The shortest distance (2.82 Å) is for N-1(A)⋯N-3(U) and the longest (2.95 Å) for N-1(G)⋯N-3(C).

Conclusions

Partial deuteration of amino and imino groups in conjugated systems leads to isotope effects on carbon-13 chemical shifts and multiplet structure of the resonances of atoms bearing such groups as well as of the resonances of vicinal atoms. In aniline derivatives the isotope effects are larger for groups involved in intramolecular hydrogen bonds. Empirical expressions relate isotope effects with amino proton chemical shifts and hydrogen bond energies. These expressions can be useful for spectral assignments of the corresponding proton and carbon-13 resonances and for estimating hydrogen bond energies. The isotopic multiplets in the base resonances of nucleosides are modified upon base-pairing through intermolecular hydrogen bonds. Intimate details regarding hydrogen isotope exchange and relative hydrogen bond energies are thus revealed. The approach of isotopic multiplets should be applicable to the study of duplexes of oligonucleotides (in aqueous solutions), for which slow proton exchange has been demonstrated by proton NMR spectroscopy.[30]

Acknowledgment. The excellent technical assistance of David S. Rice is greatly appreciated.

Registry No. 1, 62-53-3; **2**, 82-45-1; **3**, 82-38-2; **4**, 99-92-3; **5**, 613-89-8; **6**, 18358-63-9; **7**, 619-45-4; **8**, 134-20-3; **9**, 85-91-6; **10**, 3694-52-8; **11**, 89-62-3; **12**, 612-28-2; A, 58-61-7; G, 118-00-3; U, 58-96-8; T, 50-89-5; C, 65-46-3.

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Photophysics of the Intramolecular Exciplex Formation in ω-(1-Pyrenyl)-α-*N*,*N*-dimethylaminoalkanes

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Abstract: The photophysical properties of ω-(1-pyrenyl)-α-*N*,*N*-dimethylaminoethane, -propane, -butane, and -octane are investigated. Excitation of the pyrene chromophore leads, in solvents of medium polarity, to the formation of an intramolecular exciplex, but the compounds with four and eight methylene groups in the alkyl chain do not show exciplex emission. The dipole moment and the emission energy of the exciplex decrease with increasing chain length. The kinetics of exciplex formation are analyzed in solvents of medium polarity using time-correlated fluorescence measurements. These results indicate that intramolecular exciplex formation in these compounds cannot be considered as the monomolecular analogue of intermolecular exciplex formation, but must be interpreted in the framework of rotational isomerism. The influence of the chain length on the exciplex formation process is evaluated. In polar solvents, such as acetonitrile, no exciplex emission is observed except for the compound with an ethyl chain. The standard free enthalpy of the radical ion pair is in this solvent some 10 kJ mol^{-1} lower than the standard free enthalpy of the intramolecular exciplex. The formation of the ion-pair state has been confirmed by picosecond transient absorption spectroscopy.

Complex formation in the excited state, in which the acceptor is an aromatic hydrocarbon molecule and the donor an amine (aromatic or aliphatic), has received substantial attention.[1-4]

Classically the kinetics of intermolecular exciplex formation can be described by Scheme I.[5,6]

Within the framework of this scheme the following equations for fluorescence quantum yields and fluorescence decay parameters can be derived.

$$\frac{\Phi_E}{\Phi_A} = \frac{k_5}{k_1}\frac{k_3}{Y}[D] \tag{1}$$

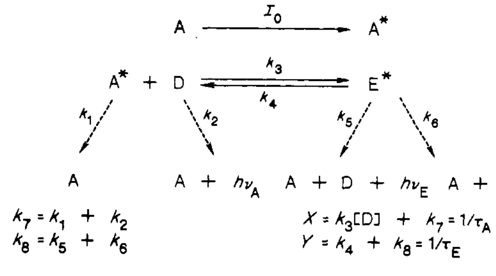
$$I_A(t) \approx \frac{k_1(\lambda_2 - X)}{\lambda_2 - \lambda_1}\{\exp(-\lambda_1 t) + C\exp(-\lambda_2 t)\} \tag{2}$$

$$I_E(t) \approx \frac{k_5 k_3[D]}{\lambda_2 - \lambda_1}\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \tag{3}$$

$$\lambda_{2,1} = \tfrac{1}{2}\{(X + Y) \pm ((X - Y)^2 + 4k_3k_4[D])^{1/2}\} \tag{4}$$

$$C = (X - \lambda_1)/(\lambda_2 - X) \tag{5}$$

Scheme I



At temperatures where k_4 is much smaller than k_8, these equations simplify to

$$\frac{\Phi_E}{\Phi_A} = \frac{k_5}{k_1}\frac{k_3}{k_8}[D] \tag{6}$$

$$I_A(t) \approx k_1\exp(-\lambda_2 t) \tag{7}$$

$$I_E(t) \approx \frac{k_5 k_3[D]}{\lambda_2 - \lambda_1}\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \tag{8}$$

$$\lambda_1 = Y \tag{9}$$

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$$\lambda_2 = X \qquad (10)$$

In this temperature region the slope of the curve ln (Φ_E/Φ_A) vs. $1/T$ equals the difference between the activation energies for k_8 and k_3 ($E_8 - E_3$).

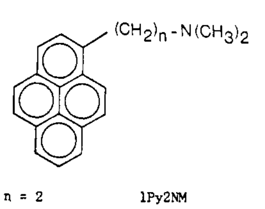
At temperatures where $k_4 >> k_8$, there exists a fast equilibrium between locally excited state and exciplex; A^* and E^* decay with the same decay parameter. In this temperature region eq 1 simplifies to

$$\frac{\Phi_E}{\Phi_A} = \frac{k_5}{k_1}\frac{k_3}{k_4}[D] \qquad (11)$$

In this case one obtains, from the variation of ln (Φ_E/Φ_A) vs. $1/T$, information about the stabilization enthalpy of the exciplex, $\Delta H° = E_3 - E_4$.

Linking donor and acceptor by an alkyl chain severely limits the translational and rotational freedom of both moieties[7] and influences the exciplex formation as well as the exciplex properties. Kinetic behavior different from that of Scheme I is observed in the formation of some intramolecular exciplexes.[8-10] Van der Auweraer and De Schryver[11] stressed the role of precursor conformations on the exciplex formation in ω-phenyl-α-N,N-dimethylaminoalkanes. A kinetic scheme was developed on the basis that when the orientation of the carbon–nitrogen bond is such that the nitrogen lone pair is trans in relation to the rest of the chain, exciplex formation, merely by chain folding, is impossible for steric reasons. Electron transfer from open-chain conformations is endothermic (except in the case of a very favorable donor–acceptor system, e.g., a cyano-substituted phenyl as acceptor[12] or in a very polar solvent, e.g., acetonitrile), and, therefore, exciplex formation in these "slow" amino rotamers becomes possible only after energy transfer to the amine, for, in the S_1 state of the amine the planar nitrogen allows the chain to fold.

In this study the photophysical properties of intramolecular exciplexes in the structure below are analyzed in solvents of different polarity in order to evaluate the influence of the chain length on exciplex formation and properties.



n = 2	1Py2NM
n = 3	1Py3NM
n = 4	1Py4NM
n = 8	1Py8NM

Experimental Section

The compounds 1PynNM (n = 2, 3, 4, 8) were obtained by the reduction of the amides, obtained from the acid chloride and the amine. Pyrenylacetic acid was obtained by hydrolysis of pyrenylacetamide, which was synthesized by a Willgerodt reaction[13,14] on acetylpyrene. A description of the synthesis of pyrenylpropanoic acid is given in ref 15. Pyrenylbutanoic acid was purchased from Eastman (Kodak). Pyrenyloctanoic acid was obtained from E. Roelants.[16]

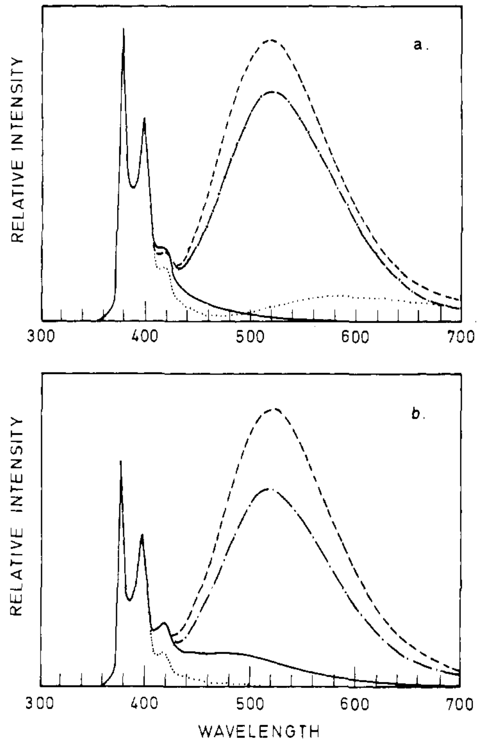


Figure 1. Fluorescence spectra of 1Py2NM (a) and 1Py3NM (b) in (—) ethyl ether (–·–) ethyl acetate, (- - -) tetrahydrofuran, and (···) acetonitrile at room temperature, normalized at 377 nm.

