# ON THE NATURE OF THE FLUORESCENT STATE
# OF METHYLATED INDOLE DERIVATIVES

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A quantitative study has been made of the solvent effects on the fluorescence properties of 1- and 3-methyl indole, with the aim of further understanding the origin of the unusually large Stokes shift in polar solvents. For the derivatives considered here the fluorescence transition probability is decreased in solvents of moderate and high polarities, and the spectrum shifts to the red. The data (in two-component, solute and solvent, systems) can be interpreted on the basis of the stabilisation, by solvent–solute relaxation, of a state with an increased charge-transfer character, relative to the initially excited state. A consideration of the decay data for other indole derivatives suggests that this state has its origin in the $^1L_a$ state ($S_2$ in non-polar media). Thus we conclude that the appropriate label of the fluorescent state of many substituted indoles in polar solvents is $^1L_a$/CT. This is consistent with the observed solvent, temperature, time and substituent dependence of the decay kinetics of these derivatives.

## 1. Introduction

The solution-phase photophysics of indole and its derivatives has been the subject of quite intensive investigation. Much of this attention has focused on the origin of the unusually large Stokes shift that is observed in polar media [1–14]. This shift arises from a red-shift in the emission, the energy of the absorption band being more or less independent of the solvent. In non-polar solvents the emission is narrow and slightly structured, whereas in polar solvents the spectrum is broad, featureless, and somewhat shifted to lower energy. The former type of spectrum has been called the locally excited (LE) emission; it bears a close mirror-image relation with the low-energy absorption spectrum. The latter is frequently referred to as the "exciplex" emission, since Lumry and co-

workers [10–14] have suggested that this broad red-shifted spectrum arises from a solvent–solute, mainly dipole–dipole stabilised, exciplex of 1 : 1 or 2 : 1 stoichiometry. However, several alternative assignments may be cited.

Kawski and co-workers [2,3] have suggested that the large Stokes shift may be explained by the relaxation of solvent dipoles about the increased dipole moment of the excited state, relative to that of the ground state, of indole. Mataga et al. [4] and Suzuki et al. [5] proposed a similar mechanism, but suggested that the (initially) second excited singlet state ($^1L_a$) becomes the fluorescent state in polar media, because it is more strongly stabilised by the solvent–solute relaxation (SSR) than is the $S_1(^1L_b)$ state; in non-polar solvents the $^1L_b$ state of indole derivatives is usually a few hundred wavenumbers below the $^1L_a$ state, the precise energy gap being dependent on the nature and position of the substituents [15–17]. Lami [8,18] has suggested that

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the emission in polar media arises from a solvated Rydberg state, the origin of which he has discussed. Skalski et al. [7] suggested that a reorganisation of the 1-methyl indole–butanol ground-state complex, that they observed, is responsible for the red-shifted emission. More recently Drickamer and co-workers [19,20] studied the effects of high pressure on the decay kinetics of indole and 5-methoxy indole in different media.

In a previous paper [21] we studied the temperature dependence of the time-resolved fluorescence of 1,3-dimethyl indole in n-butanol. We observed that the changes in spectral shape that occur when changing the medium from a non-polar to a polar one are also seen when (a) the polar butanol medium is changed from the glassy to the fluid state and (b) as a function of time after excitation in viscous polar solutions. Also, the fluorescence decay profile was highly non-exponential and emission-wavelength dependent in the viscous solutions, but not in the glassy or fluid ones. These results, and a consideration of the approximate radiative lifetime in the glass and fluid states, led us to suggest that the red-shifted emission in polar solvents arises from a new (i.e. not $^1L_a$) state that is stabilised by SSR about the initially excited state. In what follows we wish to address the question of the nature of this state.

We will present data on the electronic spectra and, more importantly, the solvent dependence of the $S_1 \rightarrow S_0$ transition probability of 1- and 3-methyl indole. The results suggest that the "exciplex" fluorescence can, in two-component (solute and solvent) solutions, be largely ascribed to a non-specific solvent perturbation of the excited states, leading to an increase in the charge-transfer character of the fluorescent state. These experimental results are discussed in relation to previous theoretical calculations, and experimental data on other indole derivatives. These considerations suggest that the new fluorescent state has its origin in the $^1L_a$ state.

## 2. Experimental

The fluorescence decays were obtained by the time-correlated single-photon counting method.

The excitation source was the frequency-doubled output of a Spectra Physics synchronously pumped, cavity-dumped dye laser, pulsewidth $\approx 6$ ps. The excitation wavelength was 295 nm, the full width at half maximum height of the instrument response function was $\approx 600$ ps. Decay times ($\tau_F$) were extracted from the raw decay data (which had $2 \times 10^4$ counts in the channel of maximum counts) by the method of non-linear least-squares iterative reconvolution. All decays reported here were well described by a single exponential decay function, as was shown by random residual and autocorrelation of residual plots, and the values of the reduced chi-square and the Durbin and Watson parameter (in the ranges of 1–1.2 and 1.8–2.0 respectively [22]). Full details of the measurement and analysis procedures have been given elsewhere [22].

Fluorescence quantum yields were measured by employing a fully corrected integrating sphere spectrofluorimeter, which eliminates the need for a "geometrical" refractive index correction, the appropriate value of which has been the subject of some recent debate [23–27]. The value of the fluorescence quantum yield ($\phi_F$) was determined relative to that of 2-aminopyridine in 1 N sulphuric acid solution ($\phi_F = 0.66$) [27]. This standard was preferred over quinine bisulphate because the latter molecule has only a weak absorbance at the excitation wavelengths used, which were at around 280 nm. Each value of $\phi_F$ was determined using at least two samples each at two excitation wavelengths. The optical density was < 0.05. Full experimental details, including the calibration, the spectral correction technique used, the method of ensuring that the correct absorbance was measured, the error determination procedure, etc., have been given elsewhere [27].

The radiative lifetime ($\tau_R$) was determined from $\phi_F$ and $\tau_F$ according to the relation $\tau_R = \tau_F \phi_F^{-1}$, and has been appropriately corrected for the different refractive indices of the solvents and the position of the emission spectrum (see below and ref. [27]).

