

The Influence of Solvent Polarity on the Nonradiative Decay of Exciplexes

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Abstract: The efficiency with which the intramolecular exciplex between pyrene and indole or between pyrene and a tertiary amine decays to the locally excited triplet state of pyrene is determined using laser-induced optoacoustic spectroscopy. Upon increasing the solvent polarity, the relative efficiency of this intersystem crossing process decreases compared to the efficiency of the internal conversion process to the singlet ground state. These results can be rationalized in the framework of the Marcus theory. The results obtained by laser-induced optoacoustic spectroscopy are confirmed by transient absorption spectroscopy of the pyrene triplet in the case of the intramolecular exciplex of 1-(1-pyrenyl)-3-*N,N*-dimethylaminopropane.

Introduction

The formation of excited-state complexes between aromatic hydrocarbons (acceptors) and aromatic or aliphatic amines (donors) has received substantial attention.¹⁻⁴ The energy of the charge-transfer state will, due to its dipole moment, depend upon the solvent polarity and upon the distance between A⁻ and D⁺ due to the Coulombic attraction between A⁻ and D⁺. This leads to the bathochromic shift of the exciplex fluorescence maxima that is observed upon increasing solvent polarity.⁵ The fluorescence quantum yields and lifetimes of these exciplexes, however, are known to decrease when the solvent polarity is increased. The decrease of the lifetime can be due to dissociation of the exciplex into a solvated radical ion pair that, for intermolecular exciplexes, can dissociate into free radical ions. This dissociation can, however, not explain why the decrease of the fluorescence quantum yield observed upon increasing the solvent polarity is more important than the decrease of the singlet lifetime.

According to Weller,^{9,10} this effect was due to a competition between the formation of a solvated radical ion pair and exciplex formation from the "encounter complex". On the other hand, Mataga et al.¹¹⁻¹³ suggested that this effect was caused by the solvent dependence of the electronic structure of the exciplex. Increasing the solvent polarity increases the energy gap between the zeroth-order CT state and the different nonpolar locally excited states leading to a less extensive mixing of those locally excited states in the exciplex.

The emission of intramolecular exciplexes with aliphatic amine donors has been observed for phenyl,^{6,7} naphthyl,⁸ and pyrenyl¹ as acceptors. Although the use of stationary and time-resolved fluorescence spectroscopy allowed the analysis of the exciplex formation, little information was obtained on the mechanism of the exciplex decay. Up to now it was not possible to separate the contributions of internal conversion and intersystem crossing in the radiationless decay process of those exciplexes. For other exciplexes, intersystem crossing (ISC) from the CT state to the locally excited triplet state has been observed by means of laser photolysis.¹⁵⁻¹⁸ The increase of the nonradiative decay in the presence of heavy atoms suggests that ISC plays an important role in the deactivation of exciplexes.¹⁹⁻²² Studies of the magnetic field effect upon the decay kinetics of triplet exciplexes in liquid media have been used to investigate the back-electron-transfer process.²³⁻²⁵ On the other hand,¹⁴ no triplet formation was observed for intermolecular exciplex between pyrene and dimethylaniline.

Reactions typical of the locally excited triplet state of either donor or acceptor, produced from the excited charge-transfer state, have been observed by Adams et al.²⁶ The effect of methyl deuteration and methyl substitution on the nonradiative decay rate, together with phosphorescence data, has been used to argue

that intersystem crossing from the CT state to a locally excited triplet state²⁷ occurs.

The role of the solvent in the formation and relaxation of molecular exciplexes has been discussed, and calculations of potential energy curves, incorporating solvent parameters,²⁸ were carried out.

However, laser-induced optoacoustic spectroscopy (LIOAS) is a method suitable to study the radiationless decay processes of excited states. Theoretical studies²⁹⁻³² leading to the understanding of the influence of different experimental parameters

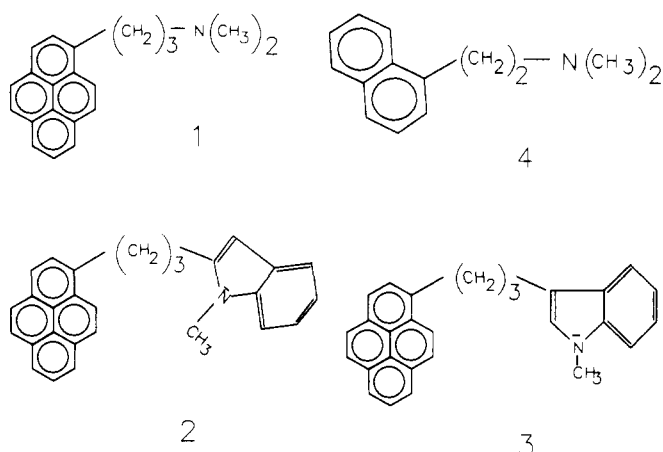
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[†] Dedicated to Professor K. Schaffner at the occasion of his 60th birthday.

on the generation of optoacoustic signals in dilute solutions made it possible to use the optoacoustic spectroscopy in a wide range of photophysical³³⁻⁴⁵ and photobiological investigations.⁴⁶⁻⁵⁵

The time resolution of the optoacoustic experiment is limited by the response time of the piezoelectric detector, which integrates (depending upon the experimental conditions) the heat that is released within about 250 ns after excitation. The amplitude of the optoacoustic deflection is directly proportional to the amount of energy released within these 250 ns. This so-called "prompt heat" differs from the "slow heat" which has its origin in the radiationless decay of long-living species (triplets, radicals,...). The first optoacoustic measurements of CT complexes and ion-pair formation were executed by Gould et al., who used LIOAS to study the electron-transfer reactions in the Marcus inverted region.⁴²

In the present contribution, the results of optoacoustic and transient absorption measurements of 1-(1-pyrenyl)-3-*N,N*-dimethylaminopropane (1Py3NM) (1), 1-(1-pyrenyl)-3-(2-(*N*-



methyl)indolyl)propane (1Py2In) (2), 1-(1-pyrenyl)-3-(3-(*N*-methyl)indolyl)propane (1Py3In) (3), and 1-(1-naphthyl)-2-(*N,N*-dimethylaminoethane) (1N2NM) (4) in solvents of different polarity are compared. These molecules are characterized by an

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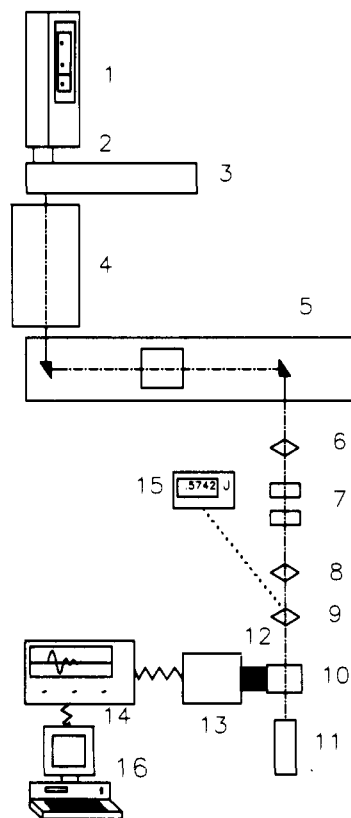


Figure 1. Optoacoustic setup: (1) DCR-3 Nd:YAG, (2) HG-2, (3) PHS-1, (4) pulsed dye laser-2, (5) WEX-1, (6) lens, (7) polarizers, (8) pinhole, (9) wedged reflector, (10) PA-cel, (11) beam dump, (12) PVF₂ transducer, (13) preamplifier and amplifier, (14) transient digitizer, (15) power meter, (16) PC.

efficient quenching of the locally excited state in different solvents which allows an accurate determination of the relative importance of the different decay channels of the exciplex.

