# PHOTOLUMINESCENCE OF 2-(*o*-AMINOPHENYL)BENZIMIDAZOLE

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(Received March 26, 1985)

## Summary

The absorption and fluorescence spectra of 2-(*o*-aminophenyl)benzimidazole in different solvents have shown the existence of two structures formed by intramolecular hydrogen bonding. Both are equally favourable in non-polar media whereas one is more stable in polar solvents. pH effects have also been discussed with the evaluation of the ground and excited state equilibrium constants of the various equilibria.

## 1. Introduction

The proton transfer spectroscopy and excited state chemistry of *N*-heterocycles is an interesting and rapidly developing subject, especially for molecules containing more than one functional group. Our recent studies of polyfunctional diazaheterocyclic molecules, *e.g.* 5- and 6-aminoindazole [1, 2], substituted benzimidazoles [3, 4] and other studies [5] on benzimidazoles, have revealed certain very interesting features: for example, (i) the presence of biprotonic phototautomerism in 5-aminoindazole [1]; (ii) the presence of different ionic species in the $S_0$ and $S_1$ states [1]; (iii) the presence of different monocations of 6-aminoindazole [2] in different solvents.

The presence of either intramolecular or intermolecular hydrogen bonding in a molecule gives rise to many further new features in both the absorption and fluorescence spectra and sometimes may alter the chemical behaviour of the molecule, depending on the nature of the solvent. 2-(*o*-aminophenyl)benzimidazole ($OBNH_2$) is a molecule of this kind and there is intramolecular hydrogen bonding leading to structure I (hydrogen atom of the amino group forming a bond with the tertiary nitrogen atom) or structure II (imino hydrogen atom forming a bond with the lone pair of the amino group), both forming a sort of four-membered condensed ring system. It does appear from models that I is more stable than II. This may be due to the presence of a lone pair on the nitrogen atom which is in the same plane as the amino hydrogen atom, and thus the ring 3 that is formed is in the same plane as 1, 2 and 4, whereas the ring 3 formed in II may not

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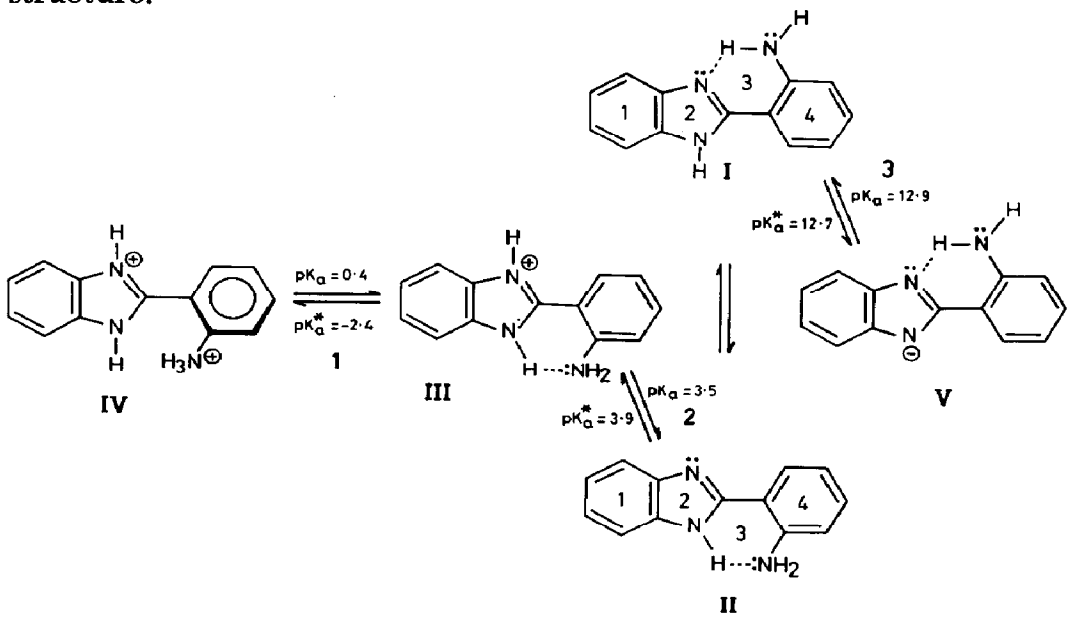
be in the same plane as 1, 2 and 4 because of steric hindrance of the amino protons by other protons, and the amino group may develop a tetrahedral structure.




