

FLUORESCENCE BEHAVIOUR OF SOME 4-SUBSTITUTED HALOBENZENES

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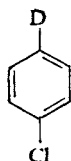
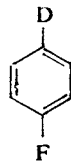
The fluorescence characteristics of 4-substituted chloro and fluorobenzenes *I* and *II* were studied in isooctane and acetonitrile solutions. It was found that all compounds exhibit a weak (substituent and solvent dependent) fluorescence in the range 305–370 nm with quantum yields $1.2 \cdot 10^{-2}$ – $2.3 \cdot 10^{-1}$. The relation between the substituent nature and fluorescence band position may be quantified by $\log \tilde{\nu}_f = \rho \sigma_p + \log \tilde{\nu}_f^0$, the magnitude of the shift paralleling the donor strength of the substituent. Fluorescence quantum yields are increased approximately by a factor 2 on going from isooctane to acetonitrile and solvent-induced shifts are proportional to the static dipole moment change $\Delta\mu$ which occurs upon excitation. Radiative decay rate varies only slightly around a mean value of $5 \cdot 10^7 \text{ s}^{-1}$ and shows no substantial difference between chloro (*I*) and fluoro (*II*) derivatives. The non-radiative decay rate (of the order $\sim 10^9 \text{ s}^{-1}$) was found to be about 5 times higher in the case of chloro compounds due to the more efficient $S_1 - T_n$ intersystem crossing.

Haloaromatic compounds substituted in *para*-position with an electron donor D, $X-C_6H_4-D$, constitute a broad class of organic molecules which are important for industry and research as well. They are produced in very large quantities and are widely used as preservatives and biocides^{1,2}. Among the environmental factors which control their fate and persistence, the influence of light appears to be one of the most important³⁻⁵.

Despite the widespread use of the compounds, the current understanding of their photo-reactivity is limited by the lack of information on the properties of their excited states. The existing data are based mostly on absorption spectra. All *p*- $X-C_6H_4-D$ derivatives, where D may change along the substituent series CH_3 , OH, OCH_3 , NH_2 , and $N(CH_3)_2$, show two systems of absorption bands in the near UV region⁶⁻¹⁰ arising from the symmetry-forbidden ${}^1L_b - {}^1A$ (${}^1B_{2u} - {}^1A_{1g}$) and ${}^1L_a - {}^1A$ (${}^1B_{1u} - {}^1A_{1g}$) transitions in benzene¹¹. The fluorescent 1L_b state is easily observed in the $X-C_6H_4-D$ derivatives because a) of vibrational borrowing from more allowed transitions and b) of the fact that the nodes of the wavefunctions of the 1L_b state do not pass exactly through the skeletal atoms permitting some overlap of 1A and 1L_b wavefunctions. Thus, in theory, the *p*- $X-C_6H_4-D$ molecules should have a higher emission efficiency than benzene.

In view of our interest in the photochemical fate of pollutants we have investigated the fluorescence behaviour of 4-substituted chloro and fluorobenzenes *I* and *II* under uniform experimental conditions.

The fluorescence behaviour of halobenzenes *I* and *II* has been hitherto studied only qualitatively¹²⁻¹⁴, the experiments being mostly restricted to phenols^{12,15} in water solutions^{13,14}. There seems to be some uncertainty as to the correct assignment of fluorescence energies and quantum yields. For example, two recent studies of 4-chlorophenol *Ia* have led to the location of the fluorescence band maximum at 27 778 cm⁻¹ (EPA solvent¹²) and 32 258 cm⁻¹ (water¹⁴).

*I**II**I, IIa*: D = OH*I, IIc*: D = NH₂*I, IIb*: D = OCH₃*I, IId*: D = N(CH₃)₂

Such energy difference certainly cannot be explained in terms of simple solvent effect. The quantum yields of *Ia* in the same solvent (water) also differ considerably (0.026 (ref.¹³) vs 0.0089 (ref.¹⁴)). Except for these fragmentary and in many respects contradictory data, detailed information concerning the fluorescence properties of derivatives *I* and *II* are scantily available.

The purpose of this paper is *a*) to obtain information about the role of OH, OCH₃, NH₂ and N(CH₃)₂ substituents in determining the properties of the lowest singlet state of compounds *I* and *II* and to compare these results with those obtained previously for corresponding monosubstituted benzenes, and *b*) to investigate variations of the photophysical characteristics along the series *a-d*.

