Journal of Fluorescence, Vol. 2, No. 2, 1992

Anomalous Fluorescence Properties of 4-*N,N*-Dimethylaminobenzoic Acid in Polar Solvents

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Received March 17, 1992; revised June 22, 1992; accepted June 26, 1992

4-*N,N*-Dimethylaminobenzoic acid exhibits anomalous fluorescence in polar and hydrogen-bonding solvents. The fluorescence spectra and kinetics suggest that this arises due to the formation of a ground-state dimer or higher polymer. Preliminary measurements in hexane containing small amounts of polar acetonitrile do not rule out the possibility of exciplex formation also occurring.

KEY WORDS: Fluorescence; anomalous fluorescence; 4-*N,N*-dimethylaminobenzoic acid; dimerization.

INTRODUCTION

Derivatives of 4-*N,N*-dimethylaminobenzoic acid such as the nitrile and various esters have been known for a number of years to show anomalous fluorescence properties [1–3]. Two fluorescence bands are observed for these compounds in some solvents. The shorter-wavelength emission, with a Stokes shift of a few thousand wavenumbers, is identified as "normal" fluorescence from the locally excited (i.e., Franck-Condon (FC) singlet state to the FC ground state [S_0(FC)]). In current terminology this is also referred to as a b* state. The anomalous, longer-wavelength emission (from a state labeled a*) has a number of possible origins.

The suggestion that the a* emission results from a twisted intramolecular change transfer (TICT) state has met with quite wide acceptance [4–6]. This transition would be labeled S_1 (CT) $\rightarrow$ S_0 (FC) in the notation adopted by Heldt *et al.* [7]. However, Varma and co-workers, at an early stage in the studies of these molecules, proposed that the a* emission was due to a solute/solvent exciplex [8] and have maintained this belief in a series of later papers [see 9 and references therein]. More recently, Phillips' group has presented evidence that the a* emission of 4-*N,N*-dimethylaminobenzonitrile and the methyl esters of 4-*N,N*-dimethylamino- and 4-*N,N*-diethylaminobenzoic acid in a supersonic jet is due to dimer formation [10,11]. We have reported a concentration dependence for the anomalous fluorescence of methyl 4-*N,N*-dimethylaminobenzoate in solution, which also points to dimer formation [12]. Although there was no evidence from the absorption spectra of ground-state dimer formation, the fluorescence properties of this ester did not conform to those expected for excimer formation and we concluded that at least a loose ground-state association exists.

We have also studied the absorption and fluorescence properties of the parent 4-*N,N*-dimethylaminobenzoic acid. Cowley *et al.* [3] have reported that this molecule also exhibits a* fluorescence (in acetonitrile), but this appears to be the only recent study on the parent acid. We therefore present our findings on this compound to date in this paper.

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1053-0509/92/0600-0107$06.50/0

EXPERIMENTAL

4-*N,N*-Dimethylaminobenzoic acid was purchased from Lancaster Synthesis Ltd. and was recrystallized twice from ethanol prior to use; m.p., 244–245°C (literature value, 242–243°C [13]). Infrared and proton and ^{13}C NMR spectra were also acceptable. The solvents used in this work were either spectrophotometric, spectrofluorimetric, or HPLC grade and were used as received with the exception of acetonitrile. This was distilled over phosphorus pentoxide and collected and stored under an inert atmosphere until it was used. The water was doubly distilled and then passed through an ion-exchange resin prior to use. The pH of the unbuffered water was 6.5.

Absorption spectra were measured on a Perkin–Elmer Lambda 3 spectrophotometer or a Hewlett–Packard HP8451A diode-array spectrometer using matched quartz cuvettes of varying path lengths. All working solutions were prepared fresh on the day of use from a stock solution which was checked at regular intervals for purity. The accuracy of the measurements made under these conditions is estimated as ± 2 nm for wavelengths and $\pm 10\%$ for extinction coefficients.

Fluorescence spectra were measured on Perkin–Elmer LS5 or LS50 spectrofluorimeters in the fully corrected mode. Excitation and emission slit widths of 5 nm were used unless otherwise indicated. For the LS5 the spectra were transferred to a BBC microcomputer to undertake quantum yield calculations. Quantum yields were measured on optically dilute samples (absorbance <0.05) which were degassed where necessary by bubbling argon or oxygen-free nitrogen through the solutions. Quinine bisulfate monohydrate (Aldrich Gold Star) in perchloric acid (BDH Analar reagent) ($\phi_f = 0.55$) [14] and 9,10-diphenylanthracene (Aldrich Gold Star) in cyclohexane ($\phi_f = 0.90$) [15] were used as quantum yield standards.

Fluorescence decays were measured by the single-photon counting technique [16]. The decay profiles were obtained using either an Edinburgh Instruments Model 199 fluorescence lifetime spectrometer with hydrogen lamp excitation [17] or at the Daresbury Synchrotron Radiation Source operating in the single bunch mode [18]. Details of the performance of the two sources are given in the references quoted. Excitation and emission slit widths of 5 nm were routinely used except at Daresbury, where the emission was monitored through interference filters which had bandpasses of approximately 10 nm at FWHM. A minimum of 10,000 counts in the peak channel of the decay profile was collected. The profiles were analyzed by computer convolution and the goodness of fit decided on the basis of chi-square values and the distribution of the residuals.

