Environmental Effects on the Absorption and Fluorescence Spectral Characteristics of Benzimidazole-2-carboxylic Acid and Its Ester

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The absorption and fluorescence spectra of benzimidazole-2-carboxylic acid (BIA) and 5-chlorobenzimidazole-2-carboxylic acid (CBIA) have clearly indicated that benzimidazole (BI) ring and -COOH group are coplanar to each other and are held together in a rigid frame by intramolecular hydrogen-bonding. Dual fluorescence in observed in polar and hydrogen bonding solvents. The short wavelength fluorescence band is assigned to a structure where the -COOH group is perpendicular to the BI moiety and the long wavelength fluorescence band to the planar configuration. This is further manifested from the spectral characteristics of the ester of 5-chlorobenzimidazole-2-carboxylic acid (CBIM). Various prototropic reactions taking place in S_0 and S_1 states for all the three molecules are studied in the H_0/pH/H_- range of −10 to 16. All the dissociation constants are determined, both in the S_0 and S_1 states and are discussed.

In the early 1950's, it was discovered that 5,6-dimethyl-1-(α-D-ribofuranosyl)benzimidazole is an integral part of the structure of vitamin B_{12}.[1,2] These findings stimulated great interest in the chemistry of benzimidazoles and related compounds. Though a detailed study of the physicochemical properties of benzimidazole molecule is available, the similar study on the derivatives of benzimidazole (BI) has received attention only recently.[3-17] We have started to look into the spectral (both absorption and fluorescence) aspects of the various derivatives of BI in detail.[6-17]

The present study on 2-substituted carboxylic acids of benzimidazole has been carried out from the following point of views: (i) The spectral characteristics of the aromatic moiety are changed by the interaction of basic substituents. It has been found in some cases that -COOH group is coplanar to the aromatic ring both in S_0 and S_1 states,[18-20] whereas in some cases, this group is coplaner in S_1 state and not in S_0 state.[21-25] In the present case, besides the transition moment vector which tries to bring the -COOH group in plane with the aromatic moiety, chances are that intramolecular hydrogen bonding will be present and thus will affect the spectral properties. (ii) Due to the competition between the inter- and intramolecular hydrogen bonding in polar and protic solvents, chances are that different conformers may be present in different solvents or there may be equilibrium distribution of conformers in the polar and protic solvents. (iii) The study on the bifunctional molecules containing both electron-withdrawing and electron-withdrawing groups are very rare.[26,27] In our molecules, the two electron-withdrawing chromophores are tertiary nitrogen atom and the carboxyl group. We would like to see the effect of one group over the other as well as overall effect of the two groups on benzimidazole moiety. Thus the absorption and fluorescence spectra of these molecules have been studied in different solvents. pH dependent study has also been carried out to identify the various prototropic species present in the ground and excited singlet states. pK_a values of the various equilibrium reactions have been calculated in the ground and excited singlet states and are discussed. Ester of the corresponding acid has been employed in the above study to supplement our results.

Methods and Materials

5-Chloro-2-(trichloromethyl)benzimidazole (CTMBI) was obtained from Aldrich Chemical Company. It was hydrolyzed to 5-chlorobenzimidazole-2-carboxylic acid (CBIA) by 2 M sodium hydroxide solution (1 M=1 mol dm^{-3}) as suggested in the literature.[28] Similarly for the preparation of benzimidazole-2-carboxylic acid (BIA), 2-(trichloromethyl)-benzimidazole (TMBI) was synthesised by a reaction of *o*-phenylenediamine with methyl trichloroacetimidate (obtained from Aldrich Chemical Company) in acetic acid medium. Several attempts to isolate only 2-(trichloromethyl)benzimidazole (as suggested in the literature)[28] failed. This method has always resulted in a mixture of two products i.e. 2-(trichloromethyl)benzimidazole and bi(benzimidazole). Later these two compounds were separated by preparative thick-layer chromatography using Merck Silicagel G for thin-layer chromatography. The eluting solvent was a mixture of ethyl acetate and benzene in 1 : 1 (v/v) ratio. TMBI was then hydrolyzed to give the corresponding acid (BIA) as mentioned in the case of CBIA. Methyl ester of CBIA (CBIM) was prepared by refluxing CTMBI in methanol for 20 hours.[28] The purity of all the compounds was checked by noting the sharp melting point as well as by spectroscopic methods. The purity was also checked by fluorescence techniques i.e. by getting same fluorescence maxima when excited with different wavelengths.