EXPERIMENTAL

Samples of 4-chlorophenol, 4-fluorophenol, 4-chloroaniline and 4-fluoroaniline (Aldrich) were purified by crystallization or fractional distillation. Their O- and N-methylated derivatives were obtained by standard phase transfer methylation procedures¹⁵ and purified by column chromatography on silica gel with petroleum ether-ether (9 : 1). Physical constants of pure products agreed with reported values. The solvents (Merck UVASOL) were found to be non-emissive under excitation wavelengths 280–340 nm. Deoxygenation of solvents was achieved by purging with argon for at least 20 min.

Electronic absorption spectra were recorded on Cary 219 spectrophotometer (Varian). Fluorescence excitation and emission spectra of solutions not exceeding absorbance of 0.02 at the excitation wavelength were taken on Fluorolog 2 spectrofluorimeter (Spex) provided with 450 W xenon lamp. Spectra were corrected for the spectral response of the light source, photomultiplier tube and optical system by means of a microprocessor. The correction curves were obtained by the quantum counter-scatterer method¹⁶. Fluorescence quantum yields were determined by a comparison with a standard isooctane solution of 9,10-diphenylanthracene (EGA-Chemie) the quantum yield of which corresponds to 0.93 (ref.¹⁷). For solutions in acetonitrile the re-

fractive index correction was applied¹⁸. The equation we used was

$$\Phi_f = \Phi_f^r \frac{\int I_f(\tilde{\nu}) d\tilde{\nu} A_r n_r^2}{\int I_f^r(\tilde{\nu}) d\tilde{\nu} A n^2}, \quad (1)$$

where Φ_f , $\int I_f(\tilde{\nu}) d\tilde{\nu}$, A , and n are the corresponding quantum yield, area of the corrected fluorescence spectra, absorbance, and refractive index of the solvent. The subscript r denotes the reference compound. All spectral measurements were carried out at $25 \pm 2^\circ\text{C}$ and recorded at least in triplicate. The wavelength-linear readout of the instrument was converted to a wave-number-linear data by using Datamate and software provided by Spex.

The fluorescence natural lifetime, τ_0 (in s), was calculated from the integrated absorption curve by using the formula¹⁹

$$\tau_0 = \frac{1}{k_r} = \frac{3 \cdot 47 \cdot 10^8}{\tilde{\nu}_0^2 n^2 \int \epsilon(\tilde{\nu}) d\tilde{\nu}}, \quad (2)$$

where k_r is the first excited state radiative rate constant, n is the solvent refractive index and $\tilde{\nu}_0$ is the wavenumber of the maximum of the absorption band. The actual lifetime, τ , was estimated according to the relation $\tau = \tau_0 \Phi_f$.

RESULTS AND DISCUSSION

Before presenting the results of fluorescence measurements, it is useful to point out two important aspects regarding absorption spectra characteristics of the compounds *I* and *II* (ref.²⁰). First, all compounds dissolved in isoctane have one moderately intense long wavelength absorption band in the region of 270–315 nm with readily apparent vibrational structure, with the exception of compounds *Id* and *IId*. Second, the bathochromic shift on going from isoctane to acetonitrile is small ($< 500 \text{ cm}^{-1}$) in all cases.

With 1L_b excitation all the compounds exhibit fluorescence of moderate intensity in both isoctane and acetonitrile solutions (Table I). Despite some differences in the vibrational progression of both the excitation and emission bands among individual compounds (Fig. 1), all fluorescence spectra show a satisfactory mirror-image relationship to the absorption spectra. Further, the excitation spectra correspond well enough to absorption spectra so that the observed emission is real and not due to impurities or other artefacts. In acetonitrile the emission is red shifted and structureless indicating partial charge transfer nature of the $^1L_b - ^1A$ transition. The bathochromic shift on going from isoctane to acetonitrile parallels the donor strength of the substituent: $\text{N}(\text{CH}_3)_2 > \text{NH}_2 > \text{OCH}_3 \cong \text{OH}$, amounting $c. 1700 \text{ cm}^{-1}$ in the case of dimethylamino derivatives *Id* and *IId*. It is also worth notice that the fluorescence maximum of 4-chlorophenol (*Ia*) in acetonitrile is located at 32579 cm^{-1} .