The corrected emission spectra were measured with the integrating sphere spectrofluorimeter, and the absorption spectra with a Perkin–Elmer model 554 spectrophotometer.

1-methyl indole (1-MI) was vacuum distilled and 3-methyl indole (3-MI) was recrystallised twice from cyclohexane. All solvents were Aldrich "Gold Label" or equivalent, and were further purified by conventional methods [28].

All experiments were performed at 293 K, unless otherwise stated. All samples were degassed by several freeze–pump–thaw cycles.

## 3. Results and discussion

This section is divided into three parts. In the first the solvent dependence of the electronic spectra of 1-MI and 3-MI is considered; in the second data are presented on the solvent dependence of their radiative lifetimes; in the final part we discuss the origins of the observed solvent effects, and reach some conclusion about the nature of the fluorescent state in polar solvents.

### 3.1. Absorption and fluorescence spectra

#### 3.1.1. Absorption spectra

The lowest-energy absorption envelope of indole derivatives is due to two electronic transitions. $^1L_b \leftarrow {}^1A$ and $^1L_a \leftarrow {}^1A$. The absorption spectra of indoles have been considered by Strickland and co-workers [15–17]. In fig. 1 we display the absorption spectra of 3-MI in three different solvents. The complete spectral data of 1-MI and 3-MI are given in tables 1 and 2. For 3-MI there is a loss of observable vibronic structure when the polarity of the medium is increased and a small red-shift in the absorption maximum. The excep-
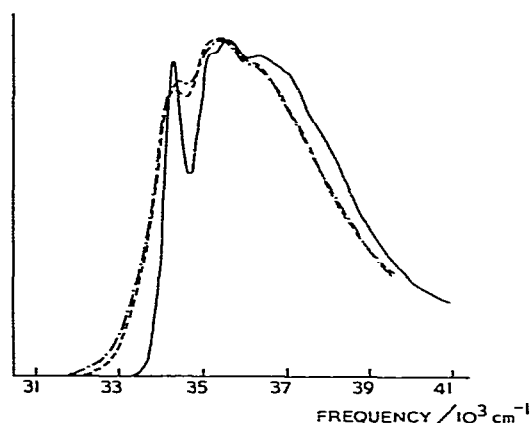


Fig. 1. Absorption spectra of 3-MI in cyclohexane (———), dichloromethane (- - - - - -) and acetonitrile (- - - - -).

tion to this trend is the aqueous solution, where the maximum is observed to be $\approx 300$ cm$^{-1}$ to the blue of the cyclohexane solution. For 1-MI there is no strong trend in the position of the band maximum, although the spectrum in acetonitrile appears to be anomalous.

For both compounds there is a well-resolved 0–0 transition in the cyclohexane solution. In the polar solvents, however, this feature is much less prominent, and the absorption broadens considerably to the red. One noteworthy feature is that the position of the 0–0 feature is, so far as can be determined, insensitive to the solvent polarity. This 0–0 feature has been assigned to the $^1L_b \leftarrow {}^1A$ absorption, whereas the band maximum is believed to be due largely to the $^1L_a \leftarrow {}^1A$ transition. These results (tables 1 and 2) then confirm that the

Table 1
Spectral data for 3-methyl indole

| Solvent | $\nu_a^{max}$ $\nu$ (10$^3$ cm$^{-1}$) | $\nu_c^{max}$ (10$^3$ cm$^{-1}$) | $\nu_c^{CG}$ a) (10$^3$ cm$^{-1}$) | $\nu_a^{max} - \nu_c^{max}$ | $\nu_a^{max} - \nu_c^{max}$ | $(\nu_a^{max} \div \nu_c^{CG})/2$ | fwhm b) (10$^3$ cm$^{-1}$) |
|---|---|---|---|---|---|---|---|
| cyclohexane | 35.84 | 32.79 | 31.91 | 3.06 | 3.93 | 33.88 | 3.51 |
| tetrahydrofuran | 35.59 | 30.19 | 29.55 | 5.40 | 6.04 | 32.57 | 4.59 |
| dichloromethane | 35.46 | 29.85 | 29.45 | 5.61 | 6.01 | 32.46 | 4.63 |
| butan-1-ol | 35.34 | 28.57 | 28.23 | 6.76 | 7.11 | 31.79 | 4.97 |
| acetonitrile | 35.59 | 28.99 | 28.67 | 6.60 | 6.92 | 32.13 | 4.81 |
| water | 36.41 | 26.85 | 26.51 | 9.57 | 9.90 | 31.46 | 5.21 |

a) Centre of gravity of emission.
b) Spectral width at half maximum height.

Table 2
Spectral data for 1-methyl indole

| Solvent | $\nu_a^{max}$ ($10^3$ cm$^{-1}$) | $\nu_c^{max}$ ($10^3$ cm$^{-1}$) | $\nu_c^{CG}$ ($10^3$ cm$^{-1}$) | $\nu_a^{max} - \nu_c^{max}$ | $\nu_a^{max} - \nu_c^{CG}$ | $(\nu_a^{max} + \nu_c^{CG})/2$ | fwhm [a] ($10^3$ cm$^{-1}$) |
|---|---|---|---|---|---|---|---|
| cyclohexane | 35.46 | 32.79 | 32.12 | 2.67 | 3.34 | 33.79 | 3.11 |
| tetrahydrofuran | 35.59 | 32.00 | 30.77 | 3.59 | 4.81 | 33.18 | 4.45 |
| dichloromethane | 35.21 | 30.77 | 30.16 | 5.44 | 5.04 | 32.69 | 4.54 |
| butan-1-ol | 35.59 | 30.77 | 30.15 | 4.88 | 5.44 | 32.87 | 5.20 |
| acetonitrile | 35.97 | 30.30 | 29.46 | 5.66 | 6.51 | 32.72 | 4.41 |
| water | 35.46 | 28.37 | 28.01 | 7.09 | 7.45 | 31.74 | 4.85 |

[a] Full width at half maximum intensity.

solvent-sensitive state is $^1L_a$. This sensitivity is probably due to the higher dipole moment (see below) of this state which will in turn give rise to significant non-specific solvent–solute interactions. Conversely the broadening on the red edge of the absorption may be due to both non-specific and weak specific interactions. A range of such interactions would be expected to cause the observed loss of vibronic structure and spectral broadening in polar solvents.

