

## Absorption and fluorescence characteristics of some 2-alkyl- and 2-aryl-benzoxazoles in different solvents and at various acid concentrations

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Absorption and fluorescence spectral characteristics of some 2-alkyl- and 2-aryl-benzoxazoles have been studied in different solvents and at various acid concentrations. Dual fluorescence observed in the monocations of 2-alkylbenzoxazoles is due to  $\pi^* \rightarrow \pi$  and charge transfer (CT) transitions, indicating the near degeneracy of excited singlet states. 2-Arylbenzoxazoles and the corresponding monocations exhibit only a single fluorescence band due to  $\pi^* \rightarrow \pi$  transition.  $pK_a$  values for the monocation-neutral equilibria in both  $S_0$  and  $S_1$  states of the molecules have been determined. Pariser-Parr-Pople method for all the molecules and CNDO/S method for 2-methyl-, and 2-phenylbenzoxazoles have been employed to calculate transition energies, transition polarization and charge densities at different atoms in the  $S_0$  and  $S_1$  states to substantiate experimental data and, hence, to verify the applicability of the methods for heterocycles containing two hetero atoms.

The importance of benzoxazole derivatives due to their use as chelating agents<sup>1</sup>, pesticides<sup>2</sup> and laser materials<sup>3</sup> in UV and visible regions as well as their therapeutic properties has led to extensive studies on these molecules. With the recent advent of studies on the excited state intramolecular proton transfer reactions 2-(2'-hydroxyphenyl)benzoxazole has been investigated extensively<sup>5</sup>. But a systematic study on the spectral characteristics of 2-substituted benzoxazoles has not received much attention except for a few sporadic attempts. Passerini<sup>6</sup> and Reiser *et al.*<sup>7</sup> have suggested that the long wavelength absorption band in 2-alkylbenzoxazoles is of  $\pi \rightarrow \pi^*$  type and is localized on the benzene ring, whereas in 2-phenylbenzoxazole, this  $\pi \rightarrow \pi^*$  band is localized on the substituent phenyl ring<sup>6-9</sup>. Earlier studies on benzimidazoles have also led to the same observations<sup>10,11</sup>. Moreover, monocations of 2-alkylbenzimidazoles exhibit dual fluorescence of which the longest wavelength band is ascribed to charge transfer (CT) transition and the short wavelength band to the normal  $\pi^* \rightarrow \pi$  transition<sup>10-12</sup>. Fluorescence spectrum of 2-phenylbenzimidazole and quantum yield indicate that the phenyl ring is coplanar with the imidazole ring both in the  $S_0$  and  $S_1$  states<sup>13</sup>. Benzoxazole being similar to benzimidazole (differing only in one of the hetero atoms), the same sort of spectral characteristics are expected for the former also.

SCF-LCAO-MO and Pariser-Parr<sup>14</sup>-Pople<sup>15</sup> (PPP), and CNDO/S<sup>16,17</sup> methods have been quite

successful in calculating electronic transition energies in many heterocycles containing one or two hetero atoms as well as benzoxazole and benzisoxazole<sup>18</sup>. However, no attempt has been made to verify the applicability of PPP and CNDO/S methods for bigger molecules like 2-alkyl- and 2-aryl-benzoxazoles.

The present study on 2-alkyl- and 2-arylbenzoxazoles has been carried out to investigate: (i) the nature of transitions and their polarizations involved in the neutral and monocation species, (ii) the geometry of the aryl group relative to the benzoxazole moiety in the  $S_0$  and  $S_1$  states, (iii) the variation in basicity of the nitrogen centre in going from 2-alkylbenzoxazole to 2-arylbenzoxazole and also with excitation, and (iv) the transition energies and charge densities at different atoms.

### Materials and Methods

Benzoxazole (BO), 2-methylbenzoxazole (MBO), 2,5-dimethylbenzoxazole (DMBO), 2-methyl-5-phenylbenzoxazole (MPBO) and 2-(4'-biphenyl)-6-phenylbenzoxazole (BPPBO) were procured from Aldrich Chemical Company (UK). 2-Phenylbenzoxazole (PBO), 2-(2'-methylphenyl)benzoxazole (OMPBO), 2-(3'-methylphenyl)benzoxazole (MMPBO) and 2-(4'-methylphenyl)benzoxazole (PMPBO) were prepared by the procedure suggested in the literature<sup>17</sup>. BO, MBO and DMBO were used as such. The other compounds, except BPPBO which was recrystallized from chloro-

