on several assumptions which should always be considered explicitly.

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Multiple Fluorescences. II. A New Scheme for 4-(*N*,*N*-Dimethylamino)benzonitrile Including Proton Transfer[1a]

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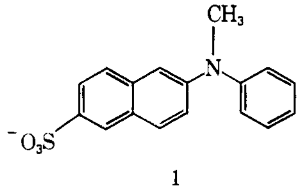
Abstract: Long-wavelength emission from 4-(*N*,*N*-dimethylamino)benzonitrile is assigned to a protonated molecule (deuterium isotope effect). Utilizing solvent polarity parameters, three other emissions are identified: planar monomer, perpendicular monomer, and dimer. The protonated emitting species occurs only in proton-donor solvents; the ratio of monomer protonated molecule emissions is viscosity and wavelength dependent.

The "abnormal" emission from *N*-methyl-2-(*N*-phenylamino)-6-naphthalenesulfonate in glycerol has been identified as that of a protonated molecule.[1a] The expected emission appeared only if the photochemical conversion to **2** were avoided, consistent with protonation occurring in the S^*_0 state, and vibrational relaxation in a high-viscosity solvent being sufficiently slow to encounter competition from a proton-transfer process, that converting structure **1** into structure **2**.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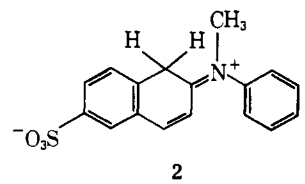
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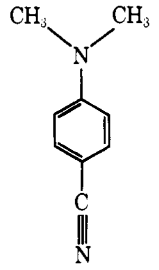
The two emissions from excited 4-(*N*,*N*-dimethylamino)benzonitrile [1-cyano-4-(*N*,*N*-dimethylamino)benzene,



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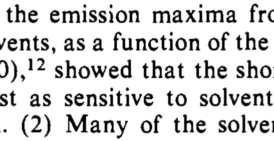
3, DMAB] were identified by Lippert as arising from two different excited states.[2] These results have been widely cited as an example of multiple fluorescence within a single electronic manifold (cf. Birks[3]). The original Lippert proposal for originating states with different polarizations was negated by the finding by Rotkiewicz et al.[4] that the two emissions arose from states with the same polarization, and they made the attractive suggestion that the two states differed in the orientation of the dimethylamino group with respect to the benzene ring.

McGlynn and coworkers[5,6] identified a ground-state dimer in a number of different solvents and suggested that a new emission which they found arose from the dimer and that the long-wavelength emission was from an excimer. Mataga[7] claimed that the "dimer" was an impurity and that the excimer assignment could not be correct because the emission did not show concentration dependence. (Our work suggests that there is a dimer emission, but not an "excimer" emission.) However, Mataga did report emissions from "aggregates".

Struve, Rentzepis, and Jortner showed by picosecond techniques that the rise times for the short- and long-wavelength bands were different in ethanol, the long-wavelength emission being produced at a markedly lower rate.[18] Mataga reported a similar result, but under conditions (MTHF solvent) for which the identification of the emitting species is not so clear.[9] Struve and Rentzepis demonstrated by further picosecond work that solvent relaxation as governed by bulk viscosity is not the factor determining the formation of the state which emits at long wavelengths,[10] but noted that its formation was delayed in viscous media.

In view of our discovery of multiple fluorescences from **1** and from **4**, in which emission from $S_{1,np}$ and $S_{1,ct}$ states can be observed in the same solution,[11] we reexamined several other cases from which multiple fluorescences had been reported. In the present instance, another look at the reported emission data for the DMAB (**3**) revealed the following. (1) Plotting the emission maxima from the literature for different solvents, as a function of the solvent polarity parameter, $E_T(30)$,[12] showed that the short-wavelength emission was at least as sensitive to solvent as the long-wavelength emission. (2) Many of the solvents for which the long-wavelength emission was reported were protic.