The procedure used for purification of the solvents, preparation of the solutions and carrying out the calculations is the same as described in our recent papers.[29-33]

Results and Discussion

Effect of Solvents. The absorption and fluorescence spectra of BI, BIA, CBIA, and CBIM are depicted in Figs. 1 and 2 respectively. The relevant spectral data of BIA, CBIA, and CBIM are compiled in Tables

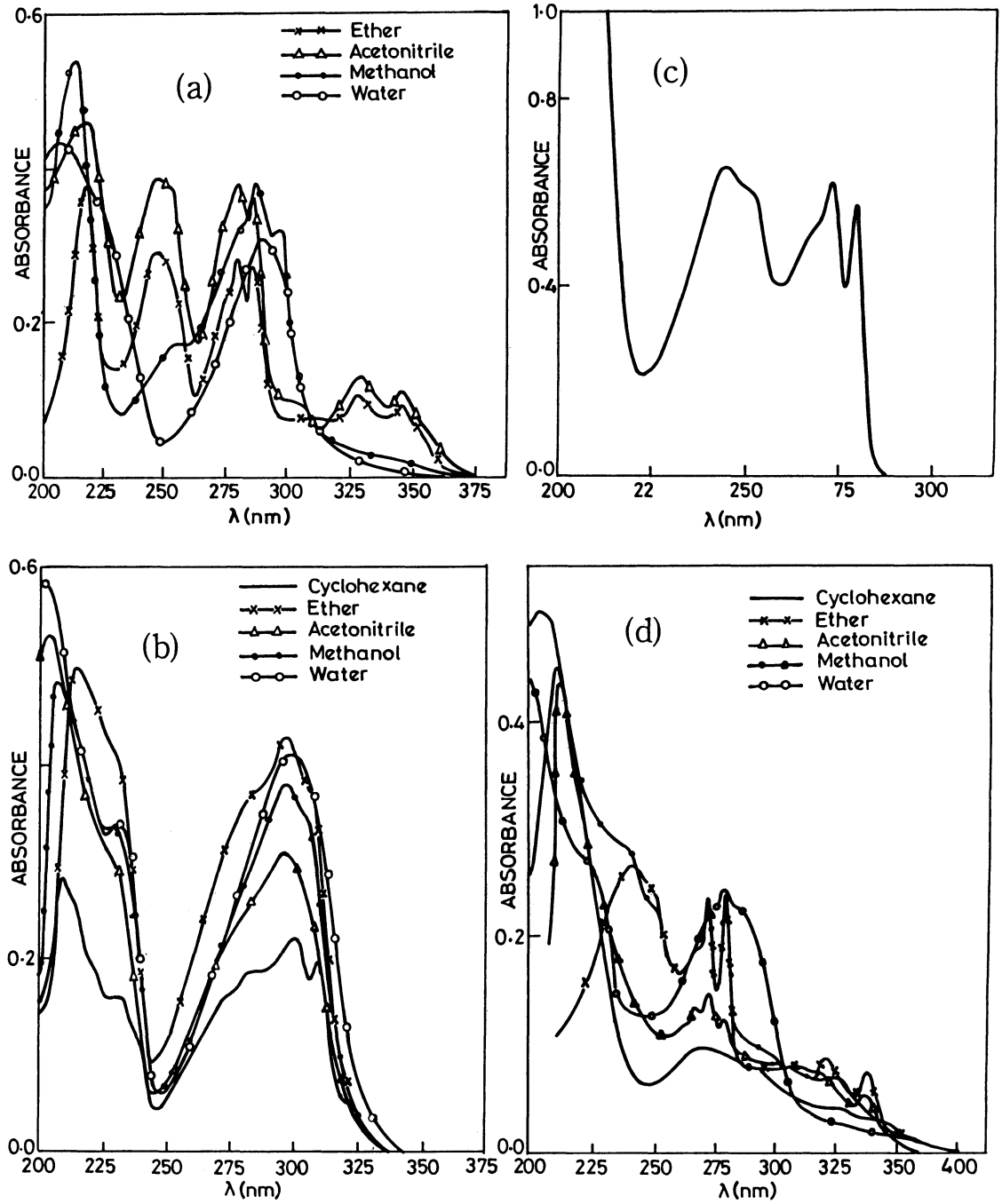

Fig. 1. Absorption spectra of (a) CBIA, (b) CBIM, (c) BI only in water and (d) BIA in different solvents at 298 K.

