Absorptiometric and Fluorimetric Study of Solvent Dependence and Prototropism of 2-Substituted Benzimidazole Derivatives

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A study of the effects of solvents on the absorption and fluorescence spectra of 2-substituted benzimidazoles has shown that the lowest-energy transition of the chloromethyl, dichloromethyl, and cyanomethyl derivatives is of π–π^* character, and that of the 5-chloro-2-trichloromethyl, 2-trifluoromethyl, and 2-chloro derivatives is of charge-transfer character. In the case of the monocations and monoanions of these compounds, the lowest-energy transitions are of charge-transfer and π–π^* nature respectively. The presence of the methylene group in between the benzimidazole and the heteroatom substituent reduces direct interaction; this is apparent from the study of proton-transfer reactions as well as from the spectral changes. The pK_a values for these reactions in the ground and excited states have been determined and discussed. Acetonitrile quenches the fluorescence of the chloromethyl, dichloromethyl, and trichloromethyl compounds. The mechanism could involve charge-transfer complex formation.

Because of its biological importance, benzimidazole has received much attention.[1–3] Recent studies have shown that the benzimidazole molecule forms a number of excited singlet states.[4] Which of these is of lowest energy depends upon the nature and position of substituents and also on the nature of the solvent.[4,5] For example, electron-donating groups on the homocyclic ring favour a charge-transfer species, even for the neutral molecule.[4] The fluorescence spectra of the monocations of benzimidazoles behave differently. Sometimes the emission is observed only from a π^* state [for example, 2-phenyl or 2-(substituted phenyl)benzimidazole cations]; in other cases, two fluorescence bands are observed, one from the π^* state and the other from a charge-transfer state (for example methyl-substituted benzimidazole cations). The π^* state is of higher energy than the charge-transfer state. The driving force behind a greater stabilisation of the charge-transfer state is the presence of positive charge on the tertiary nitrogen atom, which enhances charge migration from the benzene to the imidazole ring.

The present study is an extension of our earlier work.[5] We have taken six benzimidazoles bearing electron-withdrawing 2-substituents and studied the effect of solvents and pH on their spectral characteristics. The pK_a values for prototropic reactions have also been calculated for the S_0 and S_1 states. The results are discussed in the light of the nature of the excited singlet state.

Methods and Materials

2-(Chloromethyl)benzimidazole (CMBI),[6a] 2-(dichloromethyl)-benzimidazole (DMBI),[6b] 2-(trifluoromethyl)benzimidazole (FMBI),[6c] and 2-(cyanomethyl)benzimidazole (CNBI)[6d] were prepared by refluxing the corresponding substituted acetic acids with an equimolar quantity of *o*-phenylenediamine in 4N-HCl as reported.[6] 2-Chlorobenzimidazole (2CBI) was prepared by the reaction of $POCl_3$ with 2-hydroxybenzimidazole (Aldrich) as suggested in the literature.[7] 5-Chloro-2-trichloromethyl-benzimidazole (TMBI) was purchased from Aldrich. All these compounds were purified by repeated crystallisation from solvents as reported.[6] Their purity was checked by m.p. determination and absorption spectra, as well the similarity of fluorescence spectra obtained by excitation at different wavelengths. Spectrograde methanol (B.D.H.) and analytical grade H_2SO_4 and NaOH (both B.D.H.), trifluoroacetic acid (Fluka), and piperidine (Fluka) were used as such. Acetonitrile (Merck), cyclohexane (I.D.P.L.), ether, and ethanol were further purified by reported methods.[8] Triply distilled water was used in the preparation of all aqueous solutions. A modified Hammett acidity scale[9] below pH 1 and the Yagil basicity scale[10] above pH 13 were used for H_2SO_4–H_2O and NaOH–H_2O mixtures, respectively.

Absorption spectra were recorded with a Shimadzu 190 spectrophotometer equipped with a U135 recorder. Fluorescence measurements were carried out with a scanning spectrofluorimeter, built in our laboratory; details are available elsewhere.[11] Both exciting and emission monochromators were calibrated with a low-pressure mercury lamp from time to time. The band width used was 8 nm. The quantum yields for different solvents were calculated from the corrected fluorescence spectra by using quinine sulphate as a fluorescence standard;[12] excitation wavelengths used are given in Table 2. For absorptiometric and fluorimetric titrations, the solutions were prepared just before measurement. The fluorescence intensities at the analytical wavelength were measured by exciting the solutions at the isosbestic points. The concentration used were in the range 10^{-4}—10^{-5}M. pH Values in the range 1—13 were measured with a Toshniwal pH meter, model CL44A.

