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Intermolecular Exciplex Formation between Pyrene Derivatives and 1,2-Dimethylindole

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Abstract: The photophysics of exciplex formation between pyrene derivatives and 1,2-dimethylindole are investigated in solvents of different polarity. Thermodynamic and kinetic data are obtained by stationary- and nonstationary-state fluorescence measurements as a function of temperature. The importance of ion formation in these systems is investigated as a function of the acceptor properties of the pyrene derivative and as a function of the solvent polarity.

Quenching of the fluorescence of aromatic compounds by aromatic and aliphatic amines is a well-known phenomenon.[1-3] In many cases, fluorescent donor-acceptor complexes are formed in the excited state, which usually have a large dipole moment, evidenced by the strong dependence of their fluorescence maxima upon solvent polarity.[4] The fluorescence quantum yields of such exciplexes are known to decrease upon increasing solvent polarity, because of deactivation of the exciplex via dissociation to radical ions, although electron transfer may occur prior to complex formation in polar solvents.[5,6]

In this paper we wish to present some results concerning quenching and exciplex emission of pyrene derivatives in the presence of 1,2-dimethylindole (1,2-DMI). This quencher was chosen in view of its frequent occurrence in biological systems. The obtained information would be a basis to provide insight in the interaction between excited pyrene- and indole-like moieties in peptides or enzymes which are currently labeled with a pyrene group. From such a study information about peptide or enzyme dynamics could be gained.

Experimental Section

Hexadecane (Aldrich) was purified by being passed over activated carbon and activated SiO_2, followed by a fractional destillation under diminished pressure (T_k 149 °C (10 mm Hg)). The purity, checked by gas chromatography, exceeded 99.8%. Dibutyl ether, diethyl ether, THF, and Me-THF were refluxed for 48 h on Na/K alloy and distilled prior to use.

Acetone, dimethylacetamide, ethyl acetate, and butyl acetate were dried on molecular sieves and distilled prior to use. Acetonitrile was refluxed for 48 h on $MgSO_4$ followed by a fractional distillation.

The other solvents used were the purest commercially available and were used without further purification. 1,2-DMI (Aldrich) was purified by repetitive vacuum sublimation. The different pyrene derivatives were prepared as described in the literature[7] and purified by HPLC. The purity always exceeded 99.9%.

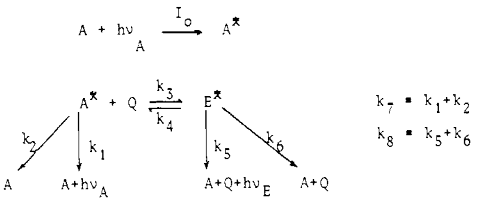
Absorption spectra were measured on a Perkin-Elmer double-beam spectrophotometer. Corrected fluorescence spectra were measured on a "Fica 55 spectrofluorimètre différentiel absolu".

The quantum yields were measured by using quinine sulfate in 1 N H_2SO_4 as a standard. The absorbance (OD) never exceeded 0.1. The quantum yield of un unknown sample is than given by

$$\phi_{\text{sample}} = \phi_{\text{standard}}\text{OD}_{\text{standard}}n^2_{\text{sample}}A_{\text{sample}}/A_{\text{standard}}\text{OD}_{\text{sample}}n^2_{\text{standard}}$$

ϕ, OD, A, and n are respectively the quantum yield, the absorbance, the area under the fluorescence spectrum, and the refractive index of the sample solution and the standard solution. All solutions were degassed by four freeze-pump-thaw cycles. The individual rate constants were determined from the decay parameters and preexponential factors obtained by a nonlinear least-squares fitting of the fluorescence decay curves obtained by time-correlated single-photon counting.

Scheme I



Four criteria were used to judge the goodness of fit: χ^2, the weighted residuals (R_i), the autocorrelation function (C_i), and the serial correlation coefficient (D).[8]

The decay curves were rejected when a visual inspection of R_i or C_i vs. channel number showed nonrandom behavior. For χ^2 the maximum allowed value was 1.25. For D, the minimum value was 1.61 to 1.57 for respectively one- and two-exponential decay.

Two different methods were used to obtain the rate constants. Whenever λ_1, λ_2, and A (eq 3 and 5) could be obtained with high accuracy ($1/\lambda_1$, $1/\lambda_2 > 3$ ns, $20 > A > 1$), measurements of λ_1, λ_2, and A were carried out at different temperatures. Whenever this condition was not fulfilled, λ_1 and λ_2 were obtained at different quencher concentrations at different temperatures, and the method of Ware[9] was used to obtain the rate constants.

The latter method is the more accurate one, but a comparison of rate constants obtained by the two methods showed that within experimental error the same values for the rate constants were found.

Results

The absorption spectrum of 1,2-DMI consists of a broad band centered around 282 nm with a maximal extinction coefficient of 7000 L mol^{-1} cm^{-1}. It does not, however, extend above 320 nm in all the solvents used. The S_0-S_1 band of pyrene (P) is situated at 372 nm, but because of the low extinction coefficient at this wavelength (ϵ = 150 L mol^{-1} cm^{-1} in isooctane) the chromophore was excited at 335 nm into its ^1L_a band with an ϵ of 3.5 × 10^4 L mol^{-1} cm^{-1}.

The excitation wavelength of 1-methylpyrene (CH_3P) was 342 nm and that of 1-cyanopyrene (CNP) 354 nm. Mixtures of 1,2-DMI with any of the pyrene derivatives did not show a new absorption band at any concentration of 1,2-DMI in any solvent used, indicating that important interactions in the ground state did not occur.

Upon excitation at 354 nm of a 2 × 10^{-5}M solution of CNP containing DMI in isooctane at room temperature, a new emission band is observed to the red of the emission of CNP (380 nm) with

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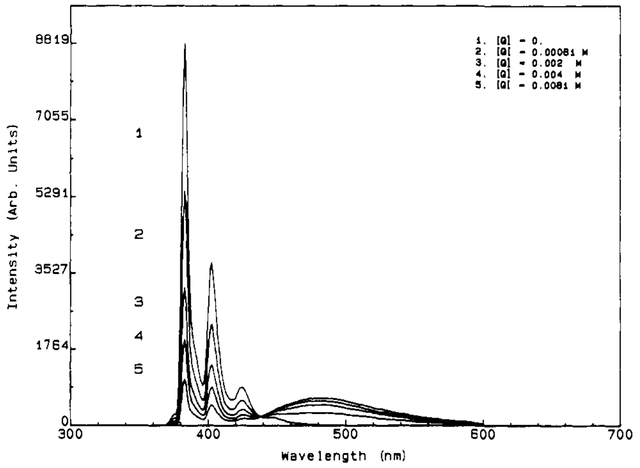

Figure 1. Fluorescence spectra of 1-cyanopyrene (2 × 10^{-5} M) in isooctane at 25 °C with varying concentrations of 1,2-dimethylindole.

a maximum at 478 ± 2 nm (Figure 1). Excitation spectra at respectively 381 and 495 nm are identical with the absorption spectrum of CNP, indicating that the emission is due to a complex in the excited state. Since this band is absent in solutions not containing DMI, the complex is formed between the excited pyrene derivative and DMI.