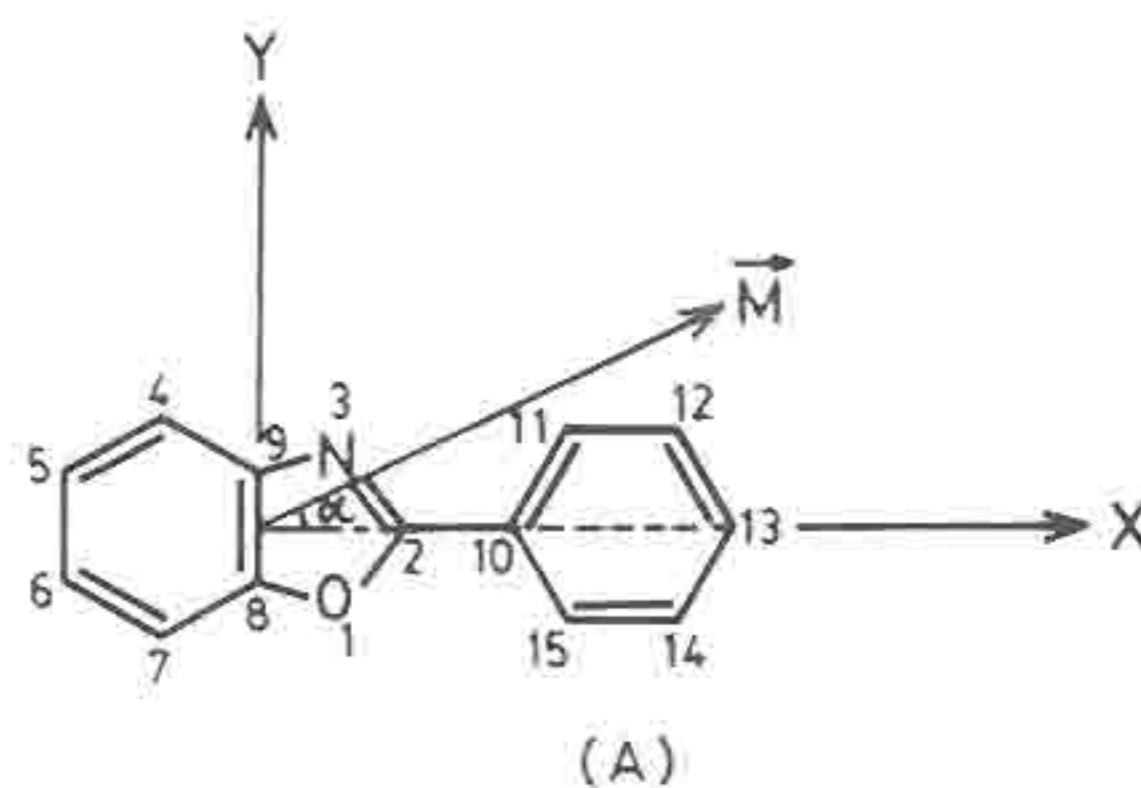


form-methanol mixture, were purified by repeated crystallizations from ethanol-water mixture. Purity of the compounds was checked on the basis of their melting points, absorption and excitation spectra and fluorescence spectra at different excitation wavelengths. Analytical reagent grade cyclohexane (SDS), dioxane (E. Merck), acetonitrile (E. Merck) and methanol (BDH) were purified as described in literature<sup>20</sup>. Triply distilled water was used for preparing aqueous solutions. Aqueous solutions having pHs in range 4-11 were prepared by mixing appropriate amounts of ortho-phosphoric acid and sodium hydroxide solutions. Modified Hammett's acidity scale<sup>21</sup> for H<sub>2</sub>SO<sub>4</sub>-water mixtures and Yagil's basicity scale<sup>22</sup> for NaOH-water mixtures were used for the solutions with pH < 1 and pH > 13 respectively.

Absorption spectra were recorded on a Shimadzu 190 UV spectrophotometer, equipped with a U135 chart recorder. Fluorescence measurements were carried out with the scanning spectrofluorimeter, fabricated in our laboratory, the details of which are reported elsewhere<sup>23</sup>. Fluorescence spectra were corrected according to the procedure of Parker<sup>24</sup> and the quantum yields were measured for the solutions having absorbances less than 0.1 using quinine sulphate<sup>25</sup> in 0.1N H<sub>2</sub>SO<sub>4</sub> as standard ( $\phi = 0.55$ ). pHs of the solutions were measured by a Toshniwal pH meter model CL44A. Concentrations of the solutions were of the order  $\sim 10^{-5}M$ , the methanol content was not more than 0.6% (v/v), except for BPPBO where it was  $\sim 10^{-6}M$ , dioxane content was 0.8% (v/v). Even at such low concentration, BPPBO was insoluble in 20% ethanol-water mixture (v/v) and thus it was impossible to find the  $pK_a$  for the monocation-neutral equilibrium either in  $S_0$  or in  $S_1$  state. To avoid hydrolysis<sup>26</sup>, the solutions were prepared just before taking measurements. No changes in the absorption spectra were observed at the end of the experiment. For fluorimetric titrations the solutions were excited at the wavelengths of isosbestic points which are 275, 278, 280, 292, 285 and 290 nm for MBO, DMBO, MPBO, PBO, OMPBO, MMPBO and PMPBO respectively. For quantum yield calculations, the wavelengths of excitation used were taken as the  $\lambda_{max}$  of the long wavelength absorption band.

The program used for Pariser-Parr-Pople (PPP)<sup>14,15</sup> calculations was obtained from QCPE, Indiana University, Bloomington. Due to lack of sufficient experimental data, molecular geometries of all these molecules were approximated as a regular hexagon bonded to a regular pentagon with

a bond length of 1.395 Å. The parameters required for the calculations were taken from literature<sup>16,17,27a</sup>. The coordinate system chosen is as shown below in structure A. The relevant data are compiled in Tables 1 and 2.



The closed shell spectroscopic CNDO/S molecular program of DelBene and Jaffe<sup>16</sup>, as developed by Ellis *et al*<sup>27b</sup>, was used for the study. The excited states were generated from the occupied ground state and virtual orbitals through the application of configuration interaction procedure among the twenty lowest singly excited states. The excited state electron densities were calculated using the equation,

$$\rho_{JA}^* = \rho_A^0 + \sum_m \sum_{\mu}^{CI} C_{jm}^2 (C_{\mu j}^2 - C_{\mu i}^2)$$

where  $\rho_A^0$  is the ground state electron density on atom A and  $C_{jm}$  is the coefficient of the mth configuration contributing to the jth state;  $C_{\mu j}$  and  $C_{\mu i}$  are the orbital coefficients of the final and initial MOs involved in the mth configuration. CNDO/S calculations have been carried out only on two molecules, i.e., MBO and PBO as representatives of the class of molecules to which they belong. The relevant data have been compiled in Table 3.