TABLE I
Fluorescence characteristics of compounds *I* and *II*

Compound	$\tilde{\nu}_{\text{exc}}^{a,b}, \text{cm}^{-1}$		$\tilde{\nu}_f^a, \text{cm}^{-1}$		$\Delta\tilde{\nu}^c, \text{cm}^{-1}$	
	IO ^d	AN ^d	IO	AN	IO	AN
<i>Ia</i>	35 461	35 335	32 895	32 679	2 566	2 656
<i>Ib</i>	35 461	35 587	32 680	32 467	2 781	3 120
<i>Ic</i>	33 557	32 786	30 120	28 818	3 437	3 968
<i>Id</i>	32 051	31 546	28 818	27 027	3 233	4 519
<i>IIa</i>	35 587	35 335	33 222	32 894	2 365	2 441
<i>IIb</i>	35 461	35 335	33 003	32 787	2 458	2 548
<i>IIc</i>	33 670	32 786	30 211	28 818	3 459	3 968
<i>IId</i>	32 154	31 645	28 735	27 027	3 419	4 618

^a The wavenumbers were not rounded, see Experimental; ^b optimized values with regard to fluorescence maxima; ^c Stokes shift; ^d IO — isoctane, AN — acetonitrile.

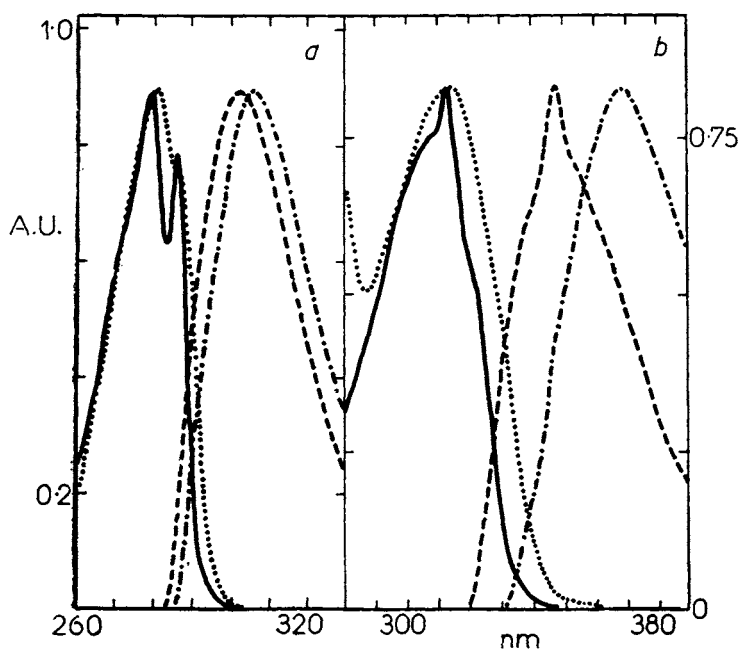


FIG. 1

Excitation and fluorescence spectra of 4-fluorophenol *a* and 4-chlorodimethylaniline *b*: isoctane (excitation ——— and emission - - - - curves); acetonitrile (excitation ······ and emission - · - · curves)

This value seems to be in a quite good agreement with previously published data^{13,14} (32 154 cm⁻¹ and 31 546 cm⁻¹, in water respectively) if we take into account the different polarities of acetonitrile and water. On the other hand, all these values markedly disagree with the reported¹² fluorescence maximum for *Ia* at 27 778 cm⁻¹ in PED mixture (pentane-ethanol-diethyl ether, 1:2:4). Such an enormous discrepancy led us to reexamine the fluorescence of *Ia* in the same solvent mixture and the fluorescence maximum was found at 32 467 cm⁻¹.

To obtain more detailed information about the substituent effects on fluorescence maxima positions we have correlated the experimental data with Hammett σ_p substituent constants. As shown in Table II, satisfactory linear correlations ($r = 0.980$ or better) with positive ρ values were obtained. The predicative ability of this relationship was tested by comparing calculated (36 907 cm⁻¹) and experimental²¹ (36 364 cm⁻¹) positions of fluorescence maxima of fluorobenzene in acetonitrile. Accordingly, data from Table II permit a reasonably accurate prediction of fluorescence shifts. The ρ values are solvent sensitive, increasing by about 45% in acetonitrile for both the series *I* and *II*. From the magnitude of ρ constants, it appears, however, that no clear distinction between the series *I* and *II* exists in the particular solvents. Moreover, all ρ values from Table II are well comparable with corresponding ρ values computed for an equivalent set of monosubstituted benzenes²¹ ($\rho_{\text{hexane}} = 0.108$, $\rho_{\text{acetonitrile}} = 0.127$). These results suggest that the extent of delocalization in compounds *I* and *II* is preferentially determined by the donor group *D*, the halogen atom exerting nearly negligible influence. In the case of fluoro derivatives *II* such a result could be expected considering the known insensitivity of aromatic π, π^* transitions to fluoro substitution²². Also the experimental observation²³ that the phenyl - substituent distance in monosubstituted benzenes shrinkages in the order NH₂ (0.0080 nm) > OH (0.0044 nm) \gg F (0.0009 nm) on going from ground state to the ¹L_b excited state provides an evidence in support of this suggestion. On the