Results in Nonpolar Solvents. In nonpolar solvents, the kinetics of exciplex formation and disappearance follow the kinetics in Scheme I.[9,10] Within the framework of this scheme, the following relations for fluorescence quantum yields and fluorescence decay parameters can be derived.

$$[\phi^{\mathrm{F}}_{\mathrm{A}_0}/\phi^{\mathrm{F}}_{\mathrm{A}}] - 1 = \frac{k_3 k_8[\mathrm{Q}]}{k_7(k_4 + k_8)} = K_{\mathrm{SV}}[\mathrm{Q}] = k_q\tau_0[\mathrm{Q}] \qquad (1)$$

$$\phi^{\mathrm{F}}_{\mathrm{E}}/\phi^{\mathrm{F}}_{\mathrm{A}} = \frac{k_5 k_3[\mathrm{Q}]}{k_1(k_4 + k_8)} \qquad (2)$$

$$i_{\mathrm{A}}(t) = \frac{k_1(\lambda_2 - X)}{(\lambda_2 - \lambda_1)}[\exp(-\lambda_1 t) + A\exp(-\lambda_2 t)] \qquad (3)$$

$$i_{\mathrm{E}}(t) = \frac{k_5 k_3[\mathrm{Q}]}{(\lambda_2 - \lambda_1)}[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \qquad (4)$$

$$\lambda_{1,2} = \tfrac{1}{2}[(X + Y) \mp \{(X - Y)^2 + 4k_3k_4[\mathrm{Q}]\}^{1/2}] \qquad (5)$$

$$A = (X - \lambda_1)/(\lambda_2 - X) \qquad (6)$$

On the basis of a study of the quantum yields and the decay parameters as a function of the quencher concentration, all relevant kinetic parameters of Scheme I can be determined. If all the rate constants are available at different temperatures, the thermodynamic properties of the exciplex can be calculated.

Stationary quenching experiments of CNP in isooctane at room temperature with varying concentrations of 1,2-DMI give a Stern–Volmer quenching constant K_{SV} equal to 702 L mol^{-1}. An identical value is obtained from the measurements of the single exponential decay curves of the fluorescence of locally excited CNP analyzed at 382 nm. Upon raising the temperature to 48 °C the K_{SV} value increases to 840 L mol^{-1}. The fluorescence decay of the exciplex, analyzed at 495 nm, could be described at these two temperatures as the difference of two exponentials.

These experimental results indicate that in this solvent in the temperature range studied $k_4 \ll k_8$, so the association rate k_3 can be calculated from K_{SV} and a value of 1.63 × 10^{10} L mol^{-1} s^{-1} is obtained at room temperature, which is equal to the rate constant for diffusion in isooctane at that temperature.

The fluorescence decay of the locally excited state remained a single exponential up to the boiling point of the solvent, so k_4 could not be determined, and a complete analysis of the thermodynamics for exciplex formation was not possible. For this reason, the system was studied in hexadecane, which has a much higher boiling temperature.

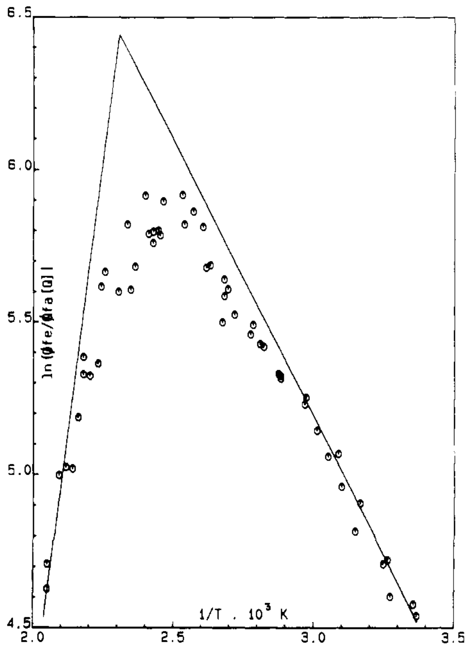

Figure 2. Stevens–Ban plot of 1-cyanopyrene (2 × 10^{-5} M)/1,2-dimethylindole (3.65 × 10^{-3} M) in hexadecane.

Table I. Kinetic and Thermodynamic Parameters for the System CNP/1,2-DMI in Hexadecane

k°_2	1.4 × 10^7 s^{-1}
k°_6	1.9 × 10^7 s^{-1}
k°_3	5.25 × 10^{11} L/(mol s)
k°_4	1.6 × 10^{14} s^{-1}
E^{a}_2	0.05 kcal mol^{-1}
E^{a}_6	0.4 kcal mol^{-1}
E^{a}_3	3.1 kcal mol^{-1}
E^{a}_4	14.0 kcal mol^{-1}
$\Delta H^\circ_{\mathrm{nstat}}$	−11.9 kcal mol^{-1}
$\Delta S^\circ_{\mathrm{nstat}}$	−13.5 esu
ΔG°(25 °C)	−7.9 kcal mol^{-1}
$\Delta H^\ddagger_3$	2.3 kcal mol^{-1}
$\Delta S^\ddagger_3$	−6.9 esu
$\Delta G^\ddagger_3$	4.4 kcal mol^{-1}
$\Delta H^\ddagger_4$	13.4 kcal mol^{-1}
$\Delta S^\ddagger_4$	5.5 esu
$\Delta G^\ddagger_4$	11.8 kcal mol^{-1}
$\Delta H^\circ_{\mathrm{stat}}$	−11.0 kcal mol^{-1}
$(E^{\mathrm{a}}_8 - E^{\mathrm{a}}_3)$	−2.9 kcal mol^{-1}

In hexadecane, a K_{SV} of 166 L mol^{-1} was obtained for the system CNP/1,2-DMI at room temperature, both from stationary and nonstationary measurements. The system is in its low-temperature limit, and for the rate constant of exciplex formation, a value of 4.8 × 10^9 L mol^{-1} s^{-1} was obtained, which is equal to the rate constant for diffusion in hexadecane. Upon increasing the temperature, the decay curve of the locally excited state remained a single exponential up to a temperature of 120 °C. At higher temperatures, exciplex dissociation became important, as evidenced by a decrease of $\phi^{\mathrm{E}}/\phi^{\mathrm{M}}$ with increasing temperature, and by the fact that biexponential decay was observed, both for the locally excited state and the exciplex. In Figure 2 a Stevens–Ban plot for a mixture of CNP (2 × 10^{-5} M) and 1,2-DMI (3.65 × 10^{-3} M) is given in hexadecane as a solvent. The exciplex stabilization enthalpy ΔH°, which was obtained from the high-temperature part of this curve, equals −11 kcal/mol, while the experimental value of $E_3 - E_8$ is equal to 2.9 kcal/mol.

The fluorescence decay curves of locally excited state and exciplex were determined in the temperature interval between room temperature and 180 °C, and the relevant kinetic and thermodynamic parameters for the system are listed in Table I.

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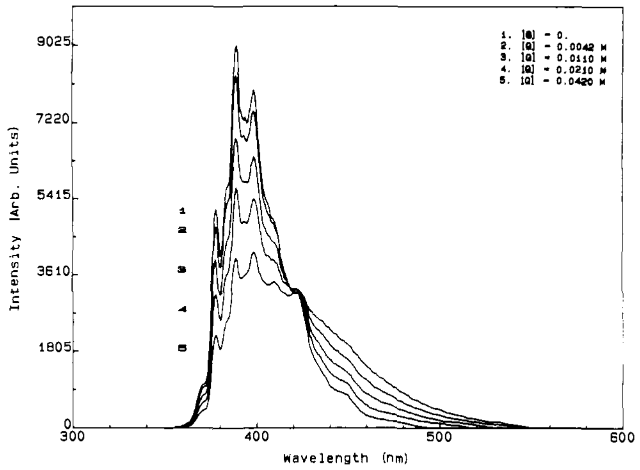


Figure 3. Fluorescence spectra of pyrene (2.2×10^{-5} M) in isooctane at 25 °C with varying concentrations of 1,2-dimethylindole.