Results and Discussion

Effect of Solvents on Absorption and Fluorescence Spectra.— The absorption and fluorescence spectra were recorded in solvents of various polarities and tendencies towards hydrogen-bond formation. The fluorescence spectra are shown in Figure 1. The relevant data are recorded in Tables 1 and 2. The absorption spectra are similar to that of 2-methylbenzimidazole (2MBI)[5] except those of TMBI and FMBI, which show red shifts much greater than those of other compounds. The effects of solvent polarity and hydrogen-bonding capacity on the absorption spectra are not appreciable, but a small blue shift is observed in going from non-polar to polar and protogenic solvents.

The fluorescence spectra of all the compounds except TMBI and FMBI are similar to that of 2MBI.[5] Table 2 shows that the effect of solvents on the fluorescence spectrum is similar to that for the absorption spectrum, *i.e.* hardly any or a very small blue shift is noticed with increase in the polarity or proton-donor capacity. On the other hand a large red shift is observed in the cases of TMBI and FMBI in the similar environments.

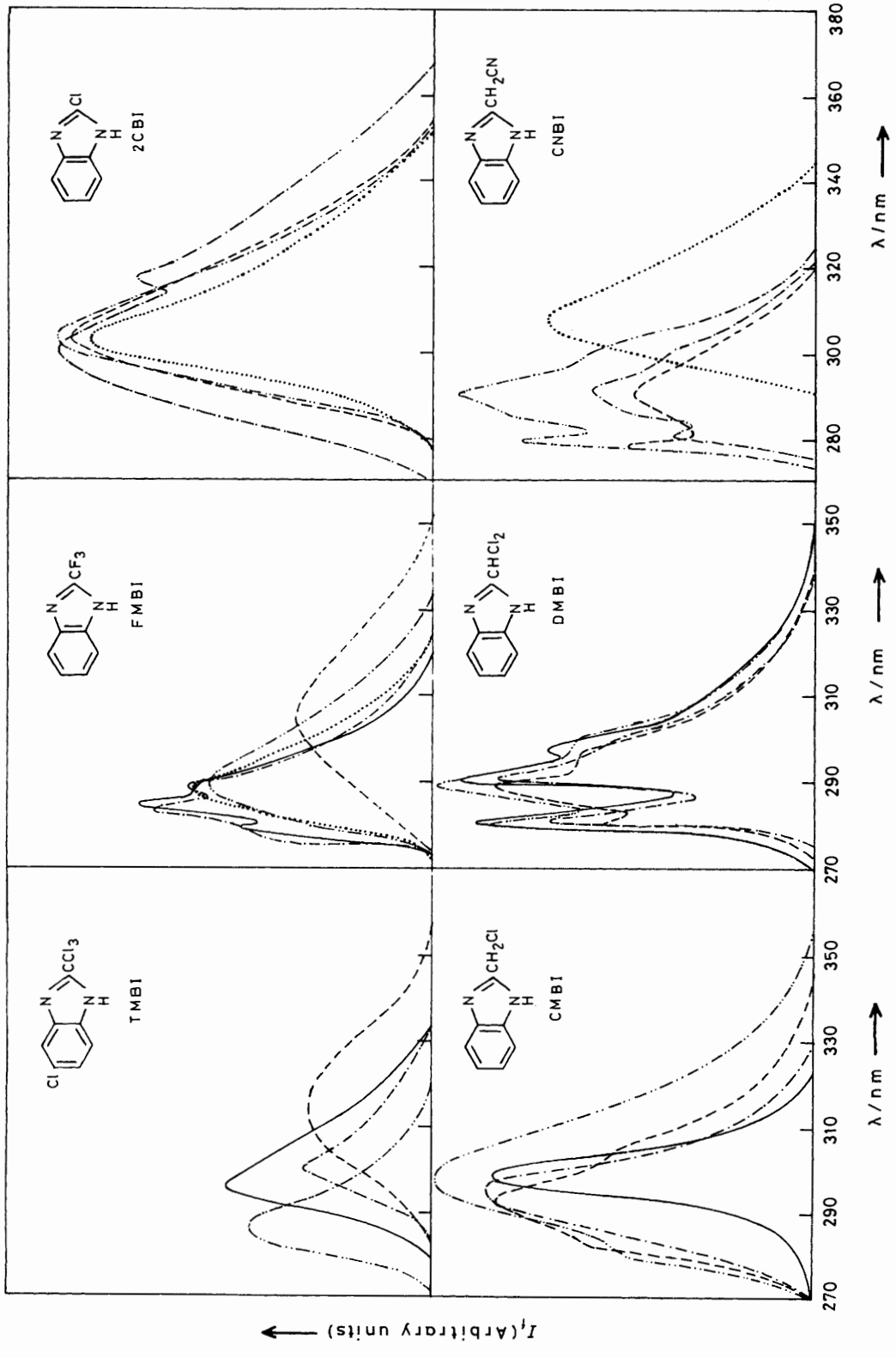

Figure 1. Fluorescence spectra of benzimidazoles in different solvents at 298 K; (——) cyclohexane, (– · – · –) ether, (– · · – · · –) methanol, (– – – –) water, (· · · ·) acetonitrile