The solvents (Merck spectrophotometric grade) were checked for purity before use and if necessary purified using standard procedures.

Sample solutions were prepared to have a concentration of 1PynNM between 3×10^{-6} M (stationary measurements) and 10^{-5} M (nonstationary measurements) and were degassed by freeze–pump–thaw cycles.

Absorption spectra were measured with a Perkin-Elmer Lambda 5 UV/Vis spectrophotometer. Fluorescence spectra were measured with a Spex Fluorolog equipped with an emission corrector; the data were transferred to a Digital Equipment Corp. (DEC) PDP-11/23 computer.[17] The decay parameters were obtained by a nonlinear least-squares fitting of the fluorescence decay curves, measured using a frequency-doubled, cavity-dumped, mode-locked, synchronously pumped DCM–dye laser as excitation source (excitation wavelength: 335 nm) with time-correlated single-photon counting (tcspc) detection.[18] The following criteria were used to judge the goodness of fit:[18] the reduced chi-square (χ_ν^2), the standard normal variate of χ_ν^2 ($Z(\chi^2)$), the serial correlation coefficient (D.W.) of the residuals (R_i), the ordinary runs (Z(OR)), and the autocorrelation function (C_n).

Time-resolved transient absorption spectra were measured with a microcomputer-controlled picosecond Nd^{3+}–YAG laser photolysis system, the details of which are published elsewhere.[19,20]

Results

Influence of Solvent Polarity on the Emission Spectra. The compounds 1PynNM (n = 2, 3, 4, 8) do not form exciplexes in apolar media. The emission spectrum and the fluorescence lifetime (τ_A) of these compounds in isooctane are identical with those of 1-methylpyrene in isooctane at the same temperature. This can be explained by the following equations:[21]

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$$h\nu_{\epsilon}(\text{hexane}) = E^{\circ}{}_{\mathrm{D^+/D}} - E^{\circ}{}_{\mathrm{A/A^-}} - 0.15 \pm 0.1\ \text{eV} \qquad (12)$$

$$h\nu_{0\text{-}0} = h\nu_{\mathrm{E}} - \Delta H^{\circ} + E_{\mathrm{rep}} \qquad (13)$$

Values for the reduction potentials of triethylamine ($E^{\circ}{}_{\mathrm{D^+/D}}$) and 1-methylpyrene ($E^{\circ}{}_{\mathrm{A/A^-}}$) vs. SCE in acetonitrile are (0.78 ± 0.1) and −2.15 eV, respectively. The excitation wavelength of the pyrene chromophore ($h\nu_{0-0}$) is equal to 3.3 eV. With a value of 0.7 eV[22,23] for E_{rep}, the repulsion energy in the ground state, one obtains for the stabilization enthalpy of the exciplex, ΔH°, a value of +0.18 eV. From this positive value for ΔH° and the fact that ΔS° is certainly negative, one can conclude that the exciplex cannot be formed in an apolar medium.

A more polar solvent has to be used to stabilize the charge-transfer state and hence make exciplex formation possible.

In Figure 1 the fluorescence spectra of 1Py2NM (a) and 1Py3NM (b) in ethyl ether ($\epsilon_r = 4.3$), ethyl acetate ($\epsilon_r = 6.0$), tetrahydrofuran ($\epsilon_r = 7.6$), and acetonitrile ($\epsilon_r = 37.5$) at room temperature are shown. The spectra consist of the emission band of the pyrene chromophore with a maximum at 377 nm and a broad bathochromic structureless band. The absorption spectrum of these compounds is identical with that of 1-methylpyrene, and an excitation spectraum at an analysis wavelength in this bathochromic band does not deviate from the absorption spectrum. One can conclude that this band is due to the emission of the intramolecular exciplex in 1Py*n*NM (n = 2, 3). With increasing solvent polarity (ϵ_r between 4 and 20) the contribution of the exciplex fluorescence increases owing to the stabilization of the charge-transfer state, except in acetonitrile where the amount of exciplex emission decreases because of the formation of a radical ion pair in this solvent.[24,25] When the chain becomes larger than two methylene groups, the emission energy of the exciplex decreases and $\Phi_{\mathrm{E}}/\Phi_{\mathrm{A}}$ increases.

Increasing solvent polarity also shifts the exciplex emission maximum to longer wavelengths. This can be correlated to the following equation:[1]

$$\tilde{\nu} = \tilde{\nu}_{\mathrm{E}}(\text{vacuum}) - \frac{2(\mu_{\epsilon})^2}{4\pi\epsilon_0 hc\rho^3}\left(\frac{\epsilon_r - 1}{2\epsilon_r + 1} - \frac{1}{2}\,\frac{n^2 - 1}{2n^2 + 1}\right) \qquad (14)$$

(μ_{E} is the exciplex dipole moment, ρ is the solvent cavity radius). A plot ofthe exciplex emission maxima of 1Py2NM and 1Py3NM as a function of the emission maxima of a reference exciplex, formed between anthracene and *N*,*N*-diethylaniline, in the same solvents[26] yields a linear relation from which the exciplex dipole moments can be determined: 19.5 and 17.5 D for 1Py2NM and 1Py3NM, respectively (assuming a value of 12.5 D for the dipole moment of the exciplex formed between anthracene and *N*,*N*-diethylaniline[26]).

For the compounds 1Py4NM and 1Py8NM no exciplex emission is observed in any of the solvents used. However, in medium and strongly polar solvents the pyrene fluorescence is quenched. In accordance with the results of semiempirical calculations on 1Py4NM,[27] one can conclude that in this case an exciplex is formed, but because of the small value of the exciplex fluorescence rate constant ($k_5{}^0 \simeq 10^5\ \mathrm{s^{-1}}$), no exciplex emission is observed.

Kinetic and Thermodynamic Aspects. Results in Ethyl Acetate. The fluorescence spectrum of 1Py2NM and 1Py3NM at low temperatures in ethyl acetate consists mainly of emission from the locally excited state. With increasing temperature the fluorescence intensity of the locally excited state decreases and the exciplex emission increases. At room temperature a maximum for $\Phi_{\mathrm{E}}/\Phi_{\mathrm{A}}$ is reached; further increasing the temperature lowers this ratio again (Figure 2). At temperatures below −20 °C the approximation $k_4 << k_8$ can be applied. From the slope of the plot of ln ($\Phi_{\mathrm{E}}/\Phi_{\mathrm{A}}$) vs. $1/T$ (Figure 3) in this temperature region, the value for $E_3 - E_8$ can be determined: 18 and 16 kJ mol^{-1} for 1Py2NM and 1Py3NM, respectively. The wavelength of the exciplex emission maximum increases from 500 nm at 70 °C to 550 nm at −80 °C and can be related to the increase of the dielectric constant of ethyl acetate with decreasing temperature (cf. eq 14).

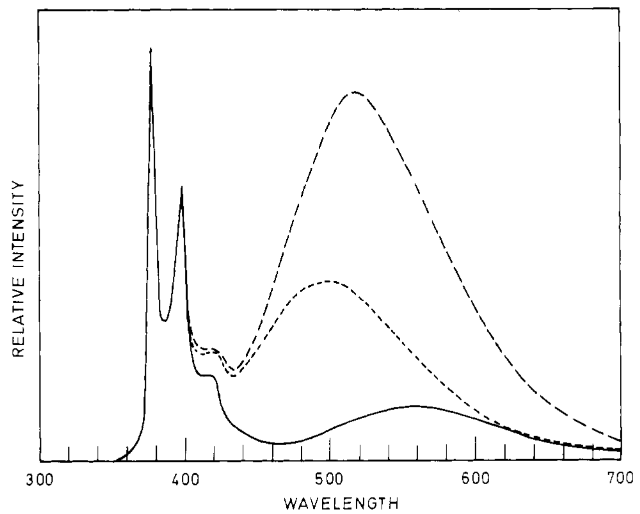

Figure 2. Fluorescence spectra of 1Py3NM in ethyl acetate at (—) −38 °C, (‒‒) 27 °C, and (‐‐‐) 70 °C, normalized at 377 nm.

