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Influence of Starting Conformations on Intramolecular Exciplex Formation in ω-Phenyl-α-N,N-dimethylaminoalkanes

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Abstract: The intramolecular complex formation of ω-phenyl-α-N,N-dimethylaminoalkanes in isopentane was investigated using stationary and nonstationary techniques. Analysis of the decay curves indicates that ground-state starting conformations influence the rate of complex formation. In deviation of the classical kinetic scheme for inter- and intramolecular exciplex and excimer formation, the emission of the locally excited state contains a slow-decaying component whose lifetime is longer than that of the exciplex. This slow-decaying emission is attributed to molecules in which the C–N bond has a conformation unfavorable for exciplex formation.

Introduction

Up to now it has been assumed that intramolecular exciplex and excimer formation[2-4] follows the same kinetic scheme as the intermolecular processes.[5] The adopted scheme could be presented as shown in Scheme I. The ratio of the quantum yields for emission from the exciplex, ϕ_E, and from the locally

Scheme I

$$AD \xrightarrow{h\nu} A^*D$$

$$A^*D \xrightarrow{k_1} AD + h\nu_A$$

$$A^*D \xrightarrow{k_2} AD$$

$$A^*D \xrightarrow{k_3} (AD)^*$$

$$(AD)^* \xrightarrow{k_4} A^*D$$

$$(AD)^* \xrightarrow{k_5} AD + h\nu$$

$$(AD)^* \xrightarrow{k_6} AD$$

$$k_7 = k_1 + k_2 \qquad A^*D = LE$$

$$k_8 = k_5 + k_6 \qquad (AD)^* = E$$

excited state, ϕ_{LE}, is within the framework of this scheme given by

$$\frac{\phi_E}{\phi_{LE}} = \frac{k_5}{k_1}\left(\frac{k_3}{k_4 + k_8}\right) \qquad (1)$$

At sufficiently high temperatures where k_4 is larger than k_8, the process is thermodynamically controlled and this expression simplifies to

$$\phi_E/\phi_{LE} = \frac{k_5}{k_1}\frac{k_3}{k_4} \qquad (2)$$

At these limiting conditions the slope of ln (ϕ_e/ϕ_m) vs. $1/T$ equals $-\Delta H/R$, the enthalpy of exciplex formation. At low temperatures where $k_4 \ll k_8$ the process is kinetically controlled and eq 1 simplifies to

$$\phi_E/\phi_{LE} = \frac{k_5}{k_1}\frac{k_3}{k_8} \qquad (3)$$

Within this scheme the slope of ln (ϕ_E/ϕ_{LE}) vs. $1/T$ equals the difference between the activation energies for k_3 and k_8. It is often found that $E_3 > E_8$ and the ratio ϕ_E/ϕ_{LE} increases with increasing temperature in this "low-temperature" region. When a temperature-dependent component of k_8, with an activation energy $E_8 > E_3$, becomes predominant, the ratio ϕ_E/ϕ_{LE} can decrease with increasing temperature. The time evolution of the emission of the exciplex $I_E(t)$ and the locally excited state $I_{LE}(t)$ are given by[3a,4b–d,5]

$$I_E(t) \sim [LE(0)]\frac{k_5 k_3}{\lambda_2 - \lambda_1}\{\exp(-\lambda_t t) - \exp(-\lambda_2 t)\} \qquad (4)$$

$$I_{LE}(t) \sim [LE(0)]\frac{k_1}{\lambda_2 - \lambda_1}\{(\lambda_2 - Y)$$
$$\times \exp(-\lambda_2 t) + (Y - \lambda_1)\exp(-\lambda_1 t)\} \qquad (5)$$

where [LE(0)] is the initial concentration of the locally excited state. Furthermore, letting

$$R = \frac{\lambda_2 - Y}{Y - \lambda_1}$$

$$X = k_7 + k_3$$

$$Y = k_8 + k_4$$

$$\lambda_{1,2} = \frac{1}{2}\{(X + Y) \mp [(X - Y)^2 + 4k_3 k_4]^{1/2}\}$$

In the "low-temperature" region

$$\lambda_1 \sim k_8 \sim Y$$

$$\lambda_2 \sim k_3 \sim X$$

In the high-temperature region

$$\lambda_1 \sim \frac{k_7 k_4 + k_3 k_8}{k_3 + k_4}$$

$$\lambda_2 \sim k_3 + k_4$$

$$X \sim k_3$$

$$Y \sim k_4$$

Deviations from this scheme were observed with carbazole-$(CH_2)_n$-terephthalic methyl ester,[6] where static quenching of the carbazole fluorescence occurred which did not lead to exciplex emission. For 3-(9-anthryl)-1-(p-dimethylamino-phenyl)propane Mataga[7] observed that the exponential decay of the anthracene emission occurred with a lifetime of 5.5 ns. This lifetime is shorter than the exciplex decay (140 ns) but much longer than the growing in of the exciplex ($\sim$40 ps)[8a] as monitored by the absorption of the anthracene radical anion and is very close to the lifetime of methylanthracene. Eisenthal suggested[8a] that the anthracene emission was due to a conformation which failed to give exciplex and not to the return from the exciplex. This behavior was not observed for the same compound in another study.[8b] For 2-(1-naphthyl)-1-diethylaminoethane[9] in acetonitrile the decay time of the naphthalene emission (57.5 ns) did not correspond to the exciplex decay time (30 ns) and was much longer than the exciplex growing in time (3 ns). No explanation for this finding was given. Morawetz[10] assumes the presence of several conformations in the intramolecular excimer formation of compounds of the type $ArCH_2XCH_2Ar$ where Ar is phenyl, 1-naphthyl, or 4-biphenyl and X is $-CH_2-$, $-O-$, $-N^+(CH_3)_2-$, or $-NCOCH_3-$. It is stated that k_3, the rate constant for excited state complex formation, is equal to the product αk_a, where α is the fraction of monomer in a conformation from which a single hindered rotation can lead to excimer formation and k_a is the rate constant for the rotation from the trans-gauche $-(+)$ to the gauche $\pm$'(gauche $\mp$) conformation of the excimer. Owing to the small variation of α within the temperature range studied this has no consequences on the plot of ln (ϕ_E/ϕ_{LE}) vs. $1/T$. This statement is based on the assumption that the interconversion among the different conformations is faster than the formation of the excimer from the trans-gauche $-(+)$ conformation. According to this line of thought, increasing the chain length would decrease α rather than k_a. Zachariasse has observed deviations from the kinetic expression for intermolecular excimer fraction in some α,ω-diarylalkanes.[11]

In the study of intramolecular photocyclization of 4-phenyl-1-N,N-dimethylaminobutane (P4NM) and 3-phenyl-1-N,N-dimethylaminopropane (P3NM) Gilbert et al.[12] observed in the fluorescence spectra of these compounds a structureless

$$\langle\!\langle \bigcirc \rangle\!\rangle - (CH_2)_n - N \begin{array}{c} CH_3 \\ \\ CH_3 \end{array}$$

