

Influence of weak and strong donor groups on the fluorescence parameters and the intersystem crossing rate constant

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Abstract

The absorption and fluorescence properties of 35 specially selected methyl and stronger donor substituted benzene, naphthalene, biphenyl, anthracene and 2-azaanthracene compounds are studied experimentally (at 293 K) and quantum chemically. The fluorescence quantum yields, γ , and decay times, τ_f , for deaerated and non-deaerated solutions are measured. The oscillator strength, f_e , natural lifetime, τ_f^0 and fluorescence and intersystem crossing rate constants, k_f and k_{ST} , are calculated for each compound. The orbital nature of the lowest excited singlet state, S_1 , is determined. The investigation shows that the introduction of methyl groups onto aromatic compounds may produce different effects. The symmetry and hence k_{ST} and k_f may change. As a result, γ will also change. Steric hindrance, possibly due to the CH_3 group, will decrease k_f while increasing k_{ST} . In cases where the introduction of the methyl group leaves the symmetry unchanged, there is a slight increase in k_{ST} and a slight decrease in k_f . This effect is cumulative (more CH_3 groups lead to a greater decrease in γ) and can be explained by the torsional vibrations of the methyl groups. The introduction of strong donor groups usually produces dramatic changes. k_{ST} always increases, as does k_f and the increase in k_f is usually greater. Hence, γ usually increases, sometimes dramatically. The nature of the S_1 state changes from $\pi\pi^*$ (for an aromatic molecule) to $\pi I, \pi^*$. There are three reasons for the observed increase in k_{ST} : (i) a decrease in symmetry; (ii) the internal heavy atom effect; and (iii) an improved mixing of the S_{I, π, π^*} state with T_i states. It is also found that, in many cases, the effect of methyl and stronger donor groups on the fluorescence parameters and k_{ST} depends on the position of substitution, as well as changes in the molecular symmetry. The substituent groups have different effects on the p - and α -bands. The fluorescence parameters obtained and trends observed may be useful for different theoretical and practical purposes.

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1. Introduction

It is well known that the methyl group, CH_3 , does not possess an electron capable of participating in π -bonding and so does not conjugate with the π -system of an aromatic or heteroaromatic molecule. However, due to hyperconjugation [1] and its weak electron donor properties, the CH_3 group can sometimes exert a significant influence upon the spectral-luminescent parameters of a molecule. Substitution of methyl groups onto a parent compound frequently causes a bathochromic shift of the long-wave absorption band [2] and can either increase [3] or, in some cases, decrease [3,4] the quantum yield of fluorescence. There are few systematic works devoted to this problem in the scientific literature, especially with regard to the influence of the CH_3 group on the intersystem crossing rate constant.

Introduction of a strong donor group (e.g. NH_2 , OH , OCH_3 , $\text{N}(\text{CH}_3)_2$) usually causes dramatic changes in all spectral-luminescent parameters, even the nature of the $S_0 \rightarrow S_1$ transition is very frequently changed. The oscillator strength of the $S_0 \rightarrow S_1$ electronic transition usually increases and, as a rule, the fluorescence quantum yield also increases [2,3,5]. Sometimes, substitution of a donor group onto a molecule that does not show laser activity will enable laser action to be obtained [6,7]. In some cases, substitution of a donor group onto a molecule that already exhibits laser action may enhance its laser properties [6,8], while in other cases, these properties are diminished [6,9]. All these effects can be explained by the change in the most important fluorescence parameters, including the intersystem crossing rate constant. However, as far as the authors are aware, a systematic treatment of the influence of donor groups on the intersystem crossing rate constant has not been reported. The objective of this work is to investigate the influence of both weak and strong donor groups on the fluorescence parameters and, in particular, the intersystem crossing rate constant. Since an approach to this topic requires analysis of a large quantity of experimental fluorescence data, as well as a theoretical treatment, 35 molecules were studied. These were

subdivided into six groups to facilitate the investigation.

Group 1: (1) Benzene, (2) Toluene, (3) *o*-xylene, (4) *m*-xylene, (5) *p*-xylene, (6) 1, 2, 4-Trimethylbenzene, (7) Mesitylene.

Group 2: (8) Phenol, (9) Aniline, (10) Anisole, (11) *N,N*-Dimethyl aniline, (12) 1,4-Dimethoxybenzene, (13) *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD).

Group 3: (14) Naphthalene, (15) 1-Methylnaphthalene, (16) 2-Methylnaphthalene, (17) 2,3-Dimethylnaphthalene, (18) 2,6-Dimethylnaphthalene, (19) 1-Naphthol, (20) 2-Naphthol, (21) 1-Naphthylamine.

Group 4: (22) Biphenyl, (23) 4-Methylbiphenyl, (24) 3,3'-Dimethylbiphenyl, (25) 2,2'-Dimethylbiphenyl, (26) 4-Methoxybiphenyl, (27) 4,4'-Dimethoxybiphenyl.

Group 5: (28) Anthracene, (29) 1-Aminoanthracene, (30) 2-Aminoanthracene.

Group 6: (31) 2-Azaanthracene, (32) 3-Methyl-2-azaanthracene, (33) 3,8-Dimethyl-2-azaanthracene, (34) 3,7,8-Trimethyl-2-azaanthracene, (35) 3,6,8-Trimethyl-2-azaanthracene.

The structural formulae of these compounds are presented in Fig. 1.