Table I. Decay Parameters (ns) of the Emission at 377 and 500 nm as a Function of Temperature (°C) for 1Py2NM in Ethyl Acetate

T	$(1/\lambda_2)^{377}$	$(1/\lambda_1)^{377}$	$(1/\lambda_2)^{500}$	$(1/\lambda_1)^{500}$
−20	4.1	108	3.7	5.5
−27	4.5	112	6.0	3.5
−35	6.5	128	7.1	3.9
−40	7.0	130	8.0	3.7
−45	9.1	133	10.2	3.7
−49	9.2	150	10.8	3.8
−55	13.1	184	14.3	3.4
−60	14.7	200	*a*	*a*
−65	20.8	209	*a*	*a*
−71	21.6	209	*a*	*a*
−78	33.9	209	*a*	*a*

[a] Exciplex emission intensity too low to allow nonstationary measurements.

Table II. Decay Parameters (ns) of the Emission at 377 and 500 nm as a Function of Temperature (°C) for 1Py3NM in Ethyl Acetate

T	$(1/\lambda_2)^{377}$	$(1/\lambda_1)^{377}$	$(1/\lambda_2)^{500}$	$(1/\lambda_1)^{500}$
−30	7.0	94	5.7	8.8
−34	7.0	111	5.4	9.0
−40	10.3	126	9.7	6.8
−46	9.9	135	12.0	5.1
−50	11.7	158	13.0	5.9
−57	15.0	170	17.0	5.5
−64	20.9	185	22.0	5.1
−71	27.4	192	*a*	*a*
−78	37.0	186	*a*	*a*

[a] Exciplex emission intensity too low to allow nonstationary measurements.

At temperatures lower than −20 °C (−30 °C for 1Py3NM) the emission of 1Py2NM (and 1Py3NM) in ethyl acetate, monitored at 377 nm, shows two-exponential decay (Figure 4). In the same temperature region the emission, monitored at 500 nm, can be analyzed as a difference of two exponentials; the ratio of the preexponential terms (A_2/A_1) equals −1 within the experimental error (Figure 5).

The lifetime of the fast decaying component, $(1/\lambda^2)^{377}$, agrees with the growing-in of the exciplex $(1/\lambda_2)^{500}$. The slow component

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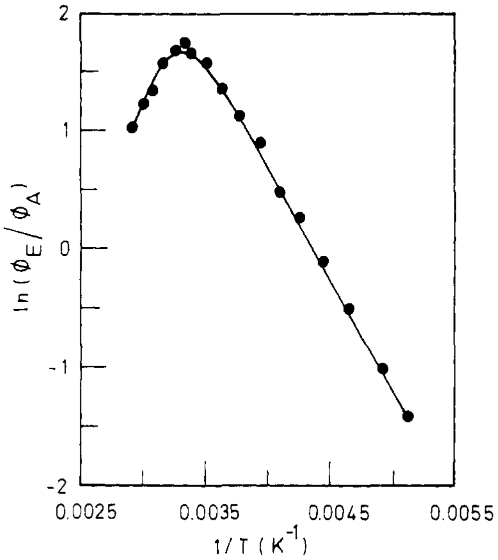


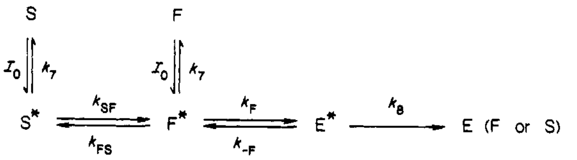
Figure 3. Influence of temperature on ln (Φ_E/Φ_A) for 1Py3NM in ethyl acetate.

of the decay, monitored at 377 nm, $(1/\lambda_1)^{377}$, decays slower than the exciplex $((1/\lambda_1)^{500})$ and converges to the lifetime of 1-methylpyrene in ethyl acetate at low temperatures (≤-65 °C) (Tables I and II). The ratio of the preexponential terms (A_2/A_1) of the fast and the slow component in the decay, monitored at 377 nm, is approximately 40 ± 10.

At temperatures above -20 °C (-30 °C for 1Py3NM) a third component is observed in the emission decay of the locally excited state of 1Py2NM and 1Py3NM in ethyl acetate; this component correlates with the exciplex decay $((1/\lambda 1)^{500})$ and comes from the dissociation of the exciplex.

It is clear that the decay measurements on 1Py2NM and 1Py3NM are not compatible with Scheme I. The intramolecular exciplex formation in these compounds can be analyzed according to Scheme II which was developed by Van der Auweraer.[11] F and F* are the ground state and the first excited singlet state of a set of conformations which have to overcome only a small energy barrier to form the exciplex; S and S* are the ground state and the first excited singlet state of a set of conformations which have first to undergo a geometrical change to F* to reach the exciplex conformation; E* and E are the exciplex and its repulsive ground state; k_7 and k_8 have the same meaning as in Scheme I.

Scheme II



When it is assumed that $k_{-F} << k_8$ and $k_{FS} << k_F + k_7$, the time evolution of the emission of the locally excited state ($I_A(t)$) and of the exciplex ($I_E(t)$) are given by the following equations.

$$I_A(t) \approx f_S\left(1 + \frac{k_{SF}}{k_F - k_{SF}}\right)\exp(-(k_{SF} + k_7)t) + \left(f_F - \frac{f_S k_{SF}}{k_F - k_{SF}}\right)\exp(-(k_F + k_7)t) \quad (15)$$

$$I_E(t) \approx \left(\frac{f_F k_F - k_{SF}}{k_D + k_7 - k_8} + \frac{f_S k_{SF}}{k_{SF} + k_7 - k_8}\right)\exp(-k_8 t) + \frac{f_F k_F - k_{SF}}{k_8 - k_F - k_7}\exp(-(k_F + k_7)t) + \frac{f_S k_{SF}}{k_S - k_{SF} - k_7}\exp(-(k_{SF} + k_7)t) \quad (16)$$

f_S is the fraction of the molecules originally in the set of conformations S; f_F is the fraction of the molecules originally in the set of conformations F.

Because of the small contribution of the slow conformations, S, to the exciplex formation in 1Py*n*NM (*n* = 2, 3) (f_S and k_{SF} small) it is possible to analyze the exciplex emission as a difference of two exponentials.

Using eq 15 and 16, k_F, k_{SF}, and k_8 can be determined from the data presented in Tables I and II. Plotting ln *k* vs. 1/*T* yields a linear relation for k_F, k_{SF}, and k_8 (Figure 6), from which the preexponential factors $k_F{}^0$, $k_{SF}{}^0$, and $k_S{}^0$ and the activation energies E_F, E_{SF}, and E_8 can be obtained (Table III).