The present investigation has been carried out to study the effect of various solvents as well as of pH on the absorption and fluorescence spectra of $OBNH_2$, and, if possible, also to identify the various species present under different conditions (of solvent and pH) and to calculate the values of the equilibrium constants of the various species in their $S_0$ and $S_1$ states.

## 2. Experimental details

$OBNH_2$ was obtained from the Aldrich Chemical Company and purified by recrystallization from ethanol. The purity of $OBNH_2$ was confirmed by the production of similar fluorescence bands on excitation with different wavelengths of radiation. BDH spectroquality methanol, analytical reagent grade trifluoroacetic acid (Aldrich), sulphuric acid and sodium hydroxide (BDH) were used as received. AnalaR grade acetonitrile (E. Merck), cyclohexane, *n*-heptane, ether (BDH) and ethanol were further purified by methods described previously [6]. Triply distilled water was used for the preparation of aqueous solutions. A modified Hammett acidity scale [7] ($H_0$) for $H_2SO_4$–$H_2O$ mixtures and Yagil's [8] basicity scale ($H_-$) for NaOH–$H_2O$ mixtures were used for solutions below pH 1 and above pH 13 respectively. Hammett's acidity and basicity functions represent the actual (or free) number of protons or hydroxyl ions available in a given solution which will react with a weak base or a weak acid respectively.

Absorption spectra were recorded using a Cary 17D spectrophotometer. Fluorescence measurements were made using a scanning spectrofluorometer

built in our laboratory and the details are available elsewhere [9]. The excitation and emission monochromators were calibrated using a calibration low pressure mercury lamp. The pH values (in the range 1 - 13) were measured using a Toshniwal pH meter model CL-44A.

The bandwidth of the exciting radiation was 8 nm. The frequency shifts (blue or red) in the study of the solvent effects are compared with the maxima in cyclohexane or *n*-heptane as the spectral maxima in both solvents are the same. The solutions for absorptiometric and fluorometric titrations were prepared just before taking the measurements. The concentrations of the solutions were of the order of $10^{-5}$ M. In fluorometric titrations, the relative fluorescence intensities were measured at the analytical wavelength as a function of $H_0$/pH/$H_-$ and the isosbestic wavelength was used for the excitation; the values for the dication–monocation, monocation–neutral form and neutral form–monoanion are 310 nm, 298 nm and 345 nm respectively. Quinine sulphate in 1.0 N $H_2SO_4$ ($\phi = 0.55$ [10]) was taken as the standard for measuring the quantum yields which were calculated using 345 nm as the wavelength of excitation.

## 3. Results and discussion

### *3.1. Absorption and fluorescence spectra*

The absorption spectra of $OBNH_2$ have been recorded in different solvents and are shown in Fig. 1. The $\lambda_{max}$(abs) and $\epsilon_{max}$ of the various bands are recorded in Table 1. The values of each quantity with ethanol as the solvent agree nicely with the literature values [11]. Unlike other substituted derivatives of benzimidazole, this compound has three band systems; this can be attributed to the presence of intramolecular hydrogen bonding which results in either structure I or structure II (*i.e.* the formation of four rings). The absorption spectrum in cyclohexane or in *n*-heptane is structured and this includes the longest wavelength band which is broad in all other solvents, whereas the structure of the other bands is lost as the polarity or the hydrogen-bonding capacity of the solvent increases. The results, as expected, could be due to the increase in the interaction between solvent and solute. Furthermore, all the bands are blue shifted in solvents of high polarity or increase in their capacity to form hydrogen bonds and the hypsochromic shift is quite large in water, especially for the longest wavelength band.

Figure 2 indicates that, except in water, the fluorescence spectra of $OBNH_2$ show two broad bands in the different solvents. The $\lambda_{max}$(flu) and $\phi_{flu}$ values of the two bands are listed in Table 2. The data in Table 2 show that the short wavelength band becomes red shifted, whereas the long wavelength band becomes blue shifted on an increase in the polarity and the tendency to form hydrogen bonds of the solvents. Furthermore, under similar conditions, the fluorescence quantum yield of the former band increases whereas that of the latter decreases and is totally absent in water.