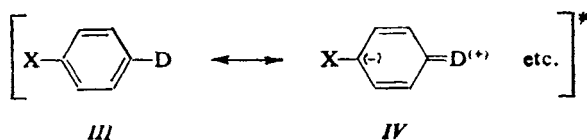
TABLE II
Statistics of Eq. $\log \tilde{\nu}_f = \rho \sigma_p + \log \tilde{\nu}_f^0$

Compounds	Solvent	ρ	$\log \tilde{\nu}_f^0$	r^a
<i>I</i>	IO ^b	0.1061	4.5489	0.980
	AN ^b	0.1537	4.5611	0.982
<i>II</i>	IO	0.1161	4.5565	0.980
	AN	0.1616	4.5671	0.985

^a Correlation coefficient; ^b see note^d, Table I.

other hand, similar type of behaviour of chloro derivatives *I* is rather surprising. To explain, at least qualitatively, this phenomenon we should assume that both the σ electron-withdrawing effect of chlorine and its capability to use d_π orbitals for an electron acceptor action with ring carbon p_π orbitals are compensated by chlorine π donor ability. As a consequence, the observed behaviour of the chloro derivatives *I* may be caused by cancellation of two roughly equal effects.

The foregoing results seem to coincide well with earlier studies^{24,25} on substituted benzenes which have revealed an appreciable quinoidal character for 1L_b singlet state of phenols, anisoles, and anilines. Thus, resonance formulae of the type *IV* (in which X represents H, F, or Cl) may be extreme representations of the 1L_b excited state structure for compounds *I* and *II*.



The often cited relationship, used for classification of a charge transfer transition^{26,27}, is based on a close similarity of the absolute value of the transition moment to the difference between the ground and excited state dipole moments $\mu_{ge} \approx \Delta\mu$. The first excited singlet state dipole moments of the compounds *I* and *II* were determined, using the solvent dependence of both the excitation and emission maxima. Considering theories of solvent influence on absorption and emission spectra²⁸, a simple semiquantitative description can be given in terms of the Onsager theory of dielectrics (Eqs 3,4).

$$\Delta E_{g-e} = \mu_g \Delta\mu_{g-e} a_g^{-3} \cos \varphi F(D, n) - (\Delta\mu)^2 a_g^{-3} F(n), \quad (3)$$

$$\Delta E_{e-g} = \mu_e \Delta\mu_{e-g} a_e^{-3} \cos \psi F(D, n) - (\Delta\mu)^2 a_e^{-3} F(n). \quad (4)$$

In these equations a is the radius of the (spherical) cavity occupied by the molecule in the solvent, and the functions $F(D, n)$ and $F(n)$ define the theoretical scale of solvent polarities in the Onsager model. Since Eqs (3) and (4) are rather complex some simplifications are needed to make practical progress. Here we follow others²⁹ and restrict the solvatochromic shifts to solvents with closely similar refractive indexes. Assuming simultaneously the negligible change in cavity radius upon excitation ($a_g = a_e = a$) and a collinearity $\mu_e \parallel \mu_g$ which could be reasonable for the compounds *I* and *II* owing to their molecular symmetry, the second terms in Eqs (3) and (4) can be neglected and their ratio simplifies to

$$\mu_e/\mu_g = (\Delta E_{e-g})_{1-2}/(\Delta E_{g-e})_{1-2}, \quad (5)$$

where $(\Delta E_{e-g})_{1-2}$ and $(\Delta E_{g-e})_{1-2}$ are the shifts of fluorescence and absorption maxima in solvents 1 and 2, respectively.