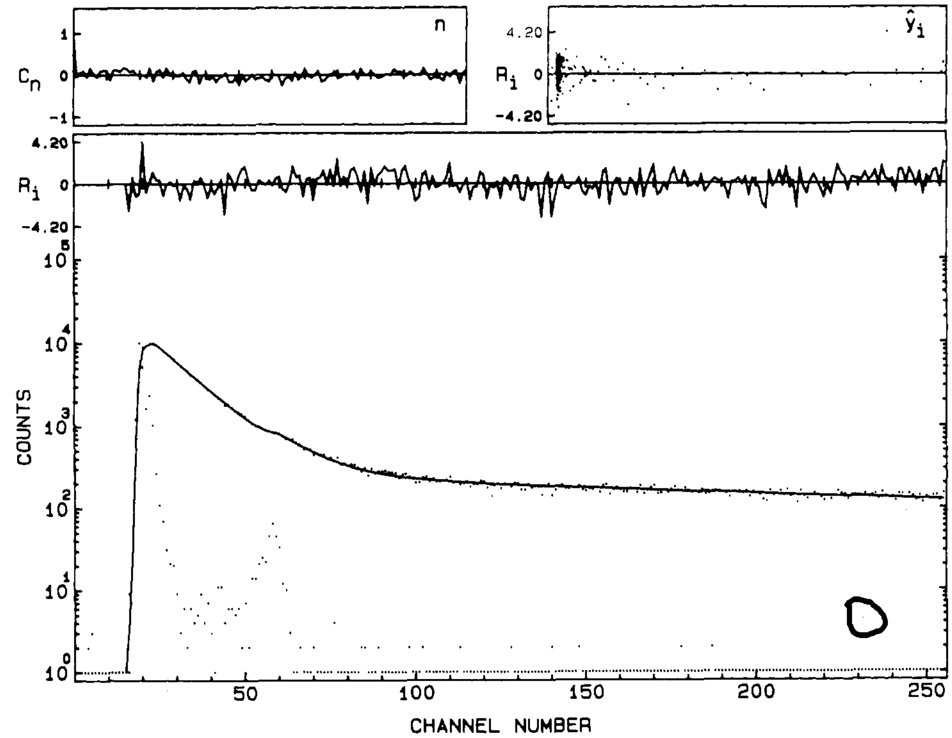


Figure 4. Decay of the emission of 1Py2NM in ethyl acetate at -20 °C monitored at 377 nm: channel width = 0.351 ns, χ_ν^2 = 1.16, $Z(\chi^2)$ = 1.78, D. W. = 2.07, Z(OR) = 0.74, $R_t[-2,2]$ = 94.6%, $1/\lambda_2$ = 4.1 ns, $1/\lambda_2$ = 108 ns, A_2/A_1 = 51.

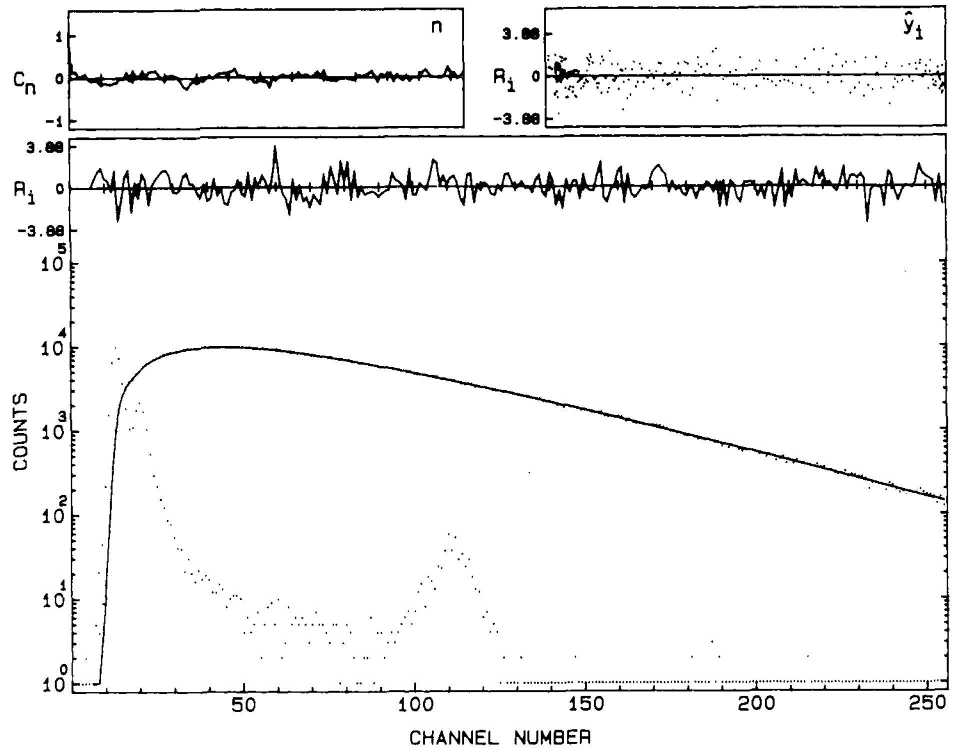


Figure 5. Decay of the emission of 1Py2NM in ethyl acetate at −20 °C monitored at 500 bm: channel width = 0.142 ns, $\chi_\nu^2 = 1.22$, $Z(\chi^2) = 2.44$, D. W. = 1.85, $Z(\text{OR}) = -0.82$, $R_i[-2.2] = 95.2\%$. $1/\lambda_2 = 3.7$ ns, $1/\lambda_1 = 5.5$ ns, $A_2/A_1 = -0.95$.

Table III. Kinetic Parameters for Exciplex Formation in 1Py*n*NM (n = 2, 3, 4, 8) in Ethyl Acetate (k_i^0 in s^{-1}, E_i in kJ mol^{-1})

	k_F^0	E_F	k_{SF}^0	E_{SF}	k_8^0	E_8
1Py2NM	5.5×10^{11}	16	9.3×10^{12}	30	9.8×10^6	−6
1Py3NM	7.1×10^{11}	17	1.9×10^{12}	26	2.6×10^6	−6
1Py4NM	1.7×10^{11}	21	*a*	*a*	*b*	*b*
1Py8NM	8.3×10^8	11	*a*	*a*	*b*	*b*

[a] Slow component in the emission decay of the locally excited state cannot be determined. [b] No exciplex emission observed.

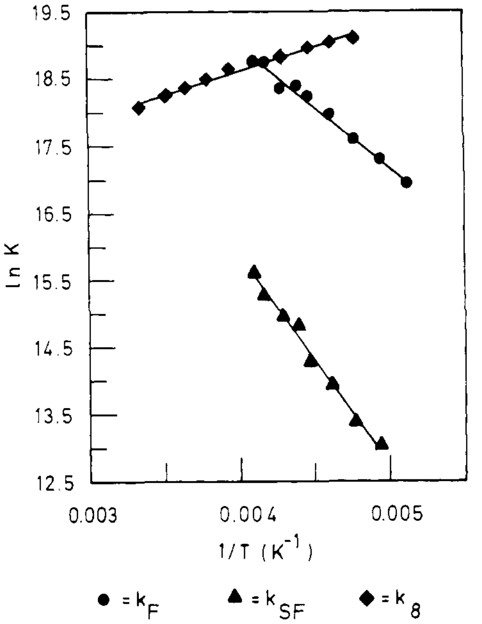


Figure 6. Influence of temperature on k_F, k_{SF}, and k_8 for 1Py3NM in ethyl acetate.

The value of $E_F - E_S$ is 22 kJ mol^{-1} for 1Py2NM and 23 kJ mol^{-1} for 1Py3NM. These values are larger than the value $E_3 - E_8$ determined by plotting ln (Φ_E/Φ_A) vs. $1/T$. This can be explained by eq 17 which gives the ratio of the quantum yields of exciplex and locally excited-state emission within the framework of Scheme II. This equation differs from eq 6 by the term between brackets.

$$\frac{\Phi_E}{\Phi_A} = \frac{k_5}{k_1}\frac{k_F}{k_8}\left[\frac{k_{SF} + f_F k_7}{f_S k_F + k_{SF} + k_7}\right] \tag{17}$$

At temperatures where $k_{SF} << f_F k_7$, this equation simplifies to

$$\frac{\Phi_E}{\Phi_A} = \frac{k_5}{k_1}\frac{k_F}{k_a}\left[\frac{f_F k_7}{f_S k_F + k_7}\right] \tag{18}$$

Assuming that k_1 and k_5 have the same temperature dependence, the derivative of ln (Φ_E/Φ_A) vs. $1/T$ is given by

$$\frac{\partial}{\partial(1/T)} \ln (\Phi_E/\Phi_A) = \frac{E_8 - E_F}{R} + \frac{\partial}{\partial(1/T)} \ln f_F + \frac{\partial}{\partial(1/T)} \ln \frac{k_7}{f_S k_F + k_7} \tag{19}$$

Upon increasing the temperature the increase of k_F will largely overcome changes in f_S, and thus the ratio $k_7/(f_S k_F + k_7)$ will decrease. When a small temperature dependence of f_F is assumed, the difference $E_3 - E_8$ observed in stationary measurements (eq 6) will be less than $E_F - E_8$, as observed.