## Results and Discussion

### Effect of solvents

The absorption and fluorescence spectral data collected in Table 4 show that the spectra of BO and MBO are nearly similar, whereas the spectra of DMBO are red-shifted compared to that of BO. The absorption as well as the fluorescence spectra of these molecules remain unaffected with the change in polarity and proton donor ability of the solvents except the loss of vibrational structure as observed in cyclohexane. The fluorescence quantum yields for BO, MBO, DMBO and MPBO are very small. Though the fluorescence intensity decreases with increase in solvent polarity, the fluorescent quantum yield could not be calculated accurately because of the limitation of



Table 1 – Electronic transitions, ground and excited state charge densities at nitrogen and oxygen atoms of BO, MBO, DMBO, MPBO and BI

Compound	Transitions (nm)		$\alpha(^{\circ})\dagger$	Electron density			
	Obs.††	Calc.		N	N*	O	O*
BO	277	286	219	1.185	1.192	1.817	1.804
	270	—	—				
	263	254	343				
MBO	277	286	181	1.224	1.211	1.826	1.812
	271	—	—				
	264	259	346				
DMBO	284	290	208	1.225	1.225	1.826	1.817
	278	—	—				
		258.6	346				
MPBO	290	277	163	1.224	1.204	1.825	1.830
	279	269	336				
	255	260	173				
		254	345				
BI	278	278	—	1.497	1.312	—	—
	271	243	—				
PBI	317	293.5	350	1.331	1.351		
	308	269.9	241				
	302.5	252.5	278				
	295,291						

†  $\alpha(^{\circ})$  is the angle (in degree) of transition moment with the positive direction of X-axis.

†† In cyclohexane.

the instrument. The absorption (Table 5) and fluorescence (Table 6) characteristics of OMPBO, MMPBO and PMPBO resemble those of PBO. In PBO, the long wavelength absorption and fluorescence bands are structured and more red-shifted than those in 2-alkylbenzoxazoles. On the other hand, the absorption and fluorescence spectra of BPPBO (Tables 5 and 6) are quite different from those of PBO in the sense that the long wavelength absorption band is highly red-shifted. All these arylbenzoxazoles exhibit a blue shift in the long wavelength absorption band with the increase in polarity and hydrogen bond forming tendency of the solvents. Unlike absorption spectra, the fluorescence spectra of 2-arylbenzoxazoles show a red shift with the increase in solvent polarity. The fluorescence quantum yield of 2-arylbenzoxazoles is very high ( $\sim 0.8$ ) and it is still higher in BPPBO ( $\sim 1.0$ ).

The molecular structure of benzoxazoles indicates the possibility of three types of transitions,

viz., (i)  $n \rightarrow \pi^*$ , (ii)  $\pi \rightarrow \pi^*$  and (iii) charge transfer (CT). Although the fluorescence quantum yield of 2-alkylbenzoxazoles is quite low, the large molar extinction coefficient ( $\epsilon$ ), high fluorescence quantum yield of arylbenzoxazoles, small Stokes shift, and the less dependence of absorption and fluorescence spectra on the solvent polarity clearly suggest that the long wavelength transition in benzoxazoles is of  $\pi \rightarrow \pi^*$  type. Data in Tables 1-3 also clearly indicate that all the transitions involved in the molecules studied are of  $\pi \rightarrow \pi^*$ .

It can be seen from the data of Table 3 that although all the HOMOs involved in the longest wavelength transition are not rigorously localised on the benzene ring, most of them are almost entirely confined to it. Similar is the case of LUMO involved in this transition. This also agrees with the earlier results on BO which show that the long wavelength transition is localised primarily on benzene ring<sup>27,28</sup>. The only major difference between the PPP and CNDO/S calculations is the



Table 2 – Electronic transitions, ground and excited state charge densities at nitrogen and oxygen atoms of PBO, OMPBO, MMPBO, PMPBO

Compound	Transitions (nm)		$\alpha(^{\circ})\dagger$	Electron density			
	Obs.	Calc.		N	N*	O	O*
PBO	313	302.7	353	1.190	1.190	1.822	1.86
	299	262.8	285				
	291.5	259.3	256				
	286.5						
OMPBO	313	307	356	1.199	1.195	1.822	1.86
	299.5	268	119				
	292.5	258	253				
	288.0						
MMPBO	314	302	353	1.19	1.192	1.822	1.86
	299.5	264.8	333				
	292.5	258.9	264				
	287.5						
PMPBO	315	306.8	353	1.195	1.204	1.823	1.856
	301	261	260				
	294	243	88				
	289						
BPPBO	326	347.8	354	0.869	0.987	1.822	1.856
	287	272.9	244				
		245.9	146				

Table 3 – Electronic transitions, ground and excited state charge densities of nitrogen and oxygen atoms of MBO and PBO calculated by CNDO/S

Molecule	Orbital promotion	$\lambda$ (nm)	$\alpha^{(0)}$	Charge density				Index of atoms on which MO's are localized	
				$S_0$ state		$S_1$ state		Initial MO	Final MO
				O <sub>1</sub>	N <sub>3</sub>	O <sub>1</sub>	N <sub>3</sub>		
MBO	$\pi \rightarrow \pi^*$	288	344	-0.106	-0.233	-0.130	-0.197	1,4,5,7,8	2,3,4,6,7
	$\pi \rightarrow \pi^*$	258	352					2,3,4,6,8,9	2,3,4,6,7
	$\pi \rightarrow \pi^*$	223	310					2,3,4,6,8,9	4,5,7,8
PBO	$\pi \rightarrow \pi^*$	320	355	-0.114	-0.222	-0.079	-0.263	2,3,4,6,8,9	2,3,10,11,13,15
	$\pi \rightarrow \pi^*$	283	340					11,12,14,15	2,3,10,11,13,15
	$\pi \rightarrow \pi^*$	275	96					1,3,4,5,6,7,8	2,3,10,11,13,15
	$\pi \rightarrow \pi^*$	242	73.4					2,3,4,6,8,9	delocalized

direction of transition moments in 2-alkylbenzoxazoles. In the former case it is towards the benzene ring, whereas in the latter case it is towards the oxazole ring. The difference could be because of the inclusion of sigma orbitals in CNDO/S calculations; otherwise, this difference is difficult to explain. The similar spectral behaviour of BO and

MBO and the red shift observed for DMBO and MPBO compared to BO also suggest that this transition is localized on the benzene ring. This view is further supported by the vibrational structure observed in the vapour phase fluorescence spectra of BO, benzimidazole (BI) and benzothiazole (BT)<sup>28</sup>. A similar structure is also observed

