INTRAMOLECULAR EXCIPLEX FORMATION IN 1-(1-PYRENYL)-3-(*N*-SKATOLYL)PROPANE†

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Summary

The photophysical properties of 1-(1-pyrenyl)-3-(*N*-skatolyl)propane were investigated. Excitation of the pyrene chromophore leads to the formation of an intramolecular exciplex. This complex has a larger dipole moment than that of the corresponding intermolecular complex. The kinetics of exciplex formation are analysed in solvents of various polarities. The binding energy of the complex increases with solvent polarity. The decay pattern of the pyrene fluorescence indicates fast equilibration between the various conformers in comparison with the rate of exciplex formation.

1. Introduction

It has previously been shown that complexes are formed between excited pyrene derivatives and 1,2-dimethylindole (1,2-DMI) [1]; more specifically 1-methylpyrene (CH_3P) forms a heteroexcimer with 1,2-DMI with a partial charge transfer character as indicated by the low value of 7550 cm^{-1} for $2\mu_c^2/4\pi\epsilon_0 hc\rho^3$ (this value is substantially lower than the values reported for *N*-methylindole–cyanonaphthalene [2] and dimethylaniline–anthracene [3]).

Intramolecular exciplex formation in 1,3-disubstituted propanes has been studied with aromatic and aliphatic amines as donors (for a recent review see ref. 4). It has been shown that in the case of α-aryl-ω-*N*-diethylaminopropane [5] and 1,3-(9-anthryl-4-*N*-dimethylphenyl)propane [6] the conformational distribution in the ground state is reflected in the

†Dedicated to Professor Dr. Dietrich Schulte-Frohlinde on the occasion of his 60th birthday.

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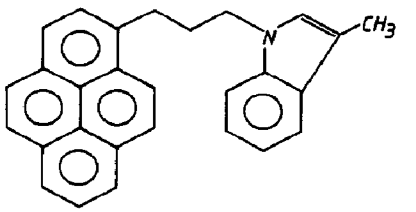

Fig. 1. Structure of 1-(1-pyrenyl)-3-(*N*-skatolyl)propane.

formation process of the exciplex. The former observation has been related to the hindered rotation around the C—N bond. In this paper we report the photophysical properties of 1-(1-pyrenyl)-3-(*N*-skatolyl)propane (P_3I) (Fig. 1) in non-polar and slightly polar solvents.

2. Experimental details

P_3I was synthesized from 1-pyrene aldehyde (Aldrich). In a first step 1-pyrene aldehyde was converted to *trans*-3-(1-pyrenyl)acrylic acid with malonic acid in pyridine. The acid was converted to the methyl ester which was reduced with Pd–H_2 at atmospheric pressure to methyl-3-(1-pyrenyl)-propanoate. The ester was treated with $LiAlH_4$ to obtain 3-(1-pyrenyl)-propan-1-ol. The alcohol was converted to the bromide by reacting with PBr_3 in a 1:1 benzene–dichloromethane mixture at 0 °C.

P_3I was obtained by reacting 1-(1-pyrenyl)-3-bromopropane with the skatol (3-methylindole) anion in dimethyl sulphoxide (all compounds were characterized using standard organic chemistry techniques). The nuclear magnetic resonance spectrum of P_3I in C_6D_6 at room temperature is shown in Fig. 2. The P_3I used in the spectroscopic studies was purified by high performance liquid chromatography on Al_2O_3 using hexane as the eluent.

The methods used to purify the solvent and the experimental techniques adopted are described elsewhere [1]. The decay parameters and pre-exponential factors were obtained by a non-linear least-squares fitting of the fluorescence decay curves measured using the single-photon-counting technique. Four criteria were used to judge the goodness of fit [7]: χ^2, the weighted residuals R_i, the autocorrelation function C_i [8] and the serial correlation coefficient D [9]. A decay fitting was rejected when one of these parameters was not acceptable.