Table II. Redox Parameters (eV) for the Three Systems under Study

system	$E(D/D^+)$	$E(A^-/A)$	$E_{00}(A)$	eq 7
P/1,2-DMI	1.12	−2.10	3.33	0.11
CH_3P/1,2-DMI	1.12	−2.15	3.30	0.03
CNP/1,2-DMI	1.12	−1.60	3.24	0.52

The value of $\Delta H°$ is the same, independent of the way the value was obtained. It is one of the largest values reported in the literature up to now,[11] and this indicates that the exciplex is a very stable one. The exciplex formation entropy change $\Delta S°$ of −13.5 esu is slightly lower than the value reported by Weller for systems consisting of aromatic acceptors and aniline derivatives.[11] The repulsion energy of 4 kcal/mol is in good agreement with the mean value of 4.5 that was obtained by Weller in exciplex systems with aniline derivatives as donors.

In Figure 3 the fluorescence spectra of 2.2×10^{-5} M solutions of pyrene with different concentrations of 1,2-DMI are given in isooctane at room temperature. A K_{SV} value of 36.5 L mol^{-1} is obtained and for k_q a value of 3.2×10^7 L mol^{-1} s^{-1} can be calculated. The fluorescence decay curves of the solutions, analyzed at 372 and 485 nm, yielded single exponential decays with the same decay parameter. These experimental facts indicate that for this system at room temperature $k_4 \gg k_8$, and the quenching is reversible. Analogous results were obtained for the system CH_3P/1,2-DMI, indicating that this system also is in its high-temperature limit at room temperature.

Measurements in isopentane showed that the fluorescence decay curves remained single exponential down to a temperature of −30 °C, from which temperature on the solubility of 1,2-DMI became a problem. It was thus not possible to obtain the values of k_3, k_4, and k_8 on the basis of nonstationary measurements. Because of the fact that $k_4 \gg k_8$, $\Delta H°$ values can be obtained from a Stevens–Ban plot, and in isopentane a value of −5.1 kcal mol^{-1} is obtained for the systems P/1,2-DMI and CH_3P/1,2-DMI. This clearly indicates that these two systems yield much less stable complexes than the system CNP/1,2-DMI.

Weller[12] proposed a classification of exciplexes on the basis of the extent of charge transfer in the complex. He found that Δ (eq 7) always exceeded 0.35 eV whenever a CT exciplex was

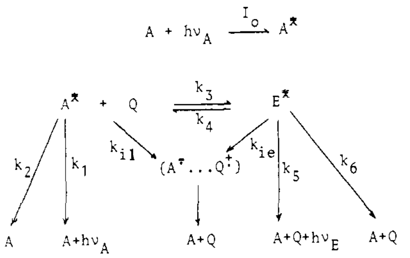
$$\Delta = \Delta E_{00} - (E(D/D^+) - E(A^-/A)) \qquad (7)$$

formed and that Δ always was smaller than 0.2 eV whenever a heteroexcimer with partial charge transfer was formed. In Table II the excitation energy, redox potentials, and Δ values are tabulated for the system used. The oxidation potential of 1,2-DMI was obtained from literature data,[13,14,22] and the redox potentials for the pyrene derivatives were measured polarographically in acetonitrile.[15]

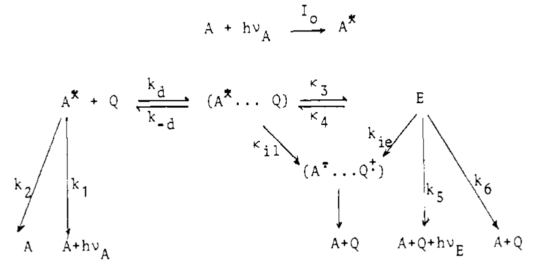
Table III. $2\mu e^2/4\pi\epsilon_0 hc\rho^3$ Values for the Three Systems under Study

system	$2\mu^2/4\pi\epsilon_0 hc\rho^3$, cm^{-1}
P/1,2-DMI	8150
CH_3P/1,2-DMI	7550
CNP/1,2-DMI	11200
anthracene/DEA	8300

Scheme II



Scheme III



The Δ values clearly indicate that CNP/1,2-DMI is a CT exciplex while the other two systems are heteroexcimers.

Influence of Solvent Polarity. Dipole Moment. With increasing solvent polarity, the exciplex fluorescence maximum shifts to longer wavelength, and this indicates the polar nature of the complex. Beens and Weller[4] derived the following equation which predicts the fluorescence maximum of an exciplex in a given solvent.

$$\bar{\nu}_E(\max) = \bar{\nu}_E{}^\circ(\max) - \frac{2\mu_e{}^2}{4\pi\epsilon_0 hc\rho^3}\left(f - \frac{1}{2}f'\right) \qquad (8)$$

On the basis of a plot of $\bar{\nu}_E(\max)$ as a function of $(f - {}^1/_2 f')$ which shows within experimental error no deviations from linearity, it was possible to obtain the value of $2\mu_e{}^2/4\pi\epsilon_0 hc\rho^3$ for the three systems, and these are given in Table III, together with the value reported for the system antracene/diethylaniline. It is very probable that the cavity ρ is about the same for the three complexes, and as can be observed, the dipole moment of the CNP/1,2-DMI exciplex is much larger than in the case of the other systems, indicating that there is a difference in extent of charge transfer in the two kinds of complexes.

Quantum Yields and Lifetimes. Upon increasing the solvent polarity, the exciplex fluorescence quantum yield and the exciplex fluorescence lifetimes both decrease, and ϕ_E^F decreases more rapidly than τ_E^F. This was rationalized by Weller[16] within the framework of Scheme II. In a function of increasing solvent polarity two processes with an ϵ_r-dependent rate constant are in competition with the other processes occurring in the system.

These two processes are ion formation via dissociation of the exciplex with a rate constant k_{ie} and ion formation directly from

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Table IV. Quenching Parameters for CNP/1,2-DMI in Different Solvents at Room Temperature (k_q, k_3', and k_d in L mol^{-1} s^{-1})

solvent	k_q	k_3'	k_d	γ_q	γ_3'
isooctane	1.6×10^{10}	1.6×10^{10}	1.3×10^{10}	1.26	1.26
hexadecane	5.3×10^{9}	5.0×10^{9}	1.9×10^{9}	2.79	2.63
benzene	1.2×10^{10}	1.0×10^{10}	1.1×10^{10}	1.1	0.95
ethyl acetate	1.4×10^{10}	1.4×10^{10}	1.5×10^{10}	0.93	0.90
THF	1.3×10^{10}	1.1×10^{10}	1.4×10^{10}	0.82	0.79
pyridine	1.0×10^{10}	9.0×10^{9}	7.0×10^{9}	1.41	1.27
methanol	1.3×10^{10}	1.2×10^{10}	1.2×10^{10}	1.09	1.03
acetonitrile	1.7×10^{10}	1.8×10^{10}	1.9×10^{10}	0.90	0.92

the locally excited state with a rate constant k_{il}. Within the framework of Scheme II the following relations can be derived.

$$[\phi^F_{A^\circ}/\phi^F_A] - 1 = \frac{Y'k_{il} + k_3(k_8 + k_{ie})}{k_7 Y'}[Q] \tag{9}$$

$$Y' = k_4 + k_8 + k_{ie} \tag{10}$$

$$\phi^F_E/\phi^F_A = \frac{k_5 k_3[Q]}{k_1(k_4 + k_8 + k_{ie})} \tag{11}$$

$$i_A(t) = k_1 \frac{(\lambda_2' - X')}{(\lambda_2' - \lambda_1')}\left[\exp(-\lambda_1' t) + \frac{X' - \lambda_1'}{\lambda_2' - X'}\exp(-\lambda_2' t)\right] \tag{12}$$

$$i_E(t) = \frac{k_5' k_3'[Q]}{(\lambda_2' - \lambda_1')}[\exp(-\lambda_1' t) - \exp(-\lambda_2' t)] \tag{13}$$

$$\lambda_{1,2}' = \tfrac{1}{2}[(X' + Y') \mp \{(X' - Y')^2 + 4k_3' k_4'[Q]\}^{1/2}] \tag{14}$$

$$X' = (k_3 + k_{il})[Q]/k_7 \tag{15}$$

$$k_3' = k_3 + k_{il} \tag{16}$$

$$k_4' = \frac{k_4 k_3}{k_3 + k_{il}} \tag{17}$$

$$k_8' = k_8 + k_{ie} + \frac{k_4 k_{il}}{k_3 + k_{il}} \tag{18}$$

$$k_5' = \frac{k_5 k_3}{k_3 + k_{il}} \tag{19}$$

Within the framework of Scheme II, the general behavior of decay curves and quantum yields is analogous to that observed in nonpolar solvents (Scheme I). The differences can be rationalized as follows.