Experimental Section

1Py3NM was synthesized using the method developed for the synthesis of 1-(1-pyrenyl)-3-(*N*-skatolyl)propane (1Py1In).⁵⁶ 1Py3NM was obtained by reacting the intermediate 1-(1-pyrenyl)-3-bromopropane with dimethylamine, 40 wt % solution in water. It was purified by preparative thin layer chromatography on silica gel using diethyl ether as eluent.

1Py2In and 1Py3In⁵⁷ were purified by HPLC. 1N2NM⁵⁸ was purified using precoated TLC silica gel plates with diethyl ether as eluent.

2-Hydroxybenzophenone (>99% purity) was purchased from Aldrich-Chemie and was used without further purification.

Methylpyrene was synthesized by reduction of 1-pyrenecarboxaldehyde⁵⁹ (Aldrich 98%) and purified by thin layer chromatography of precoated TLC silica gel plates with hexane/dichloromethane (1/1) as eluent.

The solvents used (diethyl ether and acetonitrile, Merck; tetrahydrofuran, Rathburn; isooctane, Fluka Chemical) were of spectroscopic grade and used as received.

The absorbance of the sample solutions equals 0.1 for the fluorescence and optoacoustic measurements. For the transient absorption measurements, the absorbance (*A*) equals 3.0 at 320 nm.

Absorption spectra were measured with a Perkin-Elmer Lambda 5 UV/vis spectrophotometer. Fluorescence spectra were determined with a Spex Fluorolog. The fluorescence quantum yields were determined using quinine sulfate in 1 N H₂SO₄ as a reference ($\Phi = 0.55^{60}$).

Fluorescence and transient absorption measurements were performed on samples degassed by several freeze-pump-thaw cycles, while samples used in optoacoustic measurements were degassed by bubbling argon for 15 min.

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The experimental setup used for the optoacoustic experiments is shown in Figure 1. The excitation source is a Spectra Physics DCR 3A pulsed Nd:YAG laser. By means of the HG-2 harmonic generator, the fundamental of 1064 (10 Hz, 8 ns) was frequency doubled to 532 nm. Those pulses were used to pump the Spectra Physics PDL-2 pulsed dye laser (DCM in methanol). The output of the dye laser was frequency doubled to create UV pulses (6 mJ, <4 ns) of 320 nm in the Spectra Physics WEX-1 wavelength extender. The energy of the pulsed output can be attenuated by means of two polarizers. The diameter of the laser beam, focused by a 80-cm lens, is determined by a pinhole (0.2 a 1 mm). In order to know the diameter of the laser beam in the cuvette, the focus of the lens is equidistant from the pinhole and the middle of the cuvette. A JW25 wedged reflector reflects about 5% of the incident laser beam into a RjP-735 Series energy probe power detector and a RjP 7100 power meter.

The optoacoustic wave, generated in the solution, is detected by a metallized piezoelectric poly(vinylidene difluoride) film (5-mm diameter, 40- μ m thickness, Solvay) which converts the pressure wave into a voltage signal. These signals are further amplified by a preamplifier and a wide-band high-input impedance (47 M Ω) amplifier. The analog output of the amplifier is captured by a transient digitizer (Gould 4072) triggered by the Q-switch pulse of the Nd:YAG laser. To improve the signal-to-noise ratio, the signals were averaged 128 times.

The amplitude of the optoacoustic signal is related to the energy of the incident laser pulse by:

$$H = K\alpha E_0(1 - 10^{-A}) \quad (1)$$

where H is the experimentally obtained amplitude of the optoacoustic signal, K is a constant which depends on the geometry of the experimental set-up and the thermoelastic quantities of the medium, E_0 is the incident laser pulse energy, A is the optical density of the solution, and α is the fraction of the absorbed laser energy (E_{abs}) released as thermal energy (E_{th}) within the response time of the detector (prompt heat):

$$\alpha = E_{th}/E_{abs} \quad (2)$$

where $0 \leq \alpha \leq 1$. The use of eq 1 supposes a cylindrical acoustic wave. In order to achieve this boundary condition, the absorbance is always kept below 0.1. If equal optical densities for both the reference and the sample are used and both reference and sample are dissolved in the same solvent, the ratio of the slopes of H versus E_0 is given by the following expression:

$$\frac{H_{sample}/E_0}{H_{reference}/E_0} \frac{K_{sample}\alpha_{sample}}{K_{reference}\alpha_{reference}} = \alpha_{sample}/\alpha_{reference} \quad (3)$$

When a reference characterized by $\alpha_{reference} = 1$ is used, the ratio of the two slopes yields directly α_{sample} . Comparing several reference substances suggested that for 2-hydroxybenzophenone α equals 1.⁶¹

For the transient absorption measurements, the same excitation source is used as for the optoacoustic experiments. The analytical beam is perpendicular to the excitation beam. As a light source for the analytical beam, a pulsed xenon lamp (Müller Elektronik Optik) is used. This beam is focused on the entrance slit (6 \times 1 mm) of the sample compartment. After its passage through the cell compartment, the analytical beam is focused on the entrance slit (20 mm \times 0.5 mm) of the monochromator (Baird & Tatlock) by means of two lenses. A photomultiplier (Hamamatsu R928) converts the incident light into a voltage which is recorded by a Gould 4072 transient digitizer. To avoid photodegradation of the sample, a shutter (Vincent Associates) is placed in the analytical beam in front of the cell compartment. The shutter is opened by the output signal of the oscillator of the Nd:YAG laser.

Experimental Results

Emission Spectra. The emission spectrum of 1Py3NM, in solvents of medium polarity (Figure 2) at room temperature, consists of the emission band of pyrene with a maximum at 377 nm and a broad bathochromic structureless band which is due to the emission of the intramolecular exciplex of 1Py3NM.¹ Substantial exciplex fluorescence is observed in diethyl ether ($\epsilon = 4.3$) and tetrahydrofuran ($\epsilon = 7.6$). In the more polar acetonitrile ($\epsilon = 37$), the locally excited state fluorescence is strongly quenched and a very weak exciplex emission band is observed. Table I shows the quantum yields of 1Py3NM in the different solvents. Combining the quantum yield for exciplex formation and exciplex fluorescence for 1Py3NM in diethyl ether yields a value of 0.32 for the quantum efficiency of fluorescence of the

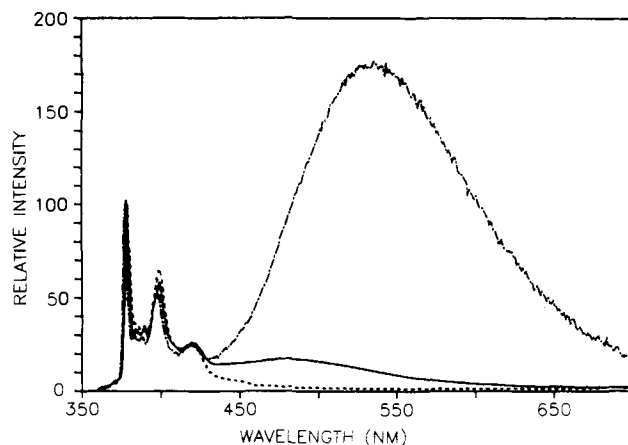


Figure 2. Fluorescence spectra of 1Py3NM in different solvents at room temperature. The spectra are normalized at 376 nm; excitation occurred at 337 nm: (—) diethyl ether, (---) tetrahydrofuran, (····) acetonitrile.