The fluorescence decay of 1Py4NM and 1Py8NM in ethyl acetate below −10 °C is monoexponential. At higher temperatures the decay becomes two-exponential; the second component probably (unambiguous assignment of this component is impossible because the data for the exciplex region are not available) originates from dissociation of the exciplex. This agrees with the fact that in this temperature region Φ_A increases with increasing temperature while below −10 °C Φ_A increases with decreasing temperature. Simulations[18] of two-exponential decay curves with a short component, comparable in decay time with the observed fluorescence lifetime of 1Py4NM (or 1Py8NM) in ethyl acetate, and a long component, comparable in decay time and contribution with the decay parameter $(1/\lambda_1)^{377}$ determined for 1Py2NM and 1Py3NM in ethyl acetate (Tables I and II), show that the fitting parameters, when these decay curves are analyzed as two-exponentials, do not improve with regard to an analysis as monoexponentials. Moreover, the error in the determination of the long component is substantial. One can therefore conclude that the

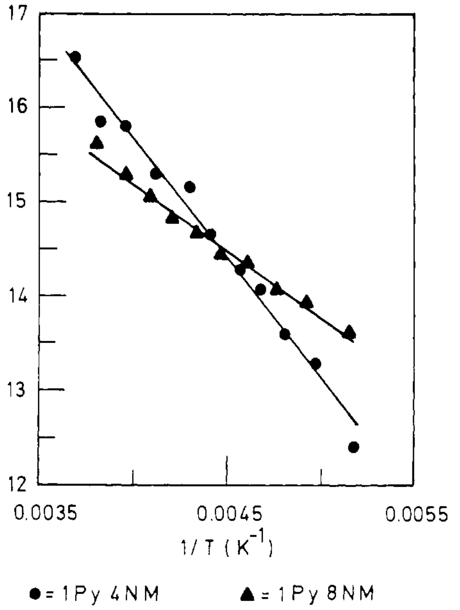


Figure 7. Influence of temperature on k_F for 1Py4NM and 1Py8NM in ethyl acetate.

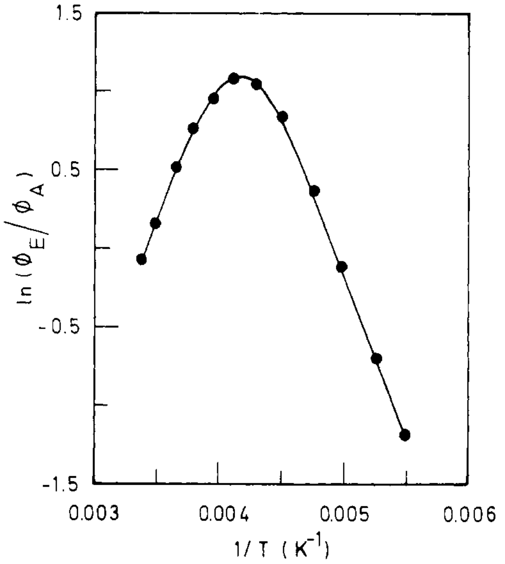


Figure 8. Influence of temperature on ln (Φ_E/Φ_A) for 1Py3NM in ethyl ether.

Table IV. Decay Parameters (ns) of the Emission at 377 and 500 nm as a Function of Temperature (°C) for 1Py2NM in Ethyl Ether

T	$(1/\lambda_2)^{377}$	$(1/\lambda_1)^{377}$	$(1/\lambda_2)^{500}$	$(1/\lambda_1)^{500}$
-20	3.1	53.1	3.2	52.5
-35	8.1	39.4	7.3	38.5
-45	7.6	34.6	8.5	34.4
-55		37.4	12.8	37.0
-65		49.9	13.0	50.7
-78		83.3	13.3	82.8
-91		131.1	*a*	*a*
-106		176.7	*a*	*a*

[a] Exciplex emission intensity too low to allow nonstationary measurements.

fluorescence lifetime of 1Py4NM and 1Py8NM below -10 °C corresponds to $(k_F + k_7)^{-1}$. The parameters k_F^0 and E_F (Table III) can be obtained from a temperature study of ln k_F (Figure 7).

Results in Ethyl Ether. Because of the very small value of Φ_E (Figure 1a), no stationary measurements (ln Φ_E/Φ_A) vs. $1/T$) were carried out on 1Py2NM in ethyl ether. The ratio Φ_E/Φ_A for 1Py3NM in ethyl ether reaches a maximum at -30 °C. From the linear part of the plot ln (Φ_E/Φ_A) as a function of $1/T$ at temperatures below -60 °C, a value of 17 kJ mol^{-1} for $E_3 - E_8$ can be determined, and from the linear part at temperatures above 1 °C, a value of -18 kJ mol^{-1} for $\Delta H°$ (Figure 8).

At temperatures above -20 °C the emission of 1Py*n*NM (n = 2, 3) in ethyl ether decays monoexponentially with the same decay time when monitored at 377 and 500 nm; in this temperature region $k_4 >> k_8$. At temperatures below -20 °C the fluorescence decay of 1Py2NM and 1Py3NM in the region of the locally excited state and in the exciplex region can be analyzed according to Scheme I (Tables IV and V). The condition $k_4 << k_8$ is valid at temperatures below -50 °C for 1Py2NM and below -60 °C for 1Py3NM.

Although slow conformations probably are present, simulations indicate that for the set of decay parameters it would not be possible to resolve them numerically. From the data in Tables IV and V k_F, k_{-F}, and k_8 can be determined; a temperature study yields values for the preexponential factors and activation energies on these rate constants (Table VI).

At temperatures lower than -40 °C, the emission of 1Py4NM in ethyl ether, monitored at 377 nm, shows monoexponential decay; the lifetime is equal to 189 ns at -40 °C and increases to 237 ns at -100 °C. Above -40 °C the decay becomes two-exponential, probably because of dissociation of the exciplex. The emission decay of 1Py8NM in ethyl ether is monoexponential; the fluorescence lifetime increases from 121 ns at -10 °C to 209 ns at -100 °C. Analysis of ln k_F as a function of temperature permits determination of k_F^0 and E_F (Table VI).

Results in Acetonitrile. The emission decay curves of 1Py*n*NM (n = 2, 3, 4) in acetonitrile, monitored at 377 nm, can be analyzed as a sum of two exponentials (Figure 9): a short and a long component which can be ascribed to fast and slow conformations. The contribution of the slow conformations in the emission of the locally excited state, $f_S(1/\lambda_1)^{377}/(f_S(1/\lambda_1)^{377} + f_F(1/\lambda_2)^{377})$, equals 45% for 1Py2NM in acetonitrile compared to 44% in ethyl acetate at the same temperature (-40 °C) (for 1Py3NM this factor equals 22% in acetonitrile and 24% in ethyl acetate). f_F/f_S equals 30 to 50. In view of a large error on the value f_F/f_S, a study of the variation with temperature of f_F/f_S or $(k_{SF} + k_7)^{-1}$ is not significant.

In Table VII the short decay parameter ($(k_F + k_7)^{-1}$) in the emission in acetonitrile of 1PynNM, monitored at 377 nm, is presented as a function of temperature. A remark concerning 1Py8NM should be made: no significant improvement is observed in the fitting parameters when the decay curves are analyzed as two-exponential compared to an exponential analysis.

Analysis of ln k_F vs. $1/T$ yields for the preexponential factors 4.6×10^{11}, 2.4×10^{11}, 2.6×10^{10}, and 2.0×10^{9} s^{-1} for n = 2, 3, 4, and 8 respectively. For the activation energies, E_F, values of 14, 13, 14, and 11 kJ mol^{-1} are obtained for n = 2, 3, 4, and 8, respectively.