1

$n = 2$, P2NM
$n = 3$, P3NM
$n = 4$, P4NM

band bathochromic to that of toluene. In a previous paper[13] the influence of the solvent polarity and temperature on the emission of P3NM and P4NM indicated that this emission was due to a highly polar exciplex. At room temperature the exciplex formation was found to be thermodynamically controlled.
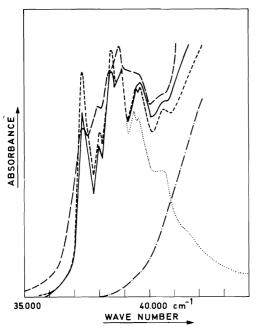
Figure 1. Absorption spectra of P2NM, P4NM, toluene, and triethylamine: - - - - -, 2×10^{-3} toluene + 2×10^{-3} triethylamine; ...., 2×10^{-3} toluene; ------, 2×10^{-3} triethylamine; ——————, 2×10^{-3} P4NM; — — — —, 2×10^{-3} P2NM.
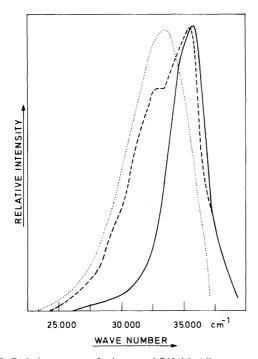

Figure 2. Emission spectra of toluene and P2NM. All spectra are normalized at the maximum: ——————, toluene at 23 °C; - - - - -, P2NM at −130 °C; ...., P2NM at 23 °C.

In this study the kinetic analysis of intramolecular exciplex formation will be attempted in the temperature region where the exciplex formation is kinetically controlled and the validity of the framework mentioned in Scheme I will be tested.

Results and Discussion

Spectra. The absorption spectra of P4NM and P3NM are comparable to those of an equimolar mixture of toluene and triethylamine with the exception of small differences in the vibronic structure. The absorption spectrum of P2NM is less structured and has a less intense 0–0 transition (Figure 1). The fluorescence spectra at 77 K are comparable with that of tol-
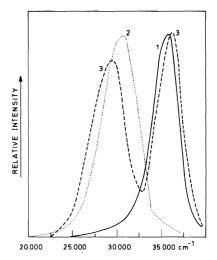

Figure 3. Emission spectra of P3NM and toluene. All spectra are normalized at the maximum: ——————, toluene at 23 °C; - - - - -, P3NM at −130 °C; ...., P3NM at 23 °C.
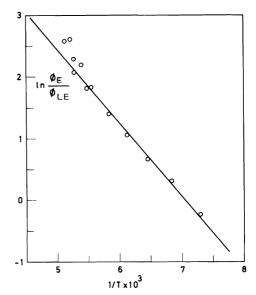

Figure 4. Influence of the temperature on the ratio of the quantum yields of emission from the locally excited state and from the exciplex of P3NM.

uene. The lifetimes at 77 K are respectively 61.4 ± 0.7 ns for toluene, 63.3 ± 2 ns for P2NM, 67.5 ± 0.9 ns for P3NM, and 66.1 ± 0.7 ns for P4NM. The emission spectrum (Figure 2) of P2NM at room temperature consists of a structureless band with a maximum at 298 nm. Whether this emission is due only to the exciplex or contains also toluene cannot be established with absolute certainty. Below −100 °C the exciplex emission shifts to 305 nm and there appears a second maximum at 283 nm due to the S_1–S_0 transition of toluene. Further lowering of the temperature decreases (Figure 2) the exciplex fluorescence and increases the toluene emission, which is characteristic for the "low-temperature behavior" of excimers and exciplexes.

The emission spectrum of P3NM at room temperature consists of a broad band with a maximum at 328 nm (Figure 3). At −55 °C the maximum has shifted to 335 nm and a shoulder appeared at 280 nm due to toluene emission. Further lowering of the temperature increases the toluene emission at the expense of the exciplex emission (Figure 3), which is typical for "low-temperature behavior" in the framework of Scheme I. For temperatures between −79 and −136 °C a plot of ln (ϕ_E/ϕ_{LE}) vs. $1/T$ yields a value of 10 kJ/mol for $E_3 - E_8$ (Figure 4).
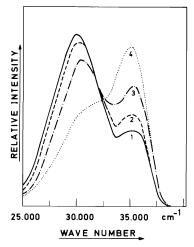
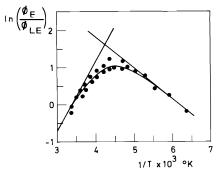**Figure 5.** Influence of the temperature on the emission spectra of P4NM: (1) −45 °C, (2) −26 °C, (3) −6 °C, (4) 23 °C.

Figure 6. Influence of the temperature on the ratio of the emission of the exciplex and of the locally excited state at P4NM.
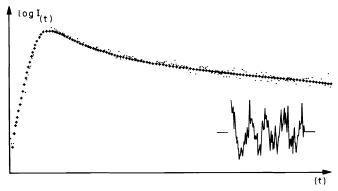
Figure 7. Decay of the toluene emission of P3NM in isopentane at −119 °C: ·, observed decay; |, lamp; +, calculated decay; channel width 0.3485 ns; ⎯, autocorrelation function of the residuals.

Figure 8. Decay of the exciplex emission of P3NM in isopentane at −121 °C: ·, observed decay; |, lamp; +, calculated decay; channel width 0.3485 ns; ⎯, autocorrelation function of the residuals.
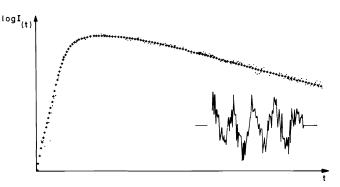
The emission of P4NM at room temperature consists of a maximum at 282 nm and a shoulder about 320 nm, due to exciplex emission. Upon cooling the exciplex emission increases at the expense of the toluene emission until −45 °C, but upon further cooling the exciplex emission starts to decrease and the toluene emission increases (Figure 5). From the slope of ln (ϕ_E/ϕ_{LE}) vs. $1/T$ in the high-temperature region a value of 15.5 kJ/mol could be obtained for the enthalpy of exciplex formation and a value of 55 kJ/mol for the ground-state repulsion. From the slope of ln (ϕ_E/ϕ_{LE}) vs. $1/T$ in the low-temperature region a value of 7.1 ± 2 kJ/mol could be obtained for the difference $E_3 - E_8$ (Figure 6).

Fluorescence Decay Measurements. Decay Measurements on P2NM. The emission of P3NM, monitored at 330 nm, in the exciplex region, decays exponentially with a lifetime of 14.3 ns at room temperature. The growing in of the emission is faster than the detection limit (0.5 ns) of our single photon counting equipment. Between −80 and −120 °C the emission can be analyzed as a difference of two exponentials (Figure 7). The decay time $(\lambda_1^{330})^{-1}$ increased from 16.5 ns at −80 °C to 18.4 ns at −120 °C and the growing-in time $(\lambda_2^{330})^{-1}$ increased from 1.3 ns at −80 °C to 7.8 ns at −120 °C (Figure 9). The ratio of the preexponential terms equals −1 within the experimental error.

