

EXCITED STATES OF AROMATIC ESTERS

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(Received December 4, 1978)

Summary

The absorption and emission spectral properties of several benzyl aromatic esters have been studied in different solvents. The geometries of ground and excited states are discussed on the basis of the Stokes shifts and solvation effects obtained in non-polar and polar solvents which are consistent with the values determined for $\mu_e - \mu_g$. The fluorescence quantum yields ϕ_f , lifetimes τ_f and spectra are in some cases strongly dependent on the solvent used. The radiative and non-radiative constants from both singlet and triplet states of benzyl 1-naphthoate and benzyl 2-naphthoate have been determined. Whilst intersystem crossing competes with fluorescence in these compounds, it is concluded that in benzyl 9-anthroate and benzyl 3-pyrenoate intersystem crossing is not efficient owing to the large energy gap between S_1 and T_1 and this increases the quantum yield of fluorescence in these esters. The data obtained are interpreted on the basis of the nature of the excited states involved.

1. Introduction

Fluorescence techniques have been used to study structural changes and solvation phenomena in electronically excited molecules [1]. The comparison of the data taken from absorption and emission spectra of aromatic molecules has in many cases allowed the detection of differences in the geometry of ground and excited states which are of great value in understanding of the photoreactivity of such molecules [2].

However, few reports have been published concerning correlations between the geometry of the lowest excited singlet state and the rates of primary photochemical processes in aromatic esters. The introduction of a polar functional group drastically affects these rates owing to considerable alteration of the charge distribution by electron donation to or from the aromatic ring [3].

In order to gain some information on the excited state properties of the aromatic esters benzyl *p*-phenyl benzoate (I), benzyl 1-naphthoate (II),

benzyl 2-naphthoate (III), benzyl 9-anthroate (IV) and benzyl 3-pyrenoate (V) shown in Fig. 1, namely as regards their use as fluorescent probes, we have investigated their fluorescence and phosphorescence quantum yields, lifetimes and emission spectra in different solvents.

2. Experimental

Compounds I - IV were synthesized from their respective acids which are commercially available products from Koch Light Laboratories and Aldrich Chemicals. The acids were converted into acid chlorides by reaction with oxalyl chloride. The acid chlorides were then treated with benzyl alcohol in pyridine to give the crude esters. The products were purified by column chromatography or thin layer chromatography and further recrystallization. Compound V was obtained from 3-acetyl pyrene which was synthesized using the reported method [4]; 3-acetyl pyrene was converted into pyrene-3-carboxylic acid [4]. The ester (m.p., 74.5 °C) was obtained by an identical procedure to that described for the other esters. All the compounds were identified by IR and nuclear magnetic resonance spectroscopy.

The absorption spectra measurements were recorded on a Perkin-Elmer Hitachi spectrophotometer and the fluorescence and phosphorescence spectra were recorded on a Hitachi Perkin-Elmer spectrofluorimeter MPF-3 with a rotating phosphoroscope. The quantum yields were measured using the method described by Parker [5].

Lifetimes were determined by the single-photon counting technique [6] using a commercial instrument from Applied Photophysics. Phosphorescence quantum yields were determined by comparing the integrated area under the corrected emission spectra with that of the prompt fluorescence of the same compounds [5].

Phosphorescence lifetimes were measured by controlling the spinning rate of the rotation slit phosphoroscope. The excitation shutter was closed following the excitation of the sample to obtain a decay signal in an oscilloscope with an adequate time base.

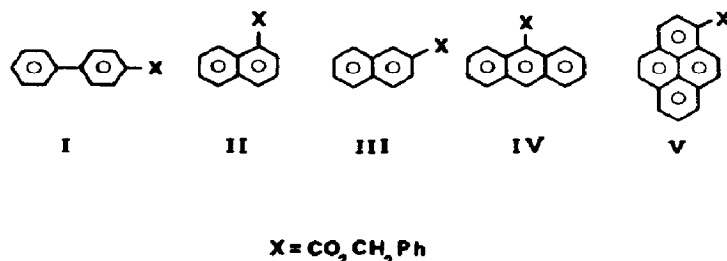


Fig. 1. Structures of compounds I - V.