Picosecond Transient Absorption Spectral Measurements. Picosecond time-resolved transient absorption spectra in strongly polar solvents have been measured for n = 3 and 4, in order to

Table V. Decay Parameters (ns) of the Emission at 377 and 500 nm as a Function of Temperature (°C) for 1Py3NM in Ethyl Ether

T	$(1/\lambda_2)^{377}$	$(1/\lambda_1)^{377}$	$(A_2/A_1)^{377}$	$(1/\lambda_2)^{500}$	$(1/\lambda_1)^{500}$	$(A_2/A_1)^{500}$
-20	2.2	77.4	0.56	1.9	75.0	-0.94
-30	3.2	59.2	0.97	3.3	59.9	-0.94
-40	6.1	47.8	1.46	6.4	45.7	-0.96
-50	11.1	38.7	2.12	11.6	37.6	-0.97
-60	13.2	36.8	3.12	16.9	35.4	-0.98
-70	27.7			25.8	33.3	-0.99

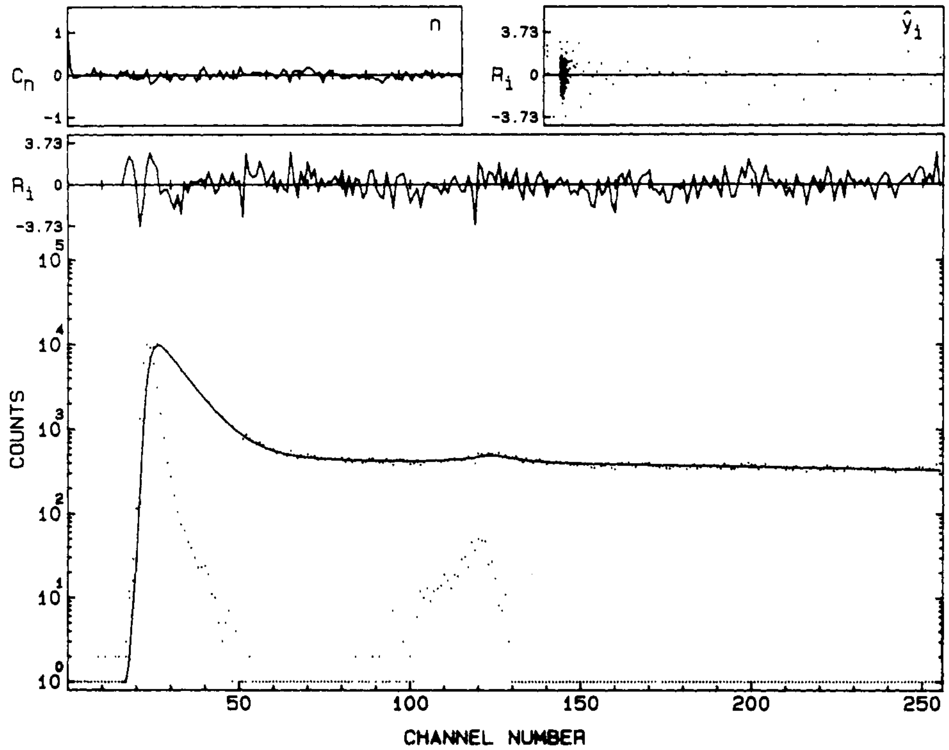


Figure 9. Decay of the emission of 1Py3NM in acetonitrile at 22 °C, monitored at 377 nm: channel width = 0.142 ns, $\chi_\nu^2 = 1.24$, $Z(\chi^2) = 2.59$, D.W. = 1.68, $Z(\mathrm{OR}) = -0.96$, $R_i[-2,2] = 92.1\%$, $1/\lambda_2 = 1.01$ ns, $1/\lambda_1 = 87$ ns, $A_2/A_1 = 34$.

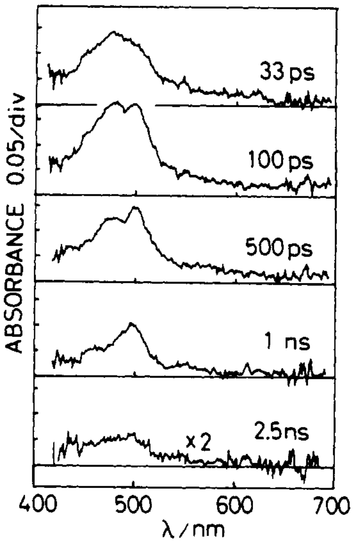


Figure 10. Picosecond time-resolved transient absorption spectra of 1Py3NM in acetonitrile at various delay times after excitation.

Table VI. Kinetic Parameters for Exciplex Formation in 1PynNM (n = 2, 3, 4,8) in Ethyl Ether (k_i^0 in s^{-1}, E_i in kJ mol^{-1})

	k_F^0	E_F	k_{-F}^0	E_{-F}	k_8^0	E_8
1Py2NM	1.7×10^{11}	16	1.0×10^{18}	47	*a*	*a*
1Py3NM	1.6×10^{11}	14	1.7×10^{17}	43	7.8×10^6	−3
1Py4NM	2.2×10^{10}	19	*b*	*b*	*a*	*a*
1Py8NM	2.6×10^8	9	*b*	*b*	*a*	*a*

[a] k_8 cannot be determined. [b] k_{-F} cannot be determined.

observe the formation of the intramolecular ion-pair state and its dynamics. Spectra for 1Py3NM in acetonitrile and acetone are shown respectively, in Figures 10 and 11.

In acetonitrile, the absorption band at 33 ps can be assigned almost completely to the $S_1 \rightarrow S_n$ transition localized in pyrene. With increase of delay time, one can observe the rise of the absorption band around 500 nm characteristic of the pyrene anion part and its successive decay. This is a direct demonstration of

Table VII. Short Decay Parameter (ns) in the Emission in Acetonitrile of 1PynNM (n = 2, 3, 4, 8), Monitored at 377 nm, As a Function of Temperature (°C)

T	1Py2NM	1Py3NM	1Py4NM	1Py8NM
79	0.25	0.45	5.2	17.5
65	0.27	0.53	6.3	20.2
50	0.35	0.62	7.6	21.6
36	0.39	0.77	9.3	
30				26.3
20	0.49	0.98	12.2	27.0
10				32.9
5	0.68	1.27	17.9	
−11	1.08	1.87	25.7	44.5
−24	1.61	2.93	32.0	
−28				59.8
−40	2.43	4.56		72.0

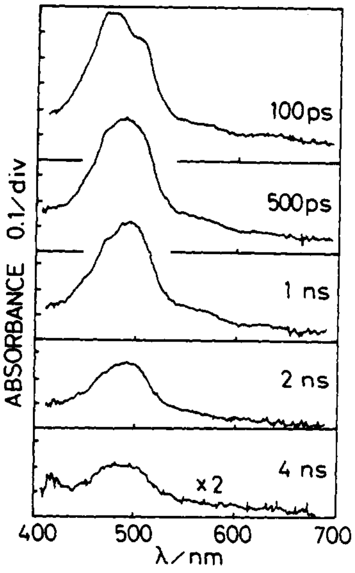


Figure 11. Picosecond time-resolved transient absorption spectra of 1Py3NM in acetone at various dealy times after excitation.

the formation and decay of intramolecular electron-transfer state for 1Py3NM in acetonitrile. In acetone, the absorption band can be assigned completely to the $S_1 \rightarrow S_n$ transition even at 100-ps delay time, reflecting the slower intramolecular electron transfer in the less polar solvent. Moreover, the absorption band shape of the electron-transfer state observed in acetone is broader compared with that in acetonitrile, indicating different structures of the electron-transfer state depending upon the nature of the solvent. This tendency, although less prominent in the present case, is similar to that observed in the case of ω-(1-pyrenyl)-α-*p*-*N*,*N*-dimethylanilinoalkane ($n = 3$) in polar solvents.[28,29]

It should be noted here, however, that the formation of a loose exciplex or ion-pair state followed by compact exciplex formation as observed in the case of ω-(1-pyrenyl)-α-*p*-*N*,*N*-dimethylanilinoalkane ($n = 3$) in acetone cannot be detected clearly in the present system. This result seems to indicate that rapid electron transfer in a loose conformation is difficult in the present system, which may be related to the pyramidal ↔ planar structural change associated with electron transfer of the present system as discussed below.

By separating the transient absorption spectra into the $S_1 \rightarrow S_n$ band of the pyrene part and the pyrene anion band at various delay times and by estimating the maximum concentration of the ion pair as well as the initial concentration of pyrene S_1 from the respective integrated absorption, we have obtained an approximate value of the quantum yield of intramolecular ion-pair formation for 1Py3NM in acetonitrile to be ca. 0.2. This value is considerably smaller than the corresponding ones of ω-(1-pyrenyl)-α-*p*-*N*,*N*-dimethylanilinoalkane ($n = 3$) (ca. 1.0), the free pyrene and *N*,*N*-dimethylaniline system (ca. 1.0), as well as the free pyrene and triethylamine system (ca. 0.5) in acetonitrile.[30,31] The much smaller ion-pair yield in the uncombined as well as combined pyrene/aliphatic amine system compared with the pyrene/*N*,*N*-dimethylaniline system may be ascribed to the higher probability of the charge recombination deactivation in the former system taking place in the course of electron transfer, to which the destablization of the ground state due to the pyramidal ↔ planar structural change will contribute.[30,31] The probability of such charge recombination deactivation will be further increased in the present $n = 3$ system compared with the free pyrene and triethylamine system owing to the restriction for the motion of the cation and anion parts in the former in contrast to their rapid dissociation in the latter.