3. Results

3.1. Spectroscopic aspects

The absorption spectrum of a solution of P_3I is identical with that of an equimolar mixture of CH_3P and 1,3-dimethylindole in the solvents used. No new band is observed, indicating that important ground state interactions are

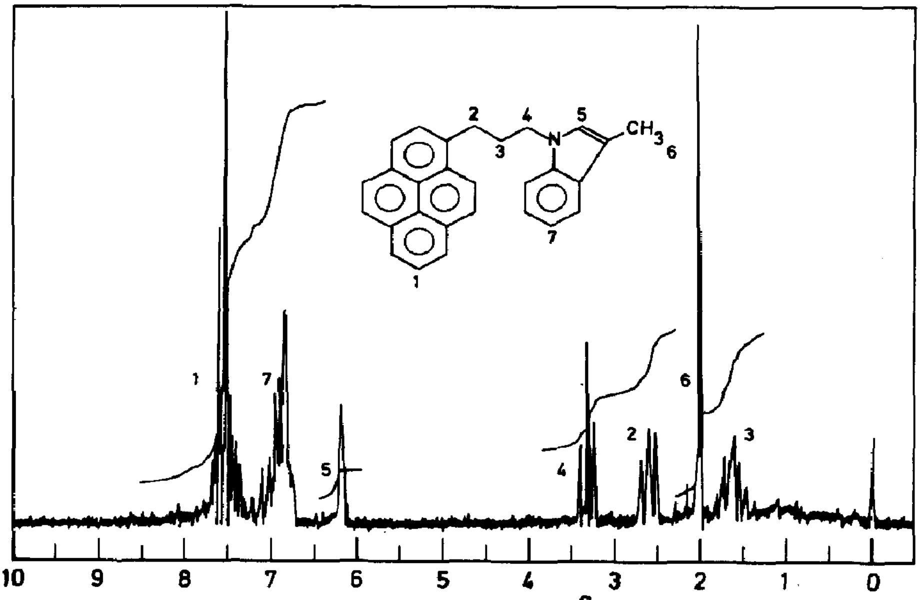

Fig. 2. ^1H nuclear magnetic resonance spectrum of P_3I in C_6D_6 at 25 °C. The internal standard is tetramethylsilane.

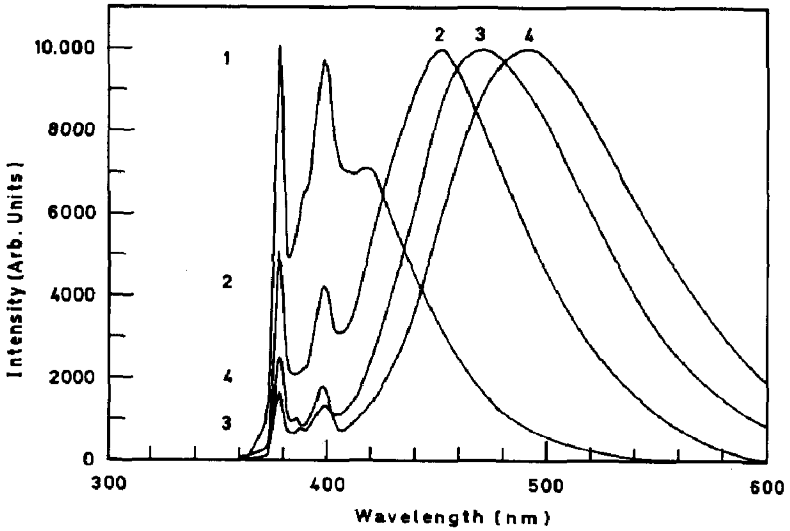

Fig. 3. Normalized fluorescence spectra of P_3I (absorbance, 0.12 at 342 nm) in various solvents at room temperature: 1, isooctane; 2, dibutyl ether; 3, butyl acetate; 4, acetonitrile.

absent. The fluorescence spectra of P_3I in various solvents are shown in Fig. 3.

The bathochromic shift of the exciplex emission depends on the solvent polarity. From a plot of the maximum of the exciplex fluorescence as a function of the solvent parameters $f - \frac{1}{2}f'$ a value of 8850 cm^{-1} is obtained for the ratio $2\mu_e^2/4\pi\epsilon_0 hc\rho^3$, where μ_e is the exciplex dipole moment and ρ is the solvent cavity (this value is substantially lower than the values reported for N-methylindole–cyanonaphthalene [2] and dimethylaniline–anthracene [3]). Compared with the value for the intermolecular system, which is 7550 cm^{-1}, this higher value indicates that the dipole moment of P_3I is larger, provided that ρ does not become smaller for P_3I in comparison with the CH_3P-1,2-DMI system. This means that in P_3I either the centres of the charges are kept slightly further apart by the chain or mixing between the charge transfer state and the locally excited state is decreased.

3.2. *Kinetic and thermodynamic aspects in solvents of low polarity ($\epsilon < 6$)*

A plot of the logarithm of $\phi^F{}_E/\phi^F{}_A$, the ratio of the quantum yield of the exciplex to the quantum yield of the locally excited state, as a function of $1/T$ is given in Fig. 4 for P_3I in isooctane, dibutyl ether (DBE) and butyl acetate (top, middle and bottom curve respectively). The decay parameters obtained from the decay curves of the locally excited state and the exciplex in the three solvents are given in Table 1 as a function of temperature.