3. Results

The absorption and fluorescence spectra of compounds I - V are shown in Fig. 2. The phosphorescence spectra of compounds I, II and III are also included. All attempts to determine the phosphorescence of compounds IV and V were unsuccessful.

From the absorption and emission shifts $\bar{\nu}_a$ and $\bar{\nu}_f$ in several solvents, the difference between the dipolar moments of ground and excited states ($\mu_e - \mu_g$) could be estimated, since $\bar{\nu}_a - \bar{\nu}_f$ correlates with solvent polarity according to the equation [7]

$$\bar{\nu}_a - \bar{\nu}_f = \frac{(\mu_e - \mu_g)^2}{hca^3} \left\{ \frac{2(\epsilon - 1)}{2\epsilon + 1} - \frac{2(n^2 - 1)}{2n^2 + 1} \right\} \quad (1)$$

The values of $\mu_e - \mu_g$ obtained are presented in Table 1.

The quantum yields of fluorescence ϕ_f , lifetimes τ_f , the singlet radiative rate constants k_f and the singlet non-radiative rate constants $k_{IC} + k_{ISC}$ are

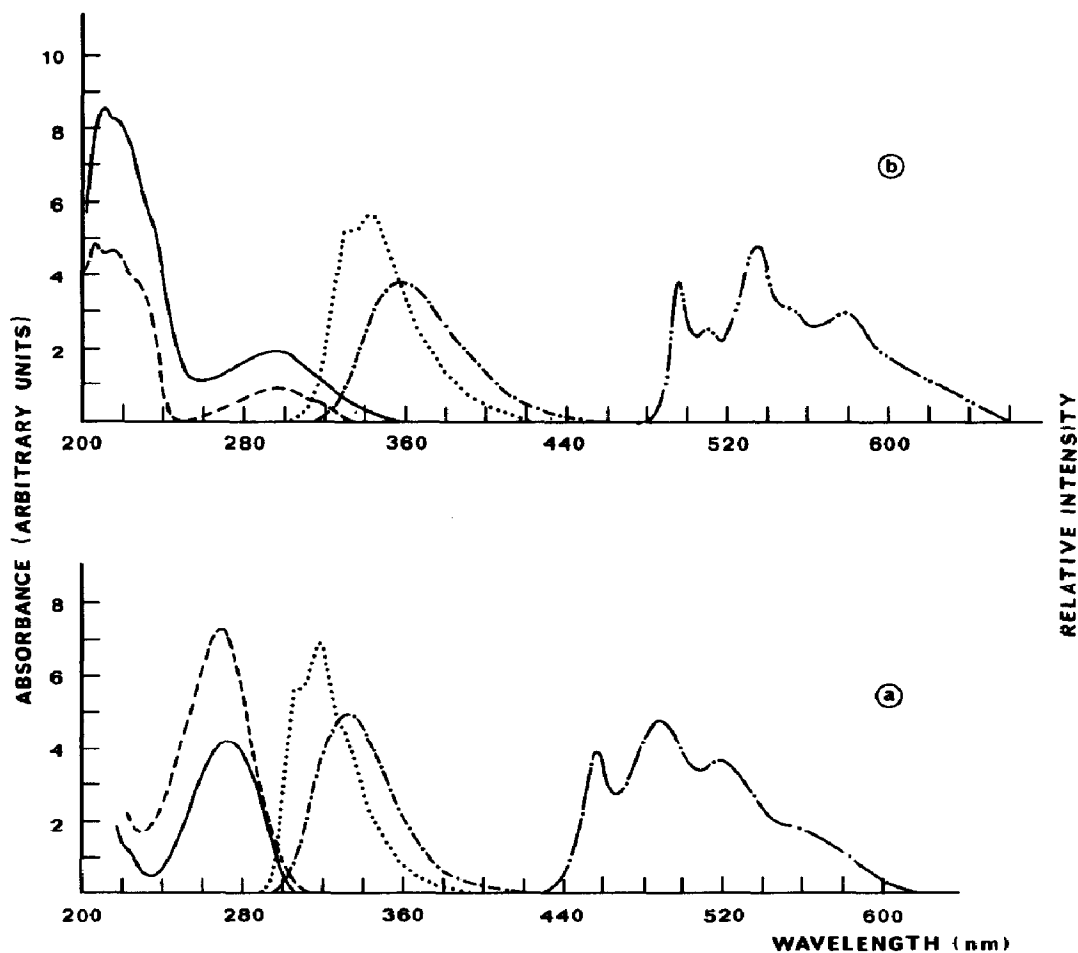


Fig. 2 (a) and (b)

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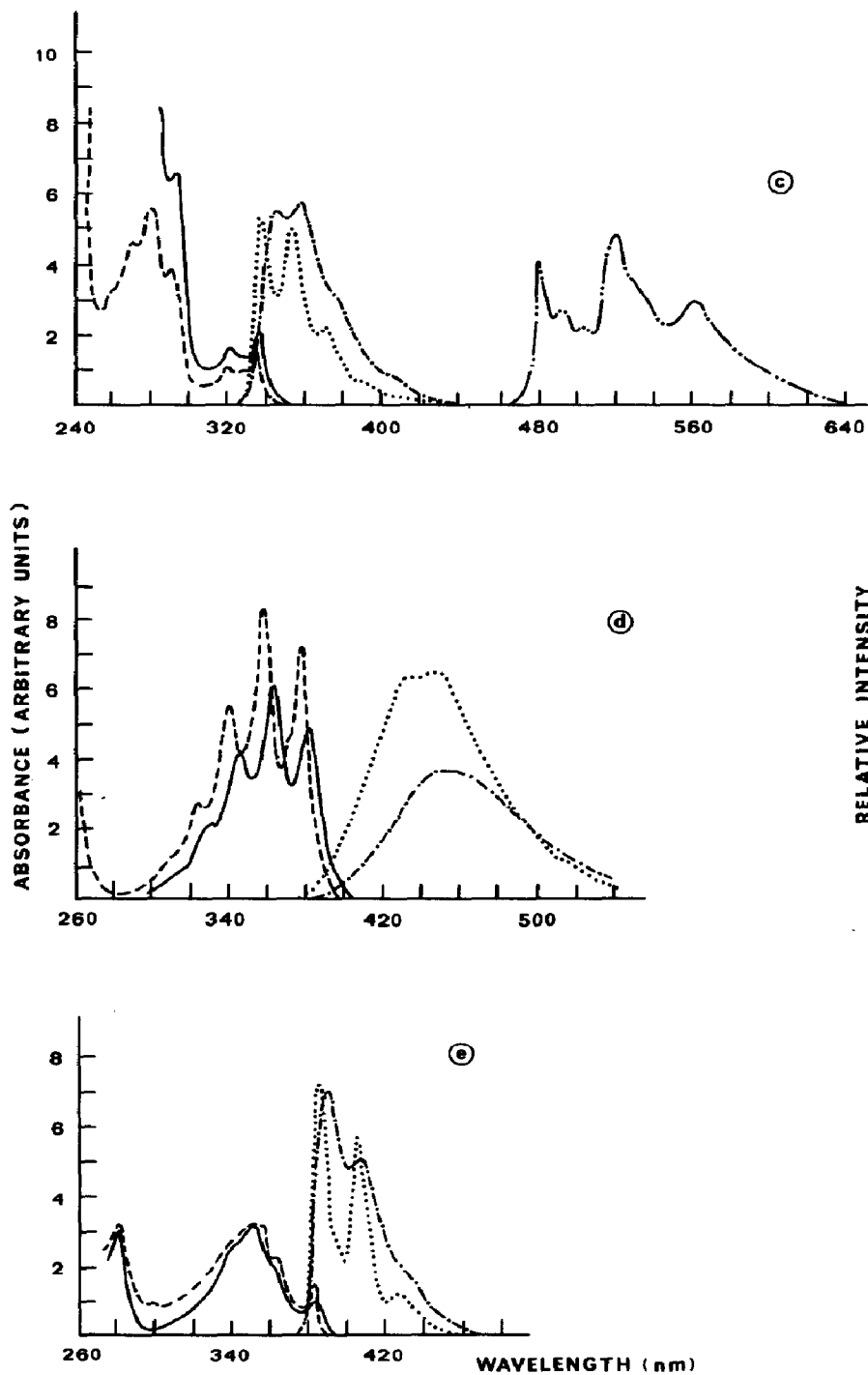