### 3.1.2. Fluorescence spectra and Stokes shift

The corrected fluorescence spectra of 1-MI are displayed in fig. 2 in each of the six solvents. Data for both molecules are shown in tables 1 and 2. The fluorescences of both compounds in cyclohexane are narrow and, in the case of 1-MI, slightly structured. This is consistent with a $^1L_b$ assignment of this fluorescent state. In more polar solvents these spectral features are lost, and the emission both broadens and shifts to the red as the polarity increases – i.e. the progression from LE to "exciplex" emission occurs. For 3-MI the emission in aqueous solution is rather broad, which is not the case for 1-MI; the absorption spectrum of 3-MI in aqueous solution is also rather broad.

The solvent-induced Stokes shift of indole and its derivatives has been considered by Mataga et al. [4] and Kawski and co-workers [2,3]. Both groups found a reasonable correlation between Stokes shift and the relevant solvent polarity parameter. This suggests that the "exciplex" emission arises via SSR about the excited state of the indole derivative. Lumry and co-workers [10] did not find such a good correlation between Stokes
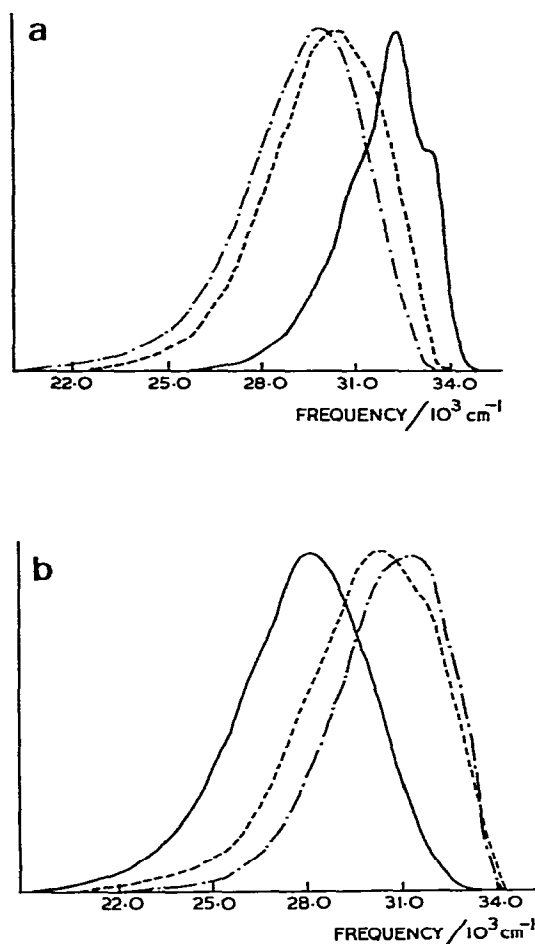
Fig. 2. (a) Emission spectra of 1-MI in cyclohexane (———), dichloromethane (------) and acetonitrile (-·--·-). (b) Emission spectra of 1-MI in water (———), butanol (------) and tetrahydrofuran (-·--·-).

shift and solvent polarity.

We have analysed our data (tables 1 and 2) according to the formulation of Bakhshiev [29]. We take the Stokes shift as being that between the absorption maximum ($\nu_a^{max}$) and the centre of gravity of the emission ($\nu_e^{CG}$), where $\nu_e^{CG} = \int \nu I(\nu)$ $d\nu / \int I(\nu)$ $d\nu$, and $I(\nu)$ is the emission intensity at frequency $\nu$. The integration is over the whole spectrum. This procedure is preferable to employing $\nu_e^{max}$ when the shape of the emission is solvent dependent. If SSR is responsible for the large Stokes shift, then it may be expressed as follows [29] ‡

$$\Delta\nu = \nu_a^{max} - \nu_e^{CG}, \tag{1}$$

where the following definitions apply

$$\nu_a^{max} = \nu_a^{sol} - \nu_a^{vap} + K$$

$$= (hca^3)^{-1} F^2(n) 2\mu_g(\mu_g - \mu_e \cos\alpha)$$

$$\times F(\epsilon, n) + (\mu_g^2 - \mu_e^2)\phi(n), \tag{2}$$

$$\nu_e^{CG} = \nu_e^{sol} - \nu_e^{vap} + K'$$

$$= (hca^3)^{-1} F^2(n) 2\mu_e(\mu_g \cos\alpha - \mu_e)$$

$$\times F(\epsilon, n) + (\mu_g^2 - \mu_e^2)\phi(n) \tag{3}$$

and

$$F(\epsilon, n) = (\epsilon - 1)/(\epsilon + 2) - (n^2 + 1)/(n^2 + 2). \tag{4}$$

$$F^2(n) = [(2n^2 + 1)/(n^2 + 2)]^2, \tag{5}$$

$$\phi(n) = (n^2 - 1)/(n^2 + 2), \tag{6}$$

where $\epsilon$ is the solvent dielectric constant, $n$ its refractive index (taken at the sodium D line). $\mu_g$ and $\mu_e$ are respectively the ground- and excited-state dipole moments of the solute, $\alpha$ is the angle between them, and $a$ is the Onsager cavity radius [31]. $K$ and $K'$ account for the difference between the spectral parameters used here and the (unresolved) frequencies of the pure electronic transition. $K$ is approximately constant. The slope of a plot of $\Delta\nu$ against $F(\epsilon, n)$ $F^2(n)$ will yield the value of $(|\mu_g - \mu_e|)^2$. Also a plot of $\Delta\nu_s$ ($\Delta\nu_s =$

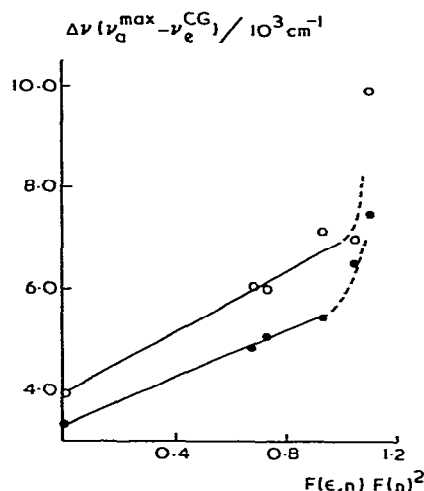‡ Other expressions [30] lead to qualitatively similar, but quantitatively different, results.