Table I. Quantum Yields of the Different Radiative and Nonradiative Processes Occurring upon the Excitation of 1Py3NM^a

| | diethyl ether | tetrahydrofuran | acetonitrile |
|----------------------------|---------------|-----------------|--------------|
| Φ_{fl} | 0.39 | 0.19 | 0.008 |
| Φ_{fe} | 0.19 | 0.17 | 0.001 |
| Φ_{fm} | 0.20 | 0.02 | 0.007 |
| Φ_{iscm} | 0.22 | 0.02 | 0.006 |
| Φ_{icm} | 0.00 | 0.00 | 0.00 |
| Φ_{for} | 0.58 | 0.96 | 0.99 |
| $\Phi_{isce} + \Phi_{ice}$ | 0.39 | 0.79 | 0.99 |

^a Φ_{fl} = total quantum yield of fluorescence. Φ_{fe} = quantum yield of exciplex fluorescence. Φ_{fm} = quantum yield of fluorescence of the locally excited state. Φ_{iscm} = quantum yield of intersystem crossing of the locally excited state. Φ_{icm} = quantum yield of internal conversion of the locally excited state. The quantum yield of the internal conversion process from the locally excited singlet state is supposed to be zero.⁶³ Φ_{for} = quantum yield of exciplex formation. $\Phi_{isce} + \Phi_{ice}$ = sum of the quantum yields of intersystem crossing and internal conversion of the exciplex.

exciplex. As the sum of the rate constants for the decay processes of the exciplex of 1Py3NM in diethyl ether equals $2.2 \times 10^7 \text{ s}^{-1}$ at room temperature,¹ a value of $7.0 \times 10^6 \text{ s}^{-1}$ can be obtained for the rate constant of exciplex fluorescence. This value corresponds within the experimental error to the value obtained in ethyl acetate.⁶²

Φ_{iscm} is calculated the following way:

$$\Phi_{iscm} = \Phi_{fm}(k_2/k_{fm}) \quad (4)$$

where k_{fm} and k_2 are the rate constants of respectively the radiative and nonradiative decay of 1-methylpyrene⁴ in the same solvent.

Φ_{for} is calculated in the following way:

$$\Phi_{for} = 1 - (\Phi_{fm}/\Phi_{fm}^0) \quad (5)$$

where Φ_{fm}^0 corresponds to the quantum yield of fluorescence of the locally excited state of 1-methylpyrene.

$\Phi_{isce} + \Phi_{ice}$ is calculated according to:

$$\Phi_{isce} + \Phi_{ice} = [1 - (\Phi_{fe}/\Phi_{for})]\Phi_{for} \quad (6)$$

Figures 3 and 4 show the emission spectra of 1Py2In and 1Py3In in isoctane, diethyl ether, and acetonitrile at room temperature. Although competition between the formation of the exciplex and a radical ion pair reduces the quantum yield of fluorescence of the exciplex (Table II), exciplex fluorescence is still observed in acetonitrile. The increase of the quantum yield of the nonradiative processes occurring from the exciplex observed for 1Py2In is due to an increase of both Φ_{for} , the quantum yield of exciplex formation,

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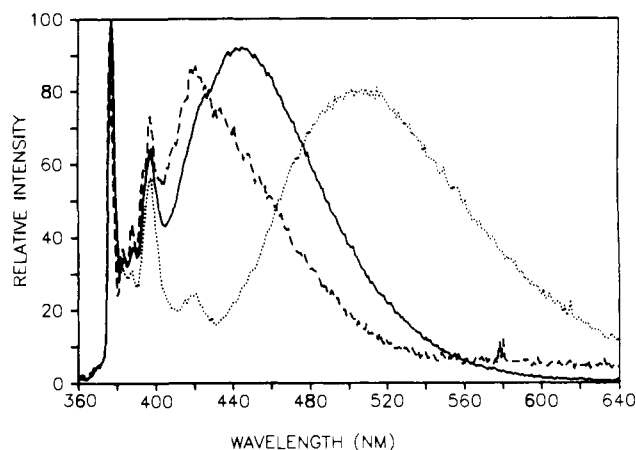


Figure 3. Fluorescence spectra of 1Py2In in different solvents at room temperature. The spectra are normalized at 376 nm, excitation at 337 nm: (—) diethyl ether, (---) isoctane, (···) acetonitrile.

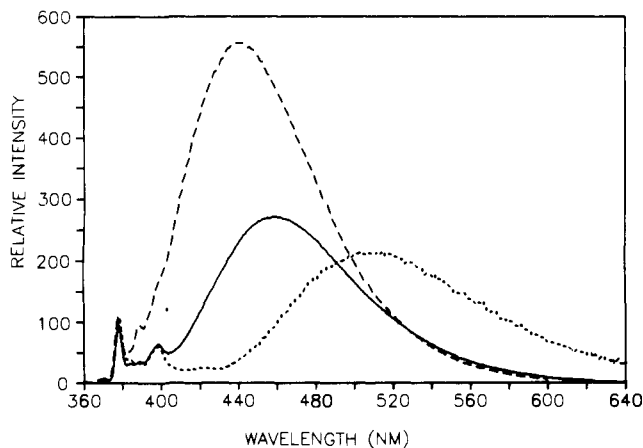


Figure 4. Fluorescence spectra of 1Py3In in different solvents at room temperature. The spectra are normalized at 376 nm, excitation at 337 nm: (—) diethyl ether, (---) isoctane, (···) acetonitrile.

Table II. Quantum Yields of the Different Radiative and Nonradiative Processes Occurring upon the Excitation of 1Py2In and 1Py3In

| | isoctane | diethyl ether | acetonitrile |
|----------------------------|-----------|---------------|--------------|
| Φ_{ft} | 0.58 0.58 | 0.54 0.59 | 0.31 0.50 |
| Φ_{fe} | 0.43 0.57 | 0.48 0.57 | 0.28 0.49 |
| Φ_{fm} | 0.15 0.01 | 0.06 0.02 | 0.03 0.01 |
| Φ_{iscm} | 0.18 0.01 | 0.07 0.02 | 0.008 0.008 |
| Φ_{icm} | 0.00 0.00 | 0.00 0.00 | 0.00 0.00 |
| Φ_{for} | 0.66 0.98 | 0.87 0.96 | 0.98 0.98 |
| $\Phi_{isce} + \Phi_{ice}$ | 0.24 0.41 | 0.39 0.39 | 0.68 0.49 |

and the quantum efficiency for the nonradiative decay processes of the exciplex ($\Phi_{isce} + \Phi_{ice}$).

The fluorescence spectrum of 1N2NM in different solvents at room temperature is shown in Figure 5. In addition to the very weak fluorescence of the locally excited state at 339 nm, a strong exciplex fluorescence band is observed at lower frequencies. Combining the quantum yield for exciplex formation and exciplex fluorescence for 1N2NM in diethyl ether yields a value of 0.20 for the quantum efficiency of fluorescence of the exciplex. As the sum of the rate constants for the decay processes of the exciplex of 1N2NM in diethyl ether equals $8.4 \times 10^7 \text{ s}^{-1}$ at room temperature,⁵⁸ a value of $1.7 \times 10^7 \text{ s}^{-1}$ can be obtained for the rate constant of exciplex fluorescence. This value is intermediate⁶² between the values obtained for the exciplex of 1-phenyl-2-dimethylaminoethane and 1-(1-pyrenyl)-2-dimethylaminoethane.

Laser-Induced Optoacoustic Data. The measured optoacoustic signal of 1Py3NM is quantitatively compared with the signal produced by the reference, 2-hydroxybenzophenone ($\alpha = 1$). Since

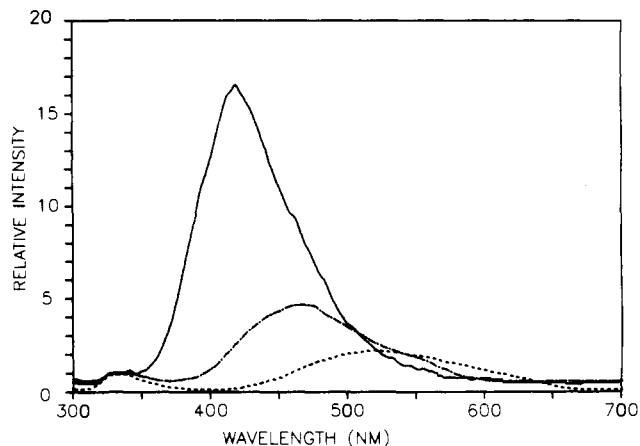


Figure 5. Fluorescence spectra of 1N2NM in different solvents at room temperature, excitation at 280 nm. The spectra are normalized at 330 nm: (—) diethyl ether, (---) tetrahydrofuran, (···) acetonitrile.