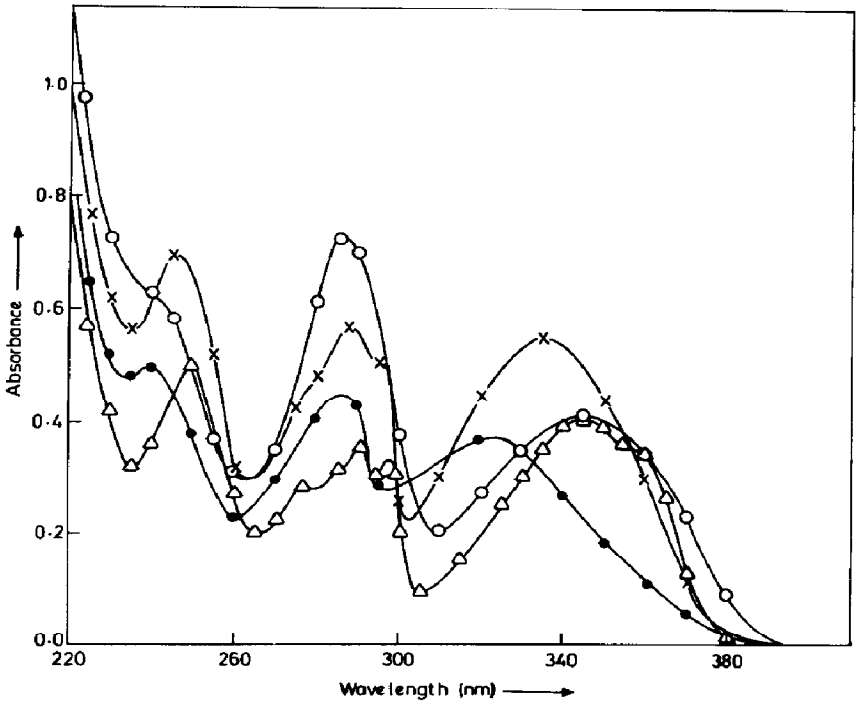



Fig. 1. Absorption spectra of $OBNH_2$ ($2 \times 10^{-5}$ M) in different solvents at 298 K: —●—, water; —○—, acetonitrile; —×—, methanol; —△—, heptane.

TABLE 1

Absorption maxima and log $\epsilon_{max}$ of $OBNH_2$ at 298 K

| *Solvent* | $\lambda_{max}$(abs) (nm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cyclohexane | 228 (4.64) | 250 (4.01) | 277 (4.05) | 286 (—) | 290 (4.13) | 297 (4.16) | 345 (4.19) | 359 (—) |
| Ether | 223 (4.70) | 251 (4.32) | 275 (—) | — | 290 (4.20) | 298 (4.30) | 345 (4.17) | — |
| Acetonitrile | 222 (4.43) | 242 (4.01) | — | 286 (3.97) | — | — | 344 (3.97) | — |
| Methanol | 222 (4.48) | 246 (4.00) | 270 | 287.5 | 294 (3.95) | | 335 (3.92) | |
| Ethanol | 221 (4.45) | 249 (3.99) | 270 | 290 | 297 (3.95) | | 341 (3.95) | |
| Water | 218 (4.70) | 240 (4.33) | | | 286 (4.27) | | 320 (4.18) | |
| 0.01 M $H_2SO_4$ | — | 245 (4.27) | | | 285 (4.32) | | 335 (3.94) | |
| 2.5 M $H_2SO_4$ | | 236 (4.37) | | | 284 (4.43) | | — | |
| 1.0 N NaOH | | 247 (4.28) | | | 297 (4.28) | | 324 (4.32) | |

Values in parentheses are log $\epsilon$.