The emission at 280 nm has, in the monomer region, a two-exponential decay (Figure 8) between −80 and −138 °C. The lifetime $(\lambda_1^{280})^{-1}$ of the slow component increases from 24.7 ns at −80 °C to 51 ns at −138 °C and the lifetime $(\lambda_2^{280})^{-1}$ of the fast component from 1.9 to 17 ns (Figure 9). The ratio of the preexponential terms of the fast and the slow component increases from 1.3 at −138 °C to 7.4 at −86 °C.

Decay Measurements on P4NM. At room temperature the emission of P4NM decays exponentially with a lifetime of 22.5

ns at 280 and at 330 nm. At temperatures below −45 °C the time evolution of the exciplex emission can be analyzed as a difference of two exponentials, but the decay is exponential only over the first and one-half decades.

At temperatures below −30 °C the decay of the emission of the locally excited state is not exponential. When analyzed as a sum of two exponentials the fast decay parameter $(\lambda_2^{280})^{-1}$ does not correspond between −30 and −85 °C with the growing-in time of the exciplex (Figure 10). The calculated value of λ_2^{280} has a poor reproducibility between −30 and −85 °C. The slow component of the decay, monitored at 280 nm $(\lambda_1^{280})^{-1}$, decays below −45 °C slower than the exciplex $(\lambda_1^{330})^{-1}$ (Figure 10) and converges to that value at higher temperatures. At temperatures between −45 and −85 °C a deviation is observed between the measured decay and the decay calculated assuming it to be two exponential. It is therefore reasonable to assume that in this region the decay is a more complex function of the time. Below −85 °C the decay of the toluene emission can be analyzed as a sum of two exponentials. The decay time of the fast-decaying component $(\lambda_2^{280})^{-1}$ equals the exciplex growing-in time $(\lambda_2^{330})^{-1}$. The decay time of the slow-decaying component $(\lambda_1^{280})^{-1}$ is much slower than the decay time of the exciplex $(\lambda_1^{330})^{-1}$; the ratio of the preexponentials equals 0.9 and is within the experimental error independent of the temperature.

Decay Measurements on P2NM. The exciplex emission of P2NM between −98 and −130 °C can be analyzed as a difference of two exponentials. The growing-in time of the exciplex increases from 2 ns at −98 °C to 9.6 ns at −130 °C and the decay time of the exciplex increases from 14 ns at −98 °C to 16 ns at −130 °C (Figure 11). Between −55 and 15 °C the growing-in time of the exciplex emission is beyond the detection limit of the single photon counting equipment (less than 0.5 ns), but its decay is two exponential. Its fast component correlates with the exciplex decay at low temperatures while its
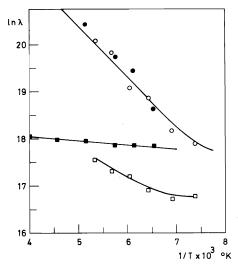
Figure 9. Influence of the temperature on the decay parameters of P3NM: ● (λ_2^{330}), growing-in time of the exciplex emission; ■ (λ_1^{330}), decay time of the exciplex emission; O (λ_2^{280}), lifetime of the fast-decaying component of the emission at 280 nm; □, lifetime λ_1^{280} of the slow-decaying component at 330 nm.

Figure 10. Influence of the temperature on the decay parameters of P4NM: □, λ_2^{280}, lifetime of the fast-decaying component of the emission at 280 nm; ■, λ_2^{330}, growing-in time of the exciplex; O, λ_1^{280}, lifetime of the slow-decaying component of the emission at 280 nm; ●, λ_2^{330}, lifetime of the exciplex.

slow component correlates at −55 °C with the lifetime of toluene and becomes shorter at higher temperatures (Figure 11). The ratio of the preexponential terms of the fast and the slow components decreases from 50 at −55 °C to 15 at 15 °C (Figure 11). At higher temperatures a one-exponential decay is observed due to the small differences between both decay times. At the intermediate temperature of −80 °C the exciplex emission shows clearly a growing in and a two-exponential decay, with a short-living component correlating with the exciplex decay time at lower temperatures and a long-living component correlating with the lifetime of toluene. The ratio of the preexponential equals 100. The emission at 280 nm has between −133 and −98 °C a two-exponential decay. The short-lived component has a lifetime corresponding to the decay of the exciplex and the long-lived component has a lifetime corresponding to that of toluene. The ratio of the preexponentials is about 3 and within the experimental error independent of the temperature.

Discussion

Interpretation of the Decay Measurements on P3NM in the Framework of Scheme I. The decay measurements on P3NM are not compatible with Scheme I for the following reasons.

1. In the framework of Scheme I the slow decay of the toluene emission $(\lambda_1^{280})^{-1}$ and the exciplex decay must have the same decay parameter (λ_1^{330}). This is clearly not observed (Figure 9).

2. The ratio of the preexponential factors of the fast- and the slow-decaying components of the toluene emission (R) increases as the temperature increases. This is in contradiction with the attribution of the slow-decaying part of the toluene emission to the return from the exciplex considering that exciplex formation is an exothermic process and that the activation energy on k_4 is mostly larger than that on k_8.

3. The small values of R observed here indicate within Scheme I an important return from the exciplex, which does not agree with the kinetic control of the exciplex formation (return from the exciplex is not important) as indicated in Figure 4.

Therefore an alternative explanation of the slow-decaying emission at 280 nm must be given. It is not due to an impurity because at 77 K the emission spectrum correlates with that of toluene. It is also not due to a toluene-like impurity because between −118 and −138 °C the ratio of the preexponential
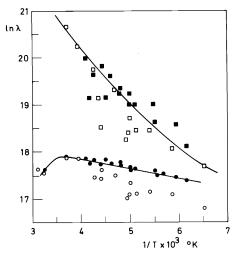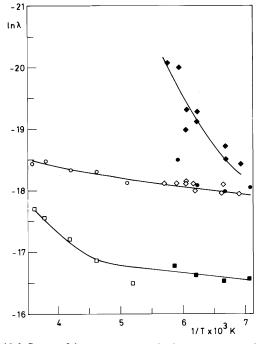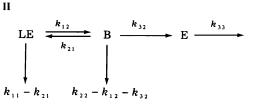

Figure 11. Influence of the temperature on the decay parameters of P2NM: ♦ growing-in time of the exciplex (−98 → −30 °C); ◊, decay time of the exciplex (−98 → −130 °C); ●, lifetime of the fast-decaying component of the emission at 280 nm (−98 → −133 °C); ■, lifetime of the slow-decaying component of the emission at 280 nm (−98 → −133 °C); O, lifetime of the fast-decaying component of the emission at 310 nm (−24 → −55 °C); □, lifetime of the slow-decaying component of the emission at 310 nm (24 → −55 °C).

factors varies between 1 and 3. Assuming that the impurity is toluene-like, this indicates that the fraction of the impurity present in the sample should amount to an impossible 25–50%.