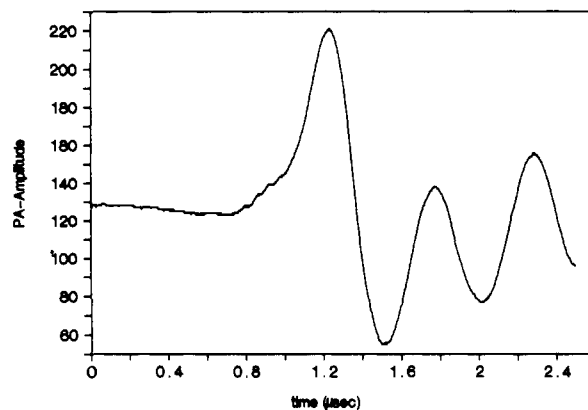


Figure 6. Optoacoustic signal detected by a 40- μm PVF₂ foil for a solution of 2-hydroxybenzophenone in acetonitrile. The energy and the diameter of the laser pulse with a wavelength of 355 nm amount to 60 μJ and 0.2 mm, respectively.

Table III. Quantum Yields of the Different Radiative and Nonradiative Processes Occurring upon the Excitation of 1N2NM

| | diethyl ether | tetrahydrofuran | acetonitrile |
|----------------------------|---------------|-----------------|--------------|
| Φ_{ft} | 0.20 | 0.17 | 0.13 |
| Φ_{fe} | 0.19 | 0.15 | 0.10 |
| Φ_{fm} | 0.01 | 0.01 | 0.03 |
| Φ_{iscm} | 0.06 | 0.09 | 0.19 |
| Φ_{icm} | 0.00 | 0.00 | 0.00 |
| Φ_{for} | 0.93 | 0.89 | 0.79 |
| $\Phi_{isce} + \Phi_{ice}$ | 0.74 | 0.74 | 0.69 |

the fluorescence decay times of the bichromophores in the different solvents used are considerably shorter^{1,57} than the response time of the optoacoustic setup (250 ns) (Figure 6), all heat emitted by the system, except that generated by the triplet decay, can be considered as "prompt" heat. Since there is, except for the locally excited triplet state, no long-living species formed, all absorbed energy must be trapped in this triplet state or be dissipated as fluorescence or heat. The heat generated by the decay of the triplet state T_1 ($\tau \approx$ several microseconds) will not contribute to the amount of prompt heat release, but will be dissipated as slow heat. Therefore, for 1Py3NM in tetrahydrofuran the amount of prompt heat ($Q_{(1\text{Py}3\text{NM})}$) can be calculated according to the scheme in Figure 7:

$$\alpha(h\nu_{ex}) = Q_{(1\text{Py}3\text{NM})} = 4650 \text{ cm}^{-1} + \Phi_{fm} \times 900 \text{ cm}^{-1} + \Phi_{iscm} \times 9800 \text{ cm}^{-1} + \Phi_{fe} \times 7910 \text{ cm}^{-1} + (\Phi_{ice} + \Phi_{isce})\beta \times 26600 \text{ cm}^{-1} + (\Phi_{ice} + \Phi_{isce})(1 - \beta) \times 9800 \text{ cm}^{-1} \quad (7)$$

The energy parameters in eq 7 are obtained in the following way:

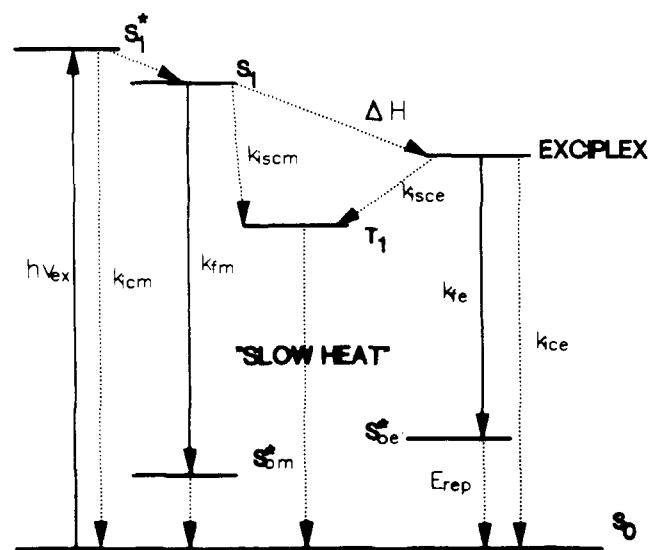


Figure 7. Kinetic scheme of the photophysics of 1Py3NM in tetrahydrofuran: k_{icm} and k_{scm} , internal conversion and intersystem crossing rate constant of the relaxed excited state S_{1m} ; k_{fm} , fluorescence rate constant of the relaxed excited state S_1 ; k_{scce} , k_{ice} , and k_{fe} , internal conversion, intersystem crossing, and fluorescence rate constant of the exciplex; ΔH° , stabilization enthalpy of the exciplex; E_{rep} , energy content of the FC ground state of the exciplex.

Table IV. Energies of the Different Excited States Involved in the Photophysics of Intramolecular Exciplexes between Pyrene and Indole or Tertiary Amines (in cm^{-1})^a

| | 1Py3NM | 1Py2In | 1Py3In | 1N2NM |
|---|--------|--------|--------|--------|
| $E(S_{1m})$ | 26 600 | 26 600 | 26 600 | 29 500 |
| $E(S_{1m}^*)$ | 31 250 | 31 250 | 31 250 | 31 250 |
| $E(S_{0m}^*)$ | 900 | 900 | 900 | 1 750 |
| $-\Delta H^\circ + E_{rep}(\text{isooctane})$ | | 3 000 | 3 980 | |
| $-\Delta H^\circ + E_{rep}(\text{ether})$ | 5 680 | 5 000 | 5 000 | 7 380 |
| $-\Delta H^\circ + E_{rep}(\text{tetrahydrofuran})$ | 7 910 | | | 10 110 |
| $-\Delta H^\circ + E_{rep}(\text{CH}_3\text{CN})$ | 8 840 | 6 840 | 7 180 | 11 950 |
| $E(T_1)$ | 16 800 | 16 800 | 16 800 | 21 300 |

^a ΔH° , E_{rep} , $E(S_{1m}^*)$, and $E(S_{0m}^*)$ correspond respectively to the enthalpy of exciplex formation, the repulsion energy in the ground state, the energy of the Franck-Condon excited state, and the energy of the Franck-Condon ground state of 1-methylpyrene.

4650 cm^{-1} = the energy difference between the Franck-Condon (FC) excited state S_{1m}^* and the relaxed locally excited state S_{1m} of pyrene. Since this conversion is very fast (10^{-13} s), it is within the time resolution of the experiment and will contribute in total to the amount of prompt heat release. The excitation energy and the energy of the relaxed locally excited state, which corresponds to the 0-0 transition of the fluorescence of 1-methylpyrene, can be determined with an accuracy of at least 200 cm^{-1} .

900 cm^{-1} = the energy difference between the FC ground state reached by fluorescence, S_{0m}^* , and the relaxed ground state, S_0 . This heat is also released promptly (10^{-13} s). This quantity corresponds to the difference between the first moment of the fluorescence spectrum of 1-methylpyrene and the 0-0 transition of the fluorescence spectrum of 1-methylpyrene, both of which are experimentally accessible.