Fig. 3. Plot of the Stokes shift ($\nu_a^{max} - \nu_e^{CG}$) as a function of the solvent polarity parameter $F(\epsilon, n)$ $F^2(n)$, for 3-MI (O) and 1-MI (●).

$(\nu_a^{max} + \nu_e^{CG})/2$) against the appropriate solvent parameter will yield the value of $(\mu_g^2 - \mu_e^2)$.

These plots are shown in figs. 3 and 4, for 1-MI and 3-MI. The data derived from them are shown in table 3. The correlations observed are reasonable in both cases, except that strong deviations are seen in the high-polarity solvents, and this is especially true for the aqueous solutions. It is note-
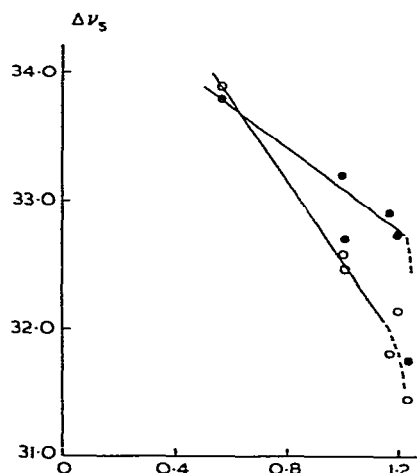


Fig. 4. Plot of $\Delta\nu_s$ against the appropriate solvent parameter (see text), for 3-MI (O) and 1-MI (●).

Table 3

Results from figs. 3 and 4. Cavity radius for both taken as $2.7 < a < 3.3$ Å. Data were calculated excluding the data for aqueous solutions. but are not much affected if these are included [30]

| | 3-MI | 1-MI |
|---|---|---|
| slope (cm$^{-1}$) | 3051 (3925)[a] | 2703 (3188) |
| $\|\Delta\mu\|$ (D) | $2.4 < \|\Delta\mu\| < 3.3$ | $2.3 < \|\Delta\mu\| < 3.1$ |
| $\Delta\mu^2$ | $-13.5 < \Delta\mu^2 < -7.4$ | $-7.4 < \Delta\mu^2 < -4.1$ |
| $\mu_e$ [b] | $3.7 < \mu_e < 4.7$ | $3.2 < \mu_e < 3.8$ |
| $\mu_g/\mu_e$ | 0.67–0.64 | 0.69–0.58 |
| cos α | 0.75–0.72 | 0.70–0.57 |

[a] Intercept on $y$ axis.

[b] Calculated assuming $2.5 < \mu_g < 3.0$ D for 3-MI and $\mu_g = 2.2$ D for 1-MI (from ref. [32]).

worthy that this deviation occurs whether or not the N atom is methylated (this is also true for 1,2-dimethyl indole [2]). thus it cannot be attributed to a simple hydrogen-bonding mechanism.

From table 3 we can see that the value of $\mu_g/\mu_e$ is very close to that of cos α. hence we expect the solvent effect on the emission spectra to be maximal. and that on the absorption minimal [29]. which is consistent with the observation (fig. 1) of an almost solvent-independent energy of the weakly resolved 0–0 ($^1L_b \leftarrow {}^1A$) absorption.

For the case of indole derivatives only qualitative conclusions may be drawn from this analysis. since (a) the large solvent effect on the shape of the emission spectrum will cause the value of $K$ and $K'$ [eq. (3)] to be different. and $K'$ to be solvent dependent. (b) the equations used here are incomplete [33]. However. the following conclusions may reasonably be drawn: (i) the positive deviation from linearity observed in fig. 3 is consistent with an increasing value of $\mu_e$ in solvents of high polarity; (ii) the deviations that are observed are not. given the widely different nature of these solvents, so large as to suggest a strong. specific. solvent–solute interaction. It would seem that the red-shifted emission does arise through some SSR mechanism, but that some change occurs in the nature of the emitting state in fluid polar solvents. Thus the solvent effects on the indole electronic spectra are consistent with the temperature dependence discussed previously.

### 3.2. Solvent effect on the radiative transition probability

In comparison with the amount of data that has been accumulated concerning solvent effects on the electronic spectra of indoles. there have been very few studies of such effects on their time-resolved fluorescence. Walker et al. [12] and Szabo and Rayner [34] have compared $\tau_R$ of several derivatives in cyclohexane and aqueous media. and found it to be longer in the latter. Recently Drickamer and co-workers [19.20] have studied $\tau_R$ of indole in several solvents at atmospheric as well as high pressure. These workers found a significant decrease in $\tau_R$ between hexane and aqueous media. In fact there is a wide scatter of values for $\tau_F$ and $\phi_F$ to be found in the literature. even for indole in aqueous media – a commonly made measurement. viz. $\tau_F = 4.1$ ns [11]. 4.8 ns [34]. 2.7 ns [19]: $\phi_F = 0.45$ [11]. 0.25 [34]. 0.23 [19]. A similar spread can be found for other indole derivatives and other solvents and. indeed. any other molecule that has been studied extensively. This merely reflects the errors to which the determinations of $\tau_F$ and $\phi_F$ (particularly the latter) are subject.

We have discussed elsewhere and at length the methods and instrumentation that we have employed to eliminate. as far as possible. errors and artefacts in our determinations of $\tau_F$ [22] and $\phi_F$ [27]. On the basis of the calibrations of these instruments we have reasonable confidence in the data presented below.