Decay Curves. λ_1' and λ_2' will be obtained and will yield values for k_3', k_4', and k_8' as given by eq 16–18. Whenever k_{ie} and k_{il} are important k_3' and k_8' will be larger than k_3 and k_8, while k_4' will be smaller than k_4. If k_8 is not much dependent on the solvent polarity, an increase of k_8' as a function of ϵ_r can be attributed to an increase of k_{ie}.

If ΔH° is calculated by plotting ln (k_3'/k_4') as a function of $1/T$, an erronous value of ΔH° will be obtained as can be seen from eq 20. Only if k_{il} is much smaller than k_3 will the exact

$$\ln\frac{k_3'}{k_4'} = \ln\frac{(k_3 + k_{il})^2}{k_3 k_4} \neq \ln\frac{k_3}{k_4} \tag{20}$$

thermodynamic parameters be found.

Stevens–Ban Plot. A comparison of eq 2 and 11 shows that ϕ^F_E/ϕ^F_A will decrease with increasing k_{ie}. It is obvious that the high-temperature limit will be less readily obtained, since whenever k_{ie} is important the condition for high-temperature behavior changes from $k_4 \gg k_8$ to $k_4 \gg k_8 + k_{ie}$. This leads to the fact that ΔH°, obtained from a Stevens–Ban plot, will likely give too small a value for $-\Delta H^\circ$ whenever ion formation is important.[17] (Appendix 1). In general, it can be stated that whenever k_{il} or k_{ie} are important, the ΔH° values, obtained by stationary and nonstationary measurements, will be different.

Table V. Quenching Parameters for CH_3P/1,2-DMI in Different Solvents at Room Temperature (k_q, k_3', and k_d in L mol^{-1} s^{-1})

solvent	k_q	k_3'	k_d	γ_q	γ_3'
Me-THF	1.5×10^{8}	9.1×10^{9}	1.4×10^{10}	0.01	0.63
pyridine	8.6×10^{8}	3.9×10^{9}	7.0×10^{9}	0.12	0.56
isopropyl alcohol	5.3×10^{8}	3.3×10^{9}	3.7×10^{9}	0.14	0.89
acetone	2.1×10^{9}	7.5×10^{9}	2.1×10^{10}	0.10	0.36
benzonitrile	9.1×10^{8}	2.4×10^{9}	4.6×10^{9}	0.20	0.52
methanol	3.9×10^{9}	7.4×10^{9}	1.2×10^{10}	0.33	0.62
acetonitrile	6.1×10^{9}	7.1×10^{9}	1.9×10^{10}	0.32	0.37
dimethylacetamide	2.5×10^{9}	2.4×10^{9}	7.2×10^{9}	0.35	0.34

Table VI. Quenching Parameters for P/1,2-DMI in Different Solvents at Room Temperature (k_q, k_3', and k_d in L mol^{-1} s^{-1})

solvent	k_q	k_3'	k_d	γ_q	γ_3'
Me-THF	3.8×10^{8}	6.9×10^{9}	1.4×10^{10}	0.03	0.48
pyridine	2.6×10^{9}	4.1×10^{9}	7.0×10^{9}	0.37	0.58
isopropyl alcohol	1.4×10^{9}	4.7×10^{9}	3.7×10^{9}	0.38	1.27
methanol	6.4×10^{9}	7.7×10^{9}	1.2×10^{10}	0.53	0.64
acetonitrile	8.4×10^{9}	9.6×10^{9}	1.9×10^{10}	0.44	0.51

Scheme II gives a general description of the most important processes that occur in exciplex forming systems. A drawback is that the diffusion step is not indicated in an explicit manner. In Scheme III[18] this is however the case.

Within the framework of this scheme the following equations can be derived, assuming stationarity for the encounter complex.

$$k_q = k_d \frac{(k_{il}Z' + \kappa_3(k_8 + k_{ie}))}{Z'(k_{-d} + \kappa_{il}) + \kappa_3(k_8 + k_{ie})} \tag{21}$$

$$Z' = \kappa_4 + k_8 + k_{ie} \tag{22}$$

$$k_q = k_d \gamma_q \tag{23}$$

$$\gamma_q = \frac{\kappa_{il} + \kappa_3(k_8 + k_{ie})/(k_8 + k_{ie} + \kappa_4)}{\kappa_{il} + k_{-d} + \kappa_3(k_8 + k_{ie})/(k_8 + k_{ie} + \kappa_4)} \tag{24}$$

$$k_3' = k_d \gamma_3' \tag{25}$$

$$\gamma_3' = \frac{\kappa_{il} + \kappa_3}{k_{-d} + \kappa_{il} + \kappa_3} \tag{26}$$

k_q is the experimental quenching constant which is connected with the diffusion constant with an efficiency factor γ_q. k_3' is the rate constant of reaction of A* and Q via the encounter state (A*···Q) and is connected with the diffusion constant with an efficiency factor γ_3'.

k_3' is related to k_3, the bimolecular rate constant for the formation of E, by the relation

$$k_3 = k_3' \frac{\kappa_3}{\kappa_3 + \kappa_{il}}$$

k_q is obtained by a Stern–Volmer analysis while k_3' is obtained by nonstationary measurements. In general

$$\gamma_3' \gg \gamma_q \tag{27}$$

Whenever $\kappa_4 \ll k_8 + k_{ie}$, $\gamma_3' = \gamma_q$. If $k_{-d} \ll \kappa_{il} + \kappa_3$ the reaction, is diffusion controlled and $\gamma_3' = 1$. In Tables IV–VI the values for k_q, k_3', k_d,[23] and the efficiency factors are given for the systems

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(22) The oxidation potential of 1,2-DMI was derived on the basis of the ionization potential of 1-methylindole[13] and an empirical relationship found between I_p and $E_{(D/D^+)}$.[14]

Table VII. Quantum Yields, Lifetimes, and Calculated Rate Constants for CNP/1,2-DMI in Different Solvents at Room Temperature[a]

solvent	ϕ_0^f	τ_0^f	ϕ_A^f	ϕ_E^f	τ_A^f	τ_E^f	K_{SV}(nstat)	K_{SV}(stat)
isooctane	0.503	43×10^{-9}	0.09	0.240	8.1×10^{-9}	81×10^{-9}	679	703
hexadecane	0.572	35×10^{-9}	0.22	0.226	13×10^{-9}	81×10^{-9}	172	182
benzene	0.805	19×10^{-9}	0.33	0.175	8.8×10^{-9}	85×10^{-9}	195	230
ethyl acetate	0.643	25×10^{-9}	0.21	0.027	8.3×10^{-9}	19×10^{-9}	338	350
THF	0.630	23×10^{-9}	0.25	0.046	9.3×10^{-9}	38×10^{-9}	250	264
pyridine	0.310	5.2×10^{-9}	0.24	0.000	4.1×10^{-9}		47	52
methanol	0.617	20×10^{-9}	0.28	0.000	9.8×10^{-9}		249	261
acetonitrile	0.591	33×10^{-9}	0.19	0.000	7.4×10^{-9}		417	408

solvent	k_1	k_2	k_3'	k_5'	k_6'	k_7	k_8'	[Q]
isooctane	1.2×10^7	1.2×10^7	1.6×10^{10}	3.7×10^6	8.7×10^6	2.4×10^7	1.2×10^7	8.2×10^{-3}
hexadecane	1.7×10^7	1.2×10^7	5.0×10^9	4.7×10^6	7.7×10^6	2.9×10^7	1.2×10^7	9.3×10^{-3}
benzene	4.3×10^7	1.0×10^7	1.0×10^{10}	3.9×10^6	7.9×10^6	5.3×10^7	1.2×10^7	5.7×10^{-3}
ethyl acetate	2.6×10^7	1.4×10^7	1.4×10^{10}	2.1×10^6	5.0×10^7	4.0×10^7	5.2×10^7	6.0×10^{-3}
THF	2.8×10^7	1.6×10^7	1.1×10^{10}	2.0×10^8	2.4×10^7	4.3×10^7	2.6×10^7	5.8×10^{-3}
pyridine	5.9×10^7	1.3×10^8	8.9×10^9			1.9×10^8		6.3×10^{-3}
methanol	3.1×10^7	1.9×10^7	1.2×10^{10}			5.0×10^7		4.2×10^{-3}
acetonitrile	2.5×10^7	1.7×10^7	1.8×10^{10}			4.2×10^7		5.3×10^{-3}