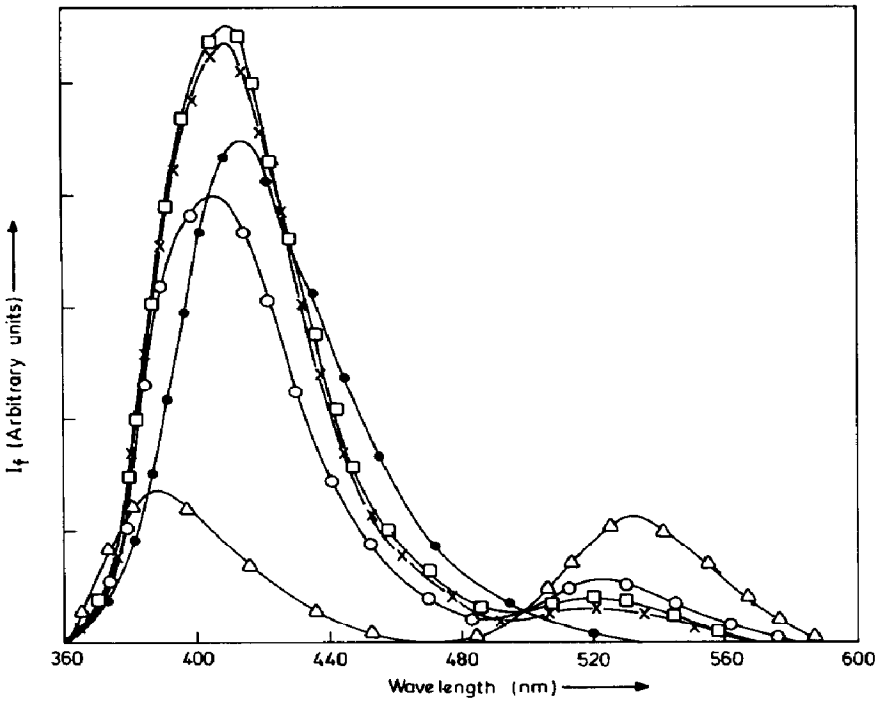



Fig. 2. Fluorescence spectra of $OBNH_2$ ($2 \times 10^{-5}$ M) in different solvents at 298 K: —●—, water; —○—, acetonitrile; —×—, methanol; —□—, ethanol; —△—, heptane.

TABLE 2

Fluorescence band maxima $\lambda_{max}(flu)$ and $\phi_{flu}$ of $OBNH_2$ in different solvents, excited at 345 ± 4 nm at 298 K

| *Solvent* | $\lambda_{max}(flu)$ (nm) | $\phi_{flu}$ | $\lambda_{max}(flu)$ (nm) | $\phi_{flu}$ |
|---|---|---|---|---|
| Cyclohexane | 390 | 0.014 | 530 | 0.013 |
| *n*-Heptane | 390 | 0.014 | 530 | 0.013 |
| Ether | 407 | | 523 | |
| Acetonitrile | 407 | 0.093 | 520 | 0.012 |
| Methanol | 410 | 0.125 | 520 | 0.008 |
| Ethanol | 413 | 0.126 | 520 | 0.008 |
| Water | 417 | 0.129 | — | — |
| 0.01 M $H_2SO_4$ | 454 | 0.102 | — | — |
| 9 M $H_2SO_4$ | 391 | 0.430 | — | — |
| 4 M NaOH | 505 | 0.375 | — | — |

The value $I_{530}/I_{390}$ of the fluorescence intensity ratio of the two bands is nearly equal to unity in *n*-heptane and this ratio decreases in the sequence *n*-heptane → ether → acetonitrile → methanol (or ethanol). Moreover, this intensity ratio in methanol could be achieved by adding only 2% (vol./vol.) methanol to *n*-heptane. It is also observed that the intensity ratio of these bands in *n*-heptane does not change for the concentration range $10^{-5}$ - $10^{-3}$

M $OBNH_2$. However, in *n*-heptane $I_{530}/I_{390}$ increases (though only slightly) with increasing the excitation wavelength, especially if this is towards the red edge of the absorption band with the longest wavelength.

The above results can be explained on the following basis. The formation of the intramolecular hydrogen bond can take place either between the tertiary nitrogen atom and the hydrogen atom of the amino group or between the lone pair of the amino group and the imino hydrogen atom (I and II). Possibly the additional ring formation at the tertiary nitrogen centre (I) will be more stable owing to the somewhat increased planarity of this ring compared with II, in which the hydrogen-bonded amino group will tend to develop a tetrahedral structure. In non-polar media both these structures are equally probable and are present in a state of dynamic equilibrium (one would only expect a low activation barrier between the two structures). Thus both forms are present in the ground state as well as in the excited state. The relatively broad, slightly structured longest wavelength absorption band in cyclohexane and *n*-heptane is due to the superposition of two bands belonging to different forms, because the uncorrected excitation spectra in *n*-heptane (Fig. 3), taken at emission wavelengths of 390 nm and 525 nm respectively, showed the presence of only one maximum in each case at the wavelengths corresponding to the respective maxima in the absorption spectrum in *n*-heptane (345 nm and 359 nm), whereas the other short wavelength bands appeared at the same wavelengths in both cases. With increasing hydrogen-bonding ability of the solvent, the lone pair on the amino group of I becomes progressively blocked owing to hydrogen bonding with the