Table 1. Absorption maxima [λ/nm; log ε[a]] of 2-substituted benzimidazoles at 298 K

Species (Solvent)	2-$ClCH_2$ (CMBI)	2-Cl_2CH (DMBI)	5-Cl-2-Cl_3C (TMBI)	2-F_3C (FMBI)	2-Cl 2CBI	2-$NCCH_2$ (CNBI)
Neutral (Cyclohexane)	279	282		285	281	
	278	275	289	276	275	
	248	269	261	246	268	
	209	250				
		244	213	210	241	
		209			211	
Neutral (Ether)	279	281 (3.88)	298	285 (3.85)	281 (3.82)	281 (3.95)
	274	275 (3.85)	290	276 (3.92)	275 (3.77)	274 (3.92)
	250	269 (3.70)	265	266 (4.03)	268 (3.59)	243 (4.00)
	219	250 (3.90)	227	254 (4.07)	242 (3.80)	219 (3.90)
		245 (3.95)		248 (4.03)		
		215 (3.50)		224 (3.67)		
Neutral (Acetonitrile)	274 (4.05)	279 (3.86)	297 (3.61)	284 (3.76)	280 (3.77)	275 (3.95)
	268 (4.02)	273 (3.81)	289 (3.64)	275 (3.81)	273 (3.75)	269 (4.00)
	250 (3.90)	268 (3.78)	266 (3.51)	269 (3.72)	266 (3.60)	243 (3.74)
	215 (4.29)	249 (3.80)	217 (3.88)	253 (3.76)	241 (3.73)	202 (4.35)
		244 (3.81)				
				204 (4.45)	211 (3.86)	
		212 (3.86)				
Neutral (Methanol)	278 (4.17)	279 (3.91)	297 (3.55)	283 (3.93)	280 (3.78)	279 (3.86)
	274 (4.12)	272 (3.90)	288 (3.61)	275 (4.03)	273 (3.76)	273 (3.84)
	250 (4.06)	265 (3.77)	259 (3.40)	268 (3.98)	266 (3.60)	243 (3.79)
	209 (4.49)	249 (3.89)		254 (4.00)	241 (3.66)	207 (4.39)
		244 (3.92)	217 (3.67)			
		208 (3.96)		206 (4.49)	213 (3.84)	
Neutral (Water, pH 7)	277	278 (3.81)		281 (3.50)	279 (3.81)	278 (3.86)
	271	271 (3.84)	292	274 (3.62)	272 (3.79)	271 (3.86)
	244	265 (3.74)	230	268 (3.58)	263 (3.71)	243 (3.78)
	203	249 (3.83)	198	255 (3.54)	245 (3.65)	200 (4.56)
		244 (3.86)			200	
		205 (4.21)				
Monocation	275 (3.95)	274 (3.98)	300 (3.65)	280 (3.70)	277 (3.90)	275 (3.92)
	270 (3.87)	267 (4.00)		273 (3.78)	270 (3.89)	269 (3.93)
		261 (3.88)	235 (3.54)		241 (3.47)	239 (3.62)
	220 (4.31)	240 (3.78)		216 (3.60)		
		203 (3.91)				
Monoanion	286 (3.93)	281 (3.68)	306 (3.78)	284 (3.75)	284 (3.83)	281 (3.86)
	280 (4.00)	277 (3.73)	220 (3.88)	277 (3.82)	278 (3.84)	275 (3.84)
					258 (3.59)	
	227 (3.54)			225 (3.59)	249 (3.59)	219 (3.75)
		225 (3.12)			226 (3.75)	

[a] ε Values in $dm^3\ mol^{-1}\ cm^{-1}$.