Examination of the picosecond time-resolved transient absorption spectra of 1Py4NM in acetonitrile does not lead to the observation of such a clear-cut spectral change from the pyrene $S_1 \rightarrow S_n$ band to the pyrene anion-like band as in the case of 1Py3NM in acetonitrile, within the 5-ns delay time, because of the much slower electron transfer in the former than in the latter system (cf. Table VII).

Although exciplex emission is not detectable in acetonitrile solution, we have tried to observe the rise processof the electron-transfer state by substracting the $S_1 \rightarrow S_n$ band of the pyrene part in accordance with the observed fluorescence decay of the pyrene part of 1Py3NM. Owing to the lower accuracy of the transient absorption measurements compared with the tcspc studies in obtaining the time profile of the decay or rise processes, the error margin in the rise time obtained is larger with the former procedure. Nevertheless, such an analysis suggests the existence of a slightly faster rise of the electron-transfer state than the one detectable in the decay curve measurements of the fluorescence from the pyrene part. At the present stage of investigation, it is not possible to derive any final conclusion on this problem.

Discussion

Structural Aspects. By linking donor and acceptor by an alkyl chain, the number of spatial positions of the nitrogen with regard to the aromatic moiety becomes strongly limited. Changes in the chain length will lead to different positions of the nitrogen. Every possible position is characterized by the distance between the positive charge localized on the amino group and the center of the negative charge on the aryl nucleus.

Table VIII. Exciplex Dipole Moments and Coulomb Attraction Terms (*C*) for ω-Aryl-α-*N*,*N*-dimethylaminoalkanes[a]

	μ_E (D)	*C* (eV)	$C + h\nu_{0-0} + EA_A$ (eV)
P2NM	15.7	4.74	8.05
1N2NM	16.2	4.06	7.34
2N2NM	18.6	3.66	7.84
1Py2NM	19.5	3.33	7.18
P3NM	12.3	5.08	8.39
1N3NM	14.1	4.45	8.13
2N3NM	14.1	4.28	8.06
1Py3NM	17.5	3.93	7.78

[a] Phenyl: $n = 2$, P2NM; $n = 3$, P3NM. 1-Naphthyl: $n = 2$, 1N2NM; $n = 3$, 1N3NM. 2-Naphthyl: $n = 2$, 2N2NM; $n = 3$, 2N3NM. 1-Pyrenyl: $n = 2$, 1Py2NM; $n = 3$, 1Py3NM.

The stabilization of the charge-transfer state, which is the main contributing state to the exciplex wave function, by Coulomb attraction between the positive and negative charge will then be different for the different chain lengths. The repulsion energy may also differ. This leads to different exciplex emission maxima. The tendency toward exciplex formation will also be different. Concerning this last aspect, one also has to take into account entropic effects which counteract the exciplex formation with increasing chain lengths. As appears from Figure 1 both the wavelength of the exciplex emission maximum and the relative intensity of exciplex emission are larger for 1Py3NM than for 1Py2NM.

The chain length influences both the exciplex emission maximum and the relative exciplex emission intensity. In this context it can be pointed out that the intermolecular exciplex formed between 1-methylpyrene and triethylamine has an emission maximum at 500 nm in ethyl ether at room temperature,[32] while for 1Py2NM and 1Py3NM this maximum is situated at 470 and 480 nm, respectively, indicating that the absence of the chain permits the nitrogen to take up a position which further enhances the Coulomb attraction.

The dipole moment of the intermolecular exciplex amounts to 12 D while for the intramolecular systems the respective values of 17.5 ($n = 3$) and 19.5 D ($n = 2$) are found. The dipole moment increases with decreasing chain length. The same effect has been observed by Mataga for ω-(1-pyrenyl)-α-*p*-*N*,*N*-dimethylanilinoalkanes ($n = 1, 2, 3$).[33,34] For an aromatic amine the dipole moment of the exciplex (with the same number of methylene groups in the alkyl chain) appears to be smaller than for an aliphatic amine, e.g., 12 D for 3-(1-pyrenyl)-1-*p*-*N*,*N*-dimethylanilinopropane compared to 17.5 D for 1Py3NM. In an aliphatic amine the positive charge is localized on the nitrogen atom, while in an aromatic amine some of the charge is delocalized in the aromatic ring. The center of the positive charge can approach the center of the negative charge more closely for the same conformation of the propane chain in the case of an aromatic amine.

The experimentally determined dipole moments[23,35] and the calculated Coulomb attraction terms[27,36,37] for the intramolecular ω-aryl-α-*N*,*N*-dimethylaminoalkane exciplexes (aryl = phenyl, naphthyl, pyrenyl) are summarized in Table VIII. The Coulomb attraction decreases in the sequence benzene–naphthalene–pyrene.

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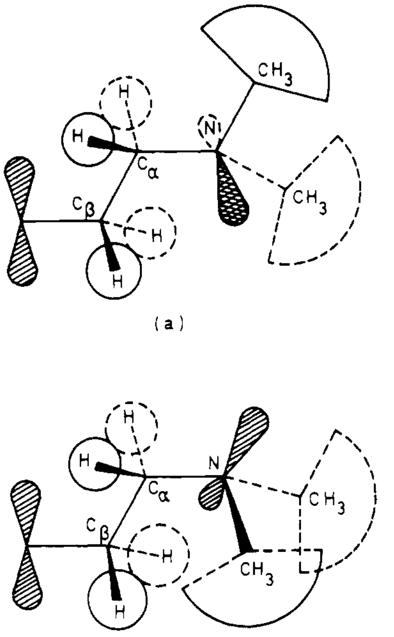


Figure 12. Scheme of the fast (a) and the slow (b) conformations at 1Py2NM. In (a) a rotation about the C_α–C_β bond leads to exciplex formation; in (b) this is not possible unless inversion of the nitrogen or rotation around the C_α–N bond takes place.

This is due to the fact that in larger aromatic systems the negative charge is more diffuse and the nitrogen is situated more excentric.

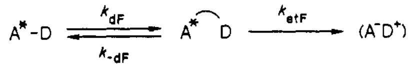
The exciplex conformation is close to an eclipsed conformation for $n = 2$ (which is a maximum in the conformational energy of an ethane chain in the ground state); for $n = 3$ the exciplex conformation is a g^+g^- conformation which is a minimum in the conformational energy of a propane chain in the ground state.

Kinetic Aspects. Fast and Slow Conformations. The fast and slow conformations may be ascribed to conformations of the alkyl chain itself or to orientations of the amino group toward the rest of the molecule.

In a linear alkyl chain conformational changes occur in 10 to 100 ps at room temperature;[38] the transition between slow and fast conformations amounts to some 10 ns. Therefore it is unlikely that the observed phenomena are related to conformational changes of the alkyl chain. Furthermore, NMR experiments carried out on 1Py2NM in chloroform at 30 °C[39] indicate that in the ground state 77% of the molecules are in the trans conformation and only 23% in the gauche conformation. NOE experiments in one-dimensional as well as in two-dimensional NMR on 1Py3NM in chloroform reveal that there is practically no interaction between the pyrene group and the methyl groups on the amine or the methylene group next to the nitrogen. So one can expect that in the ground state only a small percentage of the chain conformations are in a favorable position to form exciplex. The nonstationary measurements on these compounds show, however, that the fraction of fast conformations is much larger than the fraction of slow conformations ($f_F/f_S \geq 20$).

One can conclude therefore that the slow and fast conformations can be correlated with the orientation of the C–N bond in the same way as in the ω-phenyl-α-*N*,*N*-dimethylaminoalkanes[11,23] (Figure 12). In the case of 1Py8NM both orientations of the C–N bond permit the nitrogen lone pair to overlap with the pyrene; the difference between both conformations has disappeared.