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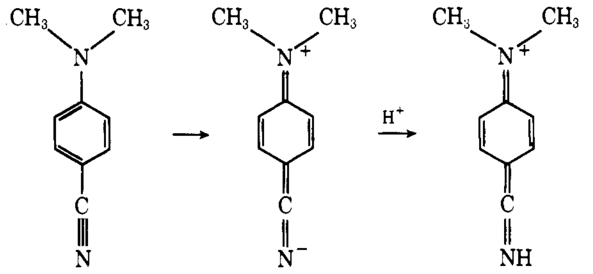
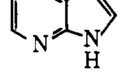
It appeared to us that the short-wavelength emission must be charge transfer and that the long-wavelength emission might arise from a molecule to which a proton had been added, as in the sequence in eq 1 showing the excitation of **3**.

We therefore made an extensive study of the fluorescence of DMAB (**3**). A previous study by El-Bayoumi and Ingham[13] on 7-azaindole (**6**) provided very convincing evidence that proton transfer could give rise to a state which emits at much longer wavelengths than the "expected" fluorescent state.



3 **4pl** **5** (1)



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Experimental Section

4-(*N,N*-Dimethylamino)benzonitrile [1-cyano-4-(*N,N*-dimethylaminobenzene] (Fluka AG, CH-9470, Buchs, Switzerland) was purified as recommended by Mataga[7] through seven recrystallizations from pure hexane. Absorption spectra in most solvents agreed with published data. Sources: F, Fluka, see above; M, E. Merck, Darmstadt, West-Germany; R, Carl Roth, Karlsruhe, West Germany; H, Hopkins and Williams, England) (s = solvents labeled spectroscopic quality): acetonitrile (s, F); tetrachloromethane (s, H); chloroform (s, M); dioxane (s, F); ethanol (s, M); benzene (s, M); cyclohexane (s, F); *tert*-butyl alcohol (AR, M); isopropyl alcohol (puriss, F); formamide (puriss, F); 1,2-propanediol (puriss, F); 1,3-butanediol (puriss, F); 1,2-ethanediol (zur Anal., M); glycerol (for fluorescence microscopy, M); water (triple distilled); deuterium oxide (s, M); dichloromethane (purified: H_2SO_4, dilute NaOH, H_2O, $MgSO_4$, distillation); chloroform-*d* (R, purified as for CH_2Cl_2, stored under nitrogen); 1,2-propanediol-d_2 (repeated distillation of water from mixture of diol and D_2O, followed by distillation of solvent). Protium content of deuterated solvents was checked by NMR and found to be negligible for $CDCl_3$ or for hydroxylic hydrogens of 1,2-propanediol.

Absorption spectra were measured with a Cary Model 17 spectrophotometer. Emission spectra were taken with a Hitachi Perkin-Elmer MPF-2A. As noted in the text, approximate corrections were made for photomultiplier sensitivity using quinine sulfate as a standard in the wavelength range 450-550 nm. Fluorescence spectra were corrected for emission of the solvent; narrow slits (5 mm) were used to simplify this task. Dilute solutions (less than 0.2 OD) were utilized to diminish contributions from self-absorption.

These precautions are particularly important for the study of DMAB because the quantum yield of emission is rather low in most solvents, ranging from ca. 0.2 in cyclohexane and benzene through ca. 0.01 in 1,2-propanediol to ca. 0.001 in water, all referred to quinine sulfate in 0.1 N H_2SO_4 as 0.55. Curiously, no quantum yield data are cited in any of the publications which we examined.

Results

Absorption and emission data for DMAB (**3**) are listed in Table I. The latter are organized according to region, with SE representing short-wavelength emission, LE, long wavelength emission, and D standing for dimer emission. Absorption maxima are plotted against the solvent polarity parameter, $E_T(30)$, in Figure 1. Two correlation lines (one for monomer and one for dimer) appear to fit most of the data.