Table 4 – Absorption maxima [ $\lambda_a$ /nm ( $\log \epsilon^a$ )] and fluorescence maxima [ $\lambda_f$ /nm ( $\phi_f$ )] of benzoxazoles at 298

Solvent	BO		MBO		DMBO		MPBO	
	$\lambda_a$ ( $\log \epsilon$ )	$\lambda_f$ ( $\phi_f$ )	$\lambda_a$ ( $\log \epsilon$ )	$\lambda_f$ ( $\phi_f$ )	$\lambda_a$ ( $\log \epsilon$ )	$\lambda_f$ ( $\phi_f$ )	$\lambda_a$ ( $\log \epsilon$ )	$\lambda_f$ ( $\phi_f$ )
Cyclohexane	277 (3.49)	<u>295</u>	277 (3.93)	<u>295</u>	284 (3.63)	300	290	<u>320</u>
	270 (3.50)	287	271 (3.92)	287	278 (3.61)	<u>293</u>	279 (3.60)	310
	263 (3.33)	(0.001)	264 sh	(0.001)	274	(0.004)	255	(0.065)
	230 (3.84)		232 (4.30)		234 (3.98)		228 (4.48)	
Dioxane	276.5 (3.19)	<u>295</u>	277 (3.89)	290	284 (3.63)	304	290	<u>320</u>
	270 (3.24)	287	270 (3.89)		278 (3.62)	<u>293</u>	279 (3.80)	310
	263 (3.09)	(0.001)	265 sh	(0.001)	— —	(0.003)	255	(0.064)
	231 (3.58)		232 (4.29)		234 (4.04)		229 (4.59)	
Acetonitrile	275.5 (3.29)	<u>295</u>	276 (3.90)	290	284 (3.62)	293	290	<u>320</u>
	269 (3.32)	287	270 (3.89)		277 (3.62)	(0.002)	279 (3.71)	310
	263 (3.17)	(0.001)	264 sh	(0.001)	—		255	(0.063)
	229 (3.71)		231 (4.29)		234 (3.99)		228 (4.50)	
Methanol	275.5 (3.46)	<u>295</u>	275 (3.97)	295	284 (3.64)	300	290	<u>320</u>
	269 (3.49)	287	269 (4.00)	(0.001)	277 (3.64)	(0.001)	279 (3.69)	310
	262.5 (3.34)	(0.001)	263 sh		— —		255	(0.064)
	230 (3.86)		229 (4.20)		233 (3.99)		227 (4.46)	
Water (pH 6)	275 (3.38)		275	<u>295</u>	283	<u>305</u>	290	<u>320</u>
	268.5 (3.45)	—	269		276	(0.0002)	279	(0.029)
	262 (3.31)		—		—		255	
	230 (3.83)		230		233		227	
Monocation $H_0$ -3	280	<u>420</u>	274 (3.60)	<u>410</u>	276 (3.67)	<u>420</u>	290 (3.85)	<u>470</u>
	232	<u>295</u>	267 (3.69)	<u>300</u>	—		—	<u>330</u>
			237 sh		240 sh	<u>308</u>	236 (4.41)	
			216		225 (3.70)			
$H_0$ -10.4	—		268	410	277 (3.68)	420	283 (4.15)	<u>410</u>
			228		228 (3.69)		—	
						242 (4.41)		



Table 5 – Absorption maxima (nm) and  $\log \epsilon_{\max}$  of the various benzoxazoles in different solvents and at different acid concentrations

Solvent/Species	PBO		OMPBO		MMPBO		PMPBO		BPPBO	
	$\lambda_{\max}$	$\log \epsilon_{\max}$	$\lambda_{\max}$	$\log \epsilon_{\max}$	$\lambda_{\max}$	$\log \epsilon_{\max}$	$\lambda_{\max}$	$\log \epsilon_{\max}$	$\lambda_{\max}$	$\log \epsilon_{\max}$
Cyclohexane	313	4.23	313	4.10	314	—	315	4.23	<u>326</u>	4.79
	<u>299</u>	4.45	<u>300</u>	4.36	<u>300</u>	4.44	<u>301</u>	4.49	287	—
	291	4.38	293	4.33	293	4.38	294	4.44		
	286	4.36	288	4.32	288	4.36	289	4.42		
Dioxane	313	4.20	312	—	314	4.16	316	4.18	<u>329</u>	4.95
	<u>299</u>	4.46	<u>299</u>	4.32	<u>300</u>	4.42	<u>302</u>	4.47	290	—
	292	4.43	292	4.32	293	4.39	295	4.43		
			274	—	239	3.85	290	s		
Acetonitrile	310	s	<u>297</u>	4.33	<u>298</u>	4.42	313	4.20	<u>326</u>	4.81
	<u>297</u>	4.38	291	4.34	291	4.40	<u>300</u>	4.50	287	—
	290	4.35	274	—	—	—	293	4.47		
					238	3.85	239	3.89		
Methanol	<u>298</u>	4.31	297	4.31	<u>299</u>	4.38	<u>300</u>	4.47	<u>326</u>	4.59
	291	4.30	<u>290</u>	4.32	292	4.37	—	—	287	—
			274	—	239	3.82	240	3.89		
Water (pH 6.1)	297		289		290		293		362	
	<u>292</u>	—		—		—		—	<u>337</u>	—
	238								304	
Monocation ( $H_0-3$ )	306	4.40	304	4.30	306	4.39	312	4.54	355	—
	248	3.92	248	3.83	247	3.85	252	3.94	248	
$H_0-10.4$	—	—	—	—	—	—	—	—	350	—
									277	
									257	

Table 6 – Fluorescence maxima ( $\lambda_f$ , nm) and quantum yields ( $\phi_f$ ) of 2-arylbenzoxazoles in different solvents and at various acid concentrations