1 and 2. The absorption band maxima of all the three molecules are largely red-shifted as compared to BI.[34] Above 300 nm, the absorption band system of BIA and CBIA are nicely structured and weak with respect to other three band systems present below 300 nm, whereas in CBIM, this band system is broad and band maximum is close to 300 nm. The absorbance of this band system further decreases with the increase in polarity and hydrogen-bond-forming tendency of the solvents. The other band systems (ca. 280 nm, ca. 250 nm, and ca. 210 nm) are similar to BI. The absorption band maxima of all the band systems are nearly insensitive to the nature of the solvents.

Similar to the absorption spectra, the fluorescence spectra of BIA, CBIA, and CBIM are largely red-shifted as compared to BI.[34] The vibrational structure is observed in all the solvents with the exception of CBIM, where the vibrational structure is present only in cyclohexane. The vibrational frequencies observed in absorption and fluorescence spectra are the same i.e. 1100±50 cm^{-1} in CBIM and 1500±50 cm^{-1} in BIA and CBIA. Besides this, the fluorescence

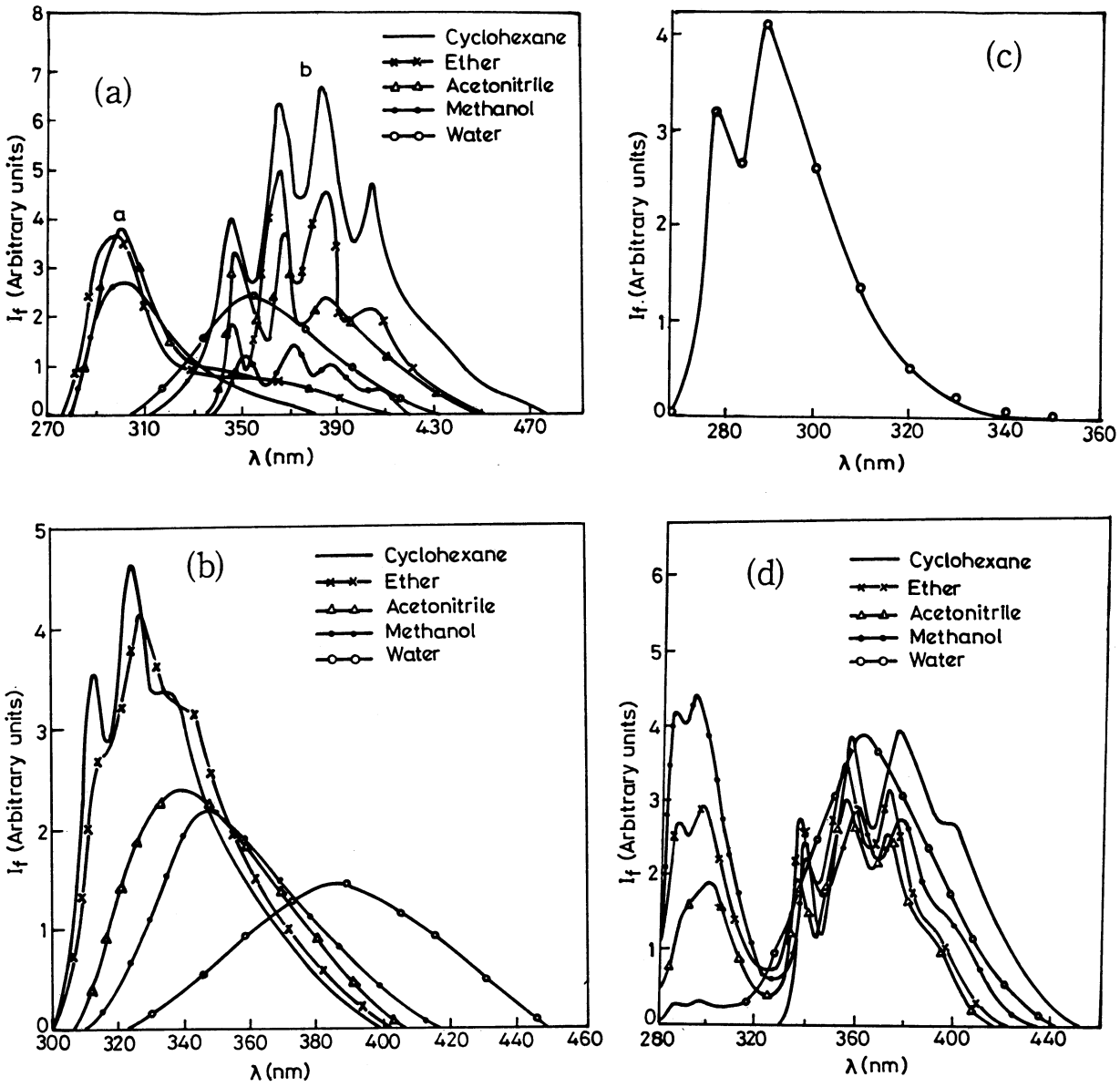

Fig. 2. Fluorescence spectra of (a) CBIA, (b) CBIM, (c) BI only in water and (d) BIA in different solvents at 298 K.

spectrum is not much separated from and makes mirror image with the absorption band.