2. Experimental methods

The compounds studied were recrystallized, sublimed or distilled and purity controlled using chromatography. The absorption spectra of the substances were recorded using a SPECORD M40 spectrophotometer with spectroquality cyclohexane or ethanol as the solvent. Compounds (1–30) were dissolved in cyclohexane and compounds (31–35) in ethanol. A Hitachi MPF-4 spectrofluorimeter was used to record the fluorescence spectra. The quantum yields of fluorescence were measured using the method described in Ref. [10] and a highly diluted solution of 9,10-diphenylanthracene in cyclohexane served as a standard. The fluorescence quantum yield of 9,10-diphenylanthracene was measured using the method described in Ref. [11] and found to be 0.90. This value is in

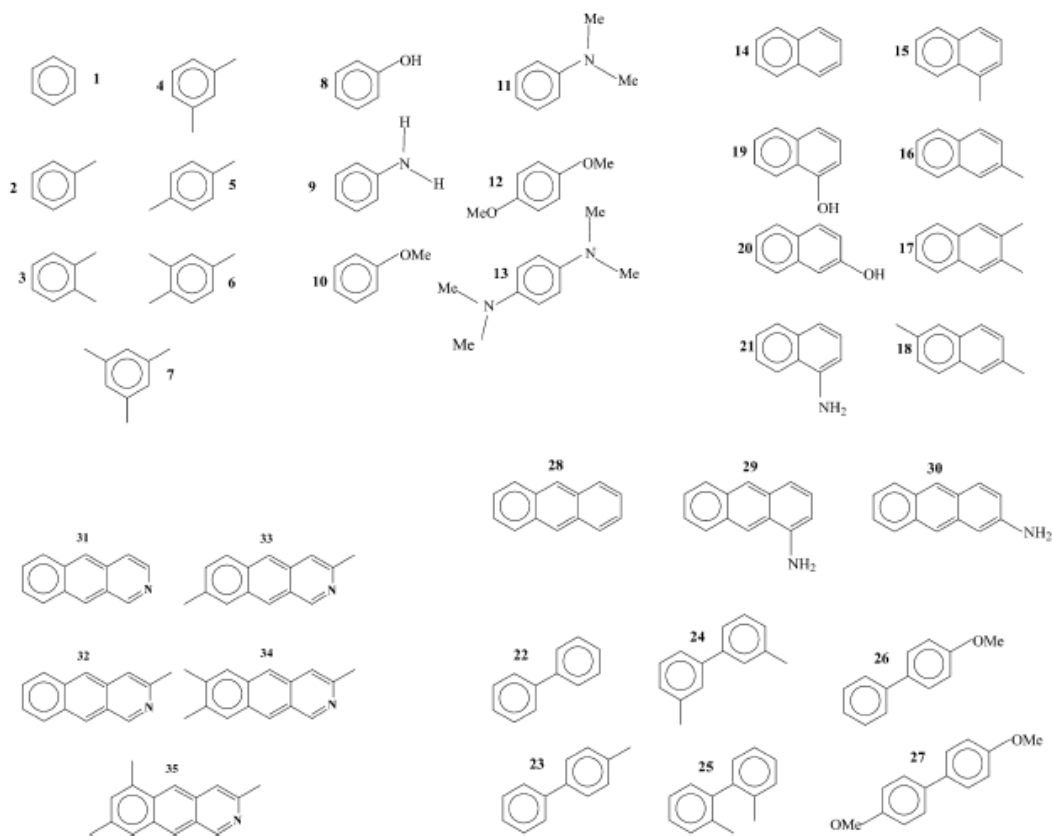


Fig. 1. Schematic representation of the structural formulae of the compounds studied.

good agreement with the results reported in Ref. [12]. The value, $\gamma = 1.00$ that is reported in Ref. [3] has never been confirmed by other researchers.

In order to minimize reabsorption effects in cases where there is a large overlap between long-wavelength absorption and fluorescence bands, solutions for fluorescence quantum yield and lifetime measurements were prepared following the recommendations given in Ref. [12]. Since some of the substances investigated reveal a very structured long-wavelength absorption band, the spectral bandpass of the excitation monochromator was chosen to be ≈ 0.5 nm in each case. The emission slit width was chosen depending on the fluores-

cence intensity, but in each case it was not large enough to cause distortion in the fluorescence spectrum.

The decay times of fluorescence, τ_f , were measured using either a SLM-4800S phase fluorimeter or installations based on the stroboscopic principle combined with single photon counting measurements [13], depending on the value of τ_f . The natural lifetimes were calculated using the formula presented in Ref. [13] and modified in Ref. [14]:

$$\frac{1}{\tau_f^T} = 2.88 \times 10^{-9} n^2 \langle \bar{\nu}_f^3 \rangle^{-1} \theta \int \frac{\epsilon(\bar{\nu}) d\bar{\nu}}{\bar{\nu}} \quad (1)$$

where $\theta = 9n/(n^2+2)^2$ is the Lorentz–Lorentz fac-

tor [15], n is the refractive index of the solvent, $\tilde{\nu}$ is the wavenumber in cm^{-1} and $\epsilon(\tilde{\nu})$ is the molar extinction coefficient. Deaeration was carried out using the method described in Ref. [16]. The value of k_{ST} was calculated by taking into account the fact that the fluorescence quantum yield of highly deaerated solutions of photostable compounds can be determined using Eq. (2), with only the intramolecular quenching processes considered [15]:

$$\gamma^* = \frac{k_f}{(k_f + k_S + k_{\text{ST}})} \quad (2)$$

where γ^* is the fluorescence quantum yield of the deaerated solution and k_S is the internal conversion rate coefficient. From Eq. (2) one obtains:

$$k_S + k_{\text{ST}} = \frac{(1 - \gamma^*)}{\tau_f^*}$$

where τ_f^* is the fluorescence decay time for the deaerated solution. For Ermolaev–Sveshnikova [17] molecules, k_S is very much less than $k_f + k_{\text{ST}}$ and in many cases $k_S \ll k_{\text{ST}}$. Hence:

$$k_{\text{ST}} = \frac{(1 - \gamma^*)}{\tau_f^*}$$

Since the vast majority of the compounds studied here have $S_1 - S_0$ energy intervals exceeding $24,000 \text{ cm}^{-1}$ and taking into account the fact that $\pi\pi^*$ and $n\pi, \pi^*$ ($l \rightarrow a_\pi$) states do not differ very much in nature [2], it is assumed that the Ermolaev–Sveshnikova principle is applicable to these compounds.