Solvent/Species	PBO		OMPBO		MMPBO		PMPBO		BPPBO	
	$\lambda_f$	$\phi_f$	$\lambda_f$	$\phi_f$	$\lambda_f$	$\phi_f$	$\lambda_f$	$\phi_f$	$\lambda_f$	$\phi_f$
Cyclohexane	317	0.81	317	0.60	318	0.90	317	0.90	360	0.98
	<u>333</u>		<u>333</u>		<u>332</u>		<u>337</u>		380	
	348		347		350		348		400	
	366		360		365		364		420	
Dioxane	320	0.80	325	0.61	320	0.91	322	0.95	370	0.74
	<u>335</u>		<u>337</u>		<u>337</u>		<u>337</u>		<u>385</u>	
	350		350		350		350		400	
	365						365		430	
Acetonitrile	320	0.79	325	0.58	320	0.87	320	0.90	390	0.80
	<u>335</u>		<u>340</u>		<u>335</u>		338			
	350		350		350		350			
Methanol	322	0.78	340	0.60	320	0.88	320	0.95	390	0.79
	335				<u>337</u>		<u>337</u>			
	<u>350</u>				350		350			
							365			
Water	360	0.78	365	0.54	360	0.86	345	0.92	385	—
							<u>360</u>		<u>410</u>	
									425	
Monocation	385	1.00	390	1.00	390	0.76	390	0.54	460	—
$H_0$ -10.4	390	—	390	—	390	—	390	—	430	—

in the spectra of 2-alkylbenzoxazoles in nonpolar solvents. The shorter wavelength band in alkylbenzoxazoles is also of  $\pi \rightarrow \pi^*$  type but it is localized on the oxazole ring. The spectral data and also our theoretical calculations (Table 1) indicate that the direction of polarization of the long wavelength band is towards the benzene ring whereas that of shorter wavelength band is towards the oxazole ring. The large Stokes shift ( $2220 \text{ cm}^{-1}$ ) observed in MPBO compared to that in MBO and DMBO could be due to the in-

creased conjugation in the excited state ( $S_1$ ) as a result of rotation of the phenyl ring at 5-position. A similar behaviour is observed in biphenyl<sup>29</sup> and 2-phenylnaphthalene<sup>30</sup> also.

The absorption spectral characteristics of PBO indicate that the long wavelength transition is of  $\pi \rightarrow \pi^*$  type. The results of Brocklehurst<sup>31</sup> and Nurmukchametov *et al.*<sup>8d</sup> on 2-biphenylbenzoxazole and other compounds confirm this explanation. Similar to those of alkylbenzoxazoles, all the transition have  $\pi \rightarrow \pi^*$  character (Tables 2 and 3).



The major contributions of HOMO and LUMO involved in the longest wavelength transition are only one each. Unlike MBO, the localization of the HOMO and LUMO at various atomic centres are distributed, but still the HOMO is primarily localised on BO moiety whereas the LUMO is localised on the phenyl ring. The polarization of the first transition, calculated by PPP and CNDO/S methods is also in the same direction. This indicates that in 2-aryl-substituted benzoxazoles, unlike that in 2-alkylbenzoxazoles, the long wavelength transition is localised on the aryl group and is perturbed by the BO ring. It is also believed that the  $\pi \rightarrow \pi^*$  transition which is localized on the benzene ring is hidden under the broad band of 2-arylbenzoxazoles. The absorption and fluorescence spectra of BPPBO resemble those of 2-biphenylbenzoxazoles (BPBO)<sup>8d</sup>. In other words, no effect of phenyl group at position-6 of benzene ring is observed on the spectrum of BPBO.

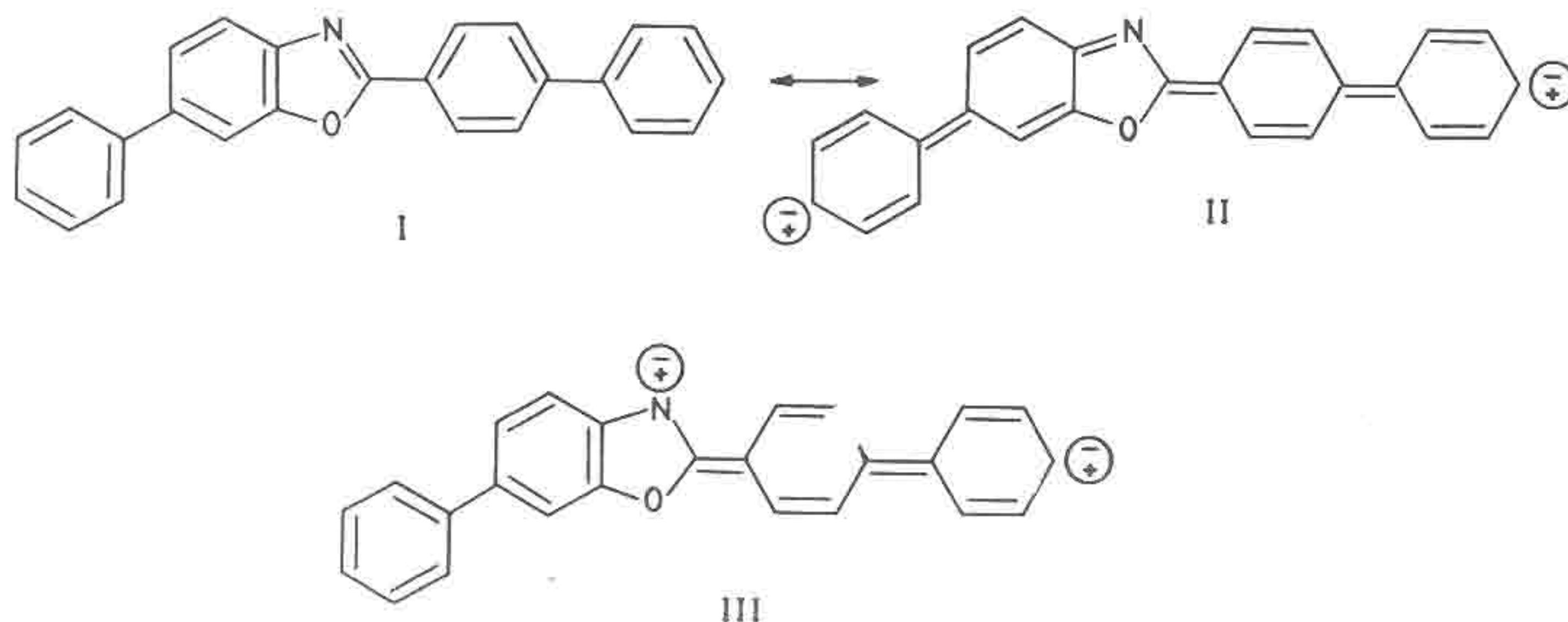
However, in the case of MPBO the phenyl group does influence the spectral characteristics of MBO. This is because in MBO the long wavelength transition is localized on the benzene ring whereas in BPBO the long wavelength band is localized on the biphenyl moiety. Further, the structured absorption and fluorescence band of BPO indicates the phenyl ring to be coplanar with the oxazole moiety in both  $S_0$  and  $S_1$  states. Our theoretical calculation (Table 2) also supports the above explanation. A similar kind of observation is noticed in the cases of 1-fluoro-2-phenyl-naphthalene<sup>32</sup>, 2-phenylbenzimidazole<sup>13</sup>, 2-benzimidazole carboxylic acid<sup>33</sup> and bibenzimidazole<sup>34a</sup> also. The same explanation can be offered in the case of BPPBO, i.e., the phenyl ring at 6-position and the biphenyl ring at 2-position attain coplanarity with the BO system in the  $S_1$  state. The greater Stokes shift ( $2700 \text{ cm}^{-1}$ ) observed for BPPBO ex-