RESULTS AND DISCUSSION

The absorption and fluorescence properties of 4-*N,N*-dimethylaminobenzoic acid (4DMABA) have been studied in a variety of solvents, including some binary solvent mixtures, at room temperature. 4DMABA is completely soluble in acetonitrile and ethanol but only partially soluble in hexane and water at concentrations up to 10^{-3} mol·dm^{-3}. In all solutions at room temperature, 4DMABA shows strong structureless UV absorption bands with a wavelength of maximum absorption varying from 280 to 310 nm, probably due to a π–π^* transition. However, in all solvents studied except water, this absorption peak exhibits asymmetry, which may be indicative of a second overlapping transition. In hexane and acetonitrile the asymmetry is on the short-wavelength side of the peak, whereas it is on the long-wavelength side in ethanol. This spectral feature is shifted approximately 10 nm from the main peak in all cases. There is also evidence of a secondary weaker absorption band in the region of 220 nm. Unlike its methyl ester (M4DMAB), where the main absorption peak is substantially red shifted in polar and hydrogen-bonding solvents, 4DMABA shows no similar trend. As with M4DMAB [12], measurement of the absorption spectrum in acetonitrile over a 10-fold concentration range (10^{-4}–10^{-5} mol·dm^{-3}) reveals that the spectrum is unchanged in terms of both its shape and its extinction coefficients as the concentration is varied. It was also found that the absorption spectrum in hexane was unaffected by small additions of acetonitrile (up to 2.2%, v/v).

Measurements in aqueous solution under pH control yield a pK_a for the deprotonation of the carboxylic acid group in 4DMABA of 4.79 and a pK_b for the protonation of the dimethylamino group of 2.34 [19]. The absorption spectrum in unbuffered water therefore corresponds to that of the 4DMABA carboxylate anion. It is possible that this deprotonation could also account for the shorter wavelength of the absorption maximum in ethanol. The absorption data are collected in Table I.

The fluorescence spectra of 4DMABA in all solvents except hexane are anomalous in that they exhibit dual fluorescence. The two fluorescence bands occur at approximately 350 nm and between 420 and 500 nm depending on the solvent (Table I). The fluorescence spectrum observed in *n*-hexane, which peaks at 340 nm, resembles that of the shorter-wavelength fluorescence observed in the other solvents. We therefore consider

Table I. Absorption and Fluorescence Properties of 4DMABA in Various Solvents at Room Temperature

Solvent	Absorption maxima (nm)	Extinction coefficient ($dm^3\ mol^{-1}\ cm^{-1}$)	Fluorescence maxima (nm)	Fluorescence excitation maxima (nm)
Hexane	302	*a*	340	300
	225	*a*		
Ethanol	295 (sh)[b]	—	350	275
	282	20,300	420	280
Acetonitrile	306	22,500	350	275
	295 (sh)	—	480	308
Water				
(unbuffered)	288	*a*	365	270
	222	*a*	500	290
Water				
Anion	284	*a*	355	274
	225	*a*	490	306
Neutral	314	*a*	370	290(sh),300
	230	*a*	480-490	300
Cation	272	*a*	*c*	—
	230	*a*		

[a] Compound only partially soluble in this solvent.
[b] sh, shoulder.
[c] No fluorescence.