In tables 4 and 5 we display the decay parameters of 3-MI and 1-MI respectively. The measured radiative lifetimes are corrected for the refractive index (high-frequency dielectric constant, $n$) of the medium. The "$n^2$" correction arises from an intrinsic dependence of $\tau_R$ on $n$, as may be seen from the Strickler–Berg relation [35,36]

$$k_R = 1/\tau_R = 2.88 \times 10^{-9}\, n^2 \langle \bar{\nu}_F^{-3}\rangle_{av}^{-1} \int \frac{\epsilon(\nu)}{\nu}\, d\bar{\nu},$$

$$(7)$$

where the integral is over the $S_1 \leftarrow S_0$ absorption spectrum ($\epsilon$ is the extinction coefficient) and

$$\langle \bar{\nu}_F^{-3}\rangle_{av}^{-1} = \int F(\nu)\, d\nu / \int F(\nu)\nu^{-3}\, d\nu.$$

$$(8)$$

Table 4

Solvent dependence of the decay kinetics of 3-methyl indole

| Solvent | $\phi_F$ [a] | $\tau_F$ (ns) | $\tau_R$ [b] (ns) | $n^2\tau_R$ (ns) | $k_{nr}$ [c] ($10^8$ s$^{-1}$) | $\langle \bar{\nu}_F^{-3} \rangle_{av}$ ($10^{13}$) |
|---|---|---|---|---|---|---|
| cyclohexane | 0.40 (0.03) | 4.36 | 10.90 (0.9) | 22.16 | 1.84 | 0.315 |
| tetrahydrofuran | 0.38 (0.02) | 5.75 | 15.13 (0.9) | 29.87 | 1.40 | 0.40 |
| dichloromethane | 0.011 (0.004) | 0.21 [d] | 19.10 (9.0) | 38.72 | 47.36 | 0.40 |
| butan-1-ol | 0.35 (0.02) | 7.41 | 21.17 (1.3) | 40.90 | 1.10 | 0.44 |
| water | 0.29 (0.015) | 9.49 | 32.72 (1.8) | 58.12 | 0.88 | 0.56 |

[a] Figure in parentheses represents estimated error. $\tau_F$ is assumed to be measured without error.
[b] Calculated from $\tau_R = \tau_F/\phi_F$. [c] Calculated from $(\tau_F^{-1} - \tau_R^{-1})$. [d] $\pm 20\%$.

where $F(\nu)$ is the fluorescence intensity at $\nu$. Eq. (7) is valid for allowed transitions where no large nuclear rearrangement occurs following excitation [36]. There have been numerous discussions concerning an $n$ dependence of the integral in (7) (see ref. [37], and references therein), but an $n^2$ correction of $\tau_R$ has been shown experimentally to be the most appropriate [26,27,23,37] for molecules which obey the conditions outlined above. No "fundamental" dependence of $\tau_R$ on the low-frequency dielectric constant has, to our knowledge, been observed.

There are a number of general trends in tables 4 and 5. For both 1-MI and 3-MI $\phi_F$ decreases as the solvent polarity increases, by a factor of 0.6 for 1-MI and 0.9 for 3-MI, between cyclohexane and butanol. The $\phi_F$ in dichloromethane is anomalously low. The $\tau_F$ of 3-MI increase as the solvent polarity increases, 1.7 times between cyclohexane and butanol. For 1-MI $\tau_F$ is decreased slightly in THF and butanol, as compared to cyclohexane, but increases in water. The lifetimes in dichloromethane are anomalously short, as expected from the $\phi_F$ values. Clearly the latter solvent acts as a quencher of indole fluorescence.

The solvent dependence of $\tau_F$ does not follow

that of $\phi_F$ for either molecule, which is reflected in the values of $\tau_R$ (and $n^2\tau_R$). These exhibit an increase as the solvent polarity is increased. For 3-MI $\tau_R$ increases by about a factor of two between cyclohexane and butanol and for 1-MI, a factor of 1.5. This is analogous to the behaviour that we have observed for some aminoaphtalenes [38]. This behaviour is in qualitative agreement with that of Szabo and Rayner [34] on some indoles in non-polar and aqueous media. Our data may be contrasted with those of Walker et al. [11], where a decrease in $\tau_R$ for indole was observed on changing the solvent from cyclohexane to methanol (or dioxane), although the spectral behaviour of indole and 1-MI or 3-MI are qualitatively similar [2]. The possible origin of this discrepancy will be discussed later. The values of $\langle \bar{\nu}_F^{-3} \rangle_{av}$ vary in the manner expected for a red-shift.

We may note a correlation between the measured radiative lifetimes and the fluorescence spectral shifts. For 3-MI there is a significant increase in $\tau_R$ between cyclohexane and THF, whereas for 1-MI the values are quite similar. The corresponding spectral shifts, $\Delta\nu$, are 3930 cm$^{-1}$ (cyclohexane) and 6040 cm$^{-1}$ (THF) for 3-MI; the corresponding figures for 1-MI being 3340 and 4810

Table 5

Solvent dependence of the decay kinetics of 1-methyl indole [a]

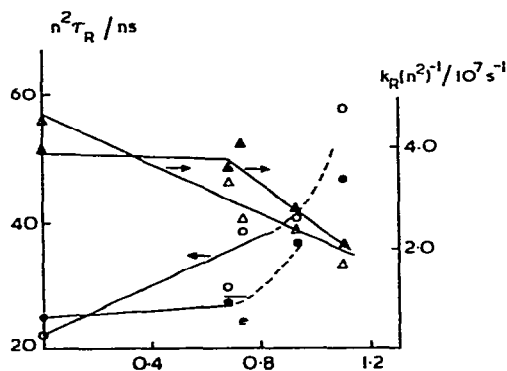| Solvent | $\phi_F$ | $\tau_F$ (ns) | $\tau_R$ (ns) | $n^2\tau_R$ (ns) | $k_{nr}$ ($10^8$ s$^{-1}$) | $\langle \nu_F^{-3} \rangle$ ($10^{13}$) |
|---|---|---|---|---|---|---|
| cyclohexane | 0.50 (0.02) | 6.25 | 12.50 (0.6) | 25.41 | 1.21 | 0.31 |
| tetrahydrofuran | 0.37 (0.025) | 5.11 | 13.80 (1.0) | 27.24 | 1.59 | 0.35 |
| dichloromethane | 0.04 (0.004) | 0.465 [b] | 11.92 (1.3) | 24.18 | 21.09 | 0.37 |
| butan-1-ol | 0.31 (0.025) | 5.45 | 17.58 (1.5) | 36.95 | 1.56 | 0.405 |
| water | 0.33 (0.014) | 8.75 | 26.52 (1.2) | 47.10 | 0.93 | 0.47 |

[a] Footnotes to table 4 apply. [b] $\pm 15\%$.