An important conclusion to be drawn from the results in Table 1 is that even at very low temperatures single exponential decay is observed for the locally excited state of P_3I. This indicates that the effect of the conformational distribution in the ground state which is observed in the photophysics of 1-aryl-3-(N,N'-dialkyl)aminopropanes and is attributed to rotations

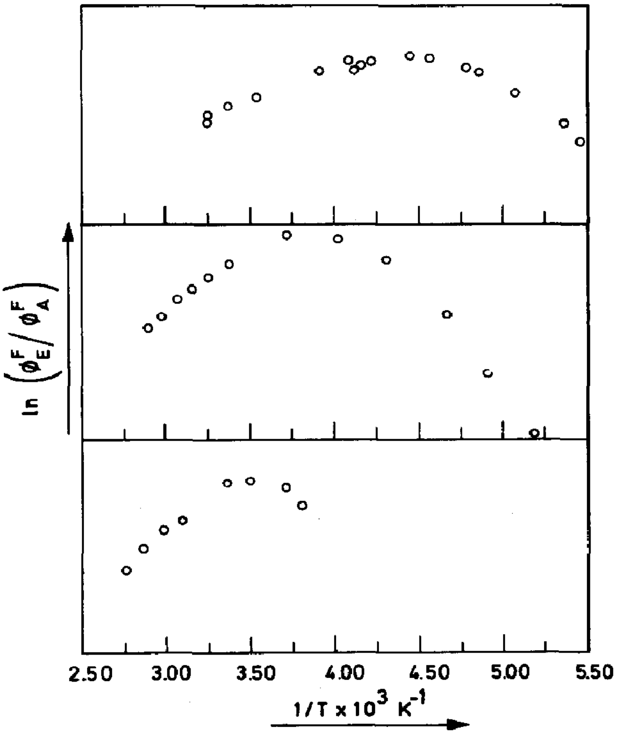

Fig. 4. Plot of $\ln(\phi^F{}_E/\phi^F{}_A)$ as a function of $1/T$ for P_3I in the three solvents.

TABLE 1

Decay parameters of P_3I in various solvents as a function of temperature

Solvent	T (°C)	Locally excited state			Exciplex		
		$1/\lambda_1$ (×10^9 s)	$1/\lambda_2$ (×10^9 s)	A	$1/\lambda_1$ (×10^9 s)	$1/\lambda_2$ (×10^9 s)	A
Isopentane	25	142	—	—	148	—	—
	−5	86.1	1.9	0.18[a]	88.2	1.75	−0.95
	−19	79.6	3.0	0.23[a]	79.5	3.17	−0.93
	−35	75.34	6.16	0.23[a]	74.13	6.11	−0.94
	−50	86.0	[a]	[a]	85.6	7.16	−0.98
	−70	87.0	[a]	[a]	86.5	14.0	−0.98
	−90	129.2	—	—	127	20.91	−0.96
	−110	205.7	—	—	207.9	21.93	−0.96
	−130	270.5	—	—	[b]	[b]	[b]
	−136	284.5	—	—	[b]	[b]	[b]
DBE	27	77.9	2.05	0.49	78.2	2.44	−0.96
	25	77.3	2.3	0.47	77.2	2.5	−0.90
	−2.5	62.7	7.0	0.44	61.1	7.1	−0.99
	−17	59.0	11.0	0.55	57.7	12.4	−0.99
	−32.5	59.8	22.9	0.38	57.3	21.9	−0.99
	−50	59.5	26	0.34	56.0	26	−0.99
	−65	83.3	—	—	86.02	32.42	−0.98
	−75	123.3	—	—	121.3	37.9	−0.96
	−85	172.1	—	—	174.6	42.12	−0.90
Butyl acetate	39.5	63.6	2.34	1.06	62.7	2.39	−0.98
	25	58.3	3.76	1.74	57.9	3.94	−1.00
	14.5	56.8	4.55	2.22	56.00	5.05	−0.99
	−5	54.8	9.28	3.73	53.1	9.7	−1.00
	−19	54.0	15.7	4.82	52.5	17.0	−1.00

[a]The decay is double exponential; the contribution of λ_2 is small and contains a large error. The analysis was performed in the following way: k_3 was extrapolated from the region where the decay of P_3I is single exponential, and k_4 and k_8 were obtained using the extrapolated value of k_3 and λ_1 and λ_2 obtained in the exciplex region.
[b]The exciplex decay could not be measured because the emission intensity was too low.