Four correlation lines are required to correlate the emission data in a wide variety of solvents, two for SE, one for D, and one for LE, as illustrated in Figure 2. All of the plot-

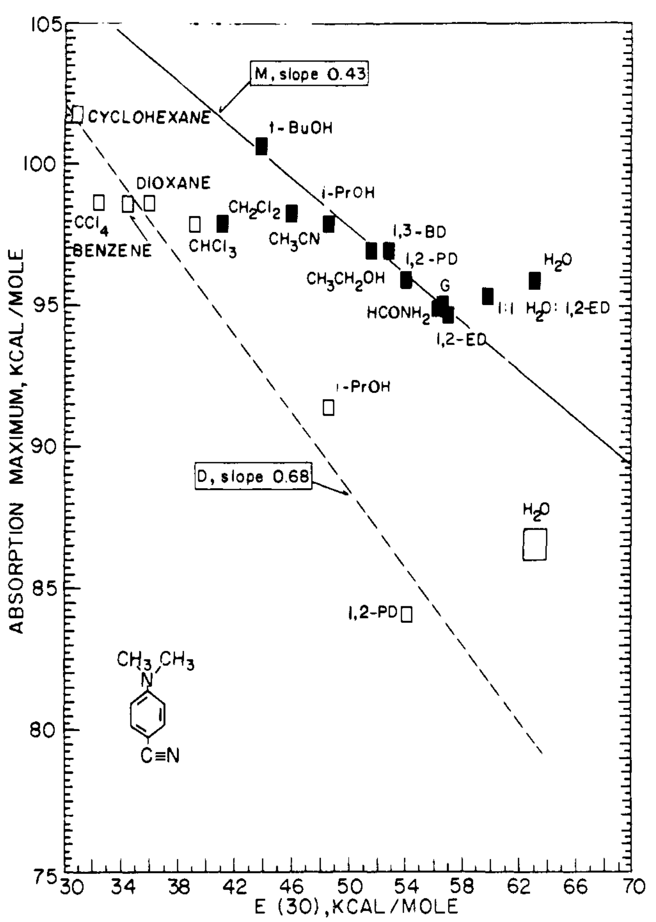


Figure 1. A plot of absorption maxima (expressed in kcal/mol) for DMAB (3) against the solvent polarity parameter, $E_T(30)$ (in kcal/mol). Filled squares (■) are assigned to monomer absorption, solid line labeled M. Empty squares (□) are assigned to dimer absorption, dashed line marked D. The values for water deviate markedly from correlation lines for both monomer and dimer. The point for dichloromethane is assigned to monomer absorption on the basis of expectation (dielectric constant 8.4 should not be conducive to dimerization at concentrations used).