Three Alternative Schemes for Intramolecular Exciplex Formation. (1) A first explanation is based on an equilibrium between the excited toluene (LE) and a nonfluorescent species B, on the pathway to the exciplex. B could in this scheme correspond to the nonrelaxed exciplex proposed by Mataga et al.[14]

Scheme II

Assuming Scheme II the time evolution of the exciplex emission would be given by

$$[E(t)] = [Le(0)]k_{32}k_{21}\left\{\frac{\exp(-\lambda_1 t)}{(\lambda_1 - \lambda_2)(\lambda_1 - k_{33})}\right.$$
$$\left. - \frac{\exp(-\lambda_2 t)}{(\lambda_1 - \lambda_2)(\lambda_2 - k_{33})} + \frac{\exp(-k_{33} t)}{(\lambda_1 - k_{33})(\lambda_2 - k_{33})}\right\} \quad (6)$$

with

$$\lambda_{1,2} = \tfrac{1}{2}\{(k_{11} + k_{22}) \pm [(k_{11} - k_{22})^2 + 4k_{12}k_{21}]^{1/2}\}$$

where $[LE(0)]$ is the initial concentration of LE, λ_1 corresponds to the observed λ_1^{280}, λ_2 corresponds to the observed λ_2^{280}, and k_{33} corresponds to the observed λ_1^{330}.

(2) Another explanation is the assumption that there are two different sets of starting conformations which can form the exciplex with a different rate. This assumption can be expressed in two models. A first model is represented in Scheme III.

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 free-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 proceed to F* to reach the exciplex conformation; E* and E are the exciplex and its repulsive ground state; k_8 and k_7 have the same meaning as in Scheme I; k_F is the rate constant for the formation of the exciplex; k_{-F} is the rate constant for back reaction from the exciplex to F*; k_S is the rate constant for the formation of F* from S*; k_{-S} is the rate constant for the formation of S* from F*.

When it is assumed that $k_{-F} \ll k_8$ (low-temperature region) and $k_{-S} \ll k_F + k_7$, the time evolution of the emission of the locally excited state ($I_{LE}(t)$) and of the exciplex $I_E(t)$ are given by

$$I_{LE}(t) \sim f_S\left(1 + \frac{k_S}{k_F - k_S}\right)\exp[-(k_S + k_7)t]$$
$$+ \left(f_F - \frac{f_S k_S}{k_F - k_S}\right)\exp[-(k_F + k_7)t] \quad (7)$$

$$I_E(t) \sim \left[\frac{f_S k_S}{(k_7 + k_S - k_8)} + \frac{f_F k_F - k_S}{(k_F + k_7 - k_8)}\right]\exp(-k_8 t)$$
$$+ \frac{(f_F k_F - k_S)}{k_8 - k_7 - k_F}\exp[-(k_7 + k_F)t]$$
$$+ \frac{f_S k_S}{k_8 - k_7 - k_S}\exp[-(k_7 + k_S)t] \quad (8)$$

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. Within the framework of Scheme III and taking into account the above-mentioned assumptions, the quantum yields for the emission of the locally excited state (ϕ_{LE}) and of the exciplex (ϕ_E) are given by

$$\phi_{LE} = k_1\left\{\frac{f_F}{k_7 + k_F} + \frac{f_S}{k_7 + k_S}\left[1 + \frac{k_S}{k_F + k_7}\right]\right\} \quad (9)$$

and

$$\phi_E = \frac{k_5}{k_8}\frac{k_F}{k_7 + k_F}\left[f_F + f_S\frac{k_S}{k_7 + k_S}\right] \quad (10)$$

Scheme III

k_1 and k_5 have the same meaning as in Scheme I.

(3) An alternative possibility is considered in Scheme IV. k_7, k_8, k_1, and k_5 have the same meaning as in Scheme I; F and F* are the ground state and first excited singlet state of a set of conformations that gives exciplex by a fast process; S and S* are the ground state and first excited singlet state of a set of conformations that gives exciplex by a slow process; k_F and k_S are rate constants for the formation of the exciplex from the "fast" and the "slow" conformations; k_{-F} and k_{-S} are rate constants for back reaction from the exciplex to F* and S*. In this scheme it is assumed that interconversion between S and F or F* and S* is much slower than all the other processes.

When it is assumed that $k_{-F} \ll k_8$ and $k_{-S} \ll k_8$ (low-temperature region), then the time evolution of the emission of the locally excited state ($I_{LE}(t)$) and of the exciplex ($I_E(t)$) are given by

$$I_{LE}(t) \sim f_S\exp[-(k_S + k_7)t] + f_F\exp[-(k_F + k_7)t] \quad (11)$$

$$I_E(t) \sim \frac{f_S k_S \exp[-(k_S + k_7)t]}{k_8 - k_S - k_7} + \frac{f_F k_F \exp[-(k_F + k_7)t]}{k_8 - k_F - k_7}$$
$$+ \left[\frac{f_S k_S}{k_7 + k_S - k_8} + \frac{f_F k_F}{k_7 + k_F - k_8}\right]\exp(-k_8 t) \quad (12)$$

f_F is the fraction of the molecules originally in the "fast" conformation; f_S is the fraction of the molecules originally in the "slow" conformation.

The quantum yields of the emission of the locally excited state (ϕ_{LE}) and of the exciplex (ϕ_E) are given by

$$\phi_{LE} = k_1\left[\frac{f_S}{k_7 + k_S} + \frac{f_F}{k_7 + k_F}\right] \quad (13)$$

$$\phi_E = \frac{k_5}{k_8}\left[\frac{f_S k_S}{k_S + k_7} + \frac{f_F k_F}{k_F + k_7}\right] \quad (14)$$

The ratio of the quantum yields of the exciplex (ϕ_E) and the locally excited state is within the framework of Scheme III given by

$$\frac{\phi_E}{\phi_{LE}} = \frac{k_5}{k_1}\frac{k_F}{k_8}\left[\frac{k_S + k_7 f_F}{k_7 + k_S + f_S k_F}\right] \quad (15)$$

This equation differs from eq 3 by the term between brackets. At temperatures where $k_F f_S > k_7 + k_S$ and $k_S > f_F k_7$ this term can be simplified to $k_S/f_S k_F$, which is smaller than one. In this limiting conditions the activation energy of the term between brackets equals $E_S - E_F$, when the temperature dependence of f_S is neglected.[10] The activation energy E_3, determined from the steady measurements, equals then E_S. When on the other hand $k_S \ll k_7 f_F$, the term between brackets simplifies to $k_7 f_F/(k_7 + f_S k_F)$.