Fig. 5. Measured radiative lifetimes of 3-MI (O) and 1-MI (●), corrected for $n^2$ effect, plotted against $F(\epsilon, n)$ $F^2(n)$. Also shown is $k_R/n^2$ for 3-MI (△) and 1-MI (▲).



Fig. 6. Plot of the solvent dependence of the (radiative transition moment, $M_{GE}^2$, of 3-MI (O) and 1-MI (●), against $F(\epsilon, n)$ $\times F^2(n)$.

$cm^{-1}$. Thus a large change in $\tau_R$ apparently correlates with a larger spectral shift. This is true even when $\tau_R$ is corrected for its dependence on the emission frequency (see below). In fig. 5 we plot $n^2\tau_R$ (and $k_R/n^2$) as a function of the solvent polarity parameter $F(\epsilon, n)$ $F^2(n)$. For 3-MI there is a gradual increase in $n^2\tau_R$ as the solvent polarity increases. whereas for 1-MI the increase is only observed in the more polar, protic, solvents.

These data are further emphasised by a consideration of the solvent dependence of the square of the electronic transition moment, $|\langle\Psi_e|\Sigma_i er_i|\Psi_g\rangle|^2 (= M_{GE}^2)$, calculated from

$$M_{GE}^2 \propto \tau_R^{-1} n^3 \langle \nu_F^{-3} \rangle_{av}.$$  (9)

This dependence is shown in fig. 6. The $S_1 \to S_0$ transition probability is found to decrease in polar media. For 3-MI in THF solution $M_{GE}^2$ decreases relative to that in cyclohexane, but for 1-MI it is approximately the same. In polar protic solvents it decreases quite rapidly for both. Again these results correlate with the larger solvent effects on 3-MI fluorescence.

It can thus be concluded that the observed decrease in the $S_1 \to S_0$ transition moment reflects an excited-state process because (a) the temperature study showed that the spectral changes, which correlate with the increase in $\tau_R$ (see above), occur via SSR as a function of time after excitation [21], (b) the reports of the solvent dependence of the absorption intensity of indoles ($^1L_a + ^1L_b$) do not
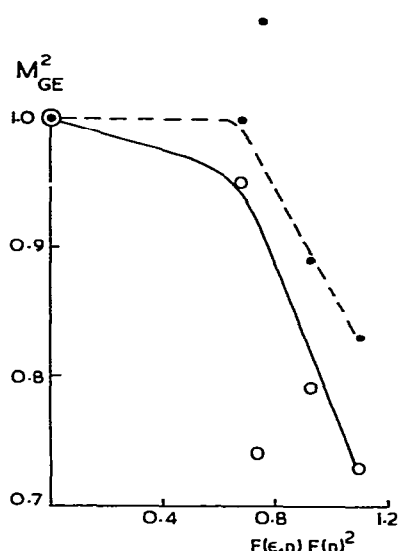
correlate with present observations. Qualitatively. Berlman [39] does not observe a strong solvent effect on the indole absorption intensity, and Strickland et al. [15] find the oscillator strength to decrease by 20% between cyclohexane and ethanol, but no change is observed between ethanol and water. Present data are not corrected for variations in the $S_1 \leftarrow S_0$ oscillator strength, because of the difficulty of separating out the two contributions to the absorption band.

The possible origin of the decrease in $\tau_R$ can now be discussed. One important conclusion that can be drawn here is that a simple inversion of the two close-lying excited electronic states, to yield a $^1L_a \to ^1A$ emission in polar media is not consistent with the results in tables 4 and 5, since it would be expected that the $^1L_a$ state, which is more intense in absorption [15], would yield a shorter radiative lifetime. Such a mechanism has previously been invoked to account for the anomalous solvent effects on the indole fluorescence spectra [4,5]. We will however show in the following section that the $^1L_a$ state is important is understanding the emission characteristics of the substituted indoles.

We should first briefly consider the non-radia-

tive decay rates, also shown in tables 4 and 5. These results are difficult to interpret due to the number of unknown parameters, particularly the levels of the triplet states (although it is known that $T_1$ is $^3L_a$ [40]) and the unknown solvent effects on them, and on higher ($\pi\sigma^*$, $\sigma\pi^*$) states. We can however see that the non-radiative decay rates generally decrease in more polar solvents, which is particularly noteworthy in aqueous solution, since an additional non-radiative pathway (electron ejection) is available in that solvent [41]. This process is not believed to be important in non-aqueous media. We may also note that a decrease in $k_{nr}$ in polar solvents is not consistent with a mechanism involving charge transfer to solvent state formation.

In general the solvent effects on the non-radiative rates are quite similar to those previously discussed for the 1-aminonaphthalenes [38].

The decay parameters of 1-MI and 3-MI do not, when corrected for the $n$ dependence and the spectral position, seem to display a strong solvent effect. Rather, the effects appear to be quite subtle, and the possible origins of these can now be considered.

### 3.3. The nature of the fluorescent state of indole derivatives

#### 3.3.1. The importance of internal charge-transfer (CT) states

Of the mechanisms that have been proposed (see section 1) to account for the solvent-induced Stokes shift of indoles, probably the most widely accepted is that of solvent–solute exciplex formation (see ref. [14], and references therein). Most recently it has been proposed that exciplexes of both 1:1 and 1:2 stoichiometry are formed between 3-MI (in hexane) and butanol [14]. Skalski et al. [7] have shown that a complex is in fact formed in the ground state between 1-MI and butanol (a tetramer in hexane). Our results in two-component (solvent and solute) solutions are not completely consistent with either of these models. In a butanol glass (85 K) 1,3-dimethyl indole displays a typical LE emission and a decay profile that is independent of emission wavelength [21]; both data are inconsistent with the emission

arising from a stoichiometric complex. The kinetic data presented above are also not consistent with such a complex formation mechanism, since we would expect the consequent changes in the transition probability to be rather larger than we in fact observe. Apparently the emitting state retains, to a significant extent, its initial identity, even in the strongly polar solvents. Other explanations, based on conventional SSR mechanisms are unsatisfactory, since they fail to explain the solvent dependence of the shape of the emission spectrum. SSR leading to a simple level inversion is also ruled out (see section 3.2); however, the spectral changes that are observed apparently occur via SSR (section 3.1 and ref. [21]).