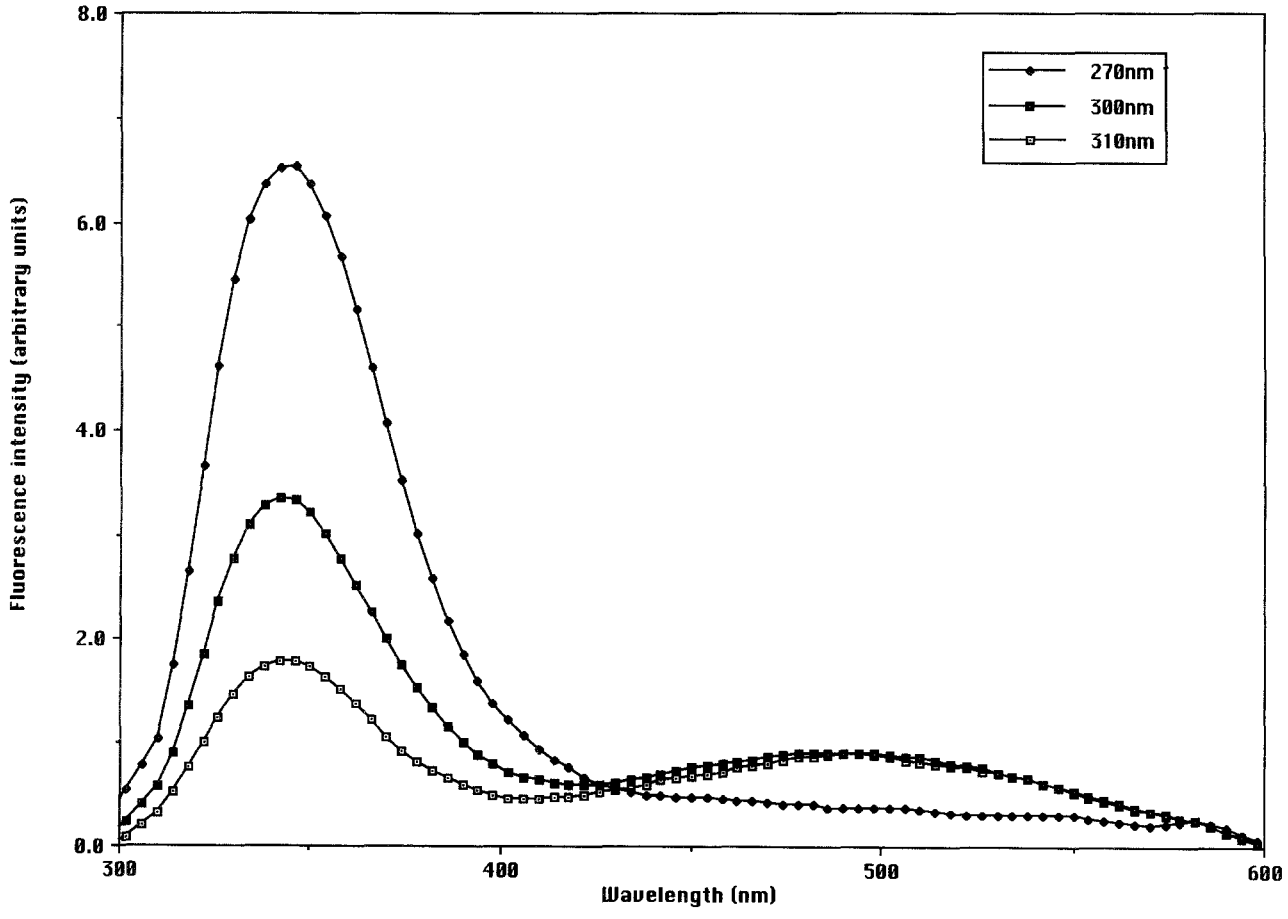

Fig. 1. Fluorescence spectra of 4DMABA (1.08×10^{-6} mol·dm^{-3}) in acetonitrile at different excitation wavelengths.

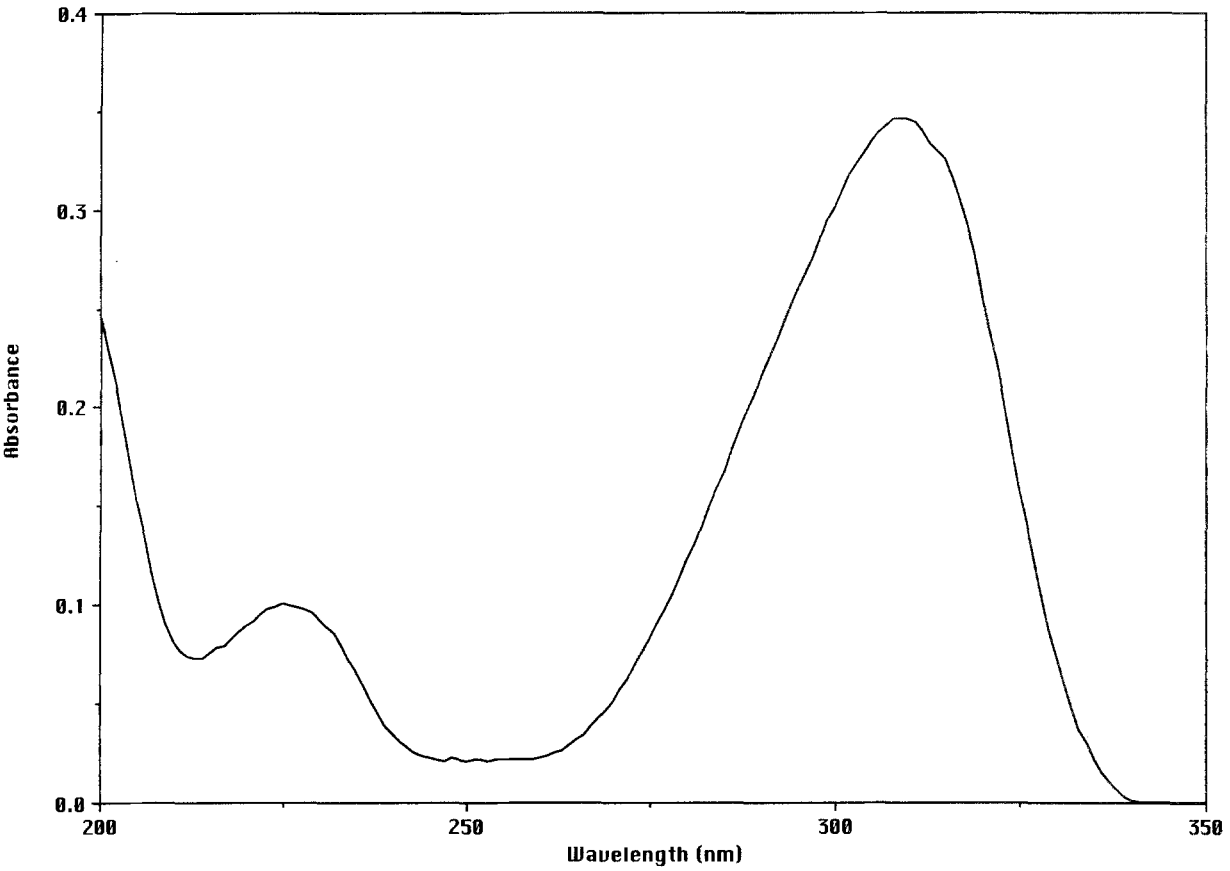

Fig. 2. Absorption spectrum of 4DMABA (5.5×10^{-4} mol·dm^{-3}) in acetonitrile.

that this band corresponds to the normal b* [S_1 (FC) → S_0 (FC) fluorescence] for 4DMABA and the longer wavelength band to anomalous (a*) fluorescence. In hexane, the fluorescence spectrum of 4DMABA is independent of excitation wavelength (except for a change in overall intensity) and the excitation spectrum is independent of emission wavelength. This is not the case in all the other solvent systems used. The measured quantum yield of 0.18 in hexane is in good agreement with the value of 0.21 in cyclohexane reported by Cowley *et al.* [3].