plains partly the above explanation. The following canonical structure (II) can also be obtained and the presence of structures (II, III) adds to the rigidity of molecule in the  $S_1$  state.

The blue shift observed in the long wavelength bands of absorption spectra of 2-arylbenzoxazoles in hydrogen bond forming solvents may be due to the partial loss of conjugation of phenyl or biphenyl ring with the BO moiety as a result of rotation, of the phenyl or biphenyl group either at the nitrogen or oxygen centre of the oxazole ring, induced by the interaction with polar solvent molecules. But in the excited state, the charge migration is completely delocalized over the whole molecule. This will increase the bond order of the interannular bond and thus reduce the rotation of the biphenyl or phenyl rings or increase the conjugation in  $S_1$  state. The interaction with the solvents is not enough to rotate the phenyl ring. This explains the red shift in the fluorescence spectra of these molecules in polar and hydrogen bond forming solvents. The greater sensitivity of fluorescence spectrum towards red shift in BPPBO in different polar solvents could be due to the canonical structure (II or III) in which the dipole moment is increased in the excited state. The larger charge displacement (transition dipole moment) in absorption and emission increases the transition probability which in turn decreases the radiative life time of the excited state. This is the reason for the high fluorescence quantum yields in 2-arylbenzoxazoles.

#### *Effect of acid concentrations: Ground state*

The absorption spectra of all the molecules remain unchanged in the  $pH/H_-$  range of 2 to 16. At higher acid concentrations, a small blue shift (of the order of 2-3 nm) is observed in the long wavelength absorption band but a major change is noticed in the 232 nm band of MBO and DMBO.





The 232 nm band is replaced by two bands; one at  $\sim 239$  nm and the other at  $\sim 222$  nm. The former appears as a shoulder to the latter. The behaviour of MPBO is different from that of MBO and DMBO at low pH region. At pH  $\sim 3$ , the 255 nm shoulder develops into a broad band and the band system at 290 nm merges with it. At  $H_0 \sim 0$ , the 255 nm band disappears and again two bands develop at 236 and 290 nm. No further change is observed in the absorption spectra of these alkylbenzoxazoles except in the case of MPBO where the long wavelength band is blue shifted at  $H_0 \sim -9.0$ . The absorption spectra of the monocations of PBO, OMPBO, MMPBO and PMPBO are closely similar and exhibit a red shift in the long wavelength band along with a new band system at 248 nm. Since BO gets hydrolysed and BPPBO is insoluble in aqueous media, the monocation-neutral equilibria could not be studied in these cases. But at  $H_0 = -9$ , BPPBO becomes soluble and the long wavelength absorption band is blue shifted. The absorption spectral characteristics of neutral and monocations of BO, MBO, DMBO and MPBO are listed in Table 4 whereas those of PBO, OMPBO, MMPBO, PMPBO and BPPBO are compiled in Table 5. The absorption spectra of various prototropic species of BPPBO are shown in Fig. 1.

The  $pK_a$  values of monocation-neutral equilibria of these molecules determined spectrophotometrically<sup>34b</sup> are listed in Table 7. The  $pK_a$  of MBO agrees with the literature value. If the change observed in the absorption spectrum of MPBO at pH  $\sim 3$  is due to prototropic reaction, the first  $pK_a$  is at 2.0 and the second one is at  $-1.2$ . The  $pK_a$  values of 2-arylbenzoxazoles are consistent with the fact that the presence of electron with-

Table 7 –  $pK_a$  values for the monocation-neutral equilibrium of various benzoxazoles in  $S_0$  and  $S_1$  states

Compound	$pK_a$	$pK_a^*$	
		abs.	flu.
MBO	0.5		2.39
DMBO	0.5		1.17
MPBO	$-1.2$		0.78
PBO	0.0	3.30	3.90
OMPBO	0.1	—	3.78
MMPBO	0.0	3.80	4.5
PMPBO	0.1	4.40	4.6
BPPBO	—	—	6.85 <sup>a</sup>

abs. and flu. = Forster cycle method using absorption and fluorescence data respectively.

$$a = \Delta pK_a = pK_a^* - pK_a$$

drawing group decreases  $pK_a$ . Further, the  $pK_a$ 's of 2-arylbenzoxazoles are much lower than that of 2-phenylbenzimidazole. The charge densities (Tables 1, 2 and 3) clearly indicate that the charge density on the tertiary N-atom in PBO is less than that in 2-alkylbenzoxazoles and 2-phenylbenzimidazole.