Scheme IV

Table I

	P2NM	P3NM	P4NM
A_S, s^{-1}	3.1×10^{10}	7.5×10^{9}	5.2×10^{8}
A_F, s^{-1}	4.6×10^{12}	6×10^{11}	3.7×10^{10}
A_8, s^{-1}	1.6×10^{8}	1.0×10^{8}	1.5×10^{8}
E_S, kJ mol^{-1}	15 ± 4	11.0	6.6 ± 1.4
E_F, kJ mol^{-1}	13.4	12.8	8.5 ± 2
E_8, kJ mol^{-1}	1.2	0.8	2

Within the framework of Scheme IV the ratio is given by

$$\frac{\phi_E}{\phi_{LE}} = \frac{k_5}{k_1}\frac{k_F}{k_8}\left\{\frac{k_S + k_7[f_F + k_S/k_Ff_S]}{[k_7 + f_Sk_F + f_Fk_S]}\right\} \quad (16)$$

At temperatures where $k_S \gg k_7[f_F + k_S/k_Ff_S]$ and $f_Sk_F \gg f_Fk_S + k_7$, the term between brackets can be simplified to (k_S/f_Sk_F) and allows the same conclusions to be drawn as in the case of Scheme III.

When $k_7f_F \gg k_S + k_7k_Sf_S/f_F$ and $k_7 + k_F = k_S \gg f_Fk_S$, the term between brackets approaches $k_7f_F/(k_7 + f_S + k_F)$. In this limiting condition eq 15 and 16 yield the same expression:

$$\frac{\phi_E}{\phi_{LE}} = \frac{k_5}{k_1}\frac{k_F}{k_8}\left[\frac{f_Fk_7}{k_7 + f_Sk_F}\right] \quad (17)$$

If $f_Sk_F \ll k_7$, the term between brackets simplifies further to f_F/f_S. At temperatures where ϕ_E/ϕ_{LE} was determined, it was possible to make the assumptions which yield eq 17 as will be shown in the next section. Assuming that k_S and k_1 are temperature independent, the derivative of ln (ϕ_E/ϕ_{LE}) vs. the absolute temperature is given by

$$\frac{\partial}{\partial T}\ln(\phi_E/\phi_{LE}) = \frac{(E_F - E_8)}{RT^2}$$
$$+ \frac{\partial}{\partial T}\ln f_F + \frac{\partial}{\partial T}\ln\left[\frac{k_7}{k_7 + f_Sk_F}\right] \quad (18)$$

Upon increasing the temperature the increase of k_F will largely overcome changes in f_S and thus the ratio $k_7/(k_7 + f_Sf_F)$ will decrease. When a small temperature dependence of f_F is assumed, the difference $(E_3 - E_8)$, observed in stationary measurements, will be less than $E_F - E_8$, as it is observed here, and will decrease upon increasing the temperature. This can cause a plot of ln (ϕ_E/ϕ_{LE}) vs. the $1/T$ to deviate from a straight line at the higher temperatures, even in the absence of back reaction from the exciplex (k_4).

Evaluation of the Kinetic Schemes for P3NM. In the framework of Scheme II the ratio of the preexponential term factors of $\exp(-\lambda_1 t)$ and $\exp(-k_{33}t)$ in eq 6 can be calculated from the observed decay parameters λ_1, λ_2, and k_{33}. That ratio is -1.08 at -98 °C and -1.37 at -120 °C. Instead of a one-exponential growing in a one-exponential decay, a two-exponential growing in, of which the most important component had a time constant equal to $(\lambda_1^{330})^{-1}$, and a one-exponential decay with the decay time equal to $(\lambda_1^{280})^{-1}$ should have been observed. This is clearly not the case. Furthermore, using this model the entropy and enthalpy for the formation of B can be calculated on the basis of the experimental data and both are found to be positive, which is rather unlikely for (some kind of) complex formation.

Within the framework of Schemes III or IV and using the assumptions that $k_{-F} \ll k_8$ and $k_{-S} \ll k_7$ or that $k_{-7} \ll k_8$, and a fortiori $k_{-S} \ll k_8$, it is possible to put λ_1^{280}, λ_2^{280}, and λ_1^{330} respectively equal to $k_S + k_7$, $k_F + k_7$, and k_8. This allows one to calculate k_S and k_F. Knowing k_S, k_F, λ_1^{280}, and λ_2^{280} it is possible to calculate from the ratio of the preexpontial factors in eq 7 or 11 the ratio f_S/f_F. This ratio is within 5% the same whether Scheme III or IV is assumed and amounts to 7.4 at -86 °C and 4 at -120 °C.
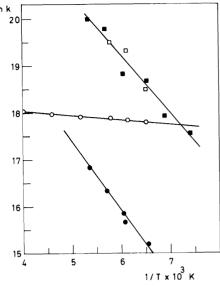

Figure 12. Influence of the temperature on ln k_S, ln k_F, and ln k_8 at P3NM: ■ ln k_F, determined from λ_2^{280}; □, ln k_F, determined from λ_2^{330}; ●, ln k_S, determined from λ_1^{280}; ○, ln k_8, determined from λ_1^{330}.

The calculated values of the ratio of the preexponential terms of $\exp[-(k_S + k_7)t]$ and $\exp(-k_8t)$ in eq 8 are, using Scheme III, respectively 0.04 and 0.017 at -87 and -120 °C. This is compatible with the fact that the exciplex decays exponentially in the first and the second decade, with a decay time that equals k_8^{-1}, and that $(\lambda_2^{330})^{-1}$, the growing-in time of the exciplex, equals $(\lambda_2^{280})^{-1}$, the decay time of the fast-decaying component of the toluene emission. Using Scheme IV gives identical results.

When it is assumed that the equilibrium constant between the "fast" and the "slow" conformations is the same in the first excited singlet state as in the ground state, where it equals f_F/f_S, then $f_F/f_S = k_S/k_{-S}$ in the framework of Scheme III. The values of the preexponential factors of the decay indicate that $f_F/f_S > 1$ and thus k_{-S} is less than k_S, but k_S is much less than k_F; then k_{-S} is surely much less than k_F and the assumption made in deriving eq 7 and 8 is reasonable. The assumptions that $k_{-F} \ll k_8$ in Scheme III or $k_{-S} \ll k_8$ in Scheme IV are justified by the steady-state measurements. The ratio f_F/f_S seems to increase upon increasing the temperature, but, because of the rather large errors on the determination of the preexponential terms of the decay, necessary to calculate f_F/f_S, no further quantitative information on this aspect is given.

While Scheme II is clearly not compatible with the observed results, there is so far no ground to choose between Schemes III or IV. Assuming an Arrhenius relationship for k_S, k_F, and k_8, it is possible to calculate the activation energy E and the preexponential term A for these rate constants (Figure 12). The results of this calculation are given in Table I.