In acetonitrile, excitation of a 1×10^{-6} mol·dm^{-3} solution at the absorption maximum of 306 nm produces a relatively weak fluorescence spectrum (Fig. 1) but with the two bands clearly visible. If the excitation is moved to a shorter wavelength (e.g., 270 nm), the intensity of the b* fluorescence increases approximately fourfold, while the a* fluorescence almost disappears. The spectra at intermediate wavelengths lie between these two extremes. It is not surprising therefore to find that the excitation spectra for the two fluorescence bands are very different, with that for the a* fluorescence peaking at 308 nm and that for the b* fluorescence at 275 nm. The latter may correspond to the asymmetry on the absorption spectrum of 4DMABA in acetonitrile (Fig. 2).

Emission spectra of 4DMABA in water exhibit an identical trend to those in acetonitrile but with overall smaller changes; the b* fluorescence intensity increases by only a factor of two as the excitation wavelength is changed from 300 to 270 nm and the a* intensity decreases by a similar amount (Fig. 3). The excitation spectra peak at approximately 290 nm (cf. absorption maximum at 288 nm) and 270 nm for the a* and b* fluorescence, respectively. In water there is no obvious absorption spectral feature at 270 nm to correspond to the latter peak. The fluorescence spectra of 4DMABA in water are also pH dependent (Fig. 4). At alkaline pH values both anomalous and normal fluorescence are observed, with the latter peaking at 355 nm. This must therefore correspond to normal fluorescence from the 4DMABA

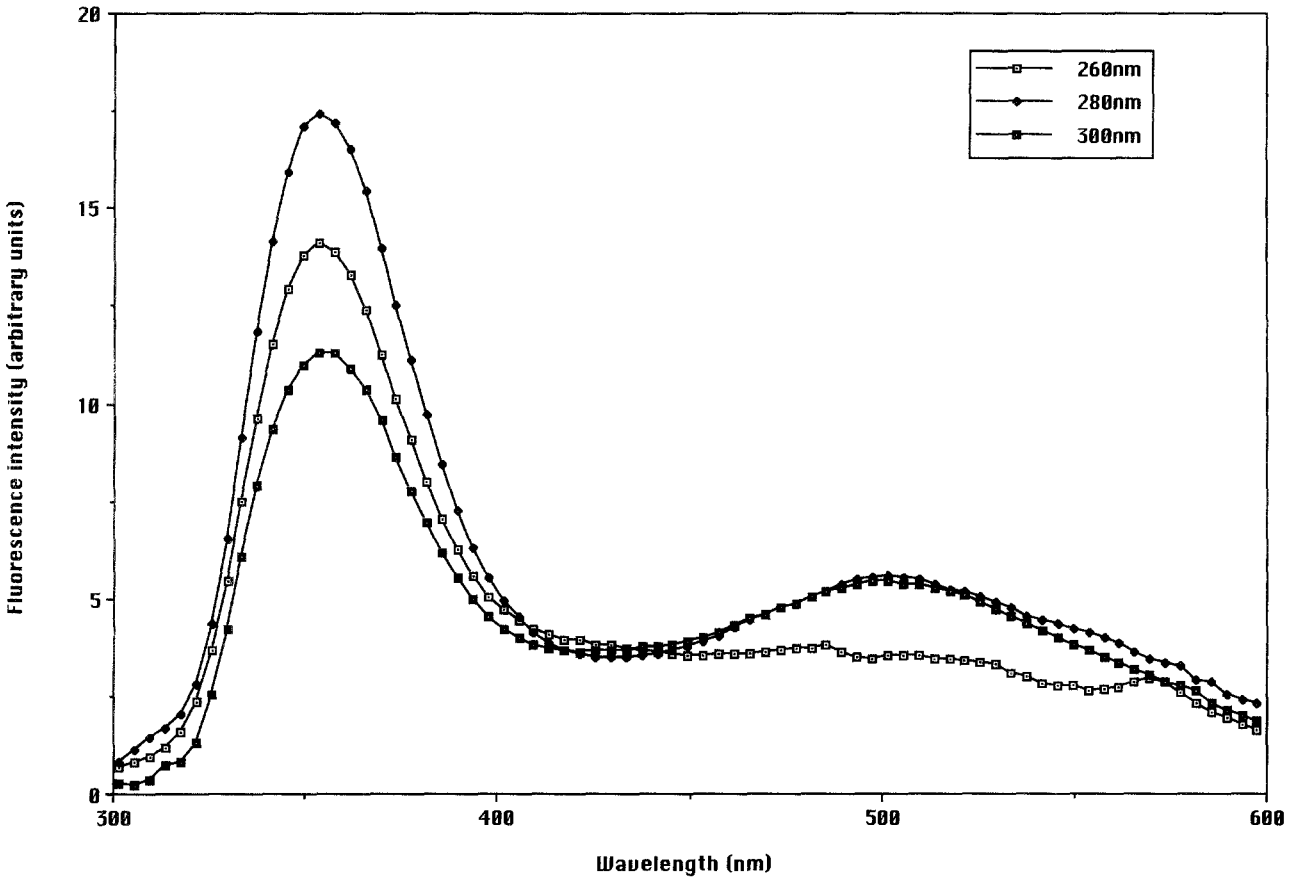

Fig. 3. Fluorescence spectra of 4DMABA in water at different excitation wavelengths.

carboxylate anion, as the ground-state pK_a is 4.79 and there is insufficient acidity present to convert the excited anion to the excited neutral species despite a calculated [20] pK_a* of 11.95 [19]. As the pH is reduced, the b* fluorescence band shifts to 375 nm and the a* fluorescence decreases in intensity until it is debatable whether it is still present. In strong acid the fluorescence disappears completely—the 4DMABA cation is nonfluorescent.