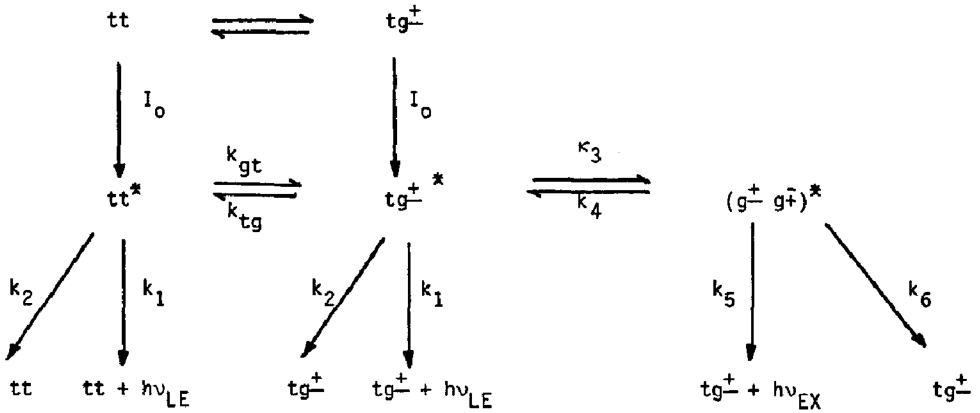

Fig. 5. The general scheme for intramolecular excited state complex formation in 1,3-disubstituted propanes [10].

around the C—N bond is, as expected, not detected in this system. Figure 5 shows the general scheme for intramolecular excited state complex formation in 1,3-disubstituted propanes [10]. tt, $tg^{\pm}$ and $g^{\pm}g^{\mp}$ refer to various chain conformations in the 1,3-disubstituted propanes, and k_{gt} and k_{tg} are the rate constants for conformational changes between the tt and the $tg^{\pm}$ conformations.

It is clear from the experimental results that in the case of P_3I k_{gt} and k_{tg} are very fast with respect to exciplex formation (rate constant, κ_3), which means that the equilibrium between the various conformations of the chain is fast with respect to exciplex formation. It can be shown that the experimental rate constant for complex formation obtained in such a system is given by

$$k_{exp} = \frac{\kappa_3(k_7 f_{tg^{\pm}} + k_{gt})}{k_{tg} + k_t + k_{gt} + f_{tt}\kappa_3} \quad (1)$$

When the condition that k_{gt} and k_{tg} are much faster than κ_3 is incorporated in eqn. (1), it simplifies to

$$k_{exp} = \kappa_3 f_{tg^{\pm}} \quad (2)$$

This means that the observed rate constant k_{exp} for exciplex formation is a function of the real rate constant κ_3 and the fraction of molecules in a specific conformation, both of which can be temperature dependent.

The following relations can be derived for the activation energy and the pre-exponential factor of k_{exp} [10]:

$$E_{a\,k_{exp}} = E_{a\,\kappa_3} + \frac{\Delta H_{pre}}{1 + K_{pre}} \quad (3)$$

where

$$K_{pre} = \frac{k_{gt}}{k_{tg}} \tag{4}$$

and

$$\ln k^{\circ}_{exp} = \ln \kappa^{\circ}_3 + \ln\left\{\frac{\exp(\Delta S_{pre}/R)}{1 + \exp(\Delta S_{pre}/R)}\right\} \tag{5}$$

ΔH_{pre} is the change in enthalpy on going from tt* to tg$^{\pm *}$ and is about 0.7 kcal mol^{-1} for most 1,3-disubstituted propanes [11]. ΔS_{pre} is usually assumed to be small (about 2 e.s.u.) [11], and this leads to values for the correction terms for $E_{a\,k_{exp}}$ and $\Delta S^{\ddagger}{}_{k_{exp}}$ of 0.4 kcal mol^{-1} and -0.6 e.s.u. respectively.