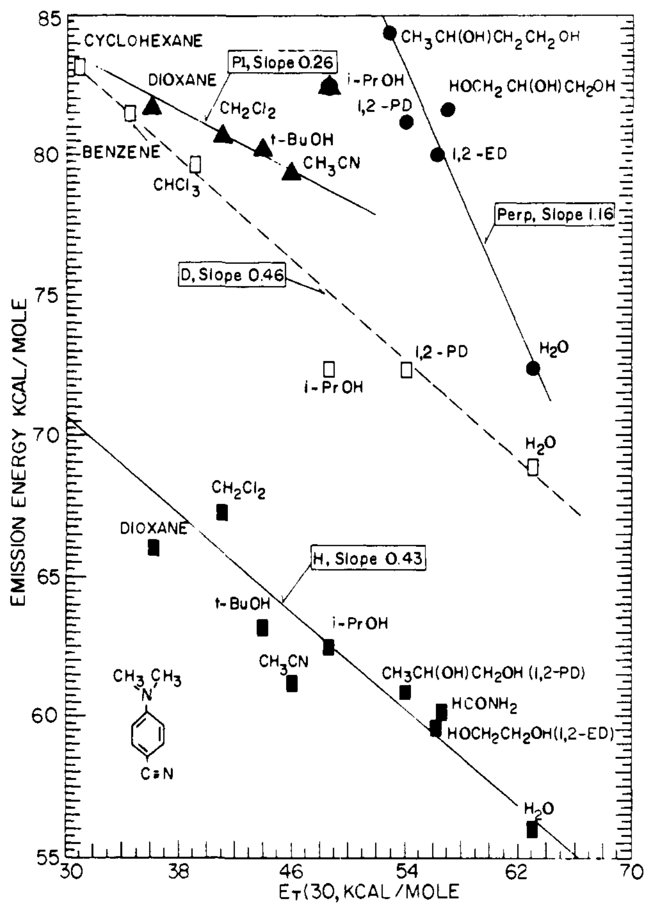


Figure 2. A plot of emission maxima for DMAB (3) expressed in kcal/mol against the solvent polarity parameter, E_T (30) (in kcal/mol). The correlation lines are as follows: (▲) planar monomer, Pl; (●) perpendicular monomer, Perp; (■) protonated monomer, H; (□) dimer, D. The dimer line is dashed; all monomer lines are full. The SE value for isopropyl alcohol falls between the Perp and Pl lines, possibly reflecting some steric hindrance to solvation. The location of the SE point for *tert*-butyl alcohol on the Pl line is consistent with the idea that steric hindrance to solvation prevents formation of the perpendicular form, which requires more solvation than the planar form to overcome the loss of overlap between the dimethylamino group and the π system of the ring.

ted points represent new measurements, which in most cases, but not all, agree with those previously reported by others.

The ratio of LE/SE emission intensities depends upon the nature of the solvent as Lippert found. In addition, the LE/SE ratio varies with the viscosity of the solvent and with the wavelength used, especially in viscous solvents. Spectra in the protic polar solvent, glycerol (Figure 3), exhibit much more short-wavelength emission than long-wavelength emission. The ratios of LE/SE emission intensities are given in Table I. A summary of the intensity ratios as a function of exciting wavelength is presented in Table II. The position of the SE in glycerol is dependent on the exciting wavelength, varying from 346 (excitation 280 nm) to 366 nm (excitation 320 nm).

To probe the nature of the LE emission, we examined the effect of solvent deuteration on the emission of DMAB. In Figure 4, we illustrate the results for H_2O and D_2O and in Figure 5, emission spectra for 1,2-propanediol and 1,2-propanediol-d_2. In both cases, the LE emission increases in the deuterated solvent, the increase being almost a factor of 5 in 1,2-propanediol-d_2. The LE/SE ratios found in deuterated solvents are included in Table II. The emission spectra of DMAB in $CHCl_3$ and $CDCl_3$ are identical.

Discussion

The variety of emissions observed for a simple molecule like DMAB is at first sight surprising, but can be accommodated by the scheme shown in Figure 6. The monomer and dimer triplet emissions mentioned by McGlynn[6] have not been included. The identification of the absorptions and emissions rests upon a variety of points which we shall summarize below.

(1) Absorption. The dipole moment of DMAB must be greater than that of benzonitrile (4.05 D). We have taken it as 6 D, slightly more than the sum of moments for the nitrile and *N,N*-dimethylaniline. In a solvent of dielectric constant 2 (cyclohexane, benzene), the interaction energy for two such dipoles would be so great that dimerization would be expected at any concentration used in our work. Thus, the line marked D in Figure 1 correlates the absorption maxima for dimers and includes the point for the dimer in 1,2-propanediol reported by McGlynn.[6] We can extend it to water, in which a weak emission near 410 nm corresponds to an excitation near 330 nm, which we assign to dimer absorption. The slope of the line is too high to be anything but an excitation which separates a substantial amount of charge. The second correlation line in Figure 1 (marked M) is assigned to monomer absorption. The slope is considerably higher than that found for absorption maxima of most conjugated carbonyl compounds and must cor-

Table I. Absorption and Emission Data for 4-(*N,N*-Dimethylamino)benzonitrile (DMAB, **3**) in Various Solvents