In ethanol, the anomalous fluorescence is shifted less to the red than in acetonitrile and water and appears as a shoulder on the long-wavelength side of the emission band (Fig. 5). Once again, the spectrum varies with excitation wavelength but the observed changes are the smallest for the three solvents where the anomalous fluorescence is observed. These observations clearly suggest that there is more than one ground-state species present in the polar solvents used in these studies. Our measurements to date have not shown any change in absorption spectra with concentration but this may be due to the fact that any changes are taking place at much lower concentrations than we have studied to date. The evidence to support this is that the fluorescence spectra for 4DMABA in acetonitrile are concentration dependent. This has also been observed for M4DMAB [12]. As the concentration of 4DMABA is varied between 10^{-5} and 10^{-8} mol·dm^{-3} (Fig. 6), the amount of a* fluorescence decreases until at 10^{-8} mol·dm^{-3} there is very little remaining, although the overall weakness of the fluorescence from 4DMABA makes measurements difficult at these low concentrations. It is possible that absorption spectral changes may be visible at these concentrations but the 4DMABA extinction coefficients preclude accurate absorption measurements at concentrations below approximately 10^{-6} mol·dm^{-3}.

The data presented so far suggest quite clearly that the anomalous fluorescence from 4DMABA arises from a ground-state species. The concentration dependence of the fluorescence in acetonitrile points to this species being a dimer or higher polymer, although we have no ab-

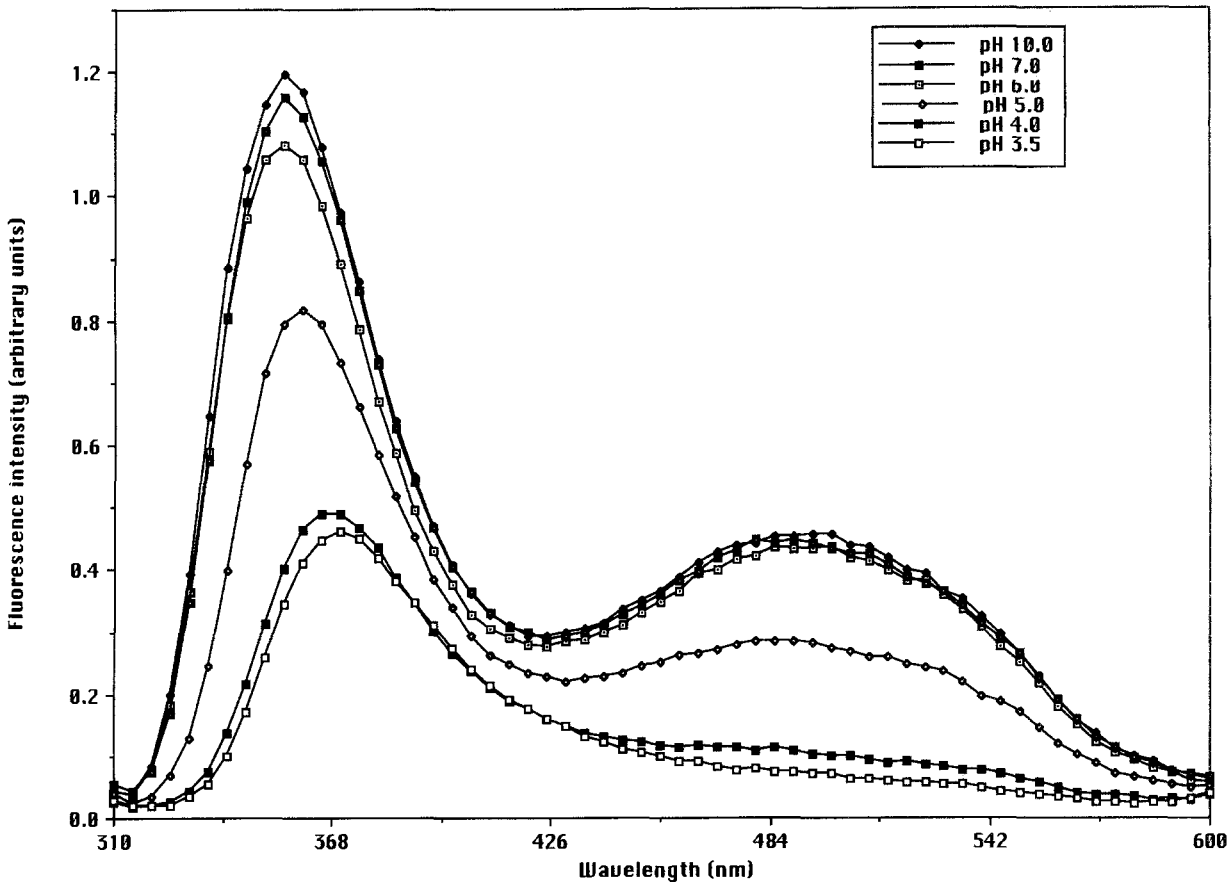

Fig. 4. Fluorescence spectra of 4DMABA in water at different pH values.

sorption evidence for this. The variation of the fluorescence spectra with concentration certainly does not agree with a mechanism involving the formation of a TICT state [4], and our attempts to analyze the data using standard excimer kinetics [21] have not been successful—the expected dependence of fluorescence intensity and kinetics on concentration is not observed. Unfortunately, the absence of any significant changes in the absorption spectra with concentration means that we are unable to verify the presence of a ground state equilibrium.