9800 cm^{-1} = the energy difference between the relaxed locally excited state S_{1m} and the locally excited triplet state T_1 of pyrene.⁶⁴

7910 cm^{-1} = the sum of the ground-state repulsion and the stabilization enthalpy of the exciplex. This amount is calculated from the difference of the fluorescence maxima of the locally excited state and the exciplex ($^1(D^+A^-)$ augmented with 900 cm^{-1} (difference between the energy of the FC state S_{0m}^* and the relaxed ground state S_0). This energy difference depends on the polarity of the solvent and equals 5680 cm^{-1} in ether, 7910 cm^{-1}

Table V. Experimental Values of α for 1Py3NM, 1Py2In, 1Py3In, and 1N2NM

| | 1Py3NM | 1Py2In | 1Py3In | 1N2NM |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| isooctane | | 0.34 ± 0.02 | 0.40 ± 0.02 | |
| diethyl ether | 0.46 ± 0.02 | 0.46 ± 0.02 | 0.47 ± 0.02 | 0.47 ± 0.02 |
| tetrahydrofuran | 0.68 ± 0.03 | | | 0.54 ± 0.03 |
| acetonitrile | 0.88 ± 0.04 | 0.64 ± 0.03 | 0.68 ± 0.03 | 0.63 ± 0.03 |

Table VI. The Values of β Obtained by LIOAS for 1Py3NM, 1Py2In, 1Py3In, and 1N2NM Using Eq 7

| | 1Py3NM | 1Py2In | 1Py3In | 1N2NM |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| isooctane | | 0.11 ± 0.13 | 0.21 ± 0.09 | |
| diethyl ether | 0.38 ± 0.10 | 0.46 ± 0.11 | 0.48 ± 0.16 | 0.34 ± 0.04 |
| tetrahydrofuran | 0.55 ± 0.08 | | | 0.45 ± 0.05 |
| acetonitrile | 0.79 ± 0.09 | 0.58 ± 0.09 | 1.00 ± 0.12 | 0.66 ± 0.06 |

in tetrahydrofuran, and 8840 cm^{-1} in acetonitrile (for 1Py3NM, see Table IV).

26600 cm^{-1} = the energy difference between the relaxed locally excited state S_{1m} and the relaxed ground state S_0 . This quantity corresponds to the energy of 0-0 transition in the fluorescence spectrum of 1-methylpyrene.

$h\nu$ = the energy of an absorbed photon.

By plotting the amplitude of the optoacoustic signal as a function of the incident laser energy for both the reference and the sample, the ratio of the two slopes, α , is calculated using eq 3 (Figure 8 and 9, Table V). The ratio of the rate constant of internal conversion of the exciplex to the sum of the rate constants of all nonradiative pathways is given by β , calculated using eq 8 (Table IV):

$$\beta = k_{ice} / (k_{ice} + k_{iscc}) \quad (8)$$

Tables V and VI suggest an important influence of the solvent polarity on the α and β values. The large errors of the β values are inherently due to a 5% error of the α values.

For 1N2NM in diethyl ether the total decay rate of the exciplex equals $8.4 \times 10^7 \text{ s}^{-1}$.⁵⁸ As the quantum efficiency of the exciplex emission equals 0.2, the sum of k_{ice} and k_{iscc} equals $6.7 \times 10^7 \text{ s}^{-1}$. Combining those data with the value of β in Table VI yields $2.3 \times 10^7 \text{ s}^{-1}$ and $4.4 \times 10^7 \text{ s}^{-1}$ for k_{ice} and k_{iscc} , respectively. In the same way $5.6 \times 10^6 \text{ s}^{-1}$ and $9.0 \times 10^6 \text{ s}^{-1}$ can be obtained for k_{ice} and k_{iscc} for 1Py3NM in diethyl ether,¹ where the sum of the rate constants of all decay paths of the exciplex equals $2.2 \times 10^7 \text{ s}^{-1}$ at room temperature.

Transient Absorption Measurements. The transient absorption intensity of a solution of 1-methylpyrene in tetrahydrofuran at 420 nm is characterized by a decay in the microsecond range (Figure 10). A transient absorption was also observed at 420 nm ($T_1 - T_0$ transition) for 1Py3NM in tetrahydrofuran and acetonitrile, but the initial value of the absorbance is considerably lower than that obtained for 1-methylpyrene. As the optical densities at the excitation wavelength (320 nm) were identical for the three solutions (3.0), one can assume that immediately after the laser pulse the optical density at 420 nm is proportional to the quantum yield of triplet formation (immediately after the laser pulse, only a negligible decay of triplet has occurred). Based on a value of 0.49⁶⁵ for the quantum yield of intersystem crossing for 1-methylpyrene in tetrahydrofuran, the quantum yield for the formation of the pyrene triplet amounts to 0.40 and 0.20 for 1Py3NM in tetrahydrofuran and acetonitrile, respectively. The ratios of the transient absorbances of 1Py3NM over 1-methylpyrene amounted to 0.82 and 0.40 in tetrahydrofuran and acetonitrile, respectively.

As the exciplex decay time amounts to only 15 ns, the optical density at 420 nm immediately after the laser pulse is due to intersystem crossing from the locally excited state of pyrene and from the exciplex. Using the experimentally determined values of

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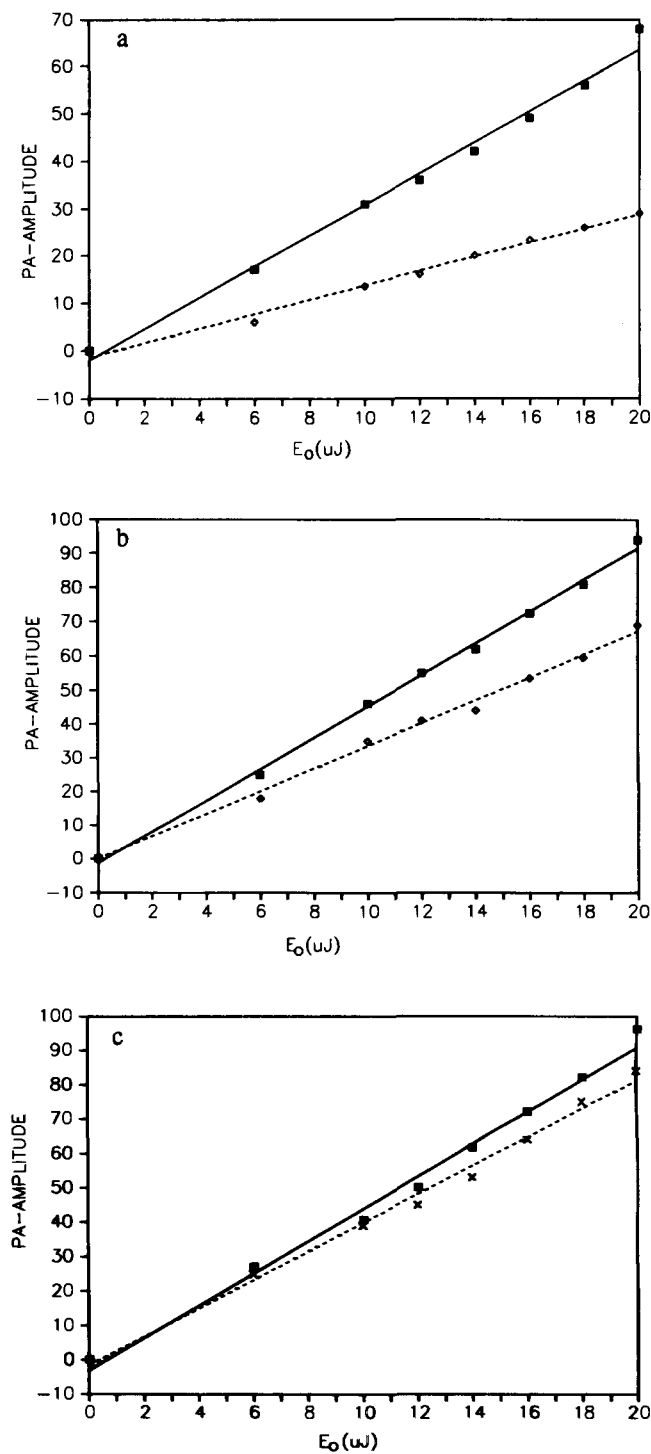