Besides the structured long wavelength fluorescence (F_1), a second band system at ca. 300 nm is also observed in case of CBIA and BIA in all the solvents except cyclohexane. The excitation spectra recorded at 365 nm in all the solvents resemble the absorption spectra above 300 nm. However no useful information could be obtained from the excitation fluorescence spectra below 300 nm as the lamp intensity is very weak below 300 nm. Both the fluorescence band systems (F_1 and F_2) are hardly affected by varying the nature of solvents whereas that of CBIM shifts from 318 nm in cyclohexane to 390 nm in water.

Data of Tables 1 and 2 clearly indicate that the carboxyl group in these compounds is coplanar with the BI ring, both in the S_0 and S_1 states and hence extensive conjugation is observed. This behavior is similar to that observed in case of 4- and 5-indolecarboxylic acids[18,19] and different to many other carboxylic acids.[20,23,26,35] We suggest that the structured long wavelength absorption and fluorescence (F_1) from BIA and CBIA are due to the presence of intramolecularly hydrogen-bonded structure (**1**). This suggestion is based on the following facts. (i) The presence of intramolecular hydrogen bonding in BIA and CBIA leads to symmetrical structure. Presumably this will lead to the complete delocalization of π cloud

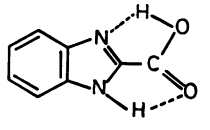

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Table 1. Absorption Maxima (λ_a/nm) and log ε_{max} of CIBIA, BIA, and CBIM in Various Solvents and at Different Hydrogen Ion Concentration at 298 K

Solvent	λ_a/nm (log ε_{max})											
	CBIA				BIA				CBIM			
Cyclohexane									322 310 300	284 271	231	210
Ether	357 344 327 305	286 280 275	254 247	216	338 321	279 274 266	250 242	209 204	— 307 298	281 271	231	216
Acetonitrile	357 344 327 305	286 280 275	254 247		337 320	279 274 266	250 242	212	— 307 298	281 271	231	216
Methanol	362 (2.00) 345 (2.36)	287 (3.88) 280 (3.81)	254 (3.55)	211 (4.15)	340 (2.21) 322 (2.35)	279 (3.90) 273 (3.83) 266 (3.51)	250 (3.62) 241 (3.69)	211 (4.10)	— 305 (3.93) 297 (3.96)	281 (3.83)	231 (3.40)	205 (4.04)
H_0—5 (Dication)		311 (3.55)	237 (3.38)	207 (3.44)		304 (3.60)	235 (3.52)	230 (3.53)		307 (3.69)	237 (3.55)	207 (3.64)
H_0—1 (Monocation)		297 (3.52)	232 (3.40)	—		293 (3.71) 275 (3.55)	232 (3.70)	229 (3.51)		302 (3.71)	235 (3.62)	207 (3.62)
pH 2 (Neutral)	—	291 (3.61)	—	227 (3.60)		285 (3.70) 273 (3.52)	—	222 (3.69)		300	232	
pH 8 (Monoanion)		289 (3.69)	260 (3.41)	202 (3.78)		281 (3.65) 278 (3.62) 271 (3.59)	—	222 (3.55)		308 (3.77)	—	212[a] (3.84)
H_-16 (Dianion)		299 (3.69)	—	226 (3.89)		295 (3.75)	—	224 (3.80)			—	

a) pH=12.