Thus it seems that the nature of the emitting ("exciplex") state is not well understood. In the following we will interpret our data in terms of a model (solvent stabilisation of intramolecular charge-transfer configurations) that is, we believe, consistent with theoretical investigations of the electronic states of indoles [8,42] as well as other experimental data in the literature (see section 3.3.2). We should note here that our data refer to indoles in single solvents. Mixed-solvent systems need further investigation, in particular accurate decay-time studies are required.

A distinguishing feature of heteroaromatic systems (as compared to carbocyclic aromatics) is that CT configurations are important in the description of the low-lying excited electronic states [8,43]. Evleth et al. [42] have shown, by means of CNDO CI calculations, that the character of the $S_1 \leftarrow S_0$ (and $S_2 \leftarrow S_0$) indole transition changes from LE to CT as the electronegativity of the atom at position 3 is adjusted. Since CT states are relatively polar a similar increase in the CT character of the indole excited state may be facilitated in polar solvents by the observed SSR about the Franck–Condon excited state. Thus the SSR can stabilise a different electronic structure of the excited state, which could also lead to changes in the nuclear structure of the excited state. If this is the case then the CT character would be expected to be observed primarily in the emission of the solvent-stabilised (relaxed) electronic state. In fluid media the SSR is complete in a few picoseconds. The emission would then exhibit a long radiative

lifetime. compared to that found in non-polar media or calculated from the absorption spectrum. The shape of the emission spectrum will also be affected if the change in the electronic configuration of the emissive state alters its potential surface relative to that of the initially excited state and the ground state. Such a model is consistent with the experimental data on 1-MI and 3-MI.

In the specific case of indoles another theoretical model has to be considered – that of emission, in polar media. from a solvated Rydberg state [8.18]. Lami has shown that such states may be important in the description of the low-lying excited electronic states of indole. Such states are likely to be strongly perturbed by solvent–solute interactions. which may also result in the increased radiative lifetime in the polar media. We cannot distinguish such behaviour from the model outlined above. but the occurrence (or not [45]) of a $3d\pi$ Rydberg state in the ethylenic fragment of indole [8] is peculiar to this molecule. whereas an increased $\tau_R$ in polar media is apparently a common phenomenon in heteroaromatics [38].

### 3.3.2. The role of the $^1L_a$ state in emission

There have been some previous attempts to correlate the emission spectra of indoles in polar media with the $^1L_a$ state and the $^1L_a/^1L_b$ energy

gap. $\Delta E$ [$\Delta E = E(^1L_a) - E(^1L_b)$] [5.8]. One important feature of the indoles is that $\Delta E$ is small. usually $< 10^3$ cm$^{-1}$, and is strongly dependent upon the position of the substituents. In the following we will consider the relationships between the decay kinetics – measured here and elsewhere – and $\Delta E$.

The $^1L_a$ and $^1L_b$ states have different values of $\Delta\bar{\mu}$ (the effective difference between the ground- and the excited-state dipole moments) and thus exhibit different solvent shifts [15–17]. Calculations show that $\Delta\bar{\mu}$ for the $^1L_a \leftarrow {}^1A$ transition is greater than that of the $^1L_b \leftarrow {}^1A$. the value of which has been directly measured as $\approx 0.14$ D. This is much smaller than is found from solvent shift studies (table 3). as would be expected from the discussion above. If we assign a reasonable value (say 2 D) to $\Delta\mu(^1L_a \leftarrow {}^1A)$ then we can calculate [eqs. (2 and 3)] a decrease in $\Delta E$ of a few hundred wavenumbers – although the exact figure depends strongly on the value chosen for $\alpha$ – when indoles are dissolved in media of moderate polarity (say $\epsilon \approx 10$–30). This may be sufficient to place $^1L_a$ below $^1L_b$. in some derivatives. and closer to it in others.

In table 6 we summarise the values of $\tau_F$ and. where available. $\tau_R$ for seven indole derivatives in non-polar and moderately polar media. and relate

Table 6

Solvent dependence of the fluorescence and radiative lifetime of indole derivatives. I = indole. DMI-dimethyl indole. 5-MeOI = 5-methoxy indole

| | $\Delta E$ (cm$^{-1}$) | | Cyclohexane | Butanol | Ethanol | Methanol | Water |
|---|---|---|---|---|---|---|---|
| 5-MeOI | | $\tau_F$ | 11.1 [c] | 7.1 [c] | | 5.6 | 4.5 [b]. 3.9 [c] |
| | | $\tau_R$ | 42.0 [c] | 24.5 [c] | | 17.5 [c] | 16.6 [b]. 13.9 [c] |
| I | 999 | $\tau_F$ | 7.9 [b]. 7.5 [g] | 6.3 [c] | 4.6 [g] | 4.3 [c]. 3.5 [d]. 4.1 [c] | 4.8 [b]. 3.7 [g] |
| | | $\tau_R$ | 16.5 [b] | 17.5 [c] | 11.0 [g] | 7.8 [c]. 12.2 [d]. 14.4 [c] | 19.3 [b] |
| 1-MI | 469 | $\tau_F$ | 6.3 [a]. 5.5 [g] | 5.4 [a] | – | – | 8.7 [a] |
| | | $\tau_R$ | 12.5 [a] | 17.6 [a] | – | – | 26.5 [a] |
| 1.2-DMI | 23 | $\tau_F$ | 3.4 [b] | – | 5.7 [a] | – | 5.5 [b] |
| | | $\tau_R$ | 7.0 [b] | – | – | – | 15.3 [b] |
| 3-MI | ~ 0 | $\tau_F$ | 4.4 [a]. 3.7 [b]. 3.2 [g] | 7.4 [a] | 8.2 [a] | 7.9 [a] | 9.5 [a]. 9.4 [b] |
| | | $\tau_R$ | 10.9 [a]. 11.9 [b] | 21.2 [a] | – | – | 32.7 [a]. 25.3 [b] |
| 1.3-DMI | | $\tau_F$ | 3.8 [a]. 3.8 [g] | 6.8 [a,b] | – | – | 15.2 [a]. 15.6 [c] |
| | | $\tau_R$ | – | – | – | – | 21.3 [c] |
| 2.3-DMI | – 573 | $\tau_F$ | 2.2 [f] | – | 8.7 [a] | – | – |
| | | $\tau_R$ | 5.5 [f] | – | – | – | – |