[a] k_1, k_2, k_4', k_5', k_6', k_7, k_8' in s^{-1}; k_3', k_q in L mol^{-1} s^{-1}; [Q] in mol L^{-1}; lifetimes in s; K_{SV} in L mol^{-1}.

Table VIII. Quantum Yields, Lifetimes, and Calculated Rate Constants for CH_3P/1,2-DMI in Different Solvents at Room Temperature[a]

solvent	$\phi_{A^\circ}^f$	τ_0^f	ϕ_A^f	ϕ_E^f	τ_A	τ_E	K_{SV}(nstat)	K_{SV}(stat)	k_q
Me-THF	0.508	209×10^{-9}	0.308	0.141	4.2×10^{-9}	1.1×10^{-9}	31	23	1.5×10^8
pyridine	0.327	74×10^{-9}	0.123	0.147	7.6×10^{-9}	9.5×10^{-9}	64	52	8.6×10^8
isopropyl alcohol	0.468	223×10^{-9}	0.101	0.241	9.7×10^{-9}	8.8×10^{-9}	117	127	5.2×10^8
acetone	0.548	202×10^{-9}	0.045	0.041	3.9×10^{-9}	5.2×10^{-9}	413	332	2.0×10^8
benzonitrile	0.587	143×10^{-9}	0.099	0.088	12.9×10^{-9}	10.1×10^{-9}	130	160	9.0×10^8
methanol	0.450	219×10^{-9}	0.016	0.058	4.4×10^{-9}	12.3×10^{-9}	849	877	3.9×10^9
acetonitrile	0.540	192×10^{-9}	0.012	0.011	4.0×10^{-9}	4.7×10^{-9}	1177	1300	6.1×10^9
dimethylacetamide	0.697	163×10^{-9}	0.045	0.013	11.3×10^{-9}		398	411	2.4×10^9

solvent	[Q]	k_1	k_2	k_3'	k_4'	k_5'	k_6'	k_7	k_8'
Me-THF	2.6×10^{-2}	2.4×10^6	2.4×10^6	9.1×10^9	9.5×10^8	3.6×10^6	8.8×10^6	4.8×10^6	1.2×10^7
pyridine	3.0×10^{-2}	4.4×10^6	9.1×10^6	3.9×10^9	6.2×10^7	4.7×10^6	1.8×10^7	1.3×10^7	2.3×10^7
isopropyl alcohol	3.0×10^{-2}	2.1×10^6	2.4×10^6	3.3×10^9	9.6×10^7	5.8×10^6	1.2×10^7	4.5×10^6	1.8×10^7
acetone	3.4×10^{-2}	2.7×10^6	2.2×10^6	7.5×10^9	1.4×10^8	1.9×10^8	5.1×10^7	5.0×10^6	5.3×10^7
benzonitrile	2.9×10^{-2}	4.1×10^6	2.9×10^6	2.4×10^9	6.1×10^7	5.1×10^6	3.2×10^7	7.0×10^6	3.8×10^7
methanol	3.0×10^{-2}	2.1×10^6	2.5×10^6	7.4×10^9	3.9×10^7	2.6×10^6	4.0×10^7	4.6×10^6	4.2×10^7
acetonitrile	3.5×10^{-2}	2.8×10^6	2.4×10^6	7.1×10^9	2.8×10^7	2.3×10^6	1.8×10^8	5.2×10^6	2.1×10^8
dimethylacetamide	3.4×10^{-2}	4.3×10^6	1.9×10^6	2.5×10^9				6.1×10^6	

[a] k_1, k_2, k_4', k_5', k_6', k_7, k_8' in s^{-1}; k_3', k_q in L mol^{-1} s^{-1}; [Q] in mol L^{-1}; lifetimes in s; K_{SV} in L mol^{-1}.

Table IX. Quantum Yields, Lifetimes, and Calculated Rate Constants for P/1,2-DMI in Different Solvents at Room Temperature[a]

solvent	ϕ_0^f	τ_0^f	ϕ_A^f	ϕ_E^f	τ_a^f	τ_E^f	K_{SV}(nstat)	K_{SV}(stat)	k_q
Me-THF	0.498	384×10^{-9}	0.163	0.263	8.1×10^{-9}	4.9×10^{-9}	144	124	4.0×10^8
pyridine	0.113	61×10^{-9}	0.029	0.117	10.6×10^{-9}	28.0×10^{-9}	159	140	2.6×10^9
isopropyl alcohol	0.375	410×10^{-9}	0.032	0.220	12.1×10^{-9}	28.1×10^{-9}	589	605	1.4×10^9
methanol	0.363	373×10^{-9}	0.009	0.039	7.7×10^{-9}	18.0×10^{-9}	2374	2560	6.4×10^9
acetonitrile	0.422	348×10^{-9}	0.008	0.008	5.8×10^{-9}	4.9×10^{-9}	2910	2923	8.4×10^9

solvent	[Q]	k_i	k_2	k_3'	k_4'	k_5'	k_6'	k_7	k_8'
Me-THF	1.8×10^{-2}	1.3×10^6	1.3×10^6	6.9×10^9	1.9×10^8	3.5×10^6	7.0×10^6	2.6×10^6	1.1×10^7
pyridine	1.9×10^{-2}	1.8×10^6	1.5×10^7	4.1×10^9	1.3×10^7	3.3×10^6	1.9×10^7	1.6×10^7	2.3×10^7
isopropyl alcohol	1.7×10^{-2}	9.0×10^5	1.5×10^6	4.7×10^9	2.4×10^7	1.6×10^6	1.0×10^7	2.5×10^6	1.2×10^7
methanol	1.7×10^{-2}	1.0×10^6	1.7×10^6	7.7×10^9	9.0×10^6	1.7×10^6	4.5×10^7	2.7×10^6	4.6×10^7
acetonitrile	1.8×10^{-2}	1.2×10^6	1.7×10^6	9.6×10^9	2.6×10^7	1.5×10^6	1.8×10^8	2.9×10^6	1.8×10^8

[a] k_1, k_2, k_4', k_5', k_6', k_7, k_8' in s^{-1}; k_3', k_q in L mol^{-1} s^{-1}; [Q] in mol L^{-1}; lifetimes in s; K_{SV} in 1 mol^{-1}.

in different solvents. The values of γ_q and γ_3' obtained for the system CNP/1,2-DMI are identical and approximating 1. This indicates that in this system κ_4 is much smaller than $k_8 + k_{ie}$ and k_{-d} much smaller than $\kappa_{il} + \kappa_3$. Therefore the quenching is diffusion controlled and irreversible in all the solvents under study at room temperature.