The Stoke's shift values were determined using the formulae:

$$\Delta\tilde{\nu}_{\text{ST}} = \tilde{\nu}_a^{\text{c.s.}} - \tilde{\nu}_f^{\text{c.s.}}$$

where

$$\tilde{\nu}_a^{\text{c.s.}} = \frac{\int \tilde{\nu}_a \epsilon(\tilde{\nu}_a) d\tilde{\nu}_a}{\int \epsilon(\tilde{\nu}_a) d\tilde{\nu}_a}$$

and

$$\tilde{\nu}_f^{\text{c.s.}} = \frac{\int \tilde{\nu}_f I(\tilde{\nu}_f) d\tilde{\nu}_f}{\int I(\tilde{\nu}_f) d\tilde{\nu}_f}$$

$\tilde{\nu}_a^{\text{c.s.}}$ and $\tilde{\nu}_f^{\text{c.s.}}$ are the 'centres of gravity' or 'first moments' of the long-wave absorption band and fluorescence spectrum, respectively.

$\tilde{\nu}_a$ and $\tilde{\nu}_f$ are the wavenumbers (in cm^{-1}) in the range of the absorption and fluorescence spectra and $I(\tilde{\nu}_f)$ is the quantum intensity of fluorescence.

The oscillator strengths of well resolved long-wave absorption bands were determined using the formula [15]:

$$f_e = 1.3 \times 10^{-8} \theta \int \epsilon(\tilde{\nu}) d\tilde{\nu} \quad (3)$$

The oscillator strengths of low intensity or submerged bands were determined using the formula:

$$f_e = \frac{4.514 \tilde{\nu}_a^{\text{c.s.}} \gamma}{n^2 (\tilde{\nu}_f^{\text{c.s.}})^3 \tau_f} \quad (4)$$

This was obtained by dividing Eq. (3) by a simplified version of Eq. (1), taking into account that $\langle \tilde{\nu}^{-3} \rangle^{-1} \approx (\tilde{\nu}_f^{\text{c.s.}})^3$ and

$$\int \frac{\epsilon(\tilde{\nu}) d\tilde{\nu}}{\tilde{\nu}} \approx \frac{1}{\tilde{\nu}_a^{\text{c.s.}}} \int \epsilon(\tilde{\nu}) d\tilde{\nu}.$$

The error limits determined for the various fluorescence parameters are as follows: quantum yield, $\pm 10\%$; decay time, $\pm 5\%$; symmetry line wavenumbers, $\pm 60 \text{ cm}^{-1}$; Stokes shift, $\pm 200 \text{ cm}^{-1}$; k_{ST} and k_f values, $\pm 15\%$. The error limits for experimental values of the oscillator strength, f_e of the $S_0 \rightarrow S_1$ transitions are within $\pm 5\%$. Where appropriate, the nature of the $S_0 \rightarrow S_1$ transitions, electron density changes accompanying these transitions and the energies of the triplet states were also found with the aid of the PPP-CI method using the program of Griffiths [18,19]. The parameters used are those detailed in the program literature with the exception of the BETA value for aromatic carbon-carbon bonds (-2.39) and electron affinity of the carbon atoms in the aromatic rings (0.3 eV). Positions of the $T_{n\pi^*}$ and $S_{n\pi^*}$ levels for the 2-azaanthracene derivatives (31–35) were calculated using the INDO/S method.

Table 1
Experimental and calculated values for the main fluorescence parameters of cyclohexane (1–30) and ethanol (31–35) solutions of the investigated aromatic and heteroaromatic compounds