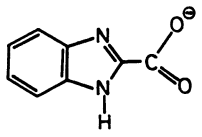
over the BI moiety and the -COOH group. This may result in small dipole moment. Because of this the effect of solvents on the spectral characteristics will be minimum. This is reflected by the data of Table 1. A similar behavior is also observed in case of bibenzimidazole.[36] Further the presence of five-menbered intramolecularly hydrogen-bonded structure in case of ninhydrin has been proposed by Dewar.[37] The same argument does not hold for CBIM, where the intramolecular hydrogen-bonding interaction with tertiary nitrogen atom is removed. Due to this, though the red shift is observed in the absorption spectrum of BI, it is not to that extent as noticed in case of BIA and CBIA. This is further manifested by the loss in the vibrational structure as well as the blue shift observed in the absorption spectrum of CBIM in polar and hydrogen-bonding solvents. This is due to the interaction of intermolecular hydrogen-bonding of the solvents with tertiary nitrogen atom and thus rotation of the -$COOCH_3$ group out of the plane of BI. (ii) The presence of long wavelength band due to the dimer formation (as observed in case of benzoic acid[38]) is rejected on the ground that the increase in the concentration of these acids does not affect the ratio of the absorbances of the two band system. Secondly, the observation of vibrational sturcture in such a loosely formed dimer is difficult to explain. (iii) The decrease in the absorbance of long wavelength absorption maxima in BIA and CBIA with increase in the proton donor/acceptor capacity of the solvents is due to the competition between the intra- and intermolecular hydrogen bonding and thereby shifting the equilibrium toward the open structure. The similar band system is also observed in the absorption spectrum of 2-(2-aminophenyl)benzimidazole,[12] which was broad and the ring formed due to intramolecular hydrogen bonding is a six member one. Observation of similar vibrational frequency in absorption and fluorescence spectra and the mirror image symmetry suggest that the molecular conjugation and the geometry of BIA and CBIA in S_1 state differ very little from that in S_0 state. The similar vibrational fre-

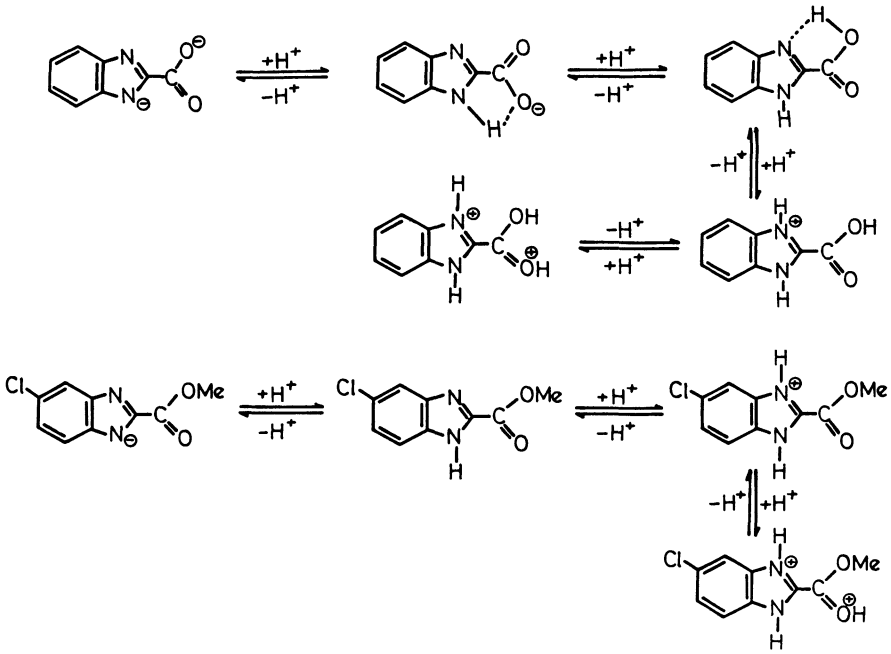
Table 2. Fluorescence Maxima (λ_f/nm) and Quantum Yield (Φ_f) of CBIA, BIA, and CBIM in Various Solvents and at Different Hydrogen Ion Concentration at 298 K

Solvent	$\lambda_f(\phi_f)$				
	CBIA		BIA		CBIM
Cyclohexane	405		400		335
	384(0.01)	—	377(0.09)	—	326(0.10)
	366		355		318
	346		339		
Ether	405		393(sh)	297	343(0.11)
	385(0.01)	300(0.03)	372(0.13)	287(0.08)	328
	366		355		316
	346		336		
Acetonitrile	—		393	300(0.02)	342(0.07)
	385	300(0.03)	372(0.12)	288	
	367(0.02)		355		
	347		336		
Methanol	—		404(sh)	294(0.11)	348(0.03)
	386(0.03)	303(0.02)	377(0.14)	285	
	368		358		
	349		339		
H_0—1 (Monocation)	410		410		410
pH 2 (Neutral)	380		392		390
pH 8 (Monoanion)	345		360		360
H–16 (Dianion)	350		365		—