It is now well established that the n–π^* transition is not observed in benzimidazoles, although the system has a lone pair of electrons on the tertiary nitrogen atom.[2–5,13c] Tables 1 and 2 show large extinction coefficients and reasonable fluorescence quantum yields, in accord with this. It is also known that benzimidazoles form a number of excited singlet states [π–π^* and charge-transfer (CT)].[4,5] The energy of the emitting state depends upon the nature and the position of the substituent as well as on the characteristics of the solvent. Moreover the spectral characteristics of the charge-transfer bands vary markedly with the polarity of the solvent, and distinction between the two types of transitions can be made only from the study of the effects of solvents on the absorption and fluorescence spectra. Tables 1 and 2 clearly indicate that the absorption and fluorescence spectra of all the benzimidazoles studied, with the exception of TMBI and FMBI, are insensitive to solvent polarity and proton-donor nature of the solvents. Thus the π–π^* transition originates from the lowest-energy state of all the benzimidazoles (as neutral species) except TMBI and FMBI. In the case of TMBI and FMBI, a large red shift in the fluorescence spectrum is noted in going from cyclohexane to water; thus the CT state is the lowest emitting state in the neutral species of these compounds. In general, charge migration takes place from the homocyclic to the heterocyclic ring and the driving force behind this migration in these cases is the presence of a strongly electron-withdrawing group (–CCl_3, –CF_3). Though –CN is also a strongly electron-withdrawing group, the presence of an intervening methylene group stops direct interaction. Similar behaviour has been observed in a number of cases.[3,14–16] This observation is supported by the spectral characteristics of 2-chlorobenzimidazole (2CBI) and CMBI. In the case of CMBI, the absorption and fluorescence spectra and pK_a values (see later) resemble those of 2MBI[5] and benzimidazole, whereas 2CBI behaves differently from BI or