In general, it can be stated that, for 1,3-disubstituted propanes, whenever k_{gt} and k_{tg} are much greater than κ_3 the overall effect is an increase in the uncertainty of $E_{a\,k_{exp}}$ and $\Delta S^{\ddagger}{}_{k_{exp}}$ which will have an effect on ΔH° and ΔS°. However, the corrections are relatively small. In the framework of the scheme shown in Fig. 5 the following equations can be derived for the time dependence of the emission intensity (k_{gt} and k_{tg} are assumed to be much greater than κ_3):

$$i_{LE}(t) = \frac{k_1(\lambda_2 - X)}{\lambda_2 - \lambda_1}\{\exp(-\lambda_1 t) + C\exp(-\lambda_2 t)\} \tag{6}$$

$$i_{E}(t) = \frac{k_5 k_{exp}}{\lambda_2 - \lambda_1}\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \tag{7}$$

where

$$C = \frac{X - \lambda_1}{\lambda_2 - X} \tag{8}$$

and

$$\lambda_{1/2} = \frac{1}{2}[(X + Y) \mp \{(Y - X)^2 + 4k_{exp}k_4\}^{1/2}] \tag{9}$$

The ratio of the fluorescence quantum yield of the excimer to that of the locally excited state is given by

$$\frac{\phi^{F}{}_{E}}{\phi^{F}{}_{LE}} = \frac{k_5}{k_1}\,\frac{k_{exp}}{\kappa_4 + k_8} \tag{10}$$

where k_1, k_2, k_4, k_5, k_6, k_7 and k_8 are defined in Fig. 5 and k_{exp} is given by eqn. (2).

When the experimental results given in Table 1 are treated within the framework of eqns. (6) - (9) values for the rate constants can be calculated and these are given in Tables 2 - 4 for P_3I in the three solvents. ΔH° and $E^{a}{}_{8} - E^{a}{}_{exp}$ can be derived from Fig. 4 using eqn. (10). The kinetic and thermodynamic parameters of P_3I are given in Tables 5 - 7.

TABLE 2

Calculated rate constants for P_3I in isopentane

T (°C)	$1/T \times 10^3$ (°C^{-1})	ϕ^F_o	ϕ^F_E	ϕ^F_A	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8
25	3.356	0.47	0.254	0.156	1.76×10^6	2.02×10^6	—	—	—	—	3.77×10^6	—
−5	3.731	0.48	0.276	0.130	1.77×10^6	1.90×10^6	9.5×10^7	4.3×10^8	1.9×10^7	3.1×10^7	3.67×10^6	5.04×10^7
−19	3.937	0.48	0.283	0.113	1.76×10^6	1.89×10^6	6.6×10^7	2.1×10^8	1.7×10^7	2.9×10^7	3.65×10^6	4.6×10^7
−35	4.202	0.49	0.298	0.107	1.78×10^6	1.85×10^6	4.1×10^7	9.1×10^7	1.6×10^7	2.6×10^7	3.63×10^6	4.2×10^7
−50	4.484	0.50	0.319	0.117	1.78×10^6	1.77×10^6	2.5×10^7	5.5×10^7	2.0×10^7	2.8×10^7	3.55×10^6	4.8×10^7
−70	4.926	0.51	0.307	0.140	1.77×10^6	1.72×10^6	1.2×10^7	1.6×10^7	2.2×10^7	3.0×10^7	3.49×10^6	5.2×10^7
−90	5.464	0.50	0.332	0.225	1.76×10^6	1.75×10^6	4.3×10^6	—	2.9×10^7	3.6×10^7	3.52×10^6	4.8×10^7
−110	6.135	0.50	0.126	0.360	1.78×10^6	1.78×10^6	1.3×10^6	—	2.5×10^7	2.6×10^7	3.56×10^6	4.6×10^7

ϕ^F_o is the quantum yield of fluorescence of CH_3P.