We have, however, studied the fluorescence decay profiles for the two fluorescence bands in some of the solvents used here. In hexane the decay is single exponential with a lifetime of 1.28 ns, very similar to the value of 1.30 ns found for M4DMAB in hexane [12]. In ethanol, the proximity of the a* and b* fluorescence bands leads to complex decay profiles which require three-exponential components to fit the data adequately. We are making further measurements at a variety of excitation and emission wavelengths to try to resolve this complexity, but in view of the various solute/solvent interactions which are possible in hydrogen-bonding solvents (in addition to any other processes taking place), decay profiles which are not single exponential are not surprising. In water and acetonitrile, the a* fluorescence decays by a single exponential, whereas the b* fluorescence requires two exponentials for an adeuqate fit (Table II). In acetonitrile, where we have accumulated a large amount of decay data, the lifetime of the a* band is independent of concentration and excitation wavelength. A lifetime in a range of 2.1–2.3 ns is always obtained and there is no evidence of a rise time indicative of an excited-state precursor. As Hasselbacher *et al.* [22] have shown, this does not absolutely rule out this mechanism but it does indicate that at least one alternative mechanism of populating the a* state is operative. We interpret these observations as confirming our earlier conclusion about the presence of a ground-state species producing the a* fluorescence. They also imply that this

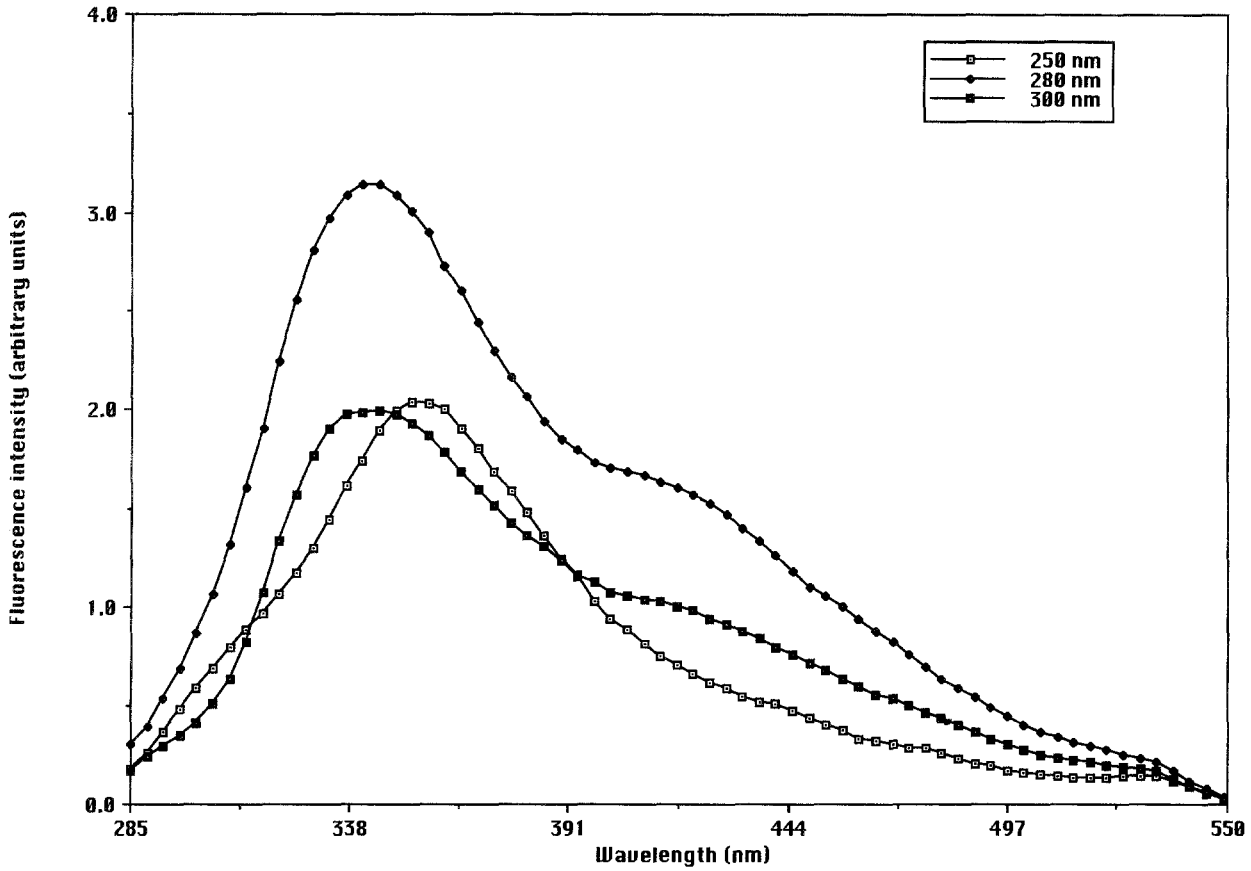

Fig. 5. Fluorescence spectra of 4DMABA (1.14×10^{-6} mol·dm^{-3}) in ethanol at different excitation wavelengths.

is the only source of the a* species—the b* excited state does not appear to be a precursor of a*, although the reverse may possibly be true given the more complex decay profiles observed for the b* fluorescence band.