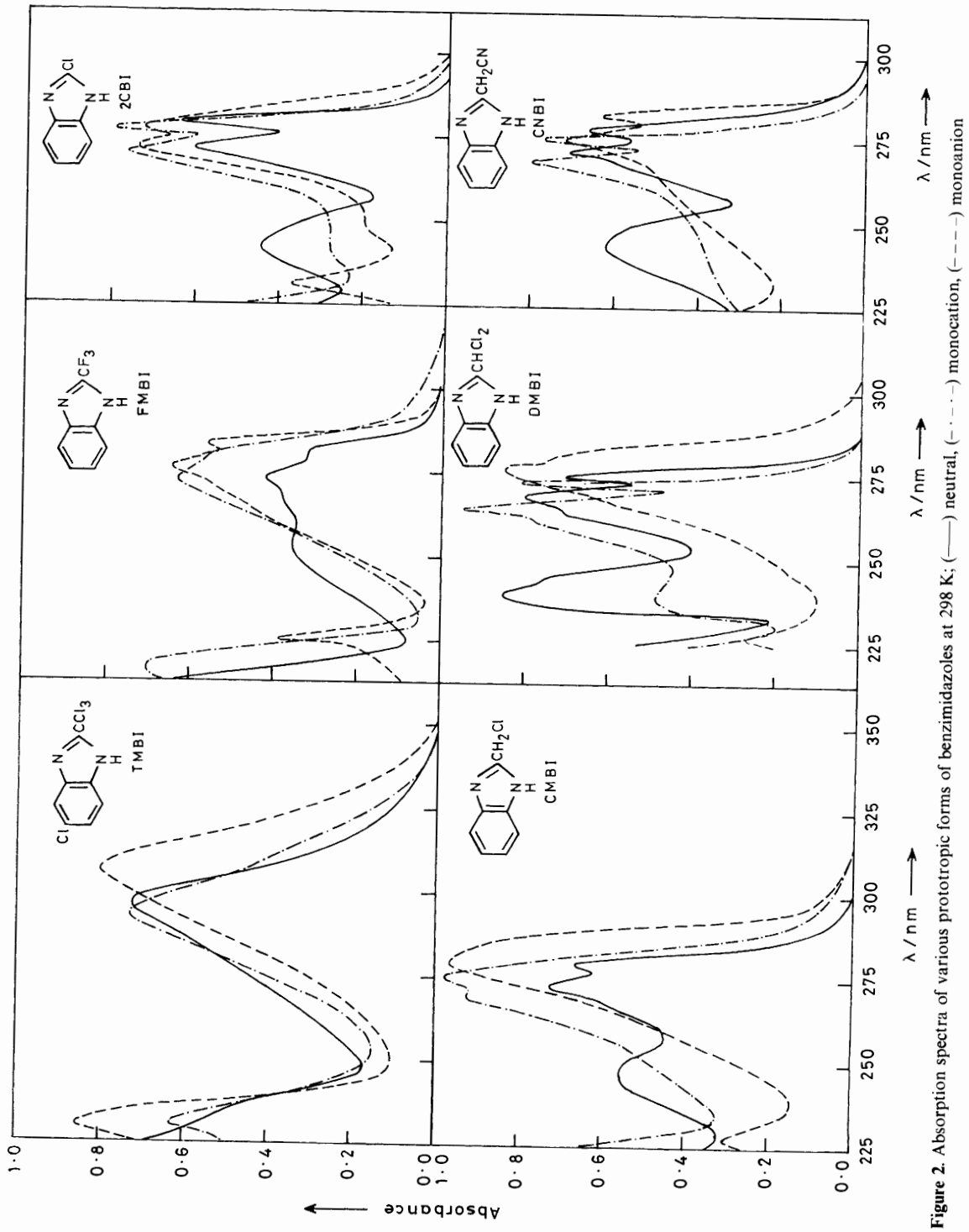

Figure 2. Absorption spectra of various prototropic forms of benzimidazoles at 298 K; (——) neutral, (– · – · –) monocation, (– – –) monoanion

Table 2. Fluorescence maxima (nm), quantum yields (in parentheses), and excitation wavelengths ($\lambda_{exc.}$) of substituted benzimidazoles at 298 K

Species (Solvent)	CMBI	DMBI	TMBI	FMBI	2CBI	CNBI
$\lambda_{exc.}$/nm[a]	280	280	290	285	281	280
Neutral (Cyclohexane)	299 (0.002)	298 (0.20) 290 280	332 (0.01)	307 (0.30) 298 288		
Neutral (Ether)	297 (0.007)	300 (0.15) 290 281	330 (0.01)	307 (0.23) 296 287	318 (0.08) 300	292 (0.16) 281
Neutral (Acetonitrile)		300 (0.01) 290		308 (0.24)	304 (0.04)	308 (0.25)
Neutral (Methanol)	297 (0.025)	297 (0.37) 289 280	303 (0.14)	310 (0.24)	304 (0.06)	290 (0.10) 280
Neutral (Water pH 7)	304 (0.115) 293 283	297 (0.59) 289 280	354 (0.03)	340 (0.18)	304 (0.07)	290 (0.01) 278
Monocation	358	375		410		390
Monoanion	308	308		310		313

[a] Used for the determination of quantum yield (Φ_f).

2MBI. Lastly the effect of solvents on the fluorescence spectrum of 2CBI is not prominent, as observed in the case of TMBI or FMBI, *i.e.* unlike other benzimidazoles studied, the fluorescence spectrum of 2CBI is slightly red-shifted, but not to the extent noticed with TMBI and FMBI. It may not be possible definitely to assign CT as the lowest-energy emitting state for 2CBI, but it certainly outweights the π–π^* transitions. In this case the chloro group can exert both inductive and resonance effects; the former favours electron withdrawal whereas the latter perturbs the π-cloud by donating the electrons to the ring. Since the effects act in the opposite directions, the net effect will be quite small.

The small blue shift observed in the absorption and fluorescence spectra of all the benzimidazoles with increase in polarity or proton donor nature of the solvent can be explained as follows. It is established that the long wavelength transition is localised on the benzene ring and the shorter wavelength transition on the imidazole ring.[17] The lone pair on the tertiary nitrogen atom can perturb the former transition like an amino group, but to a small extent, since the perturbation will be through the inductive effect. This is because the lone pair and the π-cloud of the ring are perpendicular to each other. Similar behaviour has also been observed in the case of phenanthro-[9,10-*d*]imidazole.[18] The fluorescence spectra of CMBI, DMBI, and CNBI can be explained along these lines. However in the cases of TMBI, FMBI, and 2CBI, the charge-transfer state is stabilised more than the π–π^* state, and thus a red shift is observed.

Effect of pH.—The absorption and fluorescence spectra of all the benzimidazoles were studied in the H_0/pH/H_- range -10 to 16 (see Figures 2 and 3). The relevant data are compiled in Tables 1 and 2. It is clear from Table 1 that the long-wavelength absorption bands are all slightly blue-shifted in acidic medium. The 244 nm band under the same conditions is either merged with the long-wavelength band (CMBI and FMBI) or is slightly blue-shifted (DMBI, CNBI, and 2CBI). The same band is slightly red-shifted in the case of TMBI. The species present under these conditions is the monocation, formed by protonation of the tertiary nitrogen atom. The blue shift can be explained as has been done in the case of proton-donor solvents, since protonation is the extreme case of a hydrogen-bonding interaction. No further change is observed in the absorption spectra even up to $H_0 -10$, indicating that no dication or any other species is formed in the S_0 state. The absorption spectrum is red-shifted at pH >11, by an amount depending upon the particular derivative. The spectrum in each case is assigned to the monoanion, formed by the deprotonation of the NH group. The spectral changes observed are consistent with the deprotonation reactions of similar groups.[11,19,20] The behaviour of TMBI is quite different and will be discussed later.