Figure 8. Dependence of the amplitude of the optoacoustic signal of 1Py3NM on the incident laser energy E_0 (μJ): (a) in diethyl ether, (—) 2-hydroxybenzophenone, (---) 1Py3NM; (b) in tetrahydrofuran, (—) 2-hydroxybenzophenone, (---) 1Py3NM; (c) in acetonitrile, (—) 2-hydroxybenzophenone, (---) 1Py3NM.

the fluorescence quantum yield of the locally excited state and the exciplex together with the total quantum yield for intersystem crossing, it is possible, using eq 9, to determine β from the total quantum yield of triplet formation (Φ_{isct}) obtained by transient absorption.

$$\Phi_{\text{isct}} = (1 - \Phi_{\text{for}})\Phi_{\text{iscm}}^0 + \Phi_{\text{for}}(k_{\text{isce}}/\sum k_{\text{ie}}) \quad (9)$$

with Φ_{iscm}^0 = quantum yield of intersystem crossing of 1-methylpyrene, $\sum k_{\text{im}} = k_{\text{fm}} + k_{\text{iscm}}$, and $\sum k_{\text{ie}} = k_{\text{fe}} + k_{\text{ice}} + k_{\text{isce}}$.

From the decay of the transient absorption (Figure 10) of 1-methylpyrene and 1Py3NM, a decay time of 24 μs was obtained for both samples.

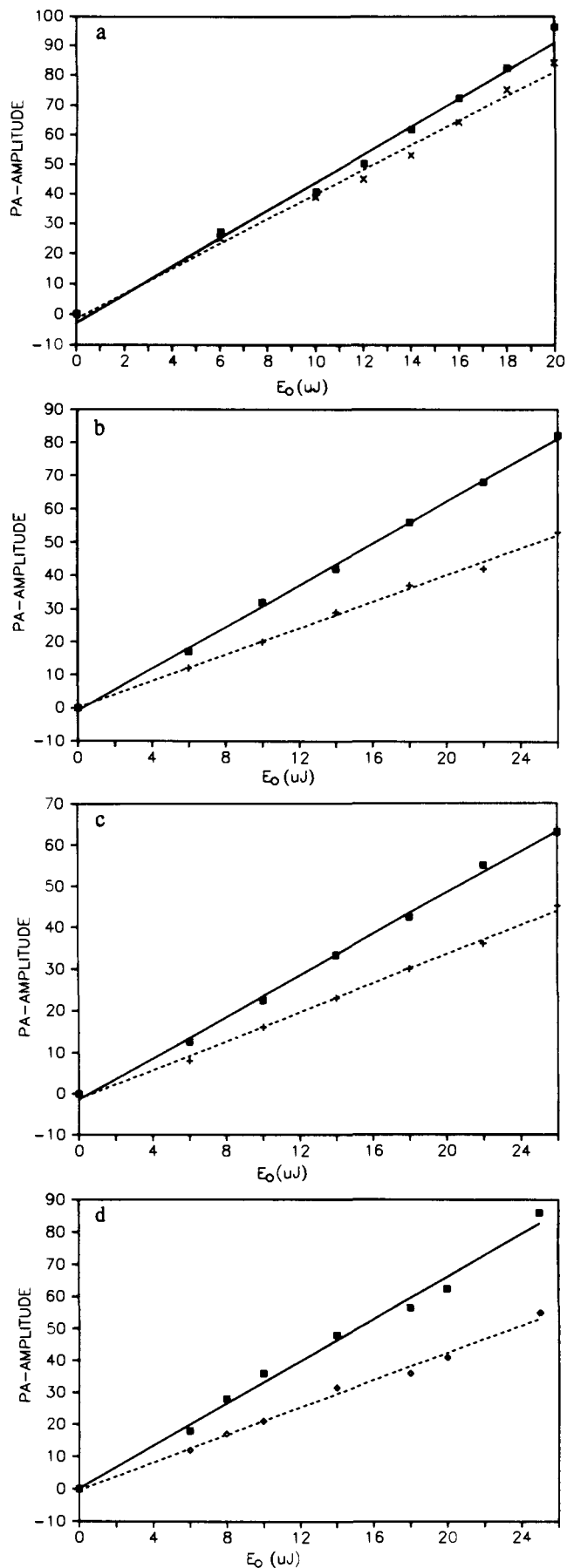


Figure 9. Dependence of the amplitude of the optoacoustic signal in acetonitrile on the incident laser energy E_0 (μJ). (a) (—) 2-hydroxybenzophenone, (---) 1Py3NM; (b) (—) 2-hydroxybenzophenone, (---) 1Py2In; (c) (—) 2-hydroxybenzophenone, (---) 1Py3In; (d) (—) 2-hydroxybenzophenone, (---) 1N2NM.

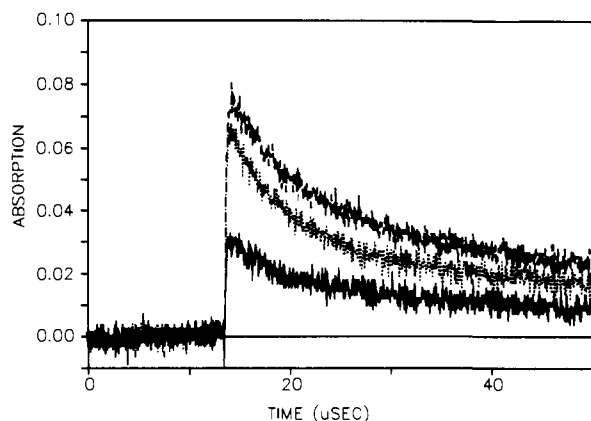


Figure 10. Decay of transient absorption at 420 nm: (---) 1-methylpyrene in tetrahydrofuran, (—) 1Py3NM in acetonitrile, (···) 1Py3NM in tetrahydrofuran.

Table VII. Calculated β Values for 1Py3NM from Optoacoustic (LIOAS) and Transient Absorption (TRABS) Experiments

| | LIOAS | TRABS |
|----------------------------------|-------|-------|
| $\beta_{\text{tetrahydrofuran}}$ | 0.55 | 0.52 |
| $\beta_{\text{CH}_3\text{CN}}$ | 0.79 | 0.81 |

Discussion

Evaluation of the Data Obtained by LIOAS. Figures 8 and 9 suggest a linear relationship between the amplitude of the optoacoustic signal H and the incident laser energy E_0 . This linearity indicates the absence of biphotonic processes and ground-state depletion. These biphotonic processes could be due to the presence of of $S_1 - S_n$ transition at the excitation wavelength. In that case the total absorption cross section of the sample would exceed that of the ground state. Because of the very short decay time of higher excited singlet states, the extra absorbed energy would be released completely as "prompt" heat. Since at 355 nm the $S_1 - S_n$ transition probability is higher⁶⁶ ($\epsilon = 21\,100\text{ L mol}^{-1}\text{ cm}^{-1}$) than the $S_0 - S_1$ transition probability ($\epsilon = 300\text{ L mol}^{-1}\text{ cm}^{-1}$) and the energy difference between the higher excited states and the lowest excited singlet state will predominantly be released as heat, the product $\epsilon_S \alpha_{S_n}$ will always exceed the product $\epsilon_{S_0} \alpha_{S_0}$. Therefore, this type of biphotonic effects can be expected to induce a positive deviation from a linear relationship between the optoacoustic amplitude H and E_0 at high incident laser energies E_0 . This effect is observed upon excitation of 1-methylpyrene at 355 nm.⁶¹ Therefore, all experiments were performed at the excitation wavelength of 320 nm where the $S_0 - S_1$ transition probability is much higher. A negative deviation from a linear relationship between H at high E_0 would indicate ground-state depletion effects. This depletion effect⁶¹ was not observed for the compounds investigated in this contribution.