No.	S	ν_{00}/cm^{-1}	$\Delta\nu_{\text{ST}}/\text{cm}^{-1}$	Non-deaerated			Deaerated			τ_1/ns	$k_f/10^7 \text{ s}^{-1}$	$k_{\text{IC}}/10^7 \text{ s}^{-1}$	f_e	Nature of $S_0 \rightarrow S_1^*$
				γ	τ/ns	$\tau_{\text{ex}}^{\text{nat}}/\text{ps}$	γ^{nat}	$\tau/\text{ns}^{\text{a}}$	$\tau_{\text{ex}}^{\text{nat}}/\text{ps}$					
1	D _{3h}	37200	4800	0.07	29.0	414.00	0.14	60.0	428.60	392.00	0.23	1.43	0.004	S ₀ →S ₀
2	C _{2v}	36940	4100	0.14	32.0	238.50	0.22	50.0	227.20	225.10	0.44	1.56	0.008	S ₀ →S ₀
3	C _{2v}	36530	4400	0.17	32.2	189.40	0.26	51.0	196.20	196.80	0.51	1.45	0.010	S ₀ →S ₀
4	C _{2v}	36400	4200	0.16	31.0	193.70	0.25	54.0	216.60	215.40	0.46	1.38	0.009	S ₀ →S ₀
5	D _{3h}	36140	3800	0.26	30.0	115.40	0.39	47.0	120.50	121.70	0.33	1.30	0.015	S ₀ →S ₀
6	C _{8h}	35860	4100	0.28	26.0	92.90	0.41	40.0	97.50	97.70	1.02	1.48	0.022	S ₀ →S ₀
7	D _{3h}	36080	4300	0.14	38.0	271.40	0.27	73.0	270.40	288.30	0.37	1.00	0.007	S ₀ →S ₀
8	C _{8h}	35750	3700	0.08	2.2	27.50	0.09	2.5	27.78	30.40	3.60	36.40	0.053	S ₀ →S ₀
9	C ₁	33120	4400	0.09	3.2	35.55	0.10	3.4	34.00	30.60	2.94	26.47	0.054	S ₀ →S ₀
10	C _{8h}	35830	3600	0.27	8.3	30.74	0.36	11.1	30.80	29.50	3.24	5.76	0.054	S ₀ →S ₀
11	C ₁	31720	4600	0.10	2.4	24.00	0.12	3.0	25.00	26.60	4.00	29.30	0.088	S ₀ →S ₀
12	C _{2h}	32940	4000	0.19	3.1	16.31	0.22	3.8	17.27	19.20	5.78	20.53	0.100	S ₀ →S ₀
13	C _{2h}	28000	5300	0.16	4.3	28.90	0.21	6.1	29.00	28.50	3.45	12.90	0.110	S ₀ →S ₀
14	D _{3h}	32060	4500	0.20	90.0	450.00	0.42	168.0	400.00	350.40	0.25	0.35	0.006	S ₀ →S ₀
15	C _{8h}	31730	4600	0.22	75.0	341.00	0.40	140.0	350.00	354.70	0.28	0.43	0.007	S ₀ →S ₀
16	C _{8h}	31220	3400	0.28	61.0	217.80	0.52	114.0	219.20	224.50	0.46	0.42	0.010	S ₀ →S ₀
17	C _{2v}	31180	3400	0.34	78.0	229.40	0.56	133.0	237.50	249.50	0.42	0.33	0.010	S ₀ →S ₀
18	C _{2h}	30720	3100	0.41	38.0	92.68	0.59	64.0	108.47	115.30	0.92	0.64	0.021	S ₀ →S ₀
19	C _{8h}	31000	3900	0.21	10.6	50.4	0.32	15.0	46.80	-	2.13	4.53	0.054	S ₀ →S ₀
20	C _{8h}	30390	3700	0.30	13.3	44.33	0.51	20.8	40.80	40.80	2.45	2.35	0.06	S ₀ →S ₀
21	C ₁	29530	6300	0.46	6.0	13.00	0.60	7.50	12.50	11.10	8.00	5.33	0.29	S ₀ →S ₀
22	D ₂	34700	9300	0.16	16.0	100.00	0.25	22.2	89.00	2.90	1.12	3.38	0.021 ^b	S ₀ →S ₀ +
23	C ₂	34400	8900	0.15	15.2	101.30	0.23	20.0	87.00	2.84	1.15	3.85	0.023 ^b	S ₀ →S ₀ +
24	C ₂	34120	8600	0.19	13.2	69.50	0.28	18.0	64.30	7.40	1.55	4.00	0.033 ^b	S ₀ →S ₀ +
25	C ₂	34900	7100	0.01	2.4	240.00	0.01	2.5	250.00	-	0.40	39.60	0.010 ^b	S ₀ →S ₀
26	C ₁	33230	8600	0.23	9.4	40.87	0.33	12.9	39.00	2.12	2.56	5.19	0.072 ^b	S ₀ →S ₀
27	C ₂	32140	9600	0.19	11.0	57.89	0.31	17.7	57.10	2.05	1.75	3.90	0.053 ^b	S ₀ →S ₀
28	D _{3h}	26580	4100	0.24	4.4	18.30	0.29	4.7	16.20	16.0	6.20	15.10	0.230	S ₀ →S ₀
29	C ₁	23280	5500	0.57	22.0	38.60	0.80	29.0	36.25	22.25	2.75	0.69	0.230	S ₀ →S ₀
30	C ₁	22800	4700	0.64	25.0	39.66	0.86	33.0	38.37	31.42	2.60	0.42	0.160	S ₀ →S ₀
31	C _{8h}	25200	3500	0.53	18.0	34.00	0.60	20.0	33.30	33.80	3.00	2.10	0.160	S ₀ →S ₀
32	C _{8h}	24830	3500	0.46	16.4	35.60	0.52	18.7	36.00	35.40	2.78	2.56	0.158	S ₀ →S ₀
33	C _{8h}	24310	3500	0.43	16.5	38.40	0.48	18.2	37.90	38.40	2.64	2.86	0.150	S ₀ →S ₀
34	C _{8h}	24290	3600	0.39	16.4	42.00	0.44	18.0	40.90	39.70	2.44	3.11	0.148	S ₀ →S ₀
35	C _{8h}	24100	3600	0.39	16.4	42.00	0.44	18.0	40.90	39.50	2.44	3.11	0.148	S ₀ →S ₀

Headings from left to right: No., compound number; S, symmetry group; ν_{00} , symmetry line wavenumber; $\Delta\nu_{\text{ST}}$, Stokes shift; γ , fluorescence quantum yield; τ_0 , fluorescence decay time; $\tau_{\text{ex}}^{\text{nat}}$, experimental natural fluorescence lifetime; $\tau_{\text{ex}}^{\text{nat}}$, natural lifetime; k_f , fluorescence rate constant; k_{IC} , intersystem crossing rate constant; f_e , $S_0 \rightarrow S_1$ transition oscillator strength. The nature of the S_1 state is given in Clar's notation.