[a] This work. [b] Ref. [34]. [c] Ref. [11]. [d] Ref. [46]. [e] Ref. [19]. [f] Ref. [47] (solvent was 2-methyl pentane). [g] Ref. [39]. [h] Undegassed.

these to the values of $\Delta E$ (in non-polar media).

It may be seen that the five derivatives with the smaller $\Delta E$ exhibit a significant increase in their radiative lifetimes in the polar solvents. 3-MI and 1-MI were discussed above, and are illustrative of the influence of $\Delta E$ on the decay kinetics. 3-MI ($\Delta E \approx 0$) showed the larger solvent effect. and its $S_1 \rightarrow S_0$ transition probability was decreased in THF; this was not the case for 1-MI ($\Delta E = 470$ cm$^{-1}$). where the decrease was only observed in butanol. $^1L_a$ could become $S_1$ in THF for 3-MI. but not 1-MI. It could however be $S_1$ for both in butanol. For 2.3-DMI only the $\tau_F$ value is available for ethanol solution. but for $\tau_R$ to be constant between it and cyclohexane $\phi_F$ would need to be $> 1$ in ethanol: obviously $\tau_R$ increases. $^1L_a$ is $S_1$ in 2.3-DMI even in non-polar media [47]. 1.3-DMI exhibits a clear increase in $\tau_R$ in polar solvents: $\Delta E$ has not been measured for it. but it is probably intermediate between that in 3-MI and 1-MI. The increase in $\tau_R$ is also apparent for 1.2-DMI ($\Delta E \approx 23$ cm$^{-1}$. thus $^1L_a$ will be $S_1$ in water).

It seems then that when the fluorescent state is likely to be $^1L_a$ the radiative lifetime is lengthened. even though this transition is more allowed in absorption. We conclude that this reflects a greater importance of CT configurations in the description of the $^1L_a$ fluorescent state. the relative weights of these being increased in polar solvents. The CT character of the $^1L_a$ state is consistent with its higher dipole moment. We hence conclude that the appropriate label of the "exciplex" emitting state in these indole derivatives is $^1L_a$/CT.

Conversely. when $\Delta E$ is quite large (indole and 5-methoxy indole). the solvent effect is very different. In indole $\tau_R$ decreases in polar media or. in water, increases only slightly. Since the indole red-shift is quite large [2] this corresponds to an overall small *increase* in the $S_1 \rightarrow S_0$ transition probability (decrease in $\tau_R$) in polar media, via eq. (7). For 5-MeOI $\tau_R$ decreases monotonically with increasing $\epsilon$. No anomalous Stokes shift is observed for 5-MeOI [48]. The origin of this behaviour is not clear, possibly a decrease in $\Delta E$ in polar solvents will lead to an increased mixing of the more allowed $^1L_a$ state with the fluorescent $^1L_b$ state. and hence a decrease in $\tau_R$. If this is the case then we would conclude that CT configura-
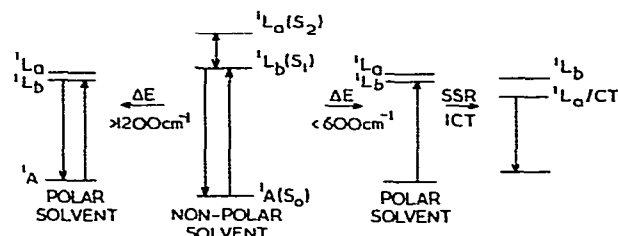


Fig. 7. Schematic representation of two extreme cases of the solvent effect on the fluorescence of substituted indoles. ICT = internal charge transfer.

tions are not important in the $^1L_b$ state.

Thus a classification of indole derivatives on the basis of $\Delta E$ leads to two types of behaviour. At one extreme ($\Delta E > 1200$ cm$^{-1}$) is 5-MeOI. with no red-shift and a decrease in $\tau_R$ in polar media. At the other extreme are the methylated indoles ($\Delta E < 600$ cm$^{-1}$) where $\tau_R$ increases in polar media. and a red-shift is observed. Indole itself ($\Delta E \approx 10^3$) is intermediate between these two classes. The behaviour is summarised in fig. 7.

## 4. Conclusions

The solvent dependence of the decay kinetics of 1-MI and 3-MI has been discussed. The "exciplex" emission. in polar solvents. can be assigned to a solvent-stabilised (by SSR) state. where the emitting state has a greater degree of CT character. and hence a higher dipole moment. than the initially excited one. A consideration of the decay kinetics of several other indole derivatives. with different values of $\Delta E$. suggests that the emission arises from the $^1L_a$ state. which is $S_1$ in non-polar media. for many of the derivatives. Thus the appropriate label of the "exciplex" emitting state may be $^1L_a$/CT.

Such a model is consistent with the observed solvent. temperature. time. and substituent dependence of the luminescence of indoles. We have not considered the pressure dependence [19,20] since to date only indole and 5-methoxy indole have been considered (with tryptophan. which has additional complexities [34]). These molecules. we have suggested. do not exhibit emission from CT states but from perturbed $^1L_b$ ($^1L_b$/$^1L_a$) states. It is

however likely that the formation and decay of the type of state discussed above will be sensitive to pressure; also the decay may be non-exponential and wavelength dependent at pressures where the spectrum is shifting.

With regard to biological studies (of tryptophan luminescence), care should be taken when – say – quenching experiments are performed that result in changes of the spectral profile, since conclusions about decay parameters based solely on measurement of either $\phi_F$ or $\tau_F$ may then lead to wrong conclusions.

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