Influence of the Solvent Polarity on the Branching Ratio between Internal Conversion and Intersystem Crossing. With increasing polarity an increase of either α and β is observed for both the pyrene and naphthalene derivatives. The increase of α correlates with the lower quantum yields of fluorescence of the locally excited state and of the exciplex observed in more polar solvents. The increase in β , giving direct information about the nonradiative behavior of the intramolecular exciplex, suggests that internal conversion is favored in more polar solvents. The values of β obtained by LIOAS for 1Py3NM correspond, within the experimental error, to those obtained by transient absorption. Both sets of β values suggest, contrary to former interpretations,^{6,7,58} that internal conversion is an important decay process of the intramolecular exciplex and that it becomes more important with increasing solvent polarity.

The difference in the solvent dependence of k_{ice} and k_{isce} can be explained in the framework of the current theory describing

electron transfer.^{67,68} The change in solvent polarity has a different influence on both reaction rates k_{ice} and k_{isce} . Assuming that the solvent is a uniform structureless dielectric, the electron-transfer rate k_{et} can be written as follows:

$$k_{\text{et}} = A \exp(-\Delta G^*/RT) \quad (10)$$

The free energy of activation ΔG^* for an electron-transfer process depends on both the overall free-energy change ΔG° and the sum of the intramolecular vibration (λ_i) and solvent (λ_s) reorganization energy accompanying electron transfer. ΔG^* for the charge recombination process is given by:^{69,70}

$$\Delta G^* = (\lambda/4)(1 + \Delta G^\circ/\lambda)^2 = \lambda/4 + \Delta G^\circ/2 + \Delta G^{\circ 2}/4\lambda \quad (11)$$

and λ is given^{7,69,70} by

$$\lambda = \lambda_i + \lambda_s \quad (12)$$

$$\lambda_s = \mu_e^2(f - f^{\text{op}})/2 \quad (13)$$

$$\lambda_i = 1/2 \sum f_i(Q_i)^2 \quad (14)$$

where f_i is the reduced force constant of the i th "inner shell" vibration and $\sum Q_i$ is the summation of the corresponding shifts of the equilibrium coordinates of all the intramolecular vibrations. f and f^{op} are two parameters describing the polarity of the solvent. For the solvation of an exciplex⁷, f and f^{op} are given by:

$$f^{\text{op}} = \frac{2}{8\pi\epsilon_0\rho^3} \left(\frac{n^2 - 1}{2n^2 + 1} \right) \quad (15)$$

and

$$f = \frac{1}{8\pi\epsilon_0\rho^3} \left(\frac{3\epsilon_r - 1}{2\epsilon_r + 1} \right) \quad (16)$$

n is the refractive index of the solvent, ϵ_r the static dielectric constant of the solvent, ρ the radius of the cavity of the solvent, and ϵ_0 the permittivity of the vacuum. λ_s is calculated using the reaction field theory,² and therefore the expressions resemble those determining the influence of solvent polarity on the emission maximum of the exciplex.^{71,72}

In strongly polar solvents competition between exciplex formation and the formation of a solvated radical ion pair can occur. For the nonradiative recombination of the radical ion pair, ΔG^* will still be given by eq 11, but the expression for λ_s must be replaced by:⁶⁹

$$\lambda_s = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r} - \frac{1}{R_c} \right) \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s} \right) \quad (17)$$

where $r(D^+) = r(A^-) = r$ are the effective radii for donor and acceptor ions, R_c the geometrical center-to-center D-A separation, and $\epsilon_{\text{op}} = n^2$ and $\epsilon_s = \epsilon_r$ are the optical and static dielectric constants of the medium.

While it has been suggested⁷³ that eq 10 and 11 are not only valid for solvent-separated radical ion pairs but also for exciplexes, the rate of internal conversion of the singlet excited state of some charge-transfer complexes could be fitted to eq 18⁷⁴ for values

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of ΔG° between -0.5 and -2.5 eV.

$$k_{\text{ice}} = A' \exp[\Delta G^\circ / B'] \quad (18)$$

As A' and B' in eq 18 are both positive constants, both expressions lead to an increase of the rate constant of the internal conversion when the charge recombination becomes less exergonic. Increasing the solvent polarity will make ΔG° less negative and increases λ_s for charge recombination from both the solvated radical ion pair and the exciplex to the ground state ($^1(D^+A^-)-S_0$ transition) or the locally excited triplet state ($^1(D^+A^-)-T_1$ transition). As for the charge recombination processes leading to the ground-state $\Delta G^\circ \ll -\lambda$ (Marcus inverted region⁶⁹), both effects will increase the rate constant of the charge recombination process. This could also explain the increase of the rate constant for internal conversion that was observed for the intermolecular exciplex between pyrene and dimethylaniline when the solvent polarity was increased.¹⁴

To a first approximation the ground-state repulsion of the exciplex E_{rep} corresponds to λ .⁷⁰ Therefore, $\Delta H^\circ - E_{\text{rep}}$ gives the difference between the relaxed locally excited singlet state and an energy content situated E_{rep} below the exciplex. Except for 1N2NM in tetrahydrofuran and acetonitrile, this demarcation level always lies between 6800 cm^{-1} (1Py2In in isoctane) and 820 cm^{-1} (1N2NM in diethyl ether) above the energy level of the locally excited triplet. This means that for 1N2NM in tetrahydrofuran and acetonitrile the free enthalpy change occurring upon intersystem crossing will be less negative than $-\lambda$ and the rate constant for intersystem crossing will decrease when the solvent polarity is increased. For the other systems the free enthalpy change occurring upon intersystem crossing will be more negative than $-\lambda$ and the rate constant for intersystem crossing will increase when the solvent polarity is increased.⁷⁵ This effect will, however, be more important for the internal conversion from the exciplex as this process is more exergonic than the intersystem crossing. Therefore, we can expect that increasing the solvent polarity leads to a considerably slower increase of the rate constant for intersystem crossing than of that for internal conversion. Increasing the solvent polarity will always favor the internal conversion process versus the intersystem crossing process for both the exciplex and the solvated radical ion pair. If it is argued that a transition to a more polar¹¹ exciplex occurs upon increasing the solvent polarity, this would, according to Mataga, decrease the rate of intersystem crossing versus that of internal conversion⁷⁵⁻⁷⁷ and therefore enhance the observed effect.

For 1N2NM and 1Py3NM the low fluorescence quantum yield of exciplex fluorescence in acetonitrile suggests that the formation of a solvent-separated radical ion pair is important.⁷⁸ However, for 1Py2In and 1Py3In the slight decrease of the quantum yield of exciplex fluorescence in acetonitrile suggests that for those molecules fluorescence quenching of the locally excited state still mainly leads to the exciplex in acetonitrile. In this aspect the results obtained for 1Py2In and 1Py3In resemble those obtained for 1-(1-pyrenyl)-1-(2-(*N*-methyl)indolyl)propane.⁴ Therefore, at least for the 1Py2In and 1Py3In, the increase of β observed upon increasing the solvent polarity can be discussed in the framework of Marcus theory. For the exciplexes with aliphatic amines, the interpretation of the increase of β in acetonitrile is less unambiguous. However, for 1N2NM the increase of β observed upon going from diethyl ether to tetrahydrofuran can still be interpreted in the framework of Marcus theory as it is not accompanied by a large decrease of the exciplex quantum efficiency which is given by the ratio $\Phi_{\text{fe}}/\Phi_{\text{for}}$.