^a Parameters for deaerated solutions.

^b Value calculated using Eq. (4).

^c $S_0 \rightarrow S_{0+}$ denotes band of α^* nature.

3. Results and discussion

The main experimental fluorescence parameters of the compounds studied are given in Table 1. In the following discussion the molecules are classified according to Berlmann [20], using the changes in geometry accompanying the $S_0 \rightarrow S_1$ transition as follows. Class I: planar \rightarrow planar (absorption and fluorescence spectra are structural). Class II non-planar \rightarrow non-planar (absorption and fluorescence spectra are non-structural). Class III: non-planar \rightarrow planar (absorption spectrum is non-structural but the fluorescence spectrum is structural). Class IV: non-planar \rightarrow

more non-planar (the absorption spectrum shows more structure than the fluorescence spectrum). Class V: planar \rightarrow non-planar (the absorption spectrum is structural while the fluorescence spectrum is not). Simulations performed using the PPP-CI method show that the long-wave absorption bands of compounds (14, 19, 20) and (22–27) are of α -nature ($^1A \rightarrow ^1L_b$) while the long-wave absorption bands of compounds (8–13), (21) and (28–35) are of p -nature ($^1A \rightarrow ^1L_a$). The nature of the long-wave absorption bands of (1–7) and (15–18) were determined from experimental measurements. It is necessary to note that the values of γ and τ_f obtained in this work for (1–30)

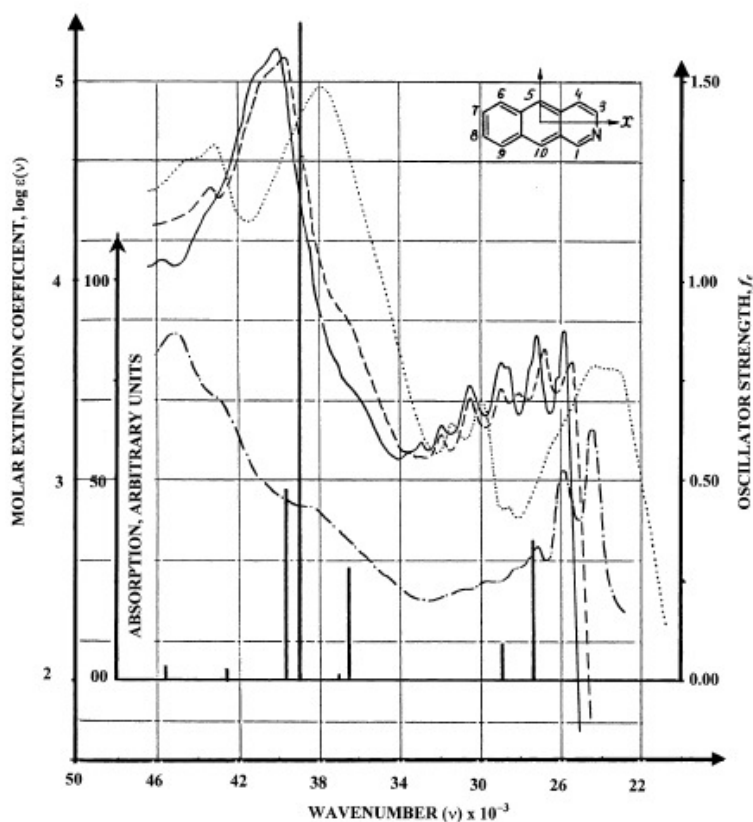


Fig. 2. UV-absorption spectra, simulated frequencies and oscillator strengths of the electronic transitions of 2-azaanthracene. (—), Cyclohexane solution; (----), ethanol solution, pH = 7; (·····), ethanol solution, pH = 2; (-·-·-·-), thin film (solid state).

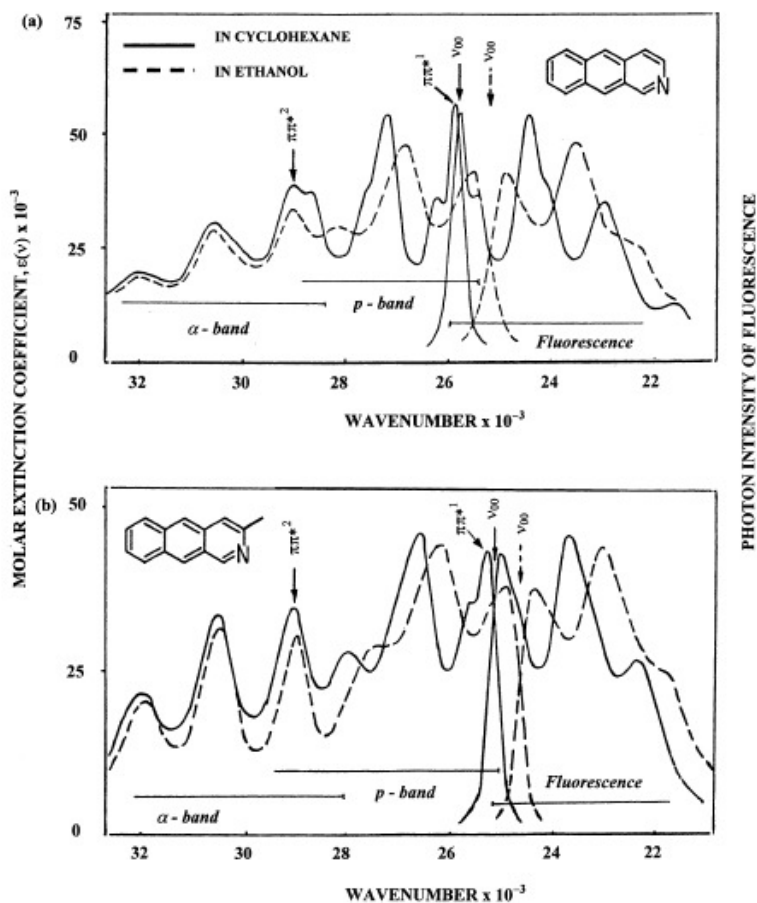


Fig. 3. Absorption and fluorescence spectra of 2-azaanthracene (a) and 3-methyl-2-azaanthracene (b).