Fig. 2. Absorption, fluorescence and phosphorescence spectra of (a) I, (b) II, (c) III, (d) IV and (e) V: absorption in cyclohexane (----) and acetonitrile (—); fluorescence in cyclohexane (.....) and acetonitrile (— · — · —); phosphorescence in ether-isopentane-ethanol (EPA) (— · — · —).

TABLE 1

Absorption and fluorescence frequency shifts ($\bar{\nu}_a - \bar{\nu}_f$) in several solvents and differences of dipole moments in the excited and ground state ($\mu_e - \mu_g$) of compounds I - V

Compound	$(\bar{\nu}_a - \bar{\nu}_f) \times 10^{-4} \text{ (cm}^{-1}\text{)}$								a (Å)	$\mu_e - \mu_g$ (debye)
	1	2	3	4	5	6	7	8		
I	0.559	0.564	0.646	0.563	0.591	0.614	0.673	0.673	5.5	7.3
II	0.483	0.487	0.604	0.548	0.489	0.531	0.630	0.615	4.5	6.5
III	0.018	0.022	0.070	0.052	0.041	0.078	0.087	0.091	4.5	4.8
IV	0.505	0.504	0.528	0.540	0.518	0.559	0.543	0.576	5.0	5.2
V	0.017	0.020	—	—	—	0.046	0.056	0.050	5.5	6.1

1, n-hexane; 2, cyclohexane; 3, benzene; 4, *p*-dioxane; 5, diethyl ether; 6, chloroform; 7, dimethylformamide; 8, acetonitrile.

presented together with the phosphorescence quantum yields ϕ_p , phosphorescence lifetimes τ_p , the triplet radiative and non-radiative rate constants (k_p and k_D) and the singlet-triplet splitting $\Delta E(S_1-T_1)$ (Table 2).

4. Discussion

The magnitude of the $\mu_e - \mu_g$ values obtained reflects the polarity of the lowest excited state S_1 in the esters studied.

The absorption spectrum of benzyl *p*-phenyl benzoate (I) is, as expected, similar to that of biphenyl [9], but is strongly red shifted indicating that the carboxyl group is coplanar with one of the phenyl groups, its excited state being more stabilized by resonance than the ground state compared with biphenyl.

The spectrum is structureless and rather broad because of the non-coplanarity of the two phenyl groups which originates a different perturbation on their modes of vibration. The lowest excited state S_1 is nearly planar and therefore the emission is structured. Since the ground state is non-planar there is a lack of mirror image relationship between the absorption and emission spectra and a large Stokes shift.

It was suggested [9] that *para* substitution on the biphenyls originated a crossover of excited states in such a way that the fluorescence associated with the strong $^1B_2 \rightarrow A$ transition [10] would be intense and long axis polarized. In contrast, the introduction of a carboxyl group, since it is an electron withdrawing group, could inhibit the fluorescence as it does in benzoic acid [11]. However, we found that compound I exhibits fluorescence in both polar and non-polar solvents with a radiative rate constant k_f of the order of 10^8 s^{-1} ; this indicates that S_1 is in all solvents a (π, π^*) state associated with the biphenyl chromophore [10]. Its fluorescence lifetime τ_f is very small in non-polar solvents and increases more than one order of magnitude with the polarity or polarizability of the solvent.