From Tables V and VI it can be seen that even for acetonitrile as a solvent, $\gamma_3' > \gamma_q$ for the systems CH_3P/1,2-DMI and P/1,2-DMI, clearly indicating that the quenching by exciplex formation remains reversible in all the solvents studied at room temperature. With increasing solvent polarity γ_q approaches γ_3', indicating that κ_4 becomes less important upon increasing ϵ_r.

A comparison of Tables IV and VI shows that the absolute value of γ_3' is, for the same solvent, always smaller for the heteroexcimers. Even in acetonitrile as a solvent, γ_3' is much less than 1, indicating that the quenching is only partially diffusion controlled in all the solvents used.

An important conclusion concerning κ_{il} can be derived from these experimental findings. One would expect κ_{il} to increase whenever ϵ_r increases. The fact that γ_3' does not increase as a function of ϵ_r indicates that κ_{il} is never larger than κ_3 for the heteroexcimers in all the solvents studied.

In Tables VII–IX quantum yields, lifetimes, and calculated rate constants are given for the three systems in solvents of different polarity at room temperature. In the case of CNP/1,2-DMI, the values of ϕ_E^F and τ_E^F show a sharp decrease, and k_8' becomes larger

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(23) The k_d values were calculated by using the simplified Smoluchowski equation $k_d = 8RT/(3000\eta)$ because of the fact that the diffusion coefficient of 1,2-DMI was not reported in the literature.

Table X. Kinetic and Thermodynamic Parameters for P/1,2-DMI and CH_3P/1,2-DMI in 2-Me-THF ($\epsilon_r = 6.24$)

parameter	CH_3P/1,2-DMI	P/1,2-DMI
$k°_2$, s^{-1}	4.0×10^6	2.7×10^6
$k°_3$, L/(mol s)	9.0×10^{11}	3.0×10^{11}
$k°_4$, s^{-1}	6.6×10^{15}	2.6×10^{15}
k_5, s^{-1}	3.6×10^6	3.9×10^6
$k°_6$, s^{-1}	8.6×10^6	8.6×10^6
E^a_2, kcal mol^{-1}	0.3	0.4
E^a_3, kcal mol^{-1}	2.6	2.2
E^a_4, kcal mol^{-1}	9.3	9.6
E^a_6, kcal mol^{-1}	0.1	0.2
$\Delta H°_{nstat}$, kcal mol^{-1}	−6.2	−7.1
$\Delta S°_{nstat}$, esu	−16.5	−16.9
$\Delta G°$(25 °C), kcal mol^{-1}	−1.2	−2.1
$\Delta H^{\ddagger}_3$ kcal mol^{-1}	2.4	1.6
$\Delta S^{\ddagger}_3$, esu	−5.7	−8.2
$\Delta G^{\ddagger}_3$, kcal mol^{-1}	3.9	4.0
$\Delta H^{\ddagger}_4$, kcal mol^{-1}	8.8	9.0
$\Delta S^{\ddagger}_4$, esu	11.9	10
$\Delta G^{\ddagger}_4$, kcal mol^{-1}	5.2	6.0
$\Delta H°_{stat}$, kcal mol^{-1}	−5.9	−6.9

Table XI. Kinetic and Thermodynamic Parameters for P/1,2-DMI and CH_3P/1,2-DMI in Isopropyl Alcohol ($\epsilon_r = 19.92$)

parameter	CH_3P/1,2-DMI	P/1,2-DMI
$k°_2$, s^{-1}	4.0×10^6	6.0×10^6
$k°_3$, L/(mol s)	4.2×10^{12}	4.8×10^{12}
$k°_4$, s^{-1}	7.7×10^{14}	5.5×10^{14}
k_5, s^{-1}	2.2×10^6	1.6×10^6
$k°_6$, s^{-1}	1.1×10^7	1.0×10^7
E^a_2, kcal mol^{-1}	0.3	0.8
E^a_3, kcal mol^{-1}	4.1	4.1
E^a_4, kcal mol^{-1}	9.6	9.8
E^a_6, kcal mol^{-1}	0.0	0.0
$\Delta H°_{nstat}$, kcal mol^{-1}	−5.6	−6.2
$\Delta S°_{nstat}$, esu	−11.2	−10
$\Delta G°$(25 °C), kcal mol^{-1}	−2.3	−3.2
$\Delta H^{\ddagger}_3$, kcal mol^{-1}	3.5	3.5
$\Delta S^{\ddagger}_3$, esu	−2.6	−2.5
$\Delta G^{\ddagger}_3$, kcal mol^{-1}	4.3	4.3
$\Delta H^{\ddagger}_4$, kcal mol^{-1}	9.0	9.2
$\Delta S^{\ddagger}_4$, esu	7.7	7
$\Delta G^{\ddagger}_4$, kcal mol^{-1}	6.7	7.1
$\Delta H°_{stat}$, kcal mol^{-1}	−5.3	−6.9

Table XII. Kinetic and Thermodynamic Parameters for CH_3P/1,2-DMI in Acetone ($\epsilon_r = 20.4$)

k_1	2.75×10^6 s^{-1}
$k°_2$	2.25×10^6 s^{-1}
$k°_3$	1.5×10^{11} L/(mol s)
$k°_4$	4.9×10^{14} s^{-1}
k_5	2.0×10^6 s^{-1}
$k°_6$	4.5×10^7 s^{-1}
E^a_2	0.0 kcal mol^{-1}
E^a_3	1.9 kcal mol^{-1}
E^a_4	9.2 kcal mol^{-1}
E^a_6	0.0 kcal mol^{-1}
$\Delta H°_{nstat}$	−7.1 kcal mol^{-1}
$\Delta S°_{nstat}$	−16.1 esu
$\Delta G°$(25 °C)	−2.3 kcal mol^{-1}
$\Delta H^{\ddagger}_3$	1.3 kcal mol^{-1}
$\Delta S^{\ddagger}_3$	−9.1 esu
$\Delta G^{\ddagger}_3$	2.7 kcal mol^{-1}
$\Delta H^{\ddagger}_4$	8.6 kcal mol^{-1}
$\Delta S^{\ddagger}_4$	7.7 esu
$\Delta G^{\ddagger}_4$	6.3 kcal mol^{-1}

when the solvent changes from a nonpolar (isooctane) to a medium-polar one (butyl acetate). From an ϵ_r of 12.4 (pyridine) no more exciplex emission can be detected. These facts indicate that ion formation becomes important, even in medium-polar solvents, which is normally the case for CT exciplexes.[19]

For the heteroexcimers, a different picture emerges. ϕ_E^F remains about constant up to an ϵ_r of 19.9 (IpOH) and k_8' shows the same behavior. The variation of τ_{ex} does not correlate with the variation of ϕ_E^F due to the fact that κ_4 becomes less important whenever ϵ_r increases at constant temperature and this has a different effect for ϕ_E^F and τ_E^F.

Whenever ϵ_r increases further, ϕ_E^F shows a rapid decrease while k_8' increases, indicating that ion formation does occur in the heteroexcimer cases.

Determination of Thermodynamic Parameters for Exciplex Formation in Different Solvents. Dibutyl Ether and 2-Me-THF. The systems P/1,2-DMI and CH_3P/1,2-DMI were investigated in different solvents as a function of T. Measurements in dibutyl ether ($\epsilon = 3.08$) indicated that in this solvent the systems were still in the high-temperature limit at room temperature. For the same reason as indicated in the case of isopentane k_3', k_4', and k_8' could not be obtained separately, but $\Delta H°$ was obtained from stationary measurements. For P/1,2-DMI a value for $\Delta H°$ of −6.2 kcal/mol and a value of the repulsion energy in the ground state E_r of 5.1 kcal/mol were obtained, while for CH_3P/1,2-DMI $\Delta H°$ equals −5.4 kcal/mol and E_r was found to be 5.5 kcal/mol.