Solvent	$E_T(30)$ value[a]	Absorption maximum λ_{max}, nm	Emission maxima, λ_{max}, nm SE[b]	LE[b]	D[b]	Ratio[b] LE/SE
Cyclohexane	30.9	281 D[e]			344	
Tetrachloromethane	32.5	290				
Benzene	34.5	290 D[e]			351	
Dioxane[c]	36.0	290	350	433		0.75
Chloroform[d]	39.2	292	359			
Dichloromethane[d]	41.1	292	354	425		1.18
tert-Butyl alcohol	43.9	284	356	452		3.5
Acetonitrile	46.0	291	360	467		5
Isopropyl alcohol	48.6	292 313 D[e,f]	345	457	395	1.05
Ethanol[g]	51.6	295				
1,3-Butanediol	52.8	295	339			Low[h]
1,2-Propanediol	54.1	298 340 D[e]	352	469	395	0.6
1,2-Ethanediol	56.3	301	357	480		0.29
Formamide	56.6	301	384	475		0.5
Glycerol[i]	57.0	302	350			Low[h]
1,2-ED/water (1:1)[j,g]	59.8	300				
Water	63.1	298 330 D[e,f]	395	510	410[k]	0.63

[a] From ref 11, or measurements made by ourselves. [b] SE, short-wavelength emission; LE, long-wavelength emission; D, dimer emission; LE/SE, ratio of intensities of emission in long-wavelength region to those in short-wavelength region, using 300 nm as exciting wavelength (see Table II). [c] Since special precautions were not utilized in transfers, solvent may have contained small quantities of water. [d] Free of ethanol (see Experimental Section). [e] Absorption assigned to dimer. [f] Detected through excitation spectrum for dimer emission. [g] Emission spectrum not measured. [h] Low, ≤0.05. [i] Dry solvent. [j] 1:1 mixture of 1,2-ethanediol and water by volume. [k] ±5 nm.

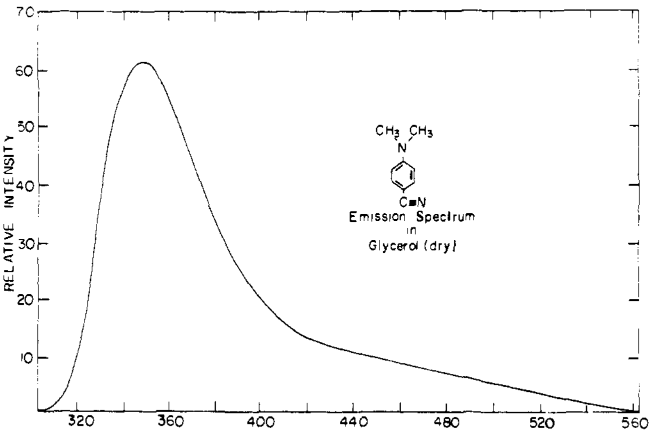


Figure 3. Emission spectrum for DMAB in glycerol. Slits used were 8 nm. The excitation wavelength used was 300 nm. The spectrum is only corrected for contributions from solvent.

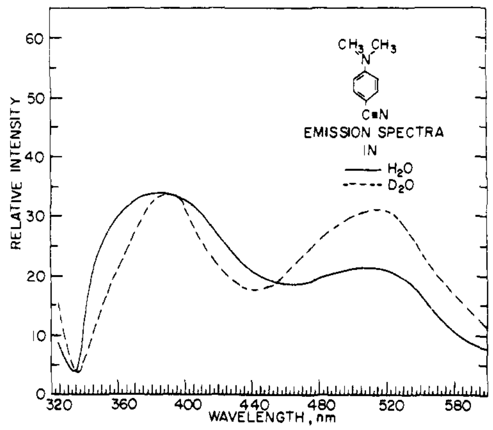


Figure 4. Emission spectra for DMAB in H_2O and D_2O: slits, 5 nm; excitation wavelength, 300 nm. The spectra are corrected only for contributions from the solvent.

respond to a reasonable increase in charge separation. The rather striking difference in slope for the correlation lines of dimer and monomer can be understood in terms of how much solvation might be expected for the Franck-Condon state. Evidently, the dimer has ground-state solvation which accommodates the substantial increase in charge easily.