quency (ca. 1500 cm^{-1}) is also observed in the specturm of other 2-substituted benzimidazoles where the structure is rigid, for example, 2-(4-aminophenyl)-[11] and 2-(4-hydroxyphenyl)benzimidazoles.[15] The insensitivity of the fluorescence spectra of BIA and CBIA towards the nature of the solvents further extablishes the existence of rigid and symmetric structure (**1**) in the S_1 state. Since similar symmetric structure is not possible in CBIM, the vibrational structure is lost in more polar and protic solvents. Unlike absorption spectrum, the large red shift observed in the fluorescence spectrum of CBIA confirms the existence of manifold degeneracy of the excited singlet states of BI.[4,17,39] Both these molecules (CBIA and CBIM) contain electron-donating (Cl atom) in the benzene ring and electron-withdrawing group (-COOH or -COOMe) in the imidazole ring and thus will favor the charge transfer state to be of lowest energy. Whereas the effect of solvents on the fluorescence spectra has indicated that the π^* is the lowest energy state in CBIA and CT in CBIM. The presence of intramolecular hydrogen-bonding perturbations in CBIA may be responsible for inhibition of charge transfer from benzene to the carboxyl group. The migration of the charge density from the benzene ring towards the carboxylic acid group is further manifested from the low pK_a value of the protonation reaction of tertiary nitrogen atom (see later).

The fluorescence (F_2) spectrum closely resembles with that of parent BI molecule[34] or the monocation of the derivatives of BI where the CT transition is absent.[4,17] This fluorescence band can be assigned to the conformer where the -COOH group and BI ring are not coplanar (open strucure). Since only one fluorescence band (F_1) is observed in cyclohexane, it suggests that the open conformer is due to the competition between the intra- and intermolecular hydrogen bonding in polar and protic solvents. The following arguments can be given for rejecting the other possibility. (i) pK_a's of aromatic acids are close to 4,[40] whereas the pK_a for the protonation of tertiary nitrogen atom of BI is 5.53.[3] One can speculate the formation of zwitterion (**5**), with the carboxylato group perpendicular to the BI, both in S_0 and S_1 states. (ii) In our earlier paper,[39] it has been reported that the presence of strong electron-withdrawing groups (-CF_3, -CCl_3) at the 2-position decreases the pK_a value for the protonation reaction of the tertiary nitrogen atom to as low as ca. 1.0. In the present case, it is also expected that the pK_a for the same reaction of BIA and CBIA will also be low (ca. 0.5 see later). This is further confirmed by the similar value of pK_a (0.3) obtained for the prototropic reaction of CBIM, where the formation of zwitterion is not possible in this range of pH. (iii) The aromatic carboxylic acids are also stronger acids in nonpolar solvents as compared





Scheme 1. Various prototropic reactions of CBIA and CBIM in the ground and excited singlet states.

to that in aqueous medium. Complete absence of F_2 in cyclohexane rejects the possibility of a zwitterion.

Effect of Acid Concentration. The absorption and fluorescence spectral data of BIA, CBIA, and CBIM at various acid concentrations are compiled in Tables 1 and 2 respectively. Scheme 1 represents the various prototropic species of BIA and CBIM identified in the H_0/pH/H_- range of −10 to 16.

CBIM. At the extreme acid conditions, the species is a dication formed by protonating the carbonyl group and tertiary nitrogen atom. With decrease of acid concentration a blue-shift, blue-shift and red-shift observed in the absorption spectra of the dication of CBIM is consistent with the deprotonation of $-C\overset{OMe}{\underset{OH^+}{<}}$, $>\overset{+}{N}$-H and >N-H groups respectively. The species formed are monocation, neutral and monoanion and the changes observed in the absorption spectra are consistent with the deprotonation reactions of various groups. On the other hand, dication is non-fluorescent, but the fluorescence specturm of monocation is blue-shifted, followed by a further blue shift under the above environments. The latter one is unusual because the deprotonation of >N-H group leads to red shift in the fluorescence spectrum of neutral species, as noticed in the absorption spectrum. This can be explained as follows. As said earlier, the lowest energy first excited singlet state of neutral CBIM is CT in character, because of the flow of charge from benzene ring to carboxyl group. In monoanion the presence of negative charge on $>N^-$ will inhibit the flow of charge towards the electron-withdrawing group and thus CT state will be destabilized. Similar behavior is also observed when strong electron-withdrawing groups ($-CF_3$, $-CCl_3$) are present at position-2.[39]

Table 3. pK_a and pK_a* of Various Prototropic Reactions of BIA, CBIA, and CBIM at 298 K