Fluorescence spectra of all the benzimidazoles are red-shifted at pH <3, with the exception of 2CBI and TMBI, which are non-fluorescent. The excited-state prototropic reaction is similar to that of the ground state, and the species formed is a monocation. The unusual large red shift is due to stabilisation of the charge-transfer state in polar solvents. The driving force behind charge migration from the carbocylic to the heterocyclic ring is the positive charge on the tertiary nitrogen atom. Thus, unlike the neutral benzimidazoles, the lowest-energy state in the monocations is the CT state. Further, unlike methyl-substituted benzimidazoles,[5] no second fluorescence band of the monocations, blue-shifted as compared with the neutral ones, is observed. This suggests either that fluorescence quantum yields of the π–π^* transitions of these cations are very low, or that the CT state is the only pathway for deactivation of the monocations from the several excited states.

On the other hand, a very small red shift is observed in the fluorescence spectra of the monoanions (with the exceptions that the monoanion of 2CBI is non-fluorescent and that a blue shift occurs in the case of FMBI monoanion). The emitting state of the monoanions is of π–π^* character. This is due to the presence of negative charge on the imidazole ring which will inhibit charge migration from the carbocyclic to the heterocyclic ring. The blue shift observed in the case of FMBI is

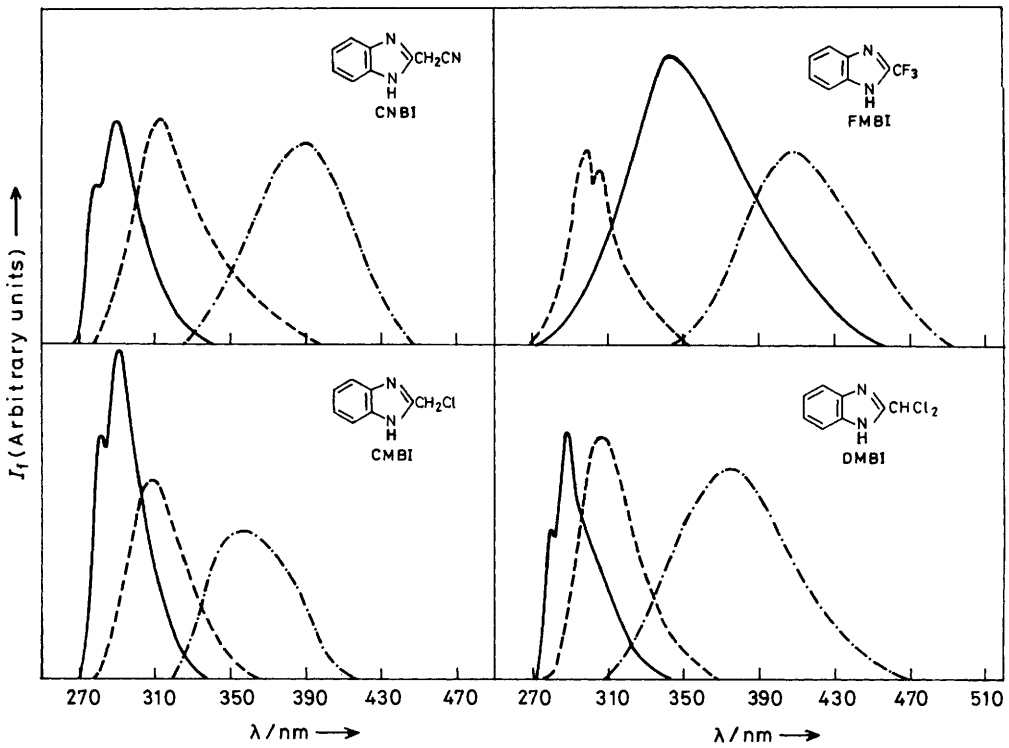

Figure 3. Fluorescence spectra of various prototropic forms of benzimidazoles at 298 K; (——) neutral, (– · – · –) monocation, (– – – –) monoanion

consistent with the foregoing explanation because of the presence of negative charge on the imidazole ring, which is absent in the neutral molecule. This is further confirmed by the results for FMBI in cyclohexane containing 1% piperidine (v/v); a 310 nm fluorescence band is observed which is due to the monoanion. The behaviour of TMBI under similar basic conditions either in aqueous media or non-polar media containing piperidine is quite different and will be discussed separately.