(2) Emission (SE). Two correlation lines were found for short-wavelength emissions. The high-slope (1.16) line is assigned to emission from a $S_{1,perp}$ state (perpendicular monomer) and the low-slope (0.26) line to a $S_{1,pl}$ (pl stands for planar) state emission (planar monomer). Even the low-slope line is more sensitive to solvent than most emissions or usual absorption bands and therefore must involve considerable change in charge separation (i.e., charge transfer). The high-slope line belongs to a species with higher energy than the species exhibiting the low-slope emission, as can be easily seen through extrapolation of the high-slope line to hydrocarbon solvents. The high-slope line must arise from a less conjugated species than the low-slope line (given the limited number of possibilities evident in a simple molecule like DMAB) and is thus assigned to a "perpendicular" S_1 state. The "perpendicular" description refers to the idea that the p orbital on the nitrogen is perpendicular to the p orbitals making up the π system of the aromatic ring and is the same designation utilized by Rotkiewicz et al.[4] The low-slope line is then assigned to a completely planar conjugated species. We had previously proposed to two such emitting states for the charge-transfer emissions of 9,9-bianthracenyl.[14] The difference in slopes is comprehensible on the basis of the ground Franck-Condon states arising from the two different S_1 states, with the slope for correlation of the perpendicular state transitions resembling those of the solvent-sensitive pyridinium iodide ion pairs from which *Z* values are derived.[15]

(3) Emission (D). The dimer emission was assigned in 1,2-propanediol on the basis of its excitation maximum at 340 nm, in excellent agreement with the results of

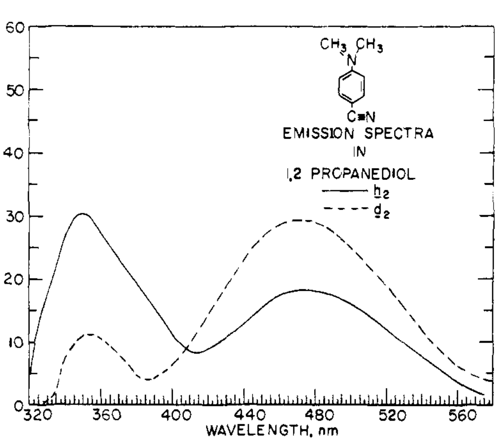


Figure 5. Emission spectra for DMAB in 1,2-propanediol-h_2 and 1,2-propanediol-d_2: slits, 5 nm. The spectrum is corrected only for contributions from solvent.

Table II. Wavelength Dependence of LE/SE Ratio[a]

Solvent	LE/SE ratio at wavelength of excitation, nm 290	300	310
Dioxane	0.69	0.75	0.86
Dichloromethane	1.06	1.17	1.18
tert-Butyl alcohol	3.0	3.4	3.45
Isopropyl alcohol	0.95	1.15	1.32
1,2-Propanediol ($-h_2$)	0.57	0.57	0.99
($-d_2$)	2.9	3.1	2.9
1,2-Ethanediol	0.28	0.38	0.54
Water (H_2O)	0.79	0.95	0.96
(D_2O)	1.20	1.40	1.25

[a] Ratio of intensities for long-wavelength and short-wavelength emissions, corrected for photomultiplier sensitivity.