In the exciplexes with an aliphatic amine, the carbon-nitrogen bending modes of the tertiary amine can be expected to be very effective "accepting modes" as they undergo an important rearrangement upon the reduction of the oxidized nitrogen.⁷⁹

Therefore, the reorganization energy will contain a large contribution of the intramolecular coordinates (eq 13). This effect is reflected in the observation that for exciplexes with aliphatic amines the ground-state repulsion is 3000 to 3600 cm^{-1} larger than for aromatic amines^{1,4,6,80,81} and that the emission spectra of exciplexes with aliphatic amines are characterized by a larger bandwidth^{6,7,81} than those with aromatic amines. Therefore, one would expect that for the aliphatic amines the internal conversion, which occurs far in the inverted region, would be enhanced versus the intersystem crossing, which occurs for values of ΔG° only slightly in the inverted region or even in the normal region. However, Table VI indicates that the values of β obtained for the aliphatic amines are not systematically larger than those obtained for the aromatic amines. While in the exciplex, where donor and acceptor are in contact with each other, the purely electronic part of the matrix element for the internal conversion process⁸² can be fairly large, that of the intersystem crossing^{17,83} will be considerably smaller. Therefore, the intersystem crossing can be expected to be a nonadiabatic electron-transfer process.^{20,83,84} The rate of this process will therefore be proportional to the square of the electronic part of the matrix element between the initial and the final state. This matrix element depends upon the nature and the relative orientation¹⁷ of donor and acceptor and will be larger when the orbitals of donor and acceptor are not parallel.¹⁷ This is the case in the equilibrium conformation of the exciplex of 1N2NM.^{85,86} This indicates that some caution is necessary when values of β obtained for different compounds are compared as the rate constants of electron transfer are not only determined by the activation energies and Franck-Condon factors but also by electronic factors. While for the exciplex of 1N2NM the intersystem crossing is in the normal region, it is in the inverted region for 1Py3NM. Although the rate constant for the intersystem crossing would change in an opposite way for both compounds upon increasing the solvent polarity, the values of β , nevertheless, exhibit the same change when the solvent polarity is increased from diethyl ether to acetonitrile. This would indicate that the increase of β is rather due to an increase of k_{ice} than to a decrease of k_{isce} . The former process is characterized by values of ΔG° close to the maximum of the Marcus parabola and will therefore be less dependent on ΔG° .

The Influence of Nuclear Tunnelling. The analysis of the LIOAS and transient absorption data indicates that the radiationless decay of the exciplex occurs, even in solvents of intermediate polarity, for a large part by internal conversion. This apparently contradicts previous results indicating a small (or even negative) activation energy and preexponential factor for the radiationless decay of exciplexes.^{1,6,7} A small activation energy and preexponential factor can, however, be obtained for electron transfer in the inverted region if important nuclear tunnelling occurs.^{67,87-89} The small preexponential factor is in this case due to a small Franck-Condon factor between the vibrational ground state of the exciplex and the vibrationally excited electronic ground state. This Franck-Condon factor will also modulate the matrix element between both states which can become several orders of magnitude smaller than in the absence of electron phonon coupling.⁹⁰ In the exciplex the undressed matrix element between the charge-transfer configuration and the ground state can be of the order of magnitude of 0.01 to 0.1 eV .^{2,85,86,91} Therefore one would expect that as far

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as this matrix element is responsible for the internal conversion, this electron-transfer process would be adiabatic and probably, in polar solvents, even controlled by solvent relaxation^{92,93} and intra- or interchromophore vibrations.^{94,95} However, the small preexponential factors obtained experimentally indicate that the transition is nonadiabatic due to the decrease⁹⁰ of the matrix elements by "phonon dressing". Following this line of thought, increasing the solvent polarity will make the electron transfer less exothermic, leading to the population of lower vibrational levels of the electronic ground-state characterized⁶⁷ by a larger Franck-Condon factor. The same effect will be obtained by an increase of the solvent reorganization energy. Both factors will increase the rate of the internal conversion when the solvent polarity is increased. As the internal conversion process is nonadiabatic, the influence of the inertial or dissipative properties⁹²⁻⁹⁴ of the solvent on this rate constant will be small. Also if the internal conversion would be induced by vibronic coupling,⁹⁶ the influence of the solvent polarity will appear mainly by a change of the Franck-Condon factors. The experimental⁶² values of the rate constants of fluorescence of different exciplexes between aromatic acceptors and aliphatic amines already differ by an order of magnitude. Therefore, the same variation can be expected for the matrix elements between the electronic part of the wave function of the exciplex and the ground state inducing the internal conversion. Therefore, it is very difficult to compare absolute values of k_{ic} and a fortiori of β obtained for different compounds. This difference of matrix elements between the electronic part of the wave functions could explain why the value of k_{ic} observed for 1N2NM in diethyl ether is larger than that observed for 1Py3NM in the same solvent in spite of the larger energy gap encountered for 1N2NM.

Conclusions

The radiationless decay of the intramolecular exciplexes between pyrene and indole or a tertiary aliphatic amine occurs by intersystem crossing, leading to the locally excited state of pyrene and internal conversion leading to the ground state. For the four compounds investigated in this contribution, both processes are important, but the internal conversion becomes more important upon increasing the solvent polarity. This can be rationalized in the framework of the current theories describing electron transfer

as the radiationless decay processes of the exciplex are actually charge recombination reactions.

These results contradict a previous interpretation that the low activation energies and small preexponential factors, obtained from Arrhenius plots of the radiationless decay of exciplexes,^{1,7,8,60} suggested intersystem crossing either to the triplet exciplex or to a locally excited state of the acceptor. As the internal conversion is a very exergonic process for the systems considered here, it is likely that the charge recombination will excite one or several high-frequency vibrational modes of the ground state. Although this process is characterized by a small Franck-Condon factor, it will, because of the smaller corresponding value of ΔG^\ddagger , still be more favorable than the formation of the vibrationally unexcited ground state.^{69,70} Beside the carbon-carbon stretching modes of the aromatic ring, also the carbon-nitrogen stretching and bending modes of the tertiary amine are very effective accepting modes as they undergo an important rearrangement upon the reduction of the oxidized nitrogen.⁷⁹

In highly polar solvents, the formation of a solvated ion pair either from the locally excited state of the pyrene or the exciplex cannot be excluded.^{9,10} In those solvents the energy of the solvated ion pair does not differ strongly from that of the exciplex, and the solvent reorganization energy for the charge recombination will be slightly larger. Therefore, one can expect that in those ion pairs the rate of intersystem crossing and internal conversion will have approximatively the same solvent dependence as in the exciplex. The value of β obtained for 1Py3NM in acetonitrile, where the quenching of the pyrene singlet mainly leads to the ion pair, is comparable to that obtained for 1Py2In, 1Py3In, or 1N2NM in acetonitrile where the quenching of the pyrene singlet still leads for at least 50% to the exciplex. This indicates that in the solvated radical ion pair the ratio between the rate constants for intersystem crossing and internal conversion is comparable to that in the exciplex.

As not only the intersystem crossing but also the internal conversion are nonadiabatic, the rates of these processes will depend upon the matrix elements between the electronic wave functions which can be considerably different for different systems. Therefore, some caution is necessary when values of β of different molecules are compared. However, the trends observed for different molecules as a function of solvent polarity will depend much less on the electronic interactions between the orbitals and can be compared for different molecules.

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