In 2-Me-THF a complete analysis based on measurements of the decay parameters and quantum yields as a function of temperature could be carried out for the two systems. The results, calculated within the assumption that ion formation can be neglected in this solvent, are tabulated in Table X.

From a comparison of Tables VIII–X, it is clear that k_8' is not much dependent on the temperature and that k_{ie} can be neglected in comparison with k_8. The fact that the values for $\Delta H°$ obtained by stationary and nonstationary measurements are identical is a strong indication for the validity of the assumption mentioned above. The repulsion energy obtained is slightly higher than that in a nonpolar solvent, indicating that there occurs an increasing solvent reorientation in a more polar solvent.

The values of E_3^a obtained are slightly higher than the activation energy for viscous flow in 2-Me-THF which is 1.9 kcal/mol. The values for E_4^a and $k_4°$ and the values of $\Delta S°$ are in good agreement with the values obtained for exciplexes between aromatic acceptors and aniline derivatives in nonpolar solvents.[11,20]

Isopropyl Alcohol and Acetone. From Tables VIII and IX it is obvious that isopropyl alcohol is the most polar solvent in which ion formation is not likely to be important, because of the high value of ϕ_E^F and the low value of k_8'. A complete analysis of thermodynamic and kinetic parameters was also carried out, and the results are given in Table XI.

If we now return to Tables V and VI and eq 21–27 the following remarks can be made.

Because of the fact that γ_3' does not increase with increasing ϵ_r, and because of the fact that κ_{il} increases with increasing ϵ_r, it is clear that κ_{il} is never larger than κ_3. This also leads to the fact that κ_3 is always of the same order of magnitude as k_{-d} which means that the reaction is only partially diffusion controlled, a fact that is corroborated by the difference between E_η and E_3^a.

If we extrapolate these ideas to eq 16 and 17, keeping in mind that

$$k_3 = \kappa_3 k_d/(\kappa_3 + k_{-d}) \tag{28}$$

we obtain the following equations:

$$k_3' \cong k_3 \qquad k_4' \cong k_4$$

which means that for these heteroexcimer systems in the solvents under study, even when ion formation due to k_{ie} is important ($\phi_E^F\downarrow$, $k_8'\uparrow$, $\Delta H°_{stat} \neq \Delta H°_{nstat}$), k_3 and k_4 can be obtained from nonstationary measurements, and $\Delta H°$, $\Delta S°$, and $\Delta G°$ can be calculated (Appendix 2).

In isopropyl alcohol, as can be seen from Tables VIII and IX, k_{ie} cannot be neglected completely to k_8, but $\Delta H°_{stat}$ is still equal to $\Delta H°_{nstat}$ for the system CH_3P/1,2-DMI. The most important features of Table XI are the values of $\Delta H°$ and $\Delta S°$, which are less negative than expected on the basis of measurements in medium-polar solvents and the fact that the repulsion energy in the ground state is about twice as large as that in the other solvents studied.

Isopropyl alcohol is a structured solvent, and solvation of a polar entity will be in competition with the autoassociation of the solvent.

Table XIII. Influence of the Solvent Polarity on k_{ie} (s^{-1})

solvent	theoretical (ref 24b, eq 3)	pyrene/DMI	methylpyrene/DMI
acetonitrile	40×10^7	17×10^7	17×10^7
methanol	16×10^7	3.8×10^7	3.2×10^7
benzonitrile	3×10^7		2.3×10^7
acetone	5×10^7		4.3×10^7
isopropyl alcohol	0.5×10^7	0.3×10^7	0.4×10^7

This leads to the fact that the solvent stabilization effect on $\Delta H°$ will be smaller then expected on the basis of ϵ_r. It also explains why $\Delta S°$ is less negative than in a nonstructured solvent; in solvating the exciplex, one goes from a structured to a more structured state, and the difference in entropy will be less than expected on the basis of measurements in nonstructured solvents.

The fact that the repulsion energy in the ground state is about twice as large as that in 2-methyl THF also fits in this picture. The solvent shell of the exciplex will show orientations of the solvent molecules which will give rise to a higher repulsion term whenever the exciplex relaxes to the (less polar) ground state.

In acetone ion formation occurs in both heteroexcimer systems (k_8' large, ϕ_E^F small), but to test the assumptions derived above, the kinetic and thermodynamic parameters for the system CH_3P/1,2-DMI were also measured in this solvent. The results are given in Table XII.

A most important fact is the difference in $\Delta H°$ values determined by the different techniques. $\Delta H°$ obtained from a Stevens–Ban plot is equal to −4.8 kcal/mol while by an analysis of k_3' and k_4', a value of −7.1 kcal/mol is found. This is an indication for the validity of the assumption that whenever ion formation is important, the $\Delta H°$ values will be different.

The $\Delta S°$ value obtained is almost identical with the value in medium-polar, nonstructured solvent, and $\Delta H°$ is slightly more negative than in Me-THF, as is expected on the basis of the more pronounced interaction of a polar solvent with a polar solute (heteroexcimer); this also gives rise to the higher value of E_r that is found in comparison with that of the nonpolar solvents.

Conclusion

Exciplex formation between pyrene derivatives and 1,2-DMI is governed by the redox properties of the pyrene derivative. The system CNP/1,2-DMI can be classified as a pure CT exciplex on the basis of the large value of $2\mu_e^2/hc\epsilon_0 4\pi\rho^3$ and on the fact that the exciplex emission maximum in nonpolar solvent can be accurately predicted by the empirical formula of Weller.[11] It forms a very stable exciplex in nonpolar solvents: the $-\Delta H°$ value is one of the largest that is indicated in the literature up to now ($\Delta H° = -11$ kcal/mol). The repulsion energy is in good agreement with the mean value of 4.5 kcal/mol indicated in the literature for exciplexes between aromatic acceptors and aromatic amines.[11] In medium-polar and polar solvents two processes by which ions are formed become important; one of them is dissociation of the exciplex via dissociation into ions with a rate constant k_{ie}, and the other one is ion formation via electron transfer in the collision complex with a rate constant k_{il}. The behavior of the system as a function of increasing solvent polarity can be completely rationalized within the framework of the description of CT exciplexes.

The rate constant for exciplex formation is diffusion controlled for the system CNP/1,2-DMI in all the solvents studied. In nonpolar solvents k_4 can be neglected with respect to k_8 up to a temperature of about 100 °C.

Exciplexes formed in the systems CH_3P/1,2-DMI and P/1,2-DMI can be classified as heteroexcimers with a partial charge-transfer character. The value of $2\mu_e^2/hc\rho^3\epsilon_0 4\pi$ is much lower than that for the CT exciplex, and the exciplex emission maximum is more bathochromic than predicted for a CT exciplex. The value of $\Delta H°$ obtained in nonpolar solvents is only about 50% of the value for the CT exciplex. The repulsion energy is identical, indicating that there is no large structural difference for the CT exciplex and the heteroexcimers in nonpolar solvents. Exciplex formation is only partially diffusion controlled in the heteroexcimer systems, as can be seen by the fact that $\gamma_3' < 1$.

From the solvent polarity dependence of ϕ_E^F and k_8' it is obvious that ion formation is not important in the heteroexcimer systems up to an ϵ_r of 19.9 (isopropyl alcohol). In solvents of higher polarity ϕ_E^F shows a sharp decrease and k_8' a sharp increase, indicating that ion formation becomes important.