McGlynn.[6] The arguments given under absorption maxima favored the assignment of emissions in cyclohexane and benzene to dimer. In support of this assignment, it appears that the quantum yield of emission is much higher than in most other solvents (the quantum efficiency for dimer emission in 1,2-propanediol is clearly greater than that of the monomer). Since the ground state of aromatic amines is twisted (the plane of the amino group is not parallel to the plane of the aromatic ring), dimerization would be expected to restrict motions favoring internal conversion. The emission in dioxane solution is problematic, either dimer emission or (probably) planar monomer emission aided by small amounts of water in the solvent. Confidence in this pattern was increased by the prediction that a dimer emission in water would occur near 420 nm, after which examination of our spectra did reveal a weak emission near 410 nm. The 410-nm emission had an excitation maximum near 330 nm which corresponded to that expected for dimer (**7**) absorption. The excited dimer is equivalent to an excimer of the monomer, but differing in that the pairs are present before excitation.

(4) **Emission (LE).** It was quite clear from the literature that the LE arose from a species created more slowly than those species responsible for SE.[8-10] The usual explanations, solvent relaxation or group rotation, seemed to us inadequate since we had already assigned SE to the two most likely charge-separated species. Noting (a) that protons in

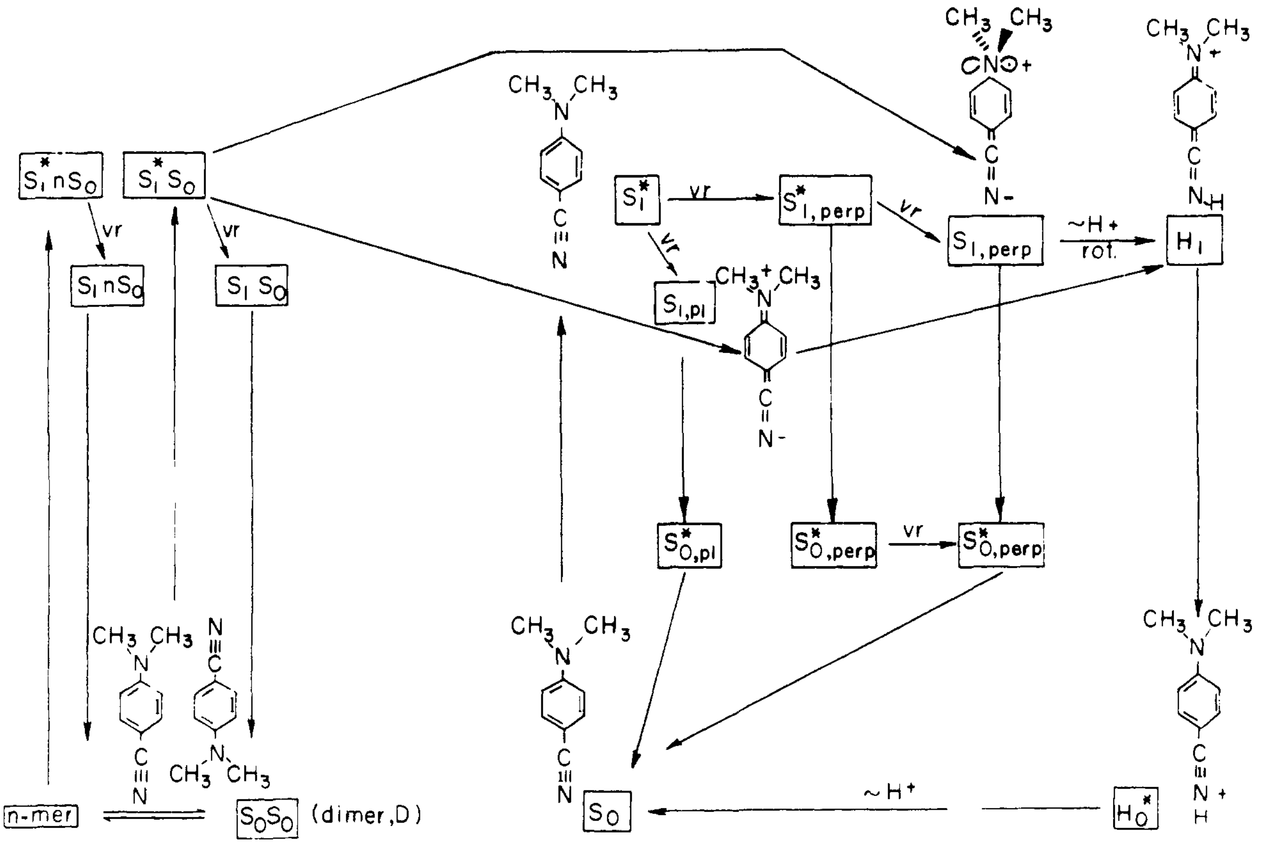
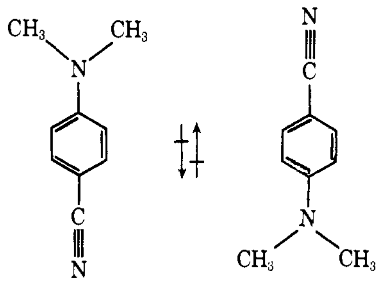