Scheme III



$$A^*\text{-}D \underset{k_{-dF}}{\overset{k_{dF}}{\rightleftharpoons}} A^*\frown D \xrightarrow{k_{etF}} (A^-D^+)$$

The activation barrier for rotation around the C–N bond in $RCH_2NR'R''$ has been established by NMR studies[41] to be 23 to 26 kJ mol^{-1} with a conformational distribution at −170 °C of 85% "fast" and 15% "slow" conformations and a difference in free enthalpy between the two conformations of 2 kJ mol^{-1}. The facts that k_{SF}^0 and E_{SF} do not depend on the chain length and that the values determined for E_{SF} correlate very well with the activation energy for rotation around the C–N bond (Table III) suggest that exciplex formation in the slow conformations starts by rotation around the C–N bond to yield a fast conformation where favorable interactions between the nitrogen lone pair and the aromatic nucleus lead to the exciplex and proves the validity of Scheme II to analyze the kinetic behavior of the compounds 1PynNM.

Rate-Limiting Step in the Exciplex Formation. Intramolecular exciplex formation requires a conformational change in the chain. Scheme III can be written,[42] where $A^*\frown D$ represents the encounter conformation (for $n = 2$, a gauche conformation; for $n = 3$, a g^+g^- conformation) and (A^-D^+) represents the exciplex. Two alternatives have to be considered.

(1) k_{etF}, the rate constant for electron transfer is much larger than k_{-dF}. In this case the chain-folding step, k_{dF}, is rate determining ($k_F = k_{dF}$). The activation energy, E_F, must then be correlated with that of rotation around a single bond and k_F^0 must decrease upon increasing the chain length.

(2) The electron transfer involving the pyramidal ↔ planar vibrational motion, causing some additional free energy of activation and resulting in slowing down the electron-transfer process in the present case compared with the case of aromatic amine donor, is the rate-determining step ($k_{-dF} >> k_{etF}$); under those conditions k_F is given by

$$k_F = (k_{dF}/k_{-dF})k_{etF} = K_F k_{etF} \qquad (20)$$

with

$$K_F = K_F^0 \exp(-w_F/RT) \qquad (21)$$

$$k_{etF} = \kappa_{el}\Gamma_n\nu_n \exp(-\Delta G^{\ddagger}_{et}/RT)^{43} \qquad (22)$$

$$\nu_n \approx (1/\eta_0) \exp(-E\eta/RT) \qquad (23)$$

w_F is the energy difference between the encounter conformation and the average conformation of the chain. w_F equals 2 to 3 kJ mol^{-1} for an ethane system and 8 to 12 kJ mol^{-1} for a propane system.[7] One can assume that electron transfer is adiabatic in these systems so κ_{el}, the electronic transmission coefficient, can be set equal to one. Γ_n is a nuclear tunneling factor and ν_n a nuclear frequency factor which appears to be inversely proportional to the viscosity η[44] which is temperature dependent via E_η (eq 23).

This last hypothesis (2) can explain the results obtained for the exciplex formation in 1Py*n*NM (n = 2, 3, 4) (Tables III and VI). The electron transfer becomes more exothermic going from n = 2 to 3 because of the larger Coulomb stabilization. This leads to a decrease in $\Delta G^{\ddagger}_{et}$ and an increase in Γn. This effect compensates for the increase in w_F and the decrease in K_F^0. In the compound with four methylene groups in the chain, k_F^0 decreases with a factor 5 to 10; this corresponds to the decrease in K_F^0, while E_F increases a little because of the increase in w_F (the Coulomb stabilization is practically the same as in 1Py3NM[27]).

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(39) The gauche–trans conformational distribution of 1,2-disubstituted ethane compounds can be studied on the basis of the ^1H NMR spectrum, which can be analyzed as an AA′BB′ system. In the staggered conformation the system can appear in three rotational isomers: one trans conformation and two gauche conformations. N_{exp}, the sum of the coupling constants J_{AS} and $j_{AB'}$, can be obtained by direct analysis of the spectrum and can be expressed as $n_+(N_+ - N_g) + N_g$. n_+ is the molar fraction of the trans form and $N_t = J_t^g + J_t^t$, $N_g = J_g^g + (J_g^t + M_g^g)/$. J_i^j is the *j* coupling in the *i* conformation (t = trans, g = gauche). N_t and N_g and be obtained from ref 40.

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When the chain length increases to eight methylene groups, $k_F{}^0$ (factor 100 to 200) as well as E_F (factor 2) decrease strongly. Increasing the chain length decreases the relative probability of a conformational transition leading to an encounter conformation ($k_{dF}{}^0$) and decreases the steric hindrance between the end groups (E_{dF}) (a cooperativity for the rotations becomes possible).

At the same temperature and for the same compound k_F increases with increasing solvent polarity. This points to electron transfer as the rate-limiting step. It is not meaningful to draw more refined conclusions from these data in view of the very complex influence of the solvent (ϵ_r, η) on k_F.

Exciplex Decay. In all the systems studied the exciplex decay (k_8) is characterized by a small preexponential factor. The apparent activation energy, E_8, is negative. In a polar solvent the exciplex can dissociate to a solvated ion pair.[24,25,45] This is demonstrated by the fact that the exciplex lifetime decreases with increasing solvent polarity. In 1Py3NM this decrease is observed by changing from ethyl ether to ethyl acetate. The decrease in exciplex lifetime of 1Py2NM in ethyl acetate and of 1Py3NM in ethyl ether and ethyl acetate upon decreasing the temperature can be explained in the same way. With decreasing temperature the solvent becomes more polar, the solvated ion pair becomes more and more stabilized compared to the exciplex[45] (also the entropy decrease associated with the larger solvation of the free ions will become less important at lower temperatures), and the energy barrier between both states decreases. When this effect is larger than E_η, the rate of exciplex ionization can increase with decreasing temperature and can lead then to a negative activation energy. In the case of the pyrenylalkylamine exciplexes the enthalpy change upon transition from the exciplex to the solvated ion pair is much larger than E_η.

There is a possibility that the radiationless transition of the exciplex itself to the ground state is enhanced in polar solvents owing to the decrease of the relevant energy gap by solvation. This effect may contribute also the observed lifetime shortening in more polar solvents.

Conclusion

The present results confirm that intramolecular excited-state interactions are possible for a variable number of methylene groups between both chromophores. The chain does, however, prevent the two chromophores from adopting the most favorable geometry which is found in the intermolecular case; this effect is more pronounced in the case of shorter chains leading to a smaller Coulomb stabilization and a larger dipole moment (17.5 D for 1Py3NM, 19.5 D for 1Py2NM).

The absence of the quenching of the pyrene emission in 1Py*n*NM in an apolar medium is due to the positive free-enthalpy gain. Kinetic analysis of the exciplex formation in 1PynNM in medium polar and polar solvents shows that in these systems k_3 must be replaced by two rate constants: k_F and k_{SF}, the last one being the rate constant for rotationa around the C–N bond; $k_{SF}{}^0 \simeq 10^{12}$ â 10^{13} s^{-1} and $E_{SF} \simeq 26$ â 30 kJ mol^{-1}.

$k_F{}^0$ and E_F do not depend much upon the chain length for $n = 2$ and 3 ($k_F{}^0 \simeq 6$ â 7×10^{11} s^{-1} and $E_F \simeq 16$ â 17 kJ mol^{-1} in ethyl acetate). This is also true in the corresponding naphthyl compounds.[35] In the phenyl compounds,[11,23,42] on the contrary, E_F and especially $k_F{}^0$ decrease by transition from $n = 2$ to 3; moreover, $k_F{}^0$ is for the same chain length and in the same solvent larger ($k_F{}^0 \simeq 10^{13}$ s^{-1} in tetrahydrofuran) than in the naphthyl or pyrenyl compounds. From this one can conclude that in the phenyl compounds k_{etF} is sufficiently exothermic to enhance the influence of the chain length. One can also point out that E_F is smaller for the naphthyl compounds ($E_F \simeq 12$ kJ mol^{-1} in tetrahydrofuran) than for the corresponding pyrenyl compounds. This can be related to the term $C + h\nu_{0-0} + \mathrm{EA_A}$ ($\mathrm{EA_A}$ is the electron affinity of the acceptor) (Table VIII); for the same donor the exciplex formation becomes less exothermic in a larger aromatic system.

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Registry No. 1Py2NM, 92977-93-0; 1Py3NM, 85425-02-1; 1Py4NM, 92989-91-8; 1Py8NM, 105501-81-3.

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