TABLE 2
Fluorescence and phosphorescence data of compounds I - V

Compound	Solvent	ϕ_f	$\tau_f \times 10^9$ (s)	ϕ_p	τ_p (s)	$k_f^a \times 10^{-7}$ (s ⁻¹)	$(k_{IC} + k_{ISC})^a \times 10^{-7}$ (s ⁻¹)	$k_{p2}^a \times 10^2$ (s ⁻¹)	$k_D^a \times 10^{-1}$ (s ⁻¹)	$\Delta E(S_1-T_1) \times 10^{-3}$ (cm ⁻¹)
Benzyl <i>p</i> -phenyl benzoate (I)	Hexane	0.07	<0.5 (0.08) ^b			>14	186			11.1
	Cyclohexane	0.08	<0.5			>16	184			10.9
	Benzene	0.52	0.7			82	76			10.0
	Acetonitrile	0.64	1.8 (0.8) ^b			36	20			9.7
Benzyl 1-naphthoate (II)	Dimethylformamide EPA	0.37 0.36	2.1	0.05	2.85	18	31 32 ^d	2.7	3.2	9.2
	Hexane	0.07	0.6 (0.2) ^b			15	199			10.6
	Cyclohexane	0.09	0.8			12	118			10.5
	Benzene	0.41	2.0			21	30			9.3
Benzyl 2-naphthoate (III)	Acetonitrile	0.20	1.8 (1.0) ^b			12	48			9.1
	Dimethylformamide EPA	0.21 0.14	2.1	0.08	1.23	7 4 ^c	22 25 ^d	7.6	7.4	9.0
	Hexane	0.41	15.9			2.6	3.7			8.9
	Cyclohexane	0.38	15.7			2.4	3.9			8.8
Benzyl 1-naphthoate (III)	Benzene	0.46	10.2			5.5	5.3			8.3
	Acetonitrile	0.31	10.2			2.5	7.1			8.2
	Dimethylformamide EPA	0.44 0.23	13.7	0.02	2.56	3.2 0.9 ^c	4.1 4.3 ^d	1.0	3.8	8.2

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TABLE 2 (contd.)

Compound	Solvent	ϕ_f	$\tau_f \times 10^9$ (s)	ϕ_p	τ_p (s)	$k_f^a \times$ 10^{-7} (s^{-1})	$(k_{IC} + k_{ISC})^a \times$ 10^{-7} (s^{-1})	$k_p^a \times$ 10^2 (s^{-1})	$k_D^a \times$ 10^{-1} (s^{-1})	$\Delta E(S_1-T_1) \times$ 10^{-3} (cm^{-1})
Benzyl 9-anthroate (IV)	Hexane	0.73	7.6			9.6	3.5			
	Cyclohexane	0.81	8.5			9.5	2.2			
	Benzene	0.79	7.1			11.0	4.6			
	Acetonitrile	0.28	8.0			3.5	9.0			
	Dimethylformamide	0.55	7.1			7.7	6.3			
Benzyl 3-pyrenoate (V)	Hexane	0.88	16.5			5.3	0.9			
	Cyclohexane	0.91	15.0			6.1	0.6			
	Acetonitrile	0.46	11.0			4.2	4.9			
	Dimethylformamide	0.98	8.7			11.3	0.2			

^a $k_f = \phi_f/\tau_f$; $k_{IC} + k_{ISC} = k_f(1/\phi_f - 1)$; $k_p = (1/\tau_p)\{\phi_p/(1 - \phi_f)\}$; $k_D = k_p\{1 - (\phi_p + \phi_f)\}/\phi_p$.