Figure 6. Scheme showing the ground and excited states of DMAB which are needed to account for the absorption and emission data. Definitions of the symbols are as follows: S_0, ground-state monomer; S_0S_0, ground-state dimer; S^*_1, vibrationally excited singlet (twisted); $S_{1,pl}$, planar charge-separated singlet; $S^*_{1,perp}$, vibrationally excited state with p orbital of nitrogen perpendicular to direction of π orbitals of aromatic ring; $S_{1,perp}$, relaxed singlet with nitrogen p orbital perpendicular to direction of π orbitals of ring; H_1, excited protonated molecule (proton on cyano nitrogen); $S^*_1S_0$, vibrationally excited singlet of dimer; *n*-mer, species containing more than two monomers. The other labels are obvious from the foregoing description.



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the solvent molecule were a sine qua non for the appearance of LE and (b) that a relatively slow appearance of the emitting species might be due to a chemical reaction, we postulated that proton transfer might produce a new emitting molecule, the protonated structure shown as **5**. Based on the idea that we might find longer lifetimes for deuterated molecules (as, for example, in the work of Rice et al. on aniline[16]), we examined the effect of solvent deuteration on the emission spectra of DMAB. The results for a particular exciting wavelength are shown in Figures 4 and 5, and the results on the LE/SE ratio are given in Table II. The large and dramatic increase in the ratio for deuterated solvents over that found for protonated solvents suggests rather strongly that the LE arises from a protonated molecule, with the structure **5** chosen to maximize conjugation in order to account for the long wavelength of the transition. Solvents without available protons do not exhibit LE (cyclohexane, benzene). The precise reasons for the magnitude of the deuterium isotope effect are no doubt complex, including solvent isotope effect, rates of proton transfer, radiative lifetimes, etc. Some of these factors have been analyzed for indoles by Eisinger and Navon,[17] and a related deuterium isotope effect has been reported for the azaindole **6** at low temperatures.[13] The increase in the rate of formation of LE species in trifluoroethanol over that noted in 1-butanol is in agreement with protonation as the mechanism of LE species formation.[18]

(**5**) **Other emissions** noted by others for DMAB (**3**) at high concentrations, low temperatures, matrices, glasses, etc., which do not fit the assignments noted seem to us to arise from polymeric species. These are noted as *n*-mers in Figure 6. Some solvents like benzonitrile present experimental problems (weak emission from solvent molecules, etc.) which do not permit simple interpretations for a solute like DMAB.

Conclusions

(1) Emissions from more than one vibrational level of excited DMAB can be observed in viscous solvents like glycerol.

(2) The multiple emissions observed for DMAB can each be assigned to a separate species, and only one emission is observed within a given manifold of states.

(3) The complex scheme describing the excited states of DMAB could apply to any conjugated system in which charge separations is effected by excitation. These are systems having a donor site and an acceptor site and could be regarded as intramolecular donor-acceptor systems (compare with ref 11).

(4) Dimers and other aggregates are commonly found for dye molecules of the cyanine class, and some of these molecules may exhibit behavior like that of DMAB.

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