For P3NM the difference $E_6 - E_8$ amounts to 12 kJ/mol and $E_5 - E_8$ equals 10.2 kJ/mol. This equals within the experimental error the slope of the plot in Figure 4. When the first simplification of eq 15 and 16, which becomes reasonable for temperatures above -96 °C, is considered, the slope of ln (ϕ_E/ϕ_{LE}) vs. $1/T$ should be equal to $E_S - E_8$, which corresponds with our observations. When the second simplification of eq 15 and 16 (which yields eq 17) is considered, the slope of ln (ϕ_E/ϕ_{LE}) vs. $1/T$ should be slightly smaller than $E_F - E_8$. This simplification is very reasonable for temperatures below -118 °C and yields no contradiction between the calculated and the observed values for the slope of ln (ϕ_E/ϕ_{LE}) vs. the reciprocal of the temperature.
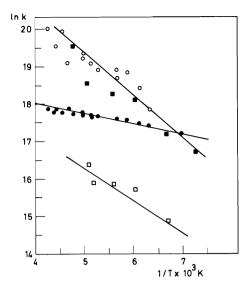
Interpretation of the Decay Measurements on P4NM and

Figure 13. Influence of the temperature on ln k_S, ln k_F, and ln k_8 at P4NM: O, ln k_F, determined from $\lambda_2{}^{330}$; ■, ln k_F, determined from $\lambda_2{}^{280}$; ●, ln k_8, determined from $\lambda_1{}^{330}$; □, ln k_S, determined from $\lambda_1{}^{280}$.

P2NM. For the same reasons as mentioned with P3NM the classical kinetic scheme for intramolecular exciplex formation cannot be used for the interpretation of the decay measurements of P4NM, but it is possible to apply the kinetics of Schemes III or IV to the observed decays. Above -30 °C the system is in the "high-temperature" region and the slow part of the decay of the emission of the locally excited state is due to dissociation of the exciplex (k_{-F} and k_{-S}). Below -85 °C the decay is due to slow and fast sets of conformations. This interpretation is compatible with the steady-state results and with the low value of the ratio of the preexponential terms of the fast and the slow components. At the intermediate temperatures the decay is three exponential[23] because neither the contribution from exciplex dissociation nor that from the "slow" conformations is negligible. Also the deviation of the exponential decay in the exciplex emission in the second and third decade can be explained. They are due to the term with $\exp[-(k_S + k_7)t]$ in eq 8 or 12. The fact that at the temperatures below -85 °C the decay is two exponential and not multiexponential indicates that, of all the conformational changes necessary to reach the exciplex, two occur a lot slower than all the others.

At temperatures below -85 °C it is possible to put $\lambda_2{}^{330}$ or $\lambda_2{}^{280}$ equal to $k_F + k_7$, $\lambda_1{}^{280}$ equal to $k_7 + k_S$, and $\lambda_1{}^{330}$ equal to k_8. Although the errors in the determination of the preexponential factors are large, they can be used to estimate an approximate value for f_S and f_F (at -106 °C $f_S \sim 0.5$ and $f_T \sim 0.5$). Using eq 33, 34, and 26 or 44, 50, and 51 this allows us to calculate that 30% of the exciplex is formed from the slow conformations and 70% from the fast conformations. The similarity of $\lambda_2{}^{330}$ and $\lambda_2{}^{280}$ indicates that the exciplex is mostly formed from the fast conformations. Relating ln k_F, ln k_S, and ln k_8 to $1/T$ allows us to calculate the activation energies E_S, E_F, and E_8 and the preexponentials A_S, A_F, and A_8 (Table I, Figure 13).

In the low-temperature region, a plot of ln (ϕ_E/ϕ_{LE}) vs. $1/T$ has a slope of 7.1 ± 2 kJ/mol, which equals $E_F - E_8 = 6.5 \pm 2$ kcal/mol within the experimental error. In the high-temperature region there is a fast equilibrium between the exciplex and at least the fast conformations. In this case the observed ΔH is the difference between the enthalpy of the exciplex and a value of the enthalpy intermediate between the enthalpy of the fast conformations and the average enthalpy of both conformations. When there is also a fast equilibrium between the exciplex and the slow conformations ($k_{-S} > k_7$ in the frame-
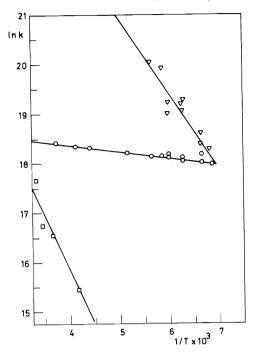

Figure 14. Influence of the temperature on ln k_S, ln k_F, and ln k_8 at P2NM: ∇, ln k_F; O, ln k_8; □, ln k_S.

work of Scheme III or $k_{-S} > k_8$ in the framework of Scheme IV), the observed ΔH is the difference between the enthalpy of the exciplex and the average enthalpy of both conformations of the locally excited state. Owing to the rather small enthalpy difference between both conformations both possibilities are nearly equivalent. It should be stressed that deviations from Scheme I cannot be observed using only steady-state measurements since the plot of ln (ϕ_E/ϕ_{LE}) vs. $1/T$ has exactly the same shape as when Scheme I is valid and since the observed values of ΔH and $E_3 - E_8$ are very reasonable in the framework of Scheme I.
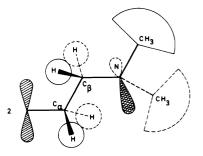
For P2NM the results are also in contradiction with Scheme I but not with Schemes III or IV. The long-living component as well at 310 nm as at 280 nm is due to "slow" conformations. At 280 nm it is due to emission from toluene in a molecule in a "slow" conformation, and at 310 nm it is due to emission of the exciplex formed from a molecule originally in a "slow" conformation (eq 8 or 12). The fast component at 280 nm is due to the overlap of the emission of spectra of toluene and of the exciplex and probably hides a component due to toluene emission and with a lifetime equal to the growing-in time of the exciplex emission. It is possible to put the lifetime of the fast-decaying component at 310 nm equal to $k_8{}^{-1}$ and the lifetime of the slow-decaying component at 310 or 280 nm equal to $(k_7 + k_S)^{-1}$; the growing-in time of the exciplex can be put equal to $(k_7 + k_F)^{-1}$. Relating ln k_S, ln k_F, and ln k_8 to $1/T$ (Figure 14) allows one to calculate E_F, E_S, E_8, A_S, A_F, and A_8 (Table I). It is not possible to extract information about f_S or f_F from the ratio of the preexponentials between -55 and $+15$ °C because k_F is not known at these temperatures.