Varma and co-workers [23,24] have proposed that the anomalous fluorescence of ethyl 4-*N,N*-dimethylaminobenzoate [23] and 4-*N,N*-dimethylaminobenzontrile [24] in acetonitrile is due to exciplex formation. We have therefore added small amounts of acetonitrile to a solution of 4DMABA in hexane up to the miscibility limit (approximately 2.2% by volume) and have found that a new fluorescence band at approximately 440 nm results (Fig. 7). The observed variations in the emission spectra do not appear to fit a standard exciplex mechanism. The b* fluorescence in hexane *is* quenched by low concentrations of acetonitrile, but at slightly higher concentrations it increases in intensity and red-shifts by some 10–20 nm. At the same time there is a steady increase in a* fluorescence as the acetonitrile concentration is increased. It would appear that there are some specific solvation effects taking place in addition to the mechanism producing the a* fluorescence. The red shift in the b* fluorescence probably results from the formation of a specific 4DMABA/acetonitrile solute/solvent interaction. The new band at 440 nm may be an exciplex or may be the same species as is seen in pure acetonitrile but with a blue-shifted fluorescence due to the nonpolar solvent environment in which it is situated. Whatever the nature of the species producing the 440-nm fluorescence, it is clear that acetonitrile plays a key role in its formation and we are undertaking further work to attempt to clarify the nature of this species.

ACKNOWLEDGMENTS

We thank the Science and Engineering Research Council for a studentship (JATR) and for access to the Daresbury Laboratory and University of Central Lancashire, the Ciba-Geigy Trust, NATO, and the British Coun-

Table II. Fluorescence Decay Properties of 4DMABA in Various Solvents

Solvent	λ_{ex} (nm)	λ_{em} (nm)	Concentration (mol·dm^{-3})	χ^2	a_1	τ_1 (ns)	a_2	τ_2 (ns)
Hexane	306	340		1.01	1.000	1.28	—	—
Ethanol	280	350		1.01	0.859	2.86	0.141	17.61
Water	290	365		1.05	0.994	0.77	0.006	5.07
	290	500		1.27	0.975	0.17	0.025	2.39
Acetonitrile	280	350	1.0×10^{-6}	1.04	1.000	2.13	—	—
	280	500	1.0×10^{-6}	1.24	1.000	2.16	—	—
	300	350	1.0×10^{-5}	1.61	1.000	1.66	—	—
	300	480	1.0×10^{-5}	1.48	1.000	2.30	—	—
	300	350	1.0×10^{-6}	1.26	0.842	1.29	0.158	2.74
	300	480	1.0×10^{-6}	1.01	1.000	2.23	—	—
	300	350	1.0×10^{-7}	1.23	0.687	0.20	0.313	1.85
	300	480	1.0×10^{-7}	1.14	1.000	2.27	—	—
	310	350	1.0×10^{-6}	1.17	1.000	2.11	—	—
	310	500	1.0×10^{-6}	1.36	1.000	2.15	—	—
	340	350	1.0×10^{-6}	1.57	1.000	2.27	—	—
	340	500	1.0×10^{-6}	1.31	1.000	2.17	—	—