The spectral changes observed in the monocations of the above mentioned molecules are due to the protonation at the tertiary nitrogen atom. The absorption characteristics of the monocations of alkylbenzoxazoles confirm our earlier assignment of spectral bands, i.e., the long wavelength band in MBO, DMBO and MPBO is localised on the benzene-ring and is long axis-polarized where-

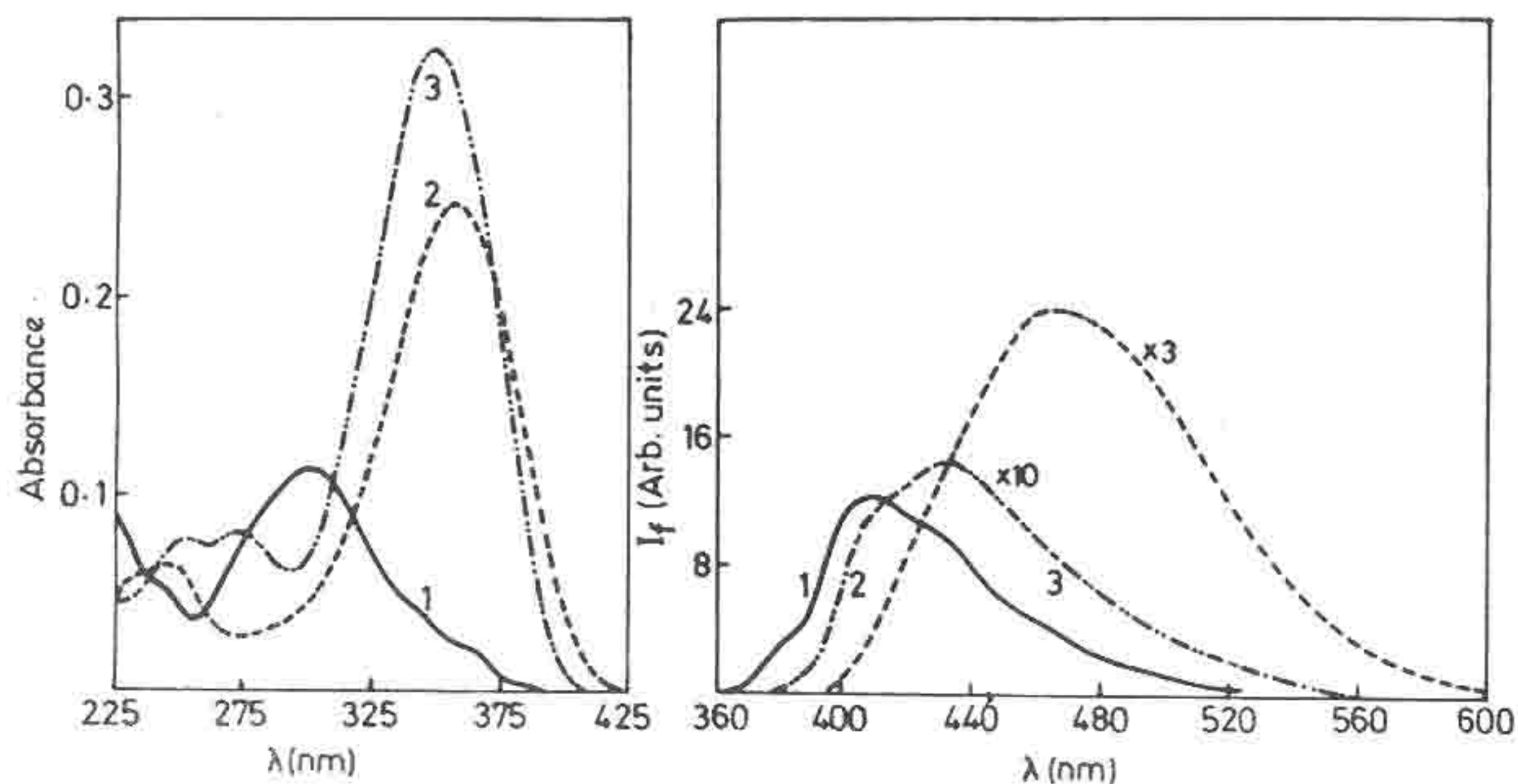


Fig. 1 – Absorption and fluorescence spectra of various prototropic species of BPPBO at 298 K [1, neutral pH 6.1; 2, monocation  $H_0-3$ ; 3,  $H_0-10.4$ ]



as the short wavelength band is localised on the oxazole ring and it is short axis-polarised. The lone pair orbital of the nitrogen atom, being in the plane of ring, cannot have resonance interaction with the  $\pi$  cloud of the molecule but can perturb weakly the transition localised on the benzene ring through inductive effect. Consequently, the long wavelength band is expected to be affected slightly when tertiary nitrogen atom is protonated. This explains the blue shift in the long wavelength band of alkylbenzoxazoles. On the other hand, the short wavelength band will be largely affected by protonation of the tertiary nitrogen. Similar behaviour has been observed in benzimidazoles<sup>11</sup> and phenanthro[9,10]imidazoles<sup>35</sup> also. On the other hand, if the long wavelength band in PBO or BPPBO had been localised on the benzene ring, one would have expected a blue shift, as is normally observed in 2-alkylbenzoxazoles. The opposite trend observed confirms our earlier assignment of transitions in arylbenzoxazoles. The small blue shift in the long wavelength band of BPPBO may be due to the formation of dication through protonation of the phenyl ring at 6-position which prevents conjugation with the benzoxazole moiety.