Several authors[4,5,24,26] indicate that the equilibrium between the solvent-separated radical ion pair and the contact ion pair (or exciplex) is shifted toward the solvent-separated ion pair upon increasing the solvent polarity. Weller et al.[5] furthermore found that upon increasing the solvent polarity direct formation of the ion pair competes with exciplex formation causing the absence of exciplex emission in acetonitrile.[11] The values Weller proposes[24] for k_{ie} correspond to those obtained for pyrene/1,2-DMI and methylpyrene/1,2-DMI assuming $k_{ie} = k_8' - k_8'$(isooctane) (Table XIII). This assumption means that the total increase of k_8' upon increasing the solvent polarity is due to k_{ie}. These results are in contradiction with those of Peters,[25] indicating that in acetonitrile the initially formed separated ion pair is converted into the contact ion pair in about 100 ps. The explanation for this difference could be found in the nature of the donor and the acceptor. In the systems of this study and in the ones studied by Weller D and A are aromatic hydrocarbons while in Peters' work a ketone (localized negative charge in the radical anion) and an aliphatic amine (localized positive charge in the radical cation) are used. This is in agreement to the results of Peters showing that a change from Na^+ to Li^+ as counterion for benzophenone favors the contact ion pair.

On the basis of the fact that γ_3' is not dependent upon solvent polarity it can be shown that κ_{il} is not important in comparison with the rate constants of the other processes occurring in the heteroexcimer system, which means that ion formation only occurs via dissociation of the exciplex in polar solvents for the systems studied.

Recent experimental results of Mataga[26b] confirm that for intermolecular systems the rise time for the formation of free ions (as observed by photoconductivity) is somewhat smaller than the fluorescence decay time of the exciplex, indicating that a fraction of the solvent-separated ion pair is formed directly. The presence of several more or less isoenergetic solvent-separated ion pairs and exciplexes interconverting between each other cannot be excluded.

They also observed a large influence of the exact nature of the donor and the acceptor on the relative importance of those processes.

On the basis of these results, it was possible to prove that k_3 and k_4, the real exciplex formation and exciplex dissociation rate constants and the thermodynamic parameters governing heteroexcimer formation, could be obtained, even in a high polar solvent (acetone, $\epsilon = 20.4$). The resulting thermodynamic parameters for the heteroexcimer systems are given in Table XIV.

As can be seen there is an increase of $-\Delta H°$ and E_r as a function of increasing solvent polarity. This can be explained as follows. As the solvent polarity increases, the heteroexcimer will be stabilized by the interaction with the solvent molecules. The stabilization is however not large, as can be derived from the relative small increase of $-\Delta H°$, and this can be explained by the partial charge-transfer character of the heteroexcimers. The increase

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(24) (a) A. Weller, *Z. Phys. Chem.* (*Frankfurt am Main*), **133**, 93 (1982). (b) A. Weller, *Z. Phys. Chem.* (*Frankfurt am Main*), **130**, 129 (1982).

(25) (a) J. D. Simon and K. S. Peters, *J. Am. Chem. Soc.*, **104**, 6542 (1982). (b) J. D. Simon and K. S. Peters, *J. Am. Chem. Soc.*, **105**, 4875 (1983).

(26) (a) Y. Hiraka, Y. Konda, and N. Mataga, *J. Phys. Chem.*, **87**, 1654 (1983). (b) N. Mataga, *Pure Appl. Chem.*, **56**, 1255 (1984).

Table XIV. Thermodynamic Parameters for the Heteroexcimer Systems in Different Solvents

solvent	parameter	P/1,2-DMI	CH_3P/1,2-DMI
isopentane	$\Delta H°$, kcal mol^{-1}	−5.1	−5.1
	E_r, kcal mol^{-1}	4.8	4.2
dibutyl ether	$\Delta H°$, kcal mol^{-1}	−6.2	−5.4
	E_r, kcal mol^{-1}	5.1	5.5
Me-THF	$\Delta H°$, kcal mol^{-1}	−7.1	−6.2
	$\Delta S°$, esu	−16.9	−16.5
	$\Delta G°$, kcal mol^{-1}	−2.1	−1.2
	E_r, kcal mol^{-1}	6.7	6.3
isopropyl alcohol	$\Delta H°$, kcal mol^{-1}	−6.2	−5.6
	$\Delta S°$, esu	−10.0	−11.2
	$\Delta G°$, kcal mol^{-1}	−3.2	−2.3
	E_r, kcal mol^{-1}	10.4	9.3
acetone	$\Delta H°$, kcal mol^{-1}		−7.1
	$\Delta S°$, esu		−16.1
	$\Delta G°$, kcal mol^{-1}		−2.3
	E_r, kcal mol^{-1}		7.8

of E_r can be due to two effects; one is the difference that must exist in the solvation layers of heteroexcimer and ground state, and the other is the possibility that the more polar solvent might introduce a change in heteroexcimer geometry.

These results concerning k_4 and $\Delta H°$ disagree with those obtained by Ware et al.[21b] for the exciplex between naphthalene and cyclopentane. The results found for isopropyl alcohol as a solvent can be rationalized in the same context. One expects for $\Delta H°$ a value rather close to the value obtained in acetone on the basis of solvent polarity. Isopropyl alcohol is however a structured, hydrogen-bonded solvent, and solvation of the exciplex has to compete with the strong autoassociation of the solvent. This leads to the fact that the energy gain caused by the interaction with the solvent is minimal ($-\Delta H°$ for isopropyl alcohol is only slightly larger than $-\Delta H°$ in isopentane).

The high repulsion energy obtained in isopropyl alcohol (higher than in acetone) reflects the fact that the solvation layer of the exciplex is farther from the ground-state configuration in a structured, compared to a nonstructured, solvent. The rather low value of $-\Delta S°$ reflects the fact that in solvating a polar entity in a structured solvent, one goes from a structured to a more structured situation, and the value of $-\Delta S°$ found will be smaller than that in a nonstructured solvent.

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Appendix

1. $\phi_E^F/\phi_A^F = k_5k_3[Q]/k_1Y'$; $Y' = k_4 + k_8 + k_{ie}$. If we assume that k_1 and k_5 show the same dependence on the temperature it follows that

$$\ln (\phi_E^F/\phi_A^F) = \text{cst} - (E_3^a - E_{Y'}^a)/RT$$

If $k_{ie} \ll k_4 + k_8$, we find the high and low-temperature regions which lead to a Stevens–Ban curve.

We can distinguish three cases:

(a) $k_8 \gg k_4, k_{ie}$

$$\ln (\phi_E^F/\phi_A^F) = \text{cst} - (E_3^a - E_8^a)/RT \cong \text{cst}' - E_3^a/RT$$

(b) $k_4 \gg k_8, k_{ie}$

$$\ln (\phi_E^F/\phi_A^F) = \text{cst} - (E_3^a - E_4^a)/RT = \text{cst} - \Delta H°/RT$$

(c) $k_{ie} \gg k_8, k_4$

$$\ln (\phi_E^F/\phi_A^F) = \text{cst} - (E_3^a - E_{ie}^a)/RT$$

In case c exciplex emission with be extremely weak. When k_{ie} is important and exciplex emission is still observable we can write in the high-temperature case:

$$k_4 + k_{ie} \gg k_8$$

$$\ln (\phi_E^F/\phi_A^F) = \text{cst} - (E_3^a - E_{Y'}^a)/RT$$

$E_{Y'}^a$ will be dependent on the preexponential factors and activation energies of k_4 and k_{ie}.

With increasing ϵ_r, E_4^a will increase and E_{il}^a will decrease, so in a polar solvent one can write

$$E_{Y'} < E_4^a$$

and this leads to

$$|\Delta H°|_{k_{ie} \neq 0} < |\Delta H°|_{k_{ie} = 0}$$

2. It was shown that, independent of ϵ_r, γ_3' is always smaller than 1, and it does not increase with increasing ϵ_r. This leads to the following conclusions:

$$\gamma_3' = \frac{\kappa_3 + \kappa_{il}}{k_{-d} + \kappa_3 + \kappa_{il}}$$

(a) k_{-d} is of the same order of magnitude as $\kappa_3 + \kappa_{il}$ and, (b) the maximal value that κ_{il} can become is about the same order of magnitude as κ_3 in acetonitrile as a solvent (in solvents with a lower ϵ_r value κ_{il} will be even smaller).

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