Equilibrium	pK_a*		
	pK_a	Abs	Flu
BIA			
Dication ⇌ Monocation	−5.0	−2.4	—
Monocation ⇌ Neutral	0.4	2.4	2.8
Neutral ⇌ Monoanion	4.8	5.9	9.6
Monoanion ⇌ Dianion	13.1	9.6	12.3
CBIA			
Dication ⇌ Monocation	−4.9	−1.7	—
Monocation ⇌ Neutral	0.0	1.1	4.1
Neutral ⇌ Monoanion	4.3	4.8	9.8
Monoanion ⇌ Dianion	12.7	10.2	11.8
CBIM			
Dication ⇌ Monocation	−4.4	−3.2	—
Monocation ⇌ Neutral	0.3	0.8	2.9
Neutral ⇌ Monoanin	9.6	7.8	—

The pK_a values for the various prototropic reactions in S_0 state are calculated by using absorption spectral data and the values are listed in Table 3. The pK_a's for the monocation-neutral and neutral-monoanion equilibria are quite low as compared to those for BI (5.53[18] and 13.35).[41] This is because of the presence of electron-withdrawing -COOMe group, which decreases the charge densities at the tertiary nitrogen atom and the imino group. The pK_a values in the S_1 state are determined by using Forster cycle method[42] (whereever possible) and the fluorimetric titrations. The pK_a values for all the prototropic equilibria, determined from the fluorometric titrations agree

nicely with the pK_a values for the similar reactions in the ground state. This indicates that prototropic equilibria are not established in the S_1 state and could be due to the shorter lifetimes of the conjugate acid-base pairs. A similar behavior is observed in the protonation and deprotonation reactions of benzimidazoles.[17,39] Spectral changes do establish that the carbonyl group and tertiary nitrogen atom become stronger bases and >N-H becomes stronger acid on excitation to S_1 state.

BIA and CBIA. The nature of prototropic species formed in S_0 and S_1 states of BIA and CBIA in the H_0/pH/H_- range of −10 to 16 are the same i.e. in S_0 and S_1 states, dication, H_0 −2; monocation, H_0 −2 to pH 2; neutral, pH 2 to 4; monoanion, pH 4 to 11 and dianion, pH>11. This is also similar to the behavior of CBIM under the similar environments, with the following exceptions. (i) Monoanions in case of BIA and CBIA are formed by the deprotonation of -COOH group, as CBIM does not possess dissociated proton at pH≈4. pK_a for the neutal-monoanion equilibrium is consistent with the earlier results of carboxyl group.[43] (ii) A normal small red shift is observed in the absorption and fluorescence spectra when >NH group is deprotonated. This is because π^* state is the lowest excited singlet state in the monoanion and dianion of BIA and CBIA as compared to CBIM where CT is the lowest excited singlet state for the neutral and π^* is that for the monoanion. (iii) The pK_a value for the monoanion-dianion equilibrium (i.e. deprotonation of >N-H) of BIA (13.1) and CBIA (12.7) is higher than that for the CBIM (9.9). This could be due to the intramolecular hydrogen bond formed between the carboxylato group and the imino proton. A similar behavior is also observed in case of 2-(2-hydroxyphenyl)benzimidazole.[14]

Various prototropic reactions taking place in the complete range of −10 to 16 are depicted in the Scheme 1 and the pK_a values are compiled in Table 3.

Conclusion

The following conclusions can be arrived at from the above study: (i) The -COOH group in S_0 and S_1 states are coplanar with the BI moiety of CBIA and BIA. The -COOMe group of CBIM is better coplanar with the BI moiety in S_1 than S_0 state. (ii) Two conformers, one cyclic rigid and the other open structure, are present in case of BIA and CBIA. The latter is more favorable in the polar solvents. (iii) Charge transfer state is the emitting state in CBIM neutral species but π^* is the emitting state of monoanion of CBIM. In case of BIA and CBIA, the lowest excited state is of π^* character. (iv) The electron-withdrawing nature of -COOH/-COOMe group reduces the charge densities at the tertiary nitrogen atom and the imino group. This decreases the pK_a values for the protonation and deprotonation reactions.

