table 1 results in the rate constants  $k_e$  for the radiative and  $k_i$  for the non-radiative decays as well as in the rates  $k_a$  of association and  $k_d$  of dissociation (Table 2).



$\text{A}-(\text{CH}_2)_3-\text{D}$  is 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane in its ground state and  $\text{A}^*(\text{CH}_2)_3-\text{D}$  is the open electronically excited singlet state with the local excitation in the anthracene moiety.  $(\text{A}-(\text{CH}_2)_3-\text{D})^*$  is the intramolecular exciplex, and  $k_e$  and  $k'_e$  are the rate constants of the radiative decay of the open electronically excited 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane and of its exciplex respectively.  $k_i$  and  $k'_i$  are the corresponding rate constants for non-radiative decays (internal conversion,

intersystem crossing and external quenching) of both excited states in the reaction scheme.

For the kinetic data in the second column of Table 2 the assumption was made that the intrinsic fluorescence lifetime  $\tau_f$  of 1-*p*-dimethylamino-phenyl-3-anthryl-(9)-propane is the same in MMA as in PMMA. This assumption is supported by the calculated value for  $\tau_f$  of 15 ns in PMMA from  $\tau_f = \tau_0^\wedge / Q_F^\wedge$ . The intrinsic lifetime of 15 ns has been measured for a sizeable number of other *meso*-substituted anthracenes in *n*-heptane [8] and for 9-methylanthracene in MMA. Because of the very low fluorescence quantum yield of the unfolded 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane in MMA (see Table 1), the direct measurement of the fluorescence decay time  $\tau_0^\wedge$  would have been associated with very high uncertainties. The kinetic data in the third column of Table 2 were calculated assuming that the rates of the radiative and non-radiative deactivations as well as the oxygen quenching for  $A^*-(CH_2)_3-D$  without exciplex formation are the same as for the anthracene moiety without the  $(CH_2)_2-D$  group, *i.e.* as for 9-methylanthracene in MMA. The fluorescence quantum yields and fluorescence decay times for 9-methylanthracene in MMA in the absence and in the presence of oxygen were determined to be  $Q_{F_0} = 0.48$  and  $Q_F = 0.32$ , and  $\tau_0 = 7.19$  ns and  $\tau = 4.16$  ns, respectively.

Using the photophysical data from Table 1 in the kinetic scheme of Klöpffer and Liptay [14, 15], it can be shown that in the presence of oxygen only 8% of the exciplex dissociates back to  $A^*-(CH_2)_3-D$ , *i.e.*  $k_d \ll (k_i)_q + k'_e$ . The measured  $Q_F^E$  and  $\tau^E$  values are always higher than the "true" fluorescence quantum yield and decay time because the former increase with the dissociation of the exciplex. Thus the error for  $k'_e$  in eqn. (2) is certainly smaller than the calculated 8%. Neglecting the dissociation of the exciplex we can write for the measured quantum yield of exciplex emission in the presence of oxygen

$$Q_F^E \approx \frac{k_a}{k_a + k_e + (k_i)_q} \frac{k'_e}{k'_e + (k'_i)_q + k_d} \quad \text{and} \quad \tau^E = \frac{1}{k'_e + (k'_i)_q + k_d} \quad (1)$$

from which follows

$$k'_e \approx \frac{Q_F^E}{\tau^E} \frac{k_a}{k_a + k_e + (k_i)_q} \approx 3.2 \times 10^6 \text{ s}^{-1} \quad (2)$$

The values of  $k'_i$ ,  $(k'_i)_q$  and  $k_d$  in Table 2 were calculated with this value. Furthermore, neglecting  $k_d$  we obtain for oxygen quenching of the exciplex

$$k'_q(O_2) = (k'_i)_q - k'_i \quad (3)$$

and for the unfolded 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane

$$k_q(O_2) = (k_i)_q - k_i \quad (4)$$

Taking into account for MMA a mean oxygen concentration of  $2.5 \times 10^{-3}$  M, similar to that for other organic solvents [16], eqns. (3) and (4) together

with the rate constants from Table 2 give rate constants for the bimolecular oxygen quenching of  $k'_q = 3.2 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$  for the exciplex and  $k_q = 2.9 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$  for the unfolded anthracene moiety.

Despite the two different geometries of the exciplex and the electronically excited unfolded 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane, oxygen quenching is in both cases a diffusion-controlled process. Thus Klöpffer's [15] assumption for the kinetic scheme that oxygen quenching of the monomer fluorescence and of the exciplex fluorescence is equally effective is demonstrated experimentally.

The kinetic data in Table 2 indicate that the rate constant  $k_a$  for the exciplex formation is much greater than the rate constants for all other deactivation processes such as the radiative ( $k_e$ ) and non-radiative deactivation ( $k_i$ ), even in the presence of an efficient quencher like oxygen. The lifetime  $\tau$  of the exciplex is of the order of  $10^{-7} \text{ s}$  as is observed for organic intramolecular excimers [15]. Because of the approximately fortyfold longer lifetime of the exciplex compared with that of the unfolded electronically excited 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane the non-radiative decay of the exciplex with and without quencher varies by more than one order of magnitude.

The intramolecular exciplex can be formed only if a conformational change, which brings the *N,N'*-dimethylaniline donor into proper juxtaposition with the anthracene ring, occurs during the lifetime of the open unfolded electronically excited  $A^*(\text{CH}_2)_3\text{-D}$  molecule. Thus the conformational change has to occur at a rate constant of faster than  $6.67 \times 10^7 \text{ s}^{-1}$ . In the polymeric matrix of PMMA the time required for the folding process is too long; thus the main deactivation channel from  $A^*(\text{CH}_2)_3\text{-D}$  to the exciplex is closed. This causes the drastic more than sixtyfold increase of the fluorescence quantum yield of 1-*p*-dimethylaminophenyl-3-anthryl-(9)-propane in PMMA. Because of the extremely rigid matrix of PMMA ( $\eta > 10^{13} \text{ P}$ ) [17] with a low oxygen diffusion coefficient ( $10^{-20} \text{ cm}^2 \text{ s}^{-1}$ ) [18] it could very well be that a certain fraction of this increase is due to restrictions of internal molecular rotations around the carbon-carbon single bonds in the trimethylene bridge. An increase of the fluorescence quantum yield from MMA to PMMA has been recently observed in two other *meso*-substituted anthracene derivatives which are not able to form an intramolecular exciplex [19].

Enhancement of the fluorescence intensity of aromatic compounds capable of internal molecular rotations in viscous and polymeric media has been previously found by Oster and Nishijima [20].

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