In the present study, Eq. (5) was used to compute μ_e values, the solvents corresponding to indexes 1 and 2 being isooctane ($D = 1.90$, $n = 1.3890$) and acetonitrile ($D = 35.50$, $n = 1.3415$).

We see in Table III that in all cases the excited states exhibit a greater dipole moment and hence more charged character than the ground states. Surprisingly, for the dimethylamino derivatives *I*d and *II*d, the dipole moment change $\Delta\mu$ on going to S_1 state is about two to three times greater than in other compounds, indicating thus the anomalously high charge transfer character of the emitting excited state. The question arises whether, in analogy with 4-acceptor substituted dimethylaminobenzenes^{33,34}, a twisted intramolecular charge transfer (TICT) state might be involved in the fluorescent transitions of the 4-halogen dimethylanilines *I*d and *II*d, as well. However, further detailed studies are necessary to solve this problem.

Let us now consider dynamic behaviour of the S_1 state of the derivatives *I* and *II* as it follows from the fluorescence quantum yield Φ_f , natural lifetime τ_0 and actual lifetime τ determination (Table IV). The use of both τ_0 and τ allows a separation of the effects due to the excited state intrinsic radiative deactivation rate (k_r) from those due to other radiationless deactivation routes. These lifetimes are related as shown in Eq. (6)

$$1/\tau_0 - 1/\tau = \sum k_{nr}, \quad (6)$$

where $\sum k_{nr}$ represents a sum of the rate constants of the non-radiative decay processes.

TABLE III
Excited state (1L_b) dipole moments of compounds *I* and *II* (in Cm)

Compound	$\mu_g \cdot 10^{30a}$	$\mu_e \cdot 10^{30b}$	$\mu_e \cdot 10^{30}$ (Lit.)
<i>I</i> a	7.39	12.65	—
<i>I</i> b	7.72	13.15	—
<i>I</i> c	9.99	16.85	14.18 ^c 16.78 ^d
<i>I</i> d	10.79	38.26	—
<i>II</i> a	6.99	9.06	8.46 ^e
<i>II</i> b	6.79	11.72	—
<i>II</i> c	8.26	13.02	10.99 ^c
<i>II</i> d	9.22	30.93	—

^a Ref. ³⁰; ^b according to Eq. (5); ^c ref. ³¹; ^d ref. ³²; ^e ref. ²⁵.

An inspection of the results given in Table IV reveals that fluorescence quantum yields of the derivatives *I* and *II* are generally low ($\sim 10^{-1} - 10^{-2}$) but exhibit interesting substituent dependences. The quantum yields of the chloro derivatives *I* in isoctane cover the small range of $9 \cdot 10^{-3}$ as the substituent series OH, OCH₃, NH₂ and N(CH₃)₂ is traversed, while the corresponding quantum yields of the fluoro derivatives *II* reflect more significantly the substituent effect by changing from $3.8 \cdot 10^{-2}$ to $17.5 \cdot 10^{-2}$. A similar behaviour is observed in acetonitrile solutions despite the fact that Φ_f values increase by a factor of about two. Considering the decay rates of the *S*₁ state, two trends are apparent: *a*) The radiative decay rate constants vary only slightly around a mean value of $5.2 \cdot 10^7 \text{ s}^{-1}$ showing no substantial difference between the chloro (*I*) and fluoro (*II*) derivatives, and *b*) the non-radiative decay rate constants are about two orders of magnitude higher than their radiative counterparts. Furthermore, they indicate a clear decrease along the series *a - d* for both fluoro and chloro derivatives.

The results outlined above suggest rather efficient radiationless processes in the singlet manifold. These processes may generally involve internal conversion process of the type *S*₁ - *S*₀ or *S*₁ - *S*_x, *S*_x being a singlet intermediate of the decomposi-

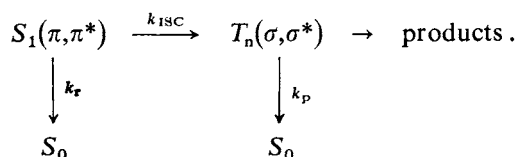
TABLE IV
Quantum yields, lifetimes, and deactivation rate constants of compounds *I* and *II*