^b Calculated values.

^c The values of k_f at 77 K for methyl 1-naphthoate and methyl 2-naphthoate given in ref. 8 were used for compounds II and III.

^d $k_{ISC} = k_p(1 - \phi_f)/\phi_f$; $k_{IC} = 0$ in EPA at 77 K.

The examination of Table 2 suggests that this variation is probably associated with the radiationless transitions from S_1 . Whereas a solvent dependence could be expected for k_{1C} , the large variation in $k_{1C} + k_{ISC}$ should be mainly ascribed to k_{ISC} since at 77 K in ether-isopentane-alcohol (EPA) ($k_{1C} \approx 0$) the value of k_{ISC} is almost identical to that found for $k_{ISC} + k_{1C}$ at room temperature in polar solvents, and besides the k_f values do not change significantly with the solvent polarity.

The efficient intersystem crossing in non-polar solvents suggests the existence of a $T_{j(n,\pi^*)}$ state close in energy to $S_{1(\pi,\pi^*)}$ state. In polar solvents, the lowering of the relative position of S_1 accounts for a decrease in k_{ISC} and consequently an increase in ϕ_f and τ_f . At 77 K in an EPA matrix, the intersystem crossing efficiency ϕ_{ISC} is 0.64 and $k_{ISC} = 3.2 \times 10^8 \text{ s}^{-1}$.

Although the vibrational spacing of T_1 is large [12], the value of $\tau_p = 2.85 \text{ s}$ is characteristic of a $T_{1(\pi,\pi^*)}$ state.

The results obtained with compound II, benzyl 1-naphthoate, are indicative of some similarity between the geometry and nature of excited states of compounds I and II. In the latter, the ground state is also non-planar, as it is known that the perihydrogen interactions prevent a complete ring carboxyl group coplanarity in the ground state [13]. The angle between the two chromophores in 1-naphthoic acid has been estimated to be 11° [14].

The substitution in the 1 position in naphthalene affects the 1L_a and 1B_b bands rather than the 1L_b band. The emission in compound II was associated with the short-axis-polarized ${}^1L_a - {}^1A$ transition, which is consistent with the magnitude of k_f values obtained. In polar solvents the emission is red shifted and structureless indicating some charge transfer content in S_1 . The large Stokes shift is again indicative of a more planar S_1 state in relationship to the ground state [13].

The fluorescence in cyclohexane is identical with the naphthalene emission in the same solvent but the very short lifetimes and small quantum yields in non-polar solvents point to the influence of the substituent.

The decrease in $k_{1C} + k_{ISC}$ with the increase of solvent polarity is explained by a similar argument to that invoked for compound I. Although it has been reported [8] that at 77 K the k_{ISC} value is not affected by the solvent polarity, we believe that in non-polar solvents the $T_{j(n,\pi^*)}$ state is located slightly above the $S_{1(\pi,\pi^*)}$ state. At room temperature there is enough activation energy to induce a fast intersystem crossing to the triplet which will decrease considerably at low temperatures.

On the basis of results from this work and those from ref. 8, a rough estimation of $\Delta E(S_{1(\pi,\pi^*)} - T_{j(n,\pi^*)})$ gave a value of about 1 kcal mol^{-1} . However, a change in geometry in going from the ground to the excited state is likely to weaken the hydrogen bond formation at 77 K and therefore the expected blue shift of the $n \rightarrow \pi^*$ transition should be much smaller. Furthermore the stabilization of $S_{1(\pi,\pi^*)}$ should be considerably decreased at 77 K. It is likely that the combination of these two factors will mask the solvent polarity dependence on k_{ISC} which we have observed at room temperature.

The phosphorescence spectrum is very similar to that of naphthalene but the introduction of the carboxyl substituent increases both k_p and k_D values by factors of 4 and 400 respectively; this may be due to some mixture with $T_{j(n,\pi^*)}$.