Conclusions

Upon increasing the chain length the activation energies E_F and E_S as well as the preexponential terms A_S and A_F decrease. For k_F and k_S between P3NM and P4NM the second factor largely overcomes the first one. The high activation energies for P2NM are perhaps due to steric effects between the phenyl group and the methyl groups on the nitrogen. In the investigated compounds some conformational changes seem to happen faster than the others, resulting in a two-exponential decay of P3NM and P4NM rather than a multiexponential

one. Each conformation, as the word is used in this context, should be understood as an ensemble of several physical conformations in fast equilibrium with each other and both ensembles are separated by a relatively high energy barrier. The decrease of A_F as the chain length increases is readily understood. Upon increasing the chain length the total number of physical conformations increases and of the "fast conformation" a smaller fraction of the molecules is in the right physical conformation to undergo the final rotation to reach the conformation of the exciplex. In the framework of Scheme IV the decrease of A_S when the chain length increases can be understood in the same way. Within the framework of Scheme III this decrease of A_S is more difficult to explain. It should perhaps signify that of all the physical conformations which belong to the "slow conformation" only a fraction, decreasing with increasing chain length, is able to be transformed in a physical conformation of the "fast conformation". In Scheme III the large difference between the preexponential terms A_S and A_F is difficult to explain. It seems reasonable to assume that the differences in rate for conformational changes are due rather to a difference in activation energy than to a difference of the preexponential factors.[15] In the framework of Scheme IV this difference means that for the slow conformations the exciplex formation occurs by a different mechanism than for the fast conformations.

The presence of "slow" and "fast" conformations suggests the following interpretation. In a linear alkyl chain conformational changes occur in 10–100 ps at room temperatures;[16a,b] therefore it is unlikely that the observed phenomena are related to some conformations of the alkyl chain. For rotation around the single bond between a phenyl and an adjacent $-CH_2-$ the activation energy is even lower.[16c,17] Rotation around a $RCH_2N R''R'$ bond has, however, an activation energy of 27.8 kJ/mol.[16d] This process is slow enough at room temperature to be responsible for the presence of slow conformations. E_S is much smaller than 27 kJ/mol; this suggests that k_S rather describes an alternative way of exciplex formation (Scheme IV) than rotation around the CH_2-N bond to yield a "fast" conformation. Studies on space-filling molecular models suggested that the slow conformations can be identified with a trans orientation of the nitrogen lone pair toward the rest of the molecule on the CH_2 α to the nitrogen, while the gauche orientation corresponds to a fast conformation. This is shown in Figure 15, where both conformations are drawn for P2NM. In the fast conformation (Figure 15, **2**) rotation around the bond between both CH_2 brings the nitrogen lone pair in overlap with the phenyl, which favors interactions leading to the exciplex. For the slow conformation it is not possible to make the large lob of the nitrogen lone pair point to the phenyl (Figure 15, **1**). Studies on molecular models on P3NM and P4NM yield the same results. Further research on the intramolecular exciplex formation of 11-phenyl-1-*N,N*-dimethylaminoethane in THF showed that for 11 CH_2 groups between the amine and phenyl this effect has disappeared.[18] Since in the exciplex the nitrogen is planar, the differences between both conformations disappear and it is reasonable to assume that both conformations give rise to the same exciplex. The small preexponential term of k_8 indicates that the main radiationless process of the exciplex is intersystem crossing and not internal conversion to the ground state. The related trigonal triplet of the amine will have an energy which is about 1000–5000 cm^{-1} above that of the exciplex[19a,b] and the toluene triplet[20] is about 8000 cm^{-1} below the exciplex in isopentane. The Franck–Condon tetrahedral triplet of the amine will have a still higher energy. It is therefore most probable that intersystem crossing will result in triplet toluene. When the solvent polarity increases, the exciplex is stabilized relative to the toluene triplet, resulting in an increase of the exciplex lifetime upon increasing the solvent polarity.[12]
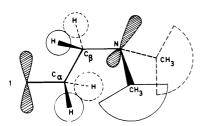

Figure 15. Scheme of the slow (**1**) and the fast (**2**) conformations at P2NM. In **2** a rotation about the $C_\alpha-C_\beta$ bond brings in the large lob of the nitrogen the lone pair above the phenyl nucleus. In **1** this is not possible.

Whether the exciplex lifetime decreases again in very polar solvents is under investigation.

Experimental Section

Absorption spectra were recorded with a Perkin-Elmer 124 double beam spectrophotometer or a Cary 17 spectrophotometer. Emission spectra were run on a Fica Fluorimètre "absolu et différentiel" and a Spex Fluorolog. Temperature control was obtained with a stream of nitrogen which was first passed through liquid nitrogen and then heated to the appropriate temperature.

Decay measurements were done using the single photon counting technique. The observed decays were deconvoluted using a nonlinear least-squares[21] method. As a criterion for the goodness of the fit the autocorrelation function[21] and the value of $X_v{}^2$ as determined by Selinger[22] were used. P2NM, P3NM, and P4NM were obtained from Professor A. Gilbert. Their purity was checked with GLC and TLC. All measurements were performed in isopentane from Merck. Its purity (GLC) was better than 99.92%. It contained no fluorescent contaminant upon excitation in the wavelength region of experimental interest (267 nm).

Appendix I. Derivation of Equation 6

In this derivation Scheme II is assumed.

The concentrations of LE and B show exactly the same time dependence as the concentration of the locally excited state and the exciplex in Scheme I.

$$[LE] = [LE(0)] \left[\frac{\lambda_2 - k_{22}}{\lambda_2 - \lambda_1} \exp(-\lambda_2 t) \right.$$

$$\left. + \frac{k_{22} - \lambda_1}{\lambda_2 - \lambda_1} \exp(-\lambda_1 t) \right] \quad (19)$$

$$[B] = \frac{[LE(0)]k_{21}}{(\lambda_2 - \lambda_1)} \{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \quad (20)$$

For the time dependence of the concentration of C the fol-

lowing differential equation can be written:

$$d[C]/dt = k_{32}[B] - k_{33}[C] \tag{21}$$

Replacing [B] by the right-hand side of eq 20 and solving the differential equation gives

$$[E] = [LE(0)]k_{32}k_{21}\left\{\frac{\exp(-\lambda_1 t)}{(\lambda_2 - \lambda_1)(k_{33} - \lambda_1)}\right.$$
$$\left. - \frac{\exp(-\lambda_2 t)}{(\lambda_2 - \lambda_1)(k_{33} - \lambda_2)} + \frac{\exp(-k_{33}t)}{(k_{33} - \lambda_1)(k_{33} - \lambda_2)}\right\} \tag{22}$$

Appendix II. Derivation of Equations 7–10

Assuming Scheme III and the assumption made the following differential equation can be written for the concentrations of [S*], [F*], and [E*]:

$$d[F^*]/dt = k_S[S^*] + I_0 f_F - (k_F + k_7)[F^*] \tag{23}$$

$$d[S^*]/dt = f_S I_0 - (k_7 + k_S)[S^*] \tag{24}$$

$$d[E^*]/dt = k_F[F^*] - k_8[E^*]$$

I_0 is the number of photons absorbed per liter and per second. The solutions of those differential equations are, using the relation $f_S + f_F = 1$

$$[S^*] = I^0 f_S \exp[-(k_S + k_7)t] \tag{25}$$

$$[F^*] = I_0\left\{\left[f_F - \frac{k_S f_S}{k_F - k_S}\right]\exp[-(k_F + k_7)t]\right.$$
$$\left. + \frac{f_S k_S}{(k_F - k_S)}\exp[-(k_S + k_7)t]\right\} \tag{26}$$

$$[E^*] = \frac{I_0 k_F}{k_F - k_S}\left\{-\left[\frac{f_F k_F - k_S}{k_8 - k_7 - k_F}\right.\right.$$
$$\left. + \frac{f_S k_S}{k_8 - k_7 - k_S}\right]\exp(-k_8 t)$$
$$+ \frac{f_F k_F - k_S}{k_8 - k_7 - k_F}\exp[-(k_7 + k_F)t]$$
$$\left. + \frac{f_S k_S}{k_8 - k_7 - k_S}\exp[-(k_7 + k_S)t]\right\} \tag{27}$$