Compound	$\Phi_f \cdot 10^{2a}$		$\tau_0 \cdot 10^9 b$ s		$\tau \cdot 10^9$ s		$k_r \cdot 10^7$ s^{-1}		$\sum k_{nr} \cdot 10^9$ s^{-1}	
	IO ^c	AN ^c	IO	AN	IO	AN	IO	AN	IO	AN
<i>Ia</i>	1.2 (0.9) ¹³ (2.6) ¹¹	1.9	23.4	24.3	0.28	0.46	4.3	4.1	3.5	2.0
<i>Ib</i>	1.5	2.1	20.3	23.3	0.30	0.49	3.9	4.3	3.3	2.0
<i>Ic</i>	1.6 (1.7) ¹³	2.9	23.3	26.5	0.37	0.77	4.3	3.8	2.7	1.3
<i>Id</i>	2.1	4.0	19.3	19.3	0.40	0.77	5.2	5.2	2.4	1.2
<i>IIa</i>	3.8 (3.0) ¹³	8.2	17.5	19.7	0.66	1.61	5.7	5.1	1.5	0.6
<i>IIb</i>	4.3	9.1	16.9	17.1	0.73	1.56	5.9	5.8	1.3	0.6
<i>IIc</i>	10.2 (12.3) ¹³	18.0	18.9	16.9	1.92	3.04	5.3	5.9	0.5	0.3
<i>IId</i>	17.5	22.9	18.8	18.8	3.29	4.30	5.3	5.3	0.3	0.2

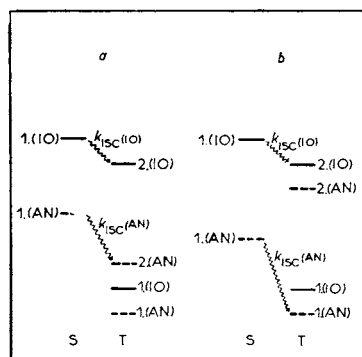
^a Literature values for water solution are given in parentheses; ^b according to Eq. (2); ^c see note^d, Table I.

tion, or intersystem crossing of the type $S_1 - T_n$. In the first approximation, the rate constants of the radiationless transition can be factorized as a product of an electronic term, related to perturbations inducing the process, and of the Franck–Condon factor. On this basis, $S_1 - S_0$ internal conversion is expected to be negligible for the 1L_b state of benzene (and the 1L_b states of its derivatives) because of the large $S_1 - S_0$ energy gap and thus of the small Franck–Condon factor. Moreover, photoexcitation of several halogen substituted aromatic compounds is known^{35,26} to induce carbon–halogen bond homolysis affording corresponding aryl and halogen radicals. It has been shown by means of picosecond laser spectroscopy³⁶ that this type of excited state energy dissipation does not proceed directly from an excited singlet state but *via* intersystem crossing to a dissociative triplet state (probably σ, σ^* in nature) that leads to homolysis of the carbon–halogen bond.

Based on above suggestions, a simplified kinetic model for the photophysical steps after the 1L_b excitation of the halobenzenes *I* and *II* may be formulated as follows



The observed differences in the intersystem crossing rate k_{ISC} when changing halogen from chlorine ($k_{ISC}^I \sim 2.4 - 3.5 \cdot 10^9 \text{ s}^{-1}$) to fluorine ($k_{ISC}^{II} \sim 3 - 15 \cdot 10^8 \text{ s}^{-1}$), are rationalized by an increased extent of spin – orbit coupling in chloro derivatives *I* owing to the heavy atom effect. Although all the k_{ISC} values should be regarded as limiting estimates due to some degree of approximation involved (the use of Eq. (2) and complete neglect of internal conversion), the magnitudes of k_{ISC}^I are well comparable with k_{ISC} estimate for parent chlorobenzene ($\sim 10^9 \text{ s}^{-1}$) (ref.³⁷).



SCHEME 1

Finally, we note that for each of the molecules investigated the nonradiative rate decreases as the solvent is changed from isooctane to acetonitrile (Table IV). The immediately following implication is that singlet-triplet energy gap is increased in acetonitrile solutions³⁸. Viewed in this way, two situations could theoretically explain such a behaviour: *a*) the existence of the T_n state (say the T_2 state) which is more polar in nature (and therefore more stabilized by polar solvents) than the $S_1(\pi, \pi^*)$ state (Scheme 1*a*), and *b*) the existence of different types of triplet states (say the T_2 and T_1 states) which take place on intersystem crossing in particular solvents (Scheme 1*b*).

We cannot distinguish unambiguously between these two variants because of the lack of phosphorescence data, but we prefer the first one (Scheme 1*a*) since it is further substantiated by our recent²⁰ CNDO/S calculations.

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