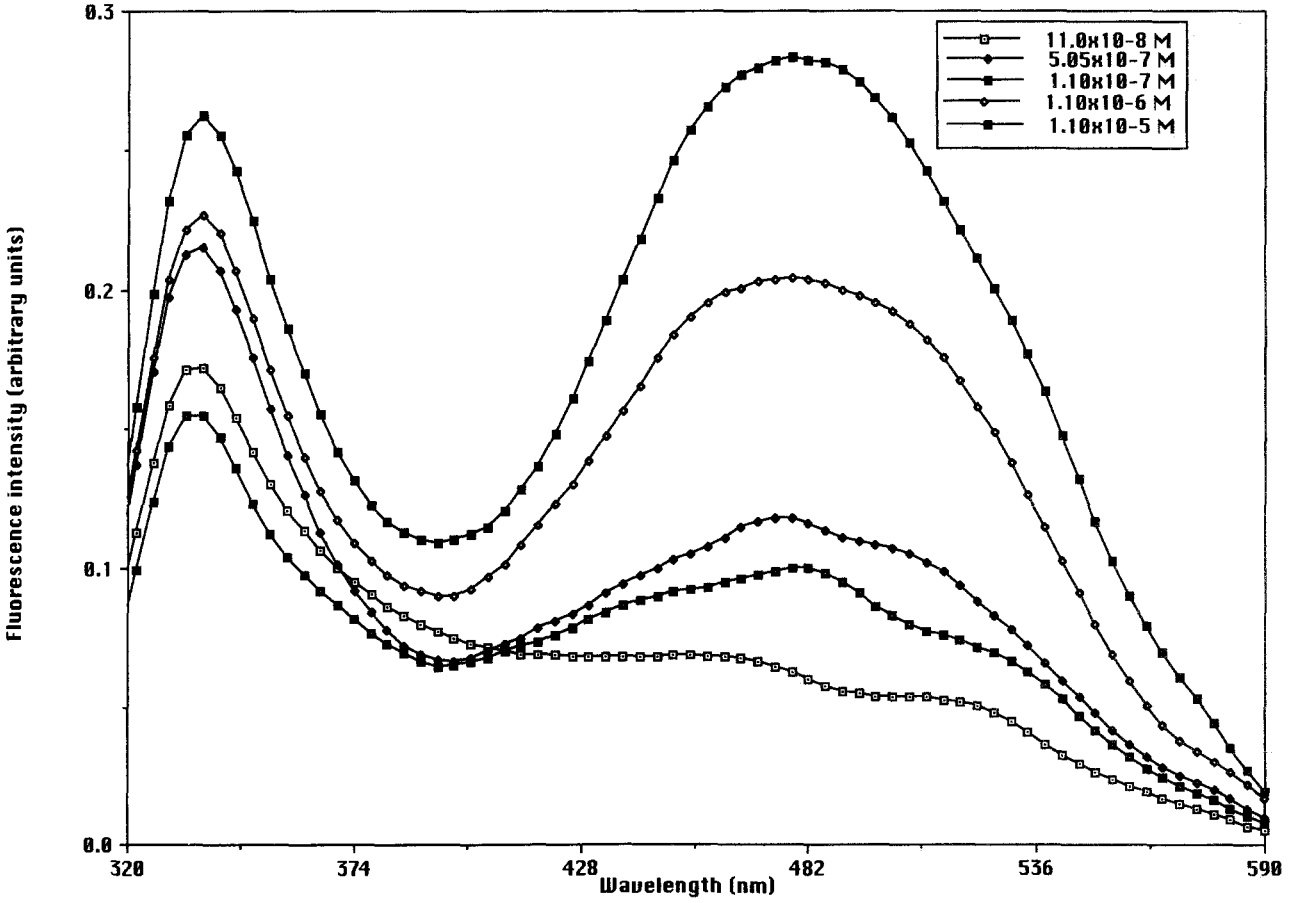

Fig. 6. Fluorescence spectra of 4DMABA in acetonitrile at different concentrations.

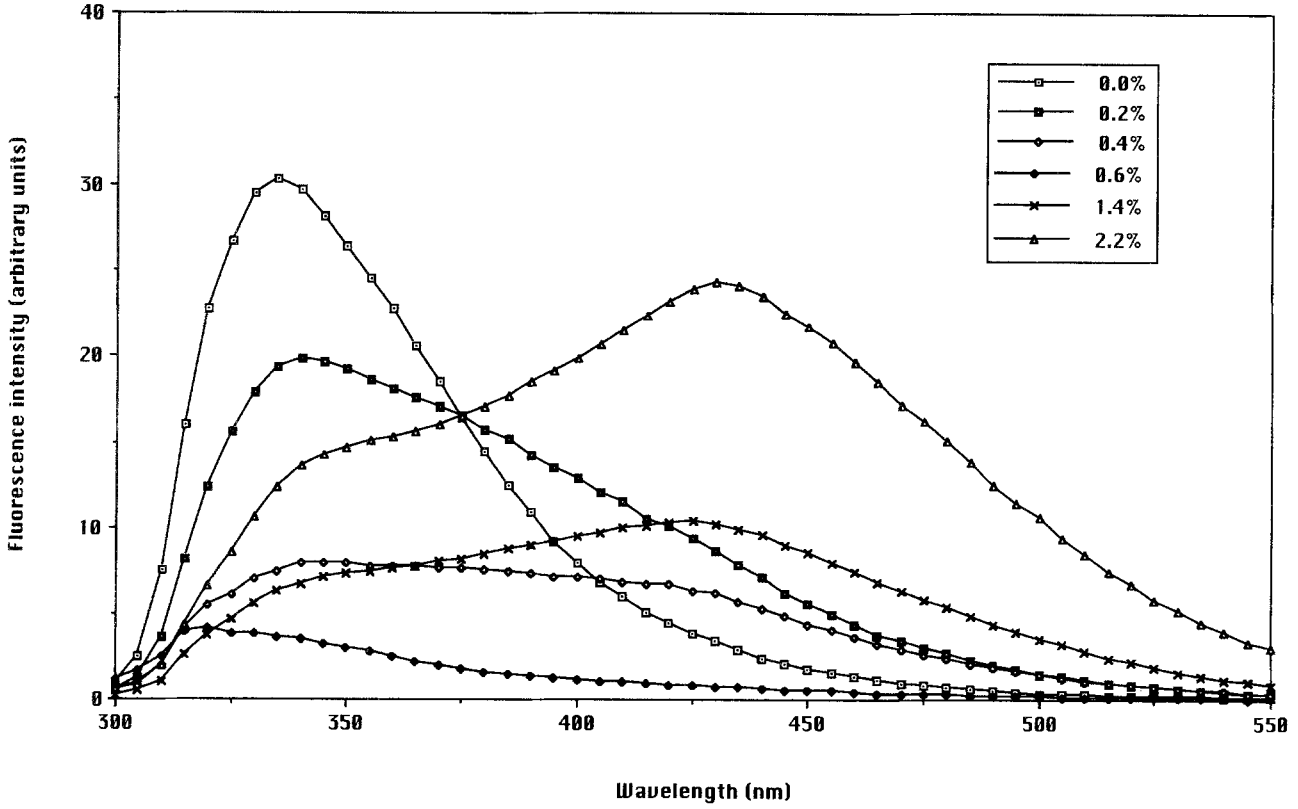

Fig. 7. Fluorescence spectra of 4DMABA in hexane with different amounts of added acetonitrile; pure hexane (%, v/v).

cil for financial support. We are grateful to Professor Wolfgang Rettig of the Technical University of Berlin for his comments and fruitful discussion and to the Photophysics Research Group at the University of Strathclyde for allowing us access to their fluorescence lifetime spectrometers.

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