are in good agreement with the corresponding values reported by other researchers [3,21,22]. Compounds (31–35) are practically unstudied previous to this work and so the fluorescence spectra of 2-azaanthracene and 3-methyl-2-azaanthracene are presented in Fig. 2 and Fig. 3.

3.1. Methyl substituted benzene derivatives

A comparison of the characteristics of the absorption and fluorescence spectra leads to the

conclusion that compounds (1) and (2) belong to the class I (showing structured absorbance and fluorescence spectra). Compounds (3–7) belong to class V (showing structured absorption, but non-structured fluorescence spectra) although the torsional vibrations of the methyl groups are responsible for some erosion of the vibrational structure in the absorption spectra.

The introduction of a methyl group onto the benzene ring produces several changes. It decreases the symmetry and hence the forbiddenness

of the $S_0 \rightarrow S_1$ transition is partially relaxed. The extent of spin-orbit coupling also changes since, in molecules of lower symmetry, more triplet levels have the appropriate symmetry to allow mixing with the S_1 state [23–25]. In addition, the extent of the vibronic coupling present in Benzene [22,26] may also change. As can be seen in Table 1, in all cases where methyl groups are introduced, the fluorescence rate constant, k_f , increases while the change in the intersystem crossing rate constant, k_{ST} , is much smaller. As a result the fluorescence quantum yield, γ , increases in all cases. For example, γ for compound (1) is four times as small as that of compound (6). The sole reason for this is the decrease in the molecular symmetry, from D_{6h} to C_s . Thus, the $S_0 \rightarrow S_1$ transition is more allowed, although the nature of the transition remains the same. The oscillator strength, f_e of $S_0 \rightarrow S_1$ increases and hence, so does k_f (from 0.23×10^7 to 1.02×10^7 s $^{-1}$). This is due to a reduction in symmetry, which can be verified by considering the difference between compounds (1) and (7). If the three methyl groups are introduced symmetrically, k_f increases 2-fold accompanied by a slight decrease in k_{ST} and hence, a 2-fold increase in γ . Compound (7) belongs to a higher symmetry group than compound (6) and so, the increase in f_e and consequently γ is not as great. We can conclude that the main effect produced by the introduction of methyl groups onto a benzene molecule is the decrease in the symmetry group. This leads to the increase in the oscillator strength of the α -band and consequently to an increase in k_f , changes in k_{ST} are small. The effect of the changes in molecular symmetry on k_{ST} is easily traced by comparison of compounds (2), (5) and (7), where there are slight decreases in k_{ST} as the symmetry increases ($k_{ST}(7)/k_{ST}(5) = 0.75$, $k_{ST}(5)/k_{ST}(2) = 0.83$). The difference in k_{ST} for compounds (3) and (4) can be explained by the steric hindrance to torsional vibration when the methyl groups are on neighbouring atoms, as in compound (3). However, it should be pointed out that the difference in k_{ST} between compounds (3) and (4) is within the error limits associated with the experimental measurement, hence this difference may be accidental.

Thus, the direct effect of CH_3 groups on k_{ST} in compounds (2–7) is not very clear. Many, sometimes opposing changes can occur, such as a decrease in symmetry (causing a change in spin-orbit coupling), a change in the intensity of vibronic coupling and so on.

3.2. Stronger donor substituted benzene derivatives

Compounds (9, 11–13) belong to class IV, showing a low or non-structured absorption spectrum and a broad, diffuse fluorescence spectrum. Compounds (8) and (10) belong to class V. In all cases, the introduction of the strong donor onto the benzene ring changes the nature of the $S_0 \rightarrow S_1$ transition from ${}^1A \rightarrow {}^1L_b$ to ${}^1A \rightarrow {}^1L_a$. There is an accompanying increase of f_e between 13 and 27 times. Moreover, the orbital nature of the S_1 state is changed from $\pi\pi^*$ to $\pi l, \pi^*$. $\pi\pi^*$ states are formed via $\pi \rightarrow \pi^*$ transitions, while $\pi l, \pi^*$ states are formed via $l \rightarrow a_z$ transitions. The quantum yield of fluorescence remains almost unchanged for compounds (8, 9, 11) but increases significantly for compounds (10, 12, 13). In all cases, k_{ST} is dramatically larger than that of benzene. This increase can be explained as follows. The excitation of the $S_0 \rightarrow S_1$ transition is localized largely on the donor group. In compound (11) this localization is $> 30\%$. These donor groups contain either nitrogen or oxygen atoms (both of which are heavier than carbon). In addition, rapid collisions with solvent molecules cause the donor groups to undergo out of plane internal rotation and vibrational motions. Hence, the increase in k_{ST} could be explained by four factors: (i) the decrease in molecular symmetry; (ii) the internal heavy atom effect; (iii) the change in the S_1 orbital nature; and (iv) the disturbance of the donor group.