5-Chloro-(2-trichloromethyl)benzimidazole in Basic Media.—The absorption spectrum of TMBI is red-shifted on increasing the pH to 13, indicating the formation of the monoanion, by deprotonation of the NH group, as generally observed. However on further increasing the basic strength, a blue shift is observed (from 310 to 300 nm). The spectrum observed in the latter case is similar to that of the dianion obtained by deprotonating the CO_2H and NH groups of 5-chlorobenzimidazole-2-carboxylic acid.[21] On the other hand the intensity of the fluorescence spectrum (350 nm) of the neutral TMBI under these conditions remains constant up to pH 12, and a sudden increase is observed at pH 13, without the appearance of any other new band at a different wavelength. The intensity of this fluorescence band increases very slowly after pH 14; this behaviour is similar to that observed in the case of the carboxylic acid. All these reactions are irreversible in the sense that on slow acidification the absorption and fluorescence spectra of the various species obtained do not agree with those of TMBI. This clearly suggests that at high pH hydrolysis takes place to give the 2-substituted carboxylic acid, as reported.[22]

The absorption and fluorescence spectra of TMBI in cyclohexane containing piperidine were recorded. Unlike the case of FMBI, the reaction seems to be more complicated than the simple removal of a proton from the NH group to form the monoanion. A preliminary study has indicated that spectral changes occur with change of solvents containing piperidine as well as with the amount of piperidine present in the solutions. This is consistent with the ground-state reactions of the $-CCl_3$ group with the base, in which a chlorine atom can be replaced[23] if the base is in excess.

Table 3. Protonation and deprotonation constants in S_0 and S_1 states

Benzimidazole	$pK_a(S_0)^a$	$pK_a(S_1)^b$	$pK_a(S_1)^c$	$pK_a(S_1)^d$
Equilibrium between monocation and neutral species				
CMBI	4.0	3.45		5.0
DMBI	4.1	3.0		5.0
TMBI	0.3	2.2		
FMBI	0.6	0.3		1.6
2CBI	2.1	1.6		0.0
CNBI	3.5	2.7		3.5
Equilibrium between monoanion and neutral species				
CMBI	12.7	10.3	11.8	12.2
DMBI	12.9	12.1	10.40	12.2
TMBI	10.3	7.0		
FMBI	10.1	9.3		9.3
2CBI	9.4	8.1		11.3
CNBI	12.0	11.2	6.7	11.0

[a] By absorptiometric titration. [b] By Förster cycle method on absorption data. [c] By Förster cycle method on fluorescence data. [d] By fluorimetric titration.

pK_a Values for S_0 and S_1 States.—The pK_a values of the monocation–neutral and neutral–monoanion reactions were calculated from spectrophotometric results (Table 3). The values for the respective prototropic reactions of benzimidazole and 2MBI are 5.48/6.19 and 13.25/14.20, respectively. Further,

the presence of electron-donating groups in the parent molecule increases the pK_a and the presence of electron-withdrawing groups decreases it. The presence of the intervening methylene group inhibits direct mutual interaction. For example, pK_a values for both the equilibria of 2CBI are lower than those of CMBI, indicating that the inductive effect of the chloro group predominates over the resonance effect. Comparison of the results for CNBI and CMBI shows that presence of the methylene group decreases direct interactions, whereas in 2CBI the chlorine atom is directly attached to the ring and can interact more effectively.

pK_a^* Values for both equilibria have been determined with the help of fluorimetric titrations and the Förster cycle method,[24] by using absorption and fluorescence data wherever applicable. For example the latter method cannot be applied to calculate the pK_a^* of the monocation–neutral equilibrium in any case except that of FMBI, because the π–π^* transition is that occurring in neutral molecules, whereas the CT transition is that of lowest energy in the case of monocations. Similarly, this method cannot be used to calculate the pK_a^* of the neutral–monoanion equilibrium of FMBI. But wherever this method is applicable the trend observed in pK_a^* is consistent with the behaviour of the benzimidazole molecule. The results obtained from fluorimetric titrations (Table 3) agree with earlier findings that (i) ground-state values of pK_a are observed from the fluorimetric titrations because of the shorter lifetimes of the conjugate species, or else the pK_a values fall in the mid-pH range 3—11,[25] where $[H^+]$ is so small that the rate of protonation or deprotonation cannot compete with radiative decay; and (ii) the tertiary nitrogen atom becomes more strongly basic and the imino group more strongly acidic on excitation. The pK_a^* value for the neutral–monoanion equilibrium of TMBI cannot be calculated from fluorimetric titration data because of the reasons mentioned earlier. In the case of 2CBI the pK_a^* values for these equilibria are different from those of the other benzimidazoles, in that the tertiary nitrogen atom becomes less basic and the imino group more basic upon excitation, an exactly opposite trend. Since monocation and monoanion of 2CBI are non-fluorescent, nothing can be inferred conclusively but it seems that (i) at low pH the inductive effect of the chloro group is predominant, therefore reducing the charge density at the tertiary nitrogen atom, and (ii) at high pH the resonance effect of the chloro group is predominant, thereby increasing the charge density at the imino group. Similar behaviour of chloro or bromo groups has been observed in other cases.[26]