TABLE 3

Calculated rate constants for P_3I in dibutyl ether

T (°C)	$1/T \times 10^3$ (°C^{-1})	ϕ^F_o	ϕ^F_E	ϕ^F_A	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8
27	3.333	0.460	0.353	0.113	2.09×10^6	2.45×10^6	1.49×10^8	2.89×10^8	1.4×10^7	1.6×10^7	4.54×10^6	3.0×10^7
25	3.356	0.466	0.358	0.115	2.11×10^6	2.42×10^6	1.27×10^8	2.58×10^8	1.5×10^7	1.66×10^7	4.53×10^6	3.16×10^7
−2.5	3.697	0.473	0.430	0.097	2.13×10^6	2.37×10^6	4.89×10^7	6.7×10^7	2.0×10^7	1.7×10^7	4.50×10^6	3.7×10^7
−17	3.914	0.496	0.462	0.088	2.11×10^6	2.14×10^6	3.56×10^7	2.6×10^7	1.8×10^7	1.4×10^7	4.25×10^6	3.2×10^7
−32.5	4.158	0.501	0.450	0.103	2.13×10^6	2.12×10^6	2.07×10^7	7.9×10^6	1.7×10^7	1.3×10^7	4.25×10^6	3.0×10^7
−50	4.484	0.512	0.305	0.106	2.16×10^6	2.06×10^6	1.86×10^7	4.3×10^6	1.1×10^7	1.76×10^7	4.22×10^6	2.86×10^7
−65	4.808	0.499	0.279	0.162	2.10×10^6	2.11×10^6	8.74×10^6	—	1.0×10^7	1.32×10^7	4.21×10^6	2.42×10^7
−75	5.051	0.507	0.204	0.263	2.13×10^6	2.07×10^6	3.9×10^6	—	1.1×10^7	1.5×10^7	4.20×10^6	2.6×10^7
−85	5.319	0.516	0.131	0.370	2.15×10^6	2.02×10^6	1.64×10^6	—	1.1×10^7	1.27×10^7	4.17×10^6	2.37×10^7

TABLE 4

Calculated rate constants for P_3I in butyl acetate

T (°C)	$1/T \times 10^3$ (°C^{-1})	ϕ^F_o	ϕ^F_E	ϕ^F_A	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8
39.5	3.2	0.479	0.428	0.075	2.35×10^6	2.56×10^6	2.20×10^8	1.88×10^8	1.3×10^7	1.3×10^7	4.91×10^6	2.56×10^7
25	3.356	0.488	0.409	0.056	2.36×10^6	2.48×10^6	1.67×10^8	8.19×10^7	1.1×10^7	1.3×10^7	4.84×10^6	2.38×10^7
14.5	3.478	0.495	0.390	0.050	2.38×10^6	2.43×10^6	1.44×10^8	5.38×10^7	1.0×10^7	1.3×10^7	4.81×10^6	2.31×10^7
−5	3.731	0.500	0.375	0.044	2.36×10^6	2.36×10^6	8.29×10^7	1.48×10^7	0.9×10^7	1.3×10^7	4.72×10^6	2.14×10^7
−19	3.931	0.505	0.387	0.053	2.36×10^6	2.31×10^6	4.94×10^7	5.07×10^6	0.9×10^7	1.2×10^7	4.67×10^6	2.08×10^7

TABLE 5

Kinetic and thermodynamic parameters for exciplex formation in P_3I in isopentane

k_1	1.78×10^6 s^{-1}	$\Delta S^{\ddagger}_3$	−10.8 e.s.u.
k°_2	2.8×10^6	$\Delta G^{\ddagger}_{3RT}$	6.2 kcal mol^{-1}
E^a_2	0.2 kcal mol^{-1}	$\Delta H^{\ddagger}_4$	4.96 kcal mol^{-1}
k°_3	7.6×10^{10}	$\Delta S^{\ddagger}_4$	−1 e.s.u.
E^a_3	3.6 kcal mol^{-1}	$\Delta G^{\ddagger}_{4RT}$	5.26 kcal mol^{-1}
k°_4	1.13×10^{10}	ΔH°	−1.9 kcal mol^{-1}
E^a_4	5.45 kcal mol^{-1}	ΔS°	−9.8 e.s.u.
k_5	2.0×10^7	ΔG°_{RT}	1.0 kcal mol^{-1}
k°_6	3.9×10^7	$-(E_6 - E_3)$	3.1 kcal mol^{-1}
E^a_6	0.1 kcal mol^{-1}	ΔH_{stat}°	−1.9 kcal mol^{-1}
$\Delta H^{\ddagger}_3$	2.96 kcal mol^{-1}	E_{rep}	6.2 kcal mol^{-1}

TABLE 6

Kinetic and thermodynamic parameters for exciplex formation in P_3I in dibutyl ether

k_1	2.13×10^6	$\Delta S^{\ddagger}_3$	−7.7 e.s.u.
k°_2	4.1×10^6	$\Delta G^{\ddagger}_{3RT}$	6.3 kcal mol^{-1}
E^a_2	0.3 kcal mol^{-1}	$\Delta H^{\ddagger}_4$	8.0 kcal mol^{-1}
k°_3	3.6×10^{11}	$\Delta S^{\ddagger}_4$	7.0 e.s.u.
E^a_3	4.6 kcal mol^{-1}	$\Delta G^{\ddagger}_{4RT}$	5.9 kcal mol^{-1}
k°_4	5.6×10^{14}	ΔH°	−3.7 kcal mol^{-1}
E^a_4	8.6 kcal mol^{-1}	ΔS°	−13.5 e.s.u.
k_5	1.5×10^7	ΔG°_{RT}	0.3 kcal mol^{-1}
k°_6	1.8×10^7	$-(E_6 - E_3)$	4.7 kcal mol^{-1}
E^a_6	0.1 kcal mol^{-1}	ΔH_{stat}°	−3.7 kcal mol^{-1}
$\Delta H^{\ddagger}_3$	4.0 kcal mol^{-1}	E_{rep}	6.5 kcal mol^{-1}