Two striking observations can be made. Firstly, compounds (8) and (10) have identical absorption and fluorescence spectra and ν_{00} and $\Delta\nu_{ST}$ are almost the same, but k_{ST} is very different (36.5×10^7 and 5.76×10^7 s $^{-1}$, respectively). This can be explained as being due to the much smaller mass of the OH donor group compared to OCH_3 . Internal rotation and vibrational modes will be of higher frequency for the OH donor group which will increase the Franck–Condon factor [23] for the

$S_1 \rightarrow T_i$ process. This is determined by the overlap of the zeroth vibrational wavefunction, v_0 , of the S_1 state with the k th active vibrational wavefunction of the T_i state (the lower k , the greater the overlap) [27,28]. The second striking observation is that k_{ST} for (12) is larger than for (10) even though a decrease might be expected, since compound (12) belongs to a higher symmetry group. A similar pattern is not seen when comparing compounds (11) and (13). The most probable explanation of these facts is the following. In compound (12), there are two atoms that are slightly heavier than carbon, while in (10) there is only one, hence an enhanced intersystem crossing rate. This effect is not as pronounced in compounds (11) and (13) since nitrogen is lighter than oxygen and so does not promote spin-orbit coupling to the same extent. Hence, in compound (12) the internal heavy atom effect (although small) prevails over the effect of molecular symmetry, while in compound (13) the effect of the molecular symmetry is dominant.

3.3. Donor derivatives of naphthalene

Compounds (14–20) belong to class I while compound (21) belongs to class IV. As in the case of the benzene derivatives, the methyl and stronger derivatives of naphthalene are affected by the decrease of symmetry. However, the position of substitution is also important. Substitution in position '1' mostly affects the $^1A \rightarrow ^1L_a$ transition, while substitution in position '2' affects both the $^1A \rightarrow ^1L_a$ and $^1A \rightarrow ^1L_b$ transitions. In all the substituted naphthalene derivatives, f_e of the $S_0 \rightarrow S_1$ transition increases (compared to naphthalene) although the nature of the transition is only different in compound (21). As for methylated benzenes, k_{ST} values for the methylated naphthalenes show no particularly significant change. The observed increase in γ is explained by the increase in k_f . The higher value of k_{ST} of compound (18) could be explained by the greater degree of allowedness of $^1A \rightarrow ^1L_b$. The more $S_0 \rightarrow S_1$ becomes allowed, the more the S_1 state can mix with the T_i triplet levels below it.

The stronger electron donors produce a large increase in k_{ST} , although the magnitude of the

increase depends on the position of substitution. Introduction of OH into position '2' produces a larger bathochromic shift of the α -band than in the case of substitution into position '1'. The k_{ST} value of compound (20) is lower than that of compound (19) although they have the same (C_1) symmetry and hence all T_i levels are allowed to mix with S_1 . The explanation of this behaviour is very simple. The PPP simulations show that in compound (20) there are only four triplet levels below S_1 , while in (19) there are five. The energy gap between S_1 and T_5 in (19) is $\approx 480 \text{ cm}^{-1}$. Thus, $S_1 \rightarrow T_5$ intersystem crossing channel is very effective, while in compound (20) this channel is significantly suppressed because the T_5 level lies 640 cm^{-1} above S_1 . Moreover, in compound (19) the S_1-T_4 energy gap is 1050 cm^{-1} , while in compound (20) the corresponding gap is 2750 cm^{-1} . This results in the $S_1 \rightarrow T_4$ channel also being quite effective in compound (19). In compound (21), the NH_2 donor group mainly affects the $^1A \rightarrow ^1L_a$ transition polarized along the short axis [3,22,26]. This transition undergoes a red shift and the orbital nature of the S_1 state changes from $\pi\pi^*$ to $\pi l, \pi^*$. f_e increases by a factor of 48 (compare with compounds (19) and (20)) and k_{ST} increases by a factor of 15. As a result, γ increases from 0.20 to 0.46.

3.4. Donor derivatives of biphenyl

Compounds (22–25) belong to class III and (26, 27) belong to class II. This difference between compounds (22–25) and (26, 27) could be explained by the following. The essential bond joining the phenyl rings of compounds (22–25) acquires a certain amount of double bond character as a result of the $S_0 \rightarrow S_1$ transition and so the rings are forced into a more planar configuration [3]. In compounds (26, 27) the S_1 state is formed by an $l \rightarrow a_\pi$ transition which usually washes out the vibrational structure [2]. In all these cases of substitution of the biphenyl parent molecule, the symmetry decreases from D_2 to C_2 (compounds 23–25, 27) or C_1 (26). The oscillator strength increases for each, except in the case of (25). This anomaly is due to the steric hindrance to torsional motion about the bond between the phenyl rings.

k_{ST} increases in all cases, especially for (25), again due to steric hindrance. As a result, γ drops from 0.16 (22) to 0.01 (25). The decrease in k_{ST} between compounds (26) and (27) is explained by the increase in the symmetry group. Thus, in all cases of donor substituted biphenyls, k_{ST} increases and the change in γ is determined by the changes in k_f and k_{ST} .

3.5. Donor derivatives of anthracene

Anthracene (28) belongs to class I, while compounds (29, 30) belong to class II, since the NH_2 group lies out of the plane of the anthracene fragment. When the amino group is substituted onto anthracene, the symmetry decreases from D_{2h} to C_1 . In both (29) and (30), the long-wave absorption band differs in nature to the $^1A \rightarrow ^1L_a$ band of anthracene. Substitution in position '1' mainly affects the p -band, which undergoes a large red shift and acquires $\pi l, \pi^*$ orbital nature. Substitution in position '2' mostly affects the α -band, which undergoes a large red shift and also acquires $\pi l, \pi^*$ orbital nature. (Therefore, the long-wave absorption bands of (29) and (30) cannot be said to be p - or α -bands, but are completely new bands formed by the $S_0 \rightarrow S_{1\pi l, \pi^*}$ transition.) Substitution into either the '1' or '2' positions leads to a significant decrease in k_{ST} . The dramatic change in the nature of the S_1 state and its position changes the system of triplet levels lying below the S_1 state. The major contribution to k_{ST} in anthracene is the $S_1 \rightarrow T_\beta$ channel [26]. However, in (29) and (30) this level is situated much higher than the S_1 state. The slight difference in the values of k_{ST} for (29) and (30) is for the same reason as in compounds (19) and (20). The role of the T_β state in the intersystem crossing process in anthracene was discussed in Ref. [26].