Fluorescence Quenching by Acetonitrile.—Fluorescence of the neutral species of CMBI, DMBI, and TMBI was completely quenched in acetonitrile as solvent. The systematic fluorescence quenching of these compounds by acetonitrile was studied. The fluorescence intensity follows a simple Stern–Volmer plot (1),

$$\varphi_0/\varphi = 1 + k_q\tau[Q] \quad (1)$$

where φ and φ_0 are the fluorescence intensity with and without quencher, k_q is the quenching constant, and τ is the lifetime of the compound. Figure 4 shows the Stern–Volmer plot; the values of $k_q\tau$ obtained from the slopes are given in Table 4. The natural lifetime, τ_{FM}, was calculated from the corrected fluorescence spectra, using Stricker and Berg's[27] equation. The value of τ was determined from the relation $\tau = \tau_{FM}\varphi$. These values, along with k_q, are also listed in Table 4. The values of k_q are much less than the diffusion-controlled limit (1.1×10^{10} $dm^3\ mol^{-1}\ s^{-1}$).[28] In this case energy transfer from the excited species to acetonitrile cannot occur directly, since the singlet-state energy of acetonitrile is much greater than that of the excited species. Although substitution reactions of these compounds by nucleophilic reagents are reported,[23] these reactions do not take place under the present conditions or are too slow to have any noticeable effect. We cannot say much about the mechanism of quenching, but formation of a collision complex cannot be the rate-determining step as the k_q value observed is much smaller than k_{diff}. The further possibilities (charge-transfer or electron-transfer mechanisms) need further investigation.

Table 4. Values of slope ($k_q\tau$), radiative lifetime (τ), and quenching constant (k_q) obtained from the Stern–Volmer plot

Neutral molecule	$k_q\tau$	τ	k_q/$dm^3\ mol^{-1}\ s^{-1}$
CMBI	0.55	0.1×10^{-9}	5.5×10^9
DMBI	0.12	0.9×10^{-9}	0.13×10^9
TMBI	0.90	0.29×10^{-9}	3.1×10^9

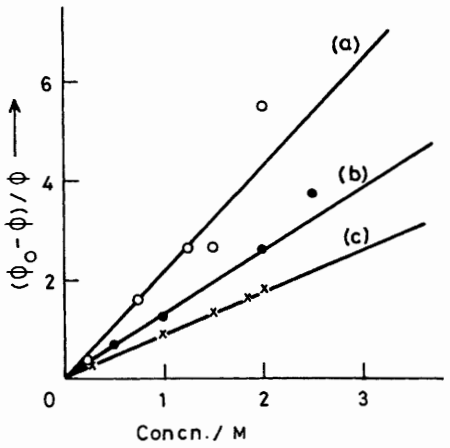

Figure 4. Stern–Volmer plot $[(\varphi_0 - \varphi)/\varphi$ *vs.* concentration] for quenching of fluorescence by acetonitrile: (a) CMBI (concn. ×4); (b) DMBI $[0.1(\varphi_0 - \varphi)/\varphi]$; (c) TMBI

Conclusions

(1) The lowest-energy transition for neutral TMBI and FMBI is of charge-transfer character, whereas in the other four molecules it is π–π^*. (2) In the case of monocations, except TMBI and 2CBI (which are non-fluorescent), the CT state is of lower energy, whereas the emitting state in the case of the monoanions is π–π^* in nature. (3) TMBI is hydrolysed to give the 2-substituted carboxylic acid in strongly basic solutions, whereas in non-aqueous solution containing a base, TMBI first forms an anion and then undergoes substitution of the chlorine atom at the 2-position. (4) The presence of a methylene group between the benzimidazole and the heteroatom substituent inhibits their direct interaction; for example pK_a values of the prototropic reactions of CMBI are close to those of BI or 2MBI, whereas those of 2CBI are much less. (5) Fluoresence quenching of neutral CMBI, DMBI, and TMBI by acetonitrile is considered to take place by either charge transfer or electron transfer.

Acknowledgements

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