In compound III the substitution of the carboxyl group in the 2 position strongly affects 1L_b and to a lesser extent 1L_a and 1B_b . The Stokes shift is very small in non-polar solvents (2 nm) which is indicative of the planarity of both ground and excited states in agreement with the work reported by McGlynn [13]. The introduction of the substituent makes the transition ${}^1L_b \leftarrow A$ more allowed [15] and red shifted. We found that lifetimes and quantum yields of this ester are not much dependent on solvent polarity. The order of magnitude of the rate constant k_f determined for compound III is lower than that obtained for compound II, in agreement with the transitions with which they are associated, ${}^1L_b \rightarrow A_1$ and ${}^1L_a \rightarrow A_1$ respectively. The non-radiative transition must have essentially the contribution of k_{ISC} , since from the phosphorescence and fluorescence at 77 K it was possible to estimate the intersystem crossing efficiency ϕ_{ISC} to be 0.77 and k_{ISC} to be $4.3 \times 10^7 \text{ s}^{-1}$. The order of magnitude of k_{ISC} is lower in compound III than in compound II and is invariant with solvent polarity, and this is consistent with a larger $\Delta E(S_{1(\pi,\pi^*)} - T_{j(n,\pi^*)})$ in compound III as proposed earlier [8]. The decay modes of $T_{1(\pi,\pi^*)}$ are also slower than in compound II, indicating that this state has a more pure π, π^* character.

Our results with benzyl 9-anthroate (IV) agree completely with the data published by Werner [3]. We have determined by flash photolysis the intersystem crossing quantum yield ϕ_{ISC} to be 0.094 in benzene and have obtained evidence of triplet sensitization by biacetyl [16] and triplet quenching of β -carotene [17]. This indicates that T_1 lies at very low energies and that therefore the intersystem crossing process is very inefficient owing to the large energy gap $\Delta E(S_1 - T_1)$. We have calculated independently by flash photolysis [16] k_{ISC} to be $1.03 \times 10^7 \text{ s}^{-1}$ in benzene which indicates that $k_{IC} = 3.6 \times 10^7 \text{ s}^{-1}$. The importance of internal conversion in this system may be associated with the formation of two new rings by hydrogen bonding to the neighbouring hydrogens.

The very high quantum yields of fluorescence (almost unity) obtained with benzyl 3-pyrenoate in both non-polar solvents and polar solvents of higher viscosity [18] may also be explained by a large singlet-triplet energy gap since we have been unable to obtain any phosphorescence emission, but we have not measured the quantum yield of intersystem crossing for this compound.

The position of the substituent in benzyl 3-pyrenoate (V) shifts the horizontal polarized band [19] which in pyrene appears at 290 - 340 nm to 335 nm (S_2) and 383.5 nm (S_1), both becoming intensified in respect to pyrene. In this compound both ground and excited states are planar and the Stokes shift observed is only due to solvation [20] of $S_{1(\pi,\pi^*)}$. An examination of Table 2 shows that the non-radiative constants are even smaller than in compound III, since internal conversion would not be efficient owing to

the rigidity of the molecule and the efficiency of intersystem crossing would be negligible as indicated earlier.

The lowering of the quantum yield in acetonitrile observed in all compounds with the exception of I may be due to a specific quenching effect induced by this solvent [21, 22]. This will favour the stabilization of S_1 by the solvent and will result in an enhanced k_{1C} (apparent in V) and a subsequent loss of excitation energy to the environment. The higher value of ϕ_f in dimethylformamide may be related to the higher viscosity of this solvent in which case that effect would not prevail.

Compounds with the anthroyl chromophore have already been used as fluorescent probes [23, 24]. We believe that the pyrenoate chromophore, which has an emission in the visible, can be of potential interest in studies of electron or energy transfer in membranes and we have already initiated an investigation using compound V in micelles [25].

Acknowledgment

The authors thank Mr. H. Onofre Moreira for his help in the fluorescence lifetime measurements.

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