3.6. Methyl derivatives of 2-azaanthracene

Compounds (31–35) belong to class I. These compounds are of special importance for the achievement of the objectives of this study, since introduction of methyl groups onto 2-azaanthracene does not change the symmetry group, nor does it significantly change f_e . Moreover, these

compounds have the same degree of planarity (i.e. the longwave absorption band and fluorescence spectrum have the same vibronic structure). This series of compounds should allow the direct effect of the weak donor (methyl group) to be elucidated. Simulations using the INDO/S method show that 2-azaanthracene and its methyl derivatives belong to the spectral-luminescent class V [29]. In other words, the $T_{\pi\pi^*}$ state is situated above $S_{1\pi\pi^*}$. In order to completely eliminate the $S_{1\pi\pi^*} \rightarrow T_{\pi\pi^*} \rightarrow T_{\pi\pi^*}$ channel of depopulation of the $S_{1\pi\pi^*}$ state, compounds (31–35) were dissolved in ethanol. This decreases the energy of $S_{1\pi\pi^*}$ and increases the energy of the $T_{\pi\pi^*}$ level due to hydrogen bonding [2,22]. Hence, the energy gap between $T_{\pi\pi^*}$ and $S_{1\pi\pi^*}$ is definitely $> 1000 \text{ cm}^{-1}$ [4,29]. Analysis of the fluorescence parameters of these compounds shows that the methyl groups cause a small decrease in k_f , a small increase in k_{ST} and consequently, a cumulative decrease in γ (which is observed to steadily decrease from (31) through (34) as the number of methyl groups increases). Compounds (31–35) were actually studied in both cyclohexane and ethanol. The quantum yields of fluorescence of these compounds in cyclohexane are 0.36, 0.34, 0.31, 0.29 and 0.31, respectively. The effect of the methyl groups in this case is mixed with the effect of the increase in the $S_{\pi\pi^*} - S_{1\pi\pi^*}$ energy interval [4].

Analysis of Fig. 2 shows that the absorption spectrum of 2-azaanthracene is quite different to the absorption spectrum of anthracene. In anthracene, the α -band ($^1A \rightarrow ^1L_b$) is forbidden, while it is allowed and clearly resolved in 2-azaanthracene. The p -band in 2-azaanthracene is sensitive to the solvent and pH of the medium, while the α -band is practically unaffected. PPP-CI simulation also confirms that the α -band of 2-azaanthracene is allowed. It is the low (C_s) symmetry that accounts for the allowed nature of the α -band. The absorption spectra of the methyl derivatives show very few differences from the spectrum of 2-azaanthracene, except that the p - and α -bands are more separated and better resolved, which is obvious from Fig. 3(b).

Finally, it is necessary to say a few words about the effect of deaeration, although this was not the objective of the study. In all cases, deaeration

caused an increase in γ and the size of this increase is dependent on τ_f . It is most probable that this effect is brought about merely by quenching of the excited S_1 state by oxygen in the non-deaerated solutions. The effect of changing the pH to 2 (see Fig. 2) could be explained by the different contribution of the N atom in the $S_{1\pi\pi^*}$ (p -band) and $S_{2\pi\pi^*}$ (α -band) states. During the $S_0 \rightarrow S_p$ transition, the π -electron density increases on the N atom, whilst during the $S_0 \rightarrow S_\alpha$ transition the π -electron density decreases on this atom. This would also explain the difference in the effects of ethanol upon the p - and α -bands.

4. Conclusions

From the experimental and quantum chemical data discussed in this paper, the following conclusions may be drawn about the influence of methyl and stronger donor groups on the fluorescence parameters and k_{ST} .

- 1) Introduction of methyl groups onto aromatic compounds may produce different effects: (a) there may be a change in the symmetry group and hence k_{ST} and k_f will change. (b) There may be increased steric hindrance and hence k_f will decrease and k_{ST} increase.
- 2) If there is no change in molecular symmetry or planarity upon introduction of methyl groups, then there will be a slight decrease in k_f and a slight increase in k_{ST} . Torsional vibrations of the methyl group(s) could explain this.
- 3) Introduction of a strong donor group usually produces dramatic changes in all of the fluorescence parameters. This is not only due to the decrease in symmetry group but also due to changes in the nature of the S_1 state. Introduction of a strong donor usually causes a significant increase in k_{ST} . This is explained by the presence of O and/or N atoms (which are slightly heavier than C) in the donor group and by the π, π^* orbital nature of the S_1 state (which mixes more readily with the T_i states than $S_{1\pi\pi^*}$) [2]. It is common for γ to increase as well, since k_f usually increases more than k_{ST} .

- 4) In many cases the effect of methyl and other donor groups on the fluorescence parameters depends on the position of substitution as well as the change in symmetry. Introduction in different positions causes different effects on the p - and α -bands.

The trends outlined in this paper could find practical use in cases where the fluorescence parameters of a compound need to be changed in a necessary direction.

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