S* as well as F* gives emission of the locally excited state with the same fluorescent rate constant k_1. Thus the time dependence of the emission of the locally excited state is given by

$$I_{LE}(t) \sim ([F^*] + [S^*])$$

$$\sim I^0\left\{\left[f_F - \frac{k_S f_S}{(k_8 - k_S)}\right]\exp[-(k_7 + k_F)t]\right.$$
$$\left. + f_S\left[1 + \frac{k_S}{k_F - k_S}\right]\exp[-(k_7 + k_S)t]\right\} \tag{28}$$

The exciplex emission intensity is proportional to [E*] and is thus given by eq 27.

Molecules originally in the slow conformation give emission of the locally excited state with a quantum yield $k_1/(k_7 + k_S)$, when they have passed to a fast conformation they can again give emission of the locally excited state with a quantum yield equal to

$$\phi = \frac{k_1 k_S}{(k_7 + k_S)(k_F + k_7)}$$

So the total quantum yield for the emission of the locally excited state, (ϕ_{LE}^S), is for molecules originally in a slow conformation

$$\phi_{LE}^S = \frac{k_1}{k_7 + k_S}\left(1 + \frac{k_S}{k_7 + k_F}\right) \tag{29}$$

For the molecules originally in the fast conformation the

quantum yield for the emission of the locally excited state is (ϕ_{LE}^F)

$$\phi_{LE}^F = k_1/(k_7 + k_F) \tag{30}$$

The total quantum yield for the LE emission is

$$\phi_{LE} = f_S \phi_{LE}^S + f_F \phi_{LE}^F$$

$$= k_1\left\{\frac{f_S}{k_7 + k_S}\left[1 + \frac{k_S}{k_7 + k_F}\right] + \frac{f_F}{k_7 + k_F}\right\} \tag{31}$$

$$= \frac{k_1[k_7 + f_S k_F]}{(k_7 + k_S)(k_7 + k_F)} \tag{32}$$

The molecules originally in the slow conformation give exciplex emission with a quantum yield ϕ_E^S:

$$\phi_E^S = \frac{k_S}{(k_7 + k_S)}\frac{k_F}{(k_7 + k_F)}\frac{k_5}{k_8} \tag{33}$$

For those originally in a fast conformation this quantum yield equals

$$\phi_E^F = \frac{k_F}{k_7 + k_S}\frac{k_5}{k_8} \tag{34}$$

The total quantum yield for exciplex emission equals

$$\phi_E = \phi_E^F f_F + \phi_E^S f_S \tag{35}$$

$$= \left[\frac{f_S k_S k_F + f_F(k_7 + k_S)k_F}{(k_7 + k_S)(k_7 + k_F)}\right]\frac{k_5}{k_8} \tag{36}$$

$$= \frac{k_5 k_F[f_F k_7 + k_S]}{k_8(k_F + k_7)(k_S + k_7)} \tag{37}$$

Appendix III. Derivation of Equations 11–14

Assuming Scheme IV and the assumptions made the differential equations for the concentrations of S*, F*, and E* are

$$d[S^*]/dt = I_0 f_S - (k_S + k_7)[S^*] \tag{38}$$

$$d[F^*]/dt = I_0 f_F - (k_F + k_7)[F^*] \tag{39}$$

$$d[E^*]/dt = [F^*]k_F + [S^*]k_S - [E^*]k_8 \tag{40}$$

I_0 is the number of photons absorbed per liter and per second. Solving these equations leads to

$$[S^*](t) = I_0 f_S \exp[-(k_S + k_7)t] \tag{41}$$

$$[F^*](t) = I_0 f_F \exp[-(k_F + k_7)t] \tag{42}$$

$$[E^*](t) = I_0\left\{\frac{f_S k_S \exp[-(k_7 + k_S)t]}{k_8 - k_S - k_7}\right.$$
$$+ \frac{f_F k_F \exp[-(k_F + k_7)t]}{k_8 - k_F - k_7}$$
$$\left. + \left[\frac{f_S k_S}{k_7 + k_S - k_8} + \frac{f_F k_F}{k_7 + k_F - k_8}\right]\exp[-k_8 t]\right\} \tag{43}$$

[F*] and [S*] give LE emission with the same fluorescent rate constant; thus

$$I_{LE}(t) \sim ([S^*] + [F^*])$$
$$\sim (f_F \exp[-(k_F + k_7)t] + f_S \exp[-(k_S + k_7)t]) \tag{44}$$

The intensity of the exciplex emission is proportional to [E*] and thus to the right-hand side of eq 43. The quantum yield of LE emission from the slow (ϕ_{LE}^S) and the fast conformations (ϕ_{LE}^F) is given by

$$\phi_{LE}^S = k_1/(k_S + k_7) \tag{45}$$

$$\phi_{LE}{}^F = k_1/(k_F + k_7) \tag{46}$$

The total quantum yield of LE emission is

$$\phi_{LE} = f_S\phi_{LE}{}^S + f_F\phi_{LE}{}^F \tag{47}$$

$$= k_1 \left[\frac{f_S}{k_S + k_7} + \frac{f_F}{k_F + k_7} \right] \tag{48}$$

$$= \frac{k_1(k_7 + f_S k_F + f_F k_S)}{(k_S + k_7)(k_F + k_7)} \tag{49}$$

The quantum yield of exciplex emission from the slow $(\phi_E{}^S)$ and the fast conformations $(\phi_E{}^F)$ is given by

$$\phi_E{}^S = \frac{k_5}{k_8} \frac{k_S}{(k_S + k_7)} \tag{50}$$

and

$$\phi_E{}^F = \frac{k_5}{k_8} \frac{k_F}{(k_F + k_7)} \tag{51}$$

The total quantum yield of exciplex emission is then given by

$$\phi_E = f_F\phi_E{}^F + f_S\phi_E{}^S$$

$$= \frac{k_5}{k_8} \left[f_F \frac{k_F}{k_F + k_7} + f_S \frac{k_S}{k_S + k_7} \right] \tag{52}$$

$$= \frac{k_5}{k_8} \frac{k_S k_F + k_7(k_F f_F + k_S f_S)}{(k_F + k_7)(k_S + k_7)} \tag{53}$$

References and Notes

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