TABLE 7

Kinetic and thermodynamic parameters for exciplex formation in P_3I in butyl acetate

k_1	2.36×10^6	$\Delta H^{\ddagger}{}_3$	3.5 kcal mol^{-1}
$k°_2$	2.8×10^6	$\Delta S^{\ddagger}{}_3$	−9 e.s.u.
$E^a{}_2$	0.2 kcal mol^{-1}	$\Delta G^{\ddagger}{}_{3RT}$	6.2 kcal mol^{-1}
$k°_3$	1.7×10^{11}	$\Delta H^{\ddagger}{}_4$	7.2 kcal mol^{-1}
$E^a{}_3$	4.1 kcal mol^{-1}	$\Delta S^{\ddagger}{}_4$	8.1 e.s.u.
$k°_4$	1.0×10^{15}	$\Delta G^{\ddagger}{}_{4RT}$	4.8 kcal mol^{-1}
$E^a{}_4$	9.6 kcal mol^{-1}	$\Delta H°$	−5.9 kcal mol^{-1}
k_5	1.0×10^7	$\Delta S°$	−18.4 e.s.u.
$k°_6$	1.3×10^7	$\Delta G°_{RT}$	−0.4 kcal mol^{-1}
$E^a{}_6$	0.0 kcal mol^{-1}	$\Delta H_{stat}°$	−5.6 kcal mol^{-1}
		ΔE_{rep}	6.7 kcal mol^{-1}

4. Discussion

4.1. Results for isopentane

The value of $\Delta H°$ in isopentane is always −1.9 kcal mol^{-1}, regardless of the method used to obtain it. This value is 3 kcal mol^{-1} less negative than that for the CH_3P–1,2-DMI system in the same solvent. The difference correlates with the difference between the exciplex energy and the repulsion energy for the intermolecular and intramolecular systems. The exciplex formation is 1.2 kcal mol^{-1} less exothermic for P_3I than for CH_3P–1,2-DMI and the repulsion energy is 1.7 kcal mol^{-1} larger for P_3I. This difference may be related to the two gauche interactions in the P_3I chain. From this it can be concluded that the chain introduces substantial changes in the thermodynamic aspects of exciplex formation.

The entropy change $\Delta S°$ for exciplex formation is −10 e.s.u., which is in good agreement with the values reported in the literature [12] for other intramolecular exciplex-forming systems in non-polar solvents. It can be attributed primarily to the entropy change in going from the tg excited state to the exciplex.

On the basis of these results a value of 1.0 kcal mol^{-1} can be calculated for $\Delta G°$ at room temperature, which explains why P_3I can be described by the Birks kinetic scheme [13] in the high temperature limit at room temperature.

4.2. Results for slightly polar solvents

The difference in solvent polarity between isopentane ($\epsilon_r = 1.84$) and DBE ($\epsilon_r = 3.1$) is small, and in the intermolecular system a decrease of only 0.5 kcal mol^{-1} in $\Delta H°$ was found in going from isopentane to DBE. A closer look at Tables 5 - 7 reveals that the change of solvent introduces a marked change in $\Delta H°$, k_4 and $\Delta S°$ for P_3I. The large increase in $-\Delta H°$ (100%) in going from isopentane to DBE reveals the fact that solvent stabilization plays an important role in the energy of the P_3I exciplex. This effect is larger for P_3I than for the intermolecular system, which is understandable because of the larger dipole moment of P_3I. The change in k_4 is due to an increase in both its pre-exponential factor and its activation energy. At the same temperature k_4 will be smaller in DBE than in isopentane. For this reason P_3I is no longer kinetically in the "high temperature" limit at room temperature. ΔS° is -13.5 e.s.u., which is a rather large value for an intramolecular system. It can be seen from Tables 5 - 7 that the change in ΔS° on going from isopentane to DBE is mainly due to an increase in $\Delta S^{\ddagger}{}_4$, which means that an additional loss of entropy occurs in the more polar solvent on going from the transition state to the exciplex.