The absorption spectrum of MPBO is very complicated and it may contain the features of both BO and the phenyl ring. It can be speculated that the long wavelength doublet (290 nm, 279 nm) and the 227 nm band may be due to the BO band system and the shoulder at 255 nm may be due to the phenyl group at 5-position. The increase in intensity of 255 nm band may be due to the intensity borrowing from the strong band systems of BO. The first change observed at  $pH \sim 2$  in the spectrum of MPBO cannot be assigned to any prototropic reactions. This may be due to some complex formation between the solute and solvent, whereas the second change may be due to protonation at the tertiary nitrogen atom. This conclusion is based on the following considerations. (i) The  $pK_a$  for the protonation of BO and MBO is  $-0.1$  and  $0.5$  respectively. The presence of electron withdrawing phenyl group should decrease the  $pK_a$ . If the first change is due to prototropic equilibrium we should have observed an opposite trend. (ii)  $pK_a$  ( $-1.2$ ) for second change agrees with the  $pK_a$  of MBO. (iii) Like MBO and DMBO, dual fluorescence (see later) is observed at  $H_0 \sim -1$  and similar explanation can be given as indicated earlier. (iv) Nearly ground state  $pK_a$  is observed from fluorimetric titration as noticed for MBO and DMBO. (v) A similar kind of com-

Table 8 – Fluorescence maxima ( $\lambda/nm$ ) of the monocation of MPBO

Solvent	$\lambda_{max}$ (nm)	
	CT	$\pi^* \rightarrow \pi$
Cyclohexane	420	325
Acetonitrile	450	328
Methanol	450	330
Water	470	330

plex formation was reported in the case of diaryloxazoles<sup>36</sup> in the acidic solutions.

#### Excited singlet state

The prototropic reactions taking place in the excited singlet state of MBO, DMBO and MPBO are the same as observed in  $S_0$  state. But a dual fluorescence appears at  $pH \sim 1$  of which the longest wavelength band is very broad. The excitation spectra recorded at both the fluorescence bands resemble the absorption spectrum of the monocation. The fluorescence intensity of MPBO is quenched in the  $pH$  range 4 to 2 without appearance of a new band. Dual fluorescence is observed at  $H_0 \sim 0$  in this case. At very high acid concentration, a blue shift is noticed in the fluorescence spectrum of MPBO monocation and the normal Stokes shifted band disappears.

Unlike alkyl BOs, monocations of 2-arylbenzoxazoles exhibit only one fluorescence band. No change observed in the fluorescence spectra of monocations at higher acid concentrations is consistent with the ground state behaviour except in the spectrum of BPPBO. In the case of BPPBO a small blue shift is noticed at  $H_0 = 10.4$  in the absorption spectrum. The fluorescence spectral data of BO, MBO, DMBO and MPBO are collected in Table 5, whereas those of PBO, OMPBO, MMPBO and PMPBO are listed in Table 6. The fluorescence spectra of various species of BPPBO are depicted in Fig. 1.

The  $pK_a$  values calculated using Forster cycle method<sup>37</sup> as well as those determined by fluorimetric titrations are collected in Table 7. The fluorimetric titrations have given only ground state values indicating that the prototropic equilibrium is not established in the  $S_1$  state. This indicates that the radiative decay rates of these molecules are faster than the rate of protonation, whereas the spectral data clearly indicate that the tertiary nitrogen atom becomes stronger base in the  $S_1$  state. Further, the agreement between the  $pK_a^*$  values obtained by absorption and fluorescence data is not bad. This is because the geometries



of the molecules are not different in the  $S_0$  and  $S_1$  states and have nearly the same solvent relaxations in these states for the conjugate acid-base pair.

Dual fluorescence band systems are assigned to the formation of monocations. The broad large Stokes-shifted band is assigned to the charge transfer (CT) transition and the normal Stokes shifted band to the  $\pi^* \rightarrow \pi$  transition. The broadness of the long wavelength band is due to the loss of vibrational quantization as a result of nuclear adjustment in the CT state. The main reason for the stabilization of this CT transition is the migration of charge from the homocyclic ring to the heterocyclic ring when the tertiary nitrogen atom is protonated. This is further supported by the fact that the large Stokes shifted band in monocation of MPBO is stabilized in more polar solvents (Table 8), while the short wavelength fluorescence band is insensitive to the solvent polarity. The existence of multiplicity of first excited singlet state ( $S_1$ ) has been proposed earlier to explain the fluorescence properties of benzimidazole monocations<sup>10,11</sup>. The absence of dual fluorescence in PBO and other 2-arylbenzoxazoles is due to the fact that the positive charge on the protonated nitrogen atom of the corresponding monocations is not localised on the nitrogen atom alone but is delocalized over the whole molecule. Similar results were obtained for 2-arylbenzimidazoles<sup>10,13,38,39</sup> also.

### Conclusions

The following conclusions can be drawn from the above studies:

(i) The long wavelength transition in neutral BOs is of  $\pi \rightarrow \pi^*$  type. It is localized on the benzene-ring in case of 2-alkylbenzoxazoles and on the phenyl/biphenyl ring in case of 2-arylbenzoxazoles. In all these molecules the long wavelength transition is polarized along the long axis of the molecule, whereas the short wavelength band in alkylbenzoxazoles is short axis-polarized and localized on the oxazole ring.

(ii) Methyl group at the 2-position of BO has no effect on its electronic absorption spectrum (long wavelength band), but a red shift is observed when the substituent is in the benzene ring.

(iii) Monocations formed by the protonation of tertiary nitrogen atom of alkylbenzoxazoles exhibit dual fluorescence of which the long wavelength band is due to CT transition and the short wavelength band is the normal  $\pi^* \rightarrow \pi$  transition.

(iv) Phenyl group present either at 2-position or at 5- or 6-position of the benzene ring reduces the  $pK_a$  value by extending the conjugation.

(v) The geometry of the 2-arylbenzoxazoles in the  $S_1$  state is not much different from that in  $S_0$  state.

(vi) A good correlation between the change in  $pK_a$  values with change in the substituent, with excitation and the charge density at the nitrogen atom has been observed. Also, good agreement of calculated transition energies with the observed values proves (a) validity of assumptions made and (b) suitability of the parameters used in PPP calculation for benzoxazoles.

(vii) The spectral behaviour of benzoxazoles and benzimidazoles is more or less similar.

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