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References

1) R. Brnnet, *Chem. Rev.*, **63**, 573 (1963).
2) J. H. Lister, "Fused Pyrimidines," Part II, Wiley Interscience, New York (1971).
3) P. N. Preston, "Benzimidazoles and Congeneric Tricyclic Compounds," Wiley Interscience, New York (1981), p. 60.
4) P. C. Tway and L. J. Clinelove, *J. Phys. Chem.*, **86**, 5223, 5227 (1982).
5) M. Kondo and H. Kuwano, *Bull. Chem. Soc. Jpn.*, **42**, 1433, 5223 (1969).
6) M. Swaminathan and S. K. Dogra, *Indian J. Chem., Sect. A*, **22**, 407 (1983).
7) A. K. Mishra and S. K. Dogra, *Spectrochim. Acta, Part A*, **39**, 609 (1983).
8) A. K. Mishra and S. K. Dogra, *J. Photochem.*, **29**, 435 (1985).
9) A. K. Mishra and S. K. Dogra, *Indian J. Phys.*, **58B**, 480 (1984).
10) A. K. Mishra and S. K. Dogra, *Indian J. Chem., Sect. A*, **24**, 364, 815 (1985).
11) A. K. Mishra and S. K. Dogra, *Bull. Chem. Soc. Jpn.*, **58**, 3587 (1985).
12) A. K. Mishra and S. K. Dogra, *J. Photochem.*, **31**, 333 (1985).
13) H. K. Sinha and S. K. Dogra, *Spectrochim. Acta, Part A*, **41**, 961 (1985).
14) H. K. Sinha and S. K. Dogra, *Chem. Phys.*, **102**, 337 (1986).
15) H. K. Sinha and S. K. Dogra, *J. Photochem.*, **36**, 149 (1987).
16) H. K. Sinha and S. K. Dogra, *Indian J. Chem., Sect. A*, **25**, 1092 (1986).
17) M. Krishnamurthy, P. Phaniraj, and S. K. Dogra, *J. Chem. Soc., Perkin Trans. 2*, **1986**, 1971 and references listed therein.
18) M. Krishnamurthy, A. K. Mishra, and S. K. Dogra, *Photochem. Photobiol.*, **45**, 359 (1987).
19) M. Krishnamurthy, H. K. Sinha, and S. K. Dogra, *J. Lumin.*, **35**, 343 (1986).
20) P. J. Kovi and S. G. Schulman, *Anal. Chim. Acta*, **63**, 39 (1973).
21) J. J. Aaron, A. Tine, M. E. Wojciechowska, and C. Parkanyi, *J. Lumin.*, **33**, 33 (1985).
22) P. S. Song and W. E. Kurtin, *J. Am. Chem. Soc.*, **91**, 4982 (1969).
23) T. C. Werner and D. M. Hercules, *J. Phys. Chem.*, **73**, 2005 (1969).
24) T. C. Werner and D. M. Hercules, *J. Phys. Chem.*, **74**, 1030 (1970).
25) R. Manoharan and S. K. Dogra, *Spectrochim. Acta, Part A*, **43**, 91 (1987).
26) P. J. Kovi, C. L. Miller, and S. G. Schulman, *Anal. Chim. Acta*, **63**, 39 (1973).
27) P. J. Kovi, C. L. Miller, and S. G. Schulman, *Anal.*

Chim. Acta, **62**, 59 (1972).
28) C. Holan, E. L. Samlel, B. C. Ennis, and R. W. Hind, *J. Chem. Soc. C*, **1967**, 20.
29) M. Swaminathan and S. K. Dogra, *Indian J. Chem., Sect. A*, **22**, 853 (1983).
30) R. Manoharan and S. K. Dogra, *Can. J. Chem.*, **65**, 2013 (1987).
31) R. Manoharan and S. K. Dogra, *J. Photochem. Photobiol. A*, **43**, 81 (1988).
32) R. Manoharan and S. K. Dogra, *Bull. Chem. Soc. Jpn.*, **60**, 4409 (1987).
33) R. Manoharan and S. K. Dogra, *J. Phys. Chem.*, **92**, 5282 (1988).
34) H. C. Borresen, *Acta Chem. Scand.*, **17**, 921 (1963).
35) R. Manoharan and S. K. Dogra, *J. Photochem. Photobiol. A*, **43**, 119 (1988).
36) A. Kumar, H. K. Sinha, and S. K. Dogra, *Can. J. Chem.*, in press.
37) M. J. S. Dewar, *Nature (London)*, **155**, 50, 499 (1945).
38) J. C. Banm and D. S. McClure, *J. Am. Chem. Soc.*, **102**, 720 (1980).
39) H. K. Sinha and S. K. Dogra, *J. Chem. Soc., Perkin Trans. 2*, **1987** 1465.
40) J. F. Ireland and P. A. H. Wyatt, *Adv. Phys. Org. Chem.*, **12**, 159 (1976).
41) C. A. Bunton, L. S. Romsted, and L. Sepulveda, *J. Phys. Chem.*, **84**, 2611 (1980).
42) Th. Forster, *Z. Elektrochem.*, **54**, 50, 531 (1950).
43) J. March, "Advanced Organic Chemistry," Wiley Interscience, New York (1986), p. 230.