Butyl acetate is a medium polar solvent with a dielectric constant of 5.2 which is approximately equal to that of 2-methyltetrahydrofuran ($\epsilon_r = 6.5$). A value of 7.3 is found for $\phi^F{}_E/\phi^F{}_A$ at room temperature, indicating that exciplex emission is much more important than emission from the locally excited state.

A comparison of the results in Tables 5 - 7 shows that the changes in k_4, ΔH° and ΔS° observed on going from isopentane to DBE become even larger than those observed on going from isopentane to the (more polar) butyl acetate. The same trend is followed: $k^\circ{}_4$ and $E^a{}_4$ increase, ΔH° and ΔS° become more negative and $\Delta S^{\ddagger}{}_4$ becomes more positive. The repulsion energy is independent of the solvent polarity, and ΔG° at room temperature changes from slightly positive in isopentane to slightly negative in butyl acetate.

5. Conclusions

The experimental observation that in P_3I k_{gt} and k_{tg} are much larger than κ_3 leads to two important conclusions concerning the photophysics of intramolecular exciplexes and excimers.

The first conclusion can be drawn from a comparison of the photophysics of P_3I and 1-aryl-3-(N,N'-dimethylamino)propane. It has been established that conformational distribution played a role in the latter compound, and this was explained by the fact that the rotation around the C—N bond was slow [7] owing to specific effects in the N,N'-dialkylated aliphatic amines. The absence of this effect in P_3I is strong support for the validity of the explanation given. The difference between this system and that studied by Wang *et al.* [6] could be due to the much faster rate of exciplex formation in the latter.

The second conclusion is related to excimer formation in 1,3-dipyrenylpropane. It has been suggested on the basis of the complexity of the decay [14] that conformational distribution of the chain controlled the photophysical behaviour of this compound. Since this is not observed in P_3I it indicates either that conformational equilibration is much faster in P_3I or that the conformational distribution is different from that of P_3I. Other possibilities are that the conditions for the relative spatial orientation in the heteroexcimer are less stringent or that the complexity may have some other source such as a high rotational barrier for the pyrene chromophore.

The experimental results obtained for P_3I and the differences with respect to the intermolecular systems can be rationalized as follows.

The value of $2\mu_e^2/4\pi\epsilon_0 hc\rho^3$ for P_3I is significantly larger than that for the CH_3P–1,2-DMI system, despite the fact that the redox properties of the two systems are identical. This means that the structures of the intramolecular and intermolecular exciplexes are different. The fact that ΔH° for exciplex formation is less negative for P_3I in isopentane than for CH_3P–1,2-DMI can be rationalized in the same way.

The chain will prevent the two chromophores from adopting the most favourable geometry (which is found in the intermolecular case) and this leads to a less favourable ΔH° for the intramolecular process. On changing the solvent polarity, the ΔH° of exciplex formation becomes more negative for both the intermolecular case and P_3I. However, the effect is much larger for P_3I, and this means that the solvent plays a much more important role in exciplex stabilization in the intramolecular system. This is understandable in view of the larger dipole moment of P_3I.

Another indication of the importance of the solvent in this system is that ΔS° becomes more negative with increasing solvent polarity. It is important to note that $\Delta S^{\ddagger}{}_3$ is almost unaffected by this change, while $\Delta S^{\ddagger}{}_4$ increases strongly on going from isopentane to butyl acetate.

This leads to the following picture for exciplex formation in P_3I. First, a transition state is formed which has some geometric restrictions but which, to a first approximation, does not depend on the solvent polarity. The transition state then produces the (polar) exciplex which interacts more strongly with the solvent, and this step, which is characterized by $\Delta H^{\ddagger}{}_4$ and $\Delta S^{\ddagger}{}_4$ is strongly dependent on the solvent polarity. No appreciable variation in the repulsion energy in the ground state as a function of solvent polarity is observed.

The importance of the correction terms for ΔH° and ΔS° can be evaluated as follows. Changing the solvent can influence the values of ΔH_{pre} and K_{pre}. This may introduce a change in ΔH°, which is not directly due to an effect of the solvent polarity on the direct process of exciplex formation. The change of ΔH° as a function of solvent polarity is substantially larger, however, than can be explained by the effect mentioned above. The experimental value of k_4 is not affected by k_{gt} and k_{tg}, and because of the fact that it is primarily the change in k_4 which determines the change in ΔS° as a function of solvent polarity the conclusions derived concerning ΔS° remain valid as well.

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