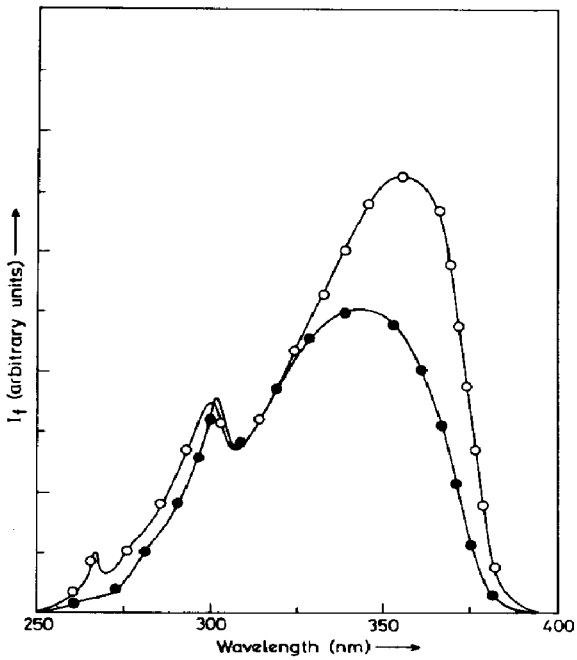
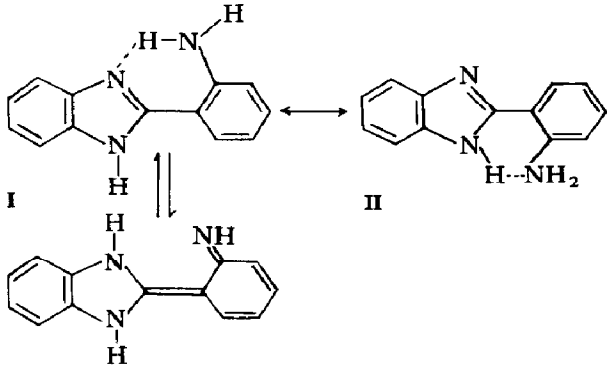



Fig. 3. Uncorrected excitation spectra of $OBNH_2$ at 298 K observed at 390 nm (—●—) and 525 nm (—○—).

solvent and this will be at a maximum with water; thus the lone pair of the amino group is stopped from participating in a charge transfer interaction between the amino group and the ring. This explains the large blue shift in the longest wavelength absorption band (which is due to the extra ring) compared with the other absorption bands [12] (which are due to the benzimidazole moiety) in water compared with the other solvents.

Similarly to the absorption spectrum, the fluorescence spectrum reflects the presence of excited state intramolecular hydrogen bonding and has two fluorescence bands. The long wavelength emission (530 nm) exhibits an anomalously large Stokes shift and thus belongs to species I′, as shown in the equilibria below in which the proton of the amino group is transferred to the tertiary nitrogen atom. Similar behaviour has been observed in many compounds [13]. The short wavelength (normally Stokes shifted) emission (390 nm) could be assigned to II or to I, where the proton of the amino group is not transferred to the tertiary nitrogen atom, but the latter can be rejected on the grounds that the intramolecular proton transfer process is very rapid and can take place during the lifetime of the species. Furthermore, for II, intramolecular hydrogen transfer will not occur in the $S_1$ state because the acidity of the imino group in this state does not increase to the extent that it will protonate the amino group, which becomes less basic.




The increase in $I_{390}/I_{530}$ with increase in solvent polarity and particularly with using hydrogen-bonding solvents can be explained in two ways. Firstly, in polar solvents there is a strong possibility of disruption of intramolecular hydrogen bonding, which is a prerequisite of proton transfer, leading to a decrease in the concentration of I and an increase in the concentration of II. The second factor is the solvent effect on the relative quantum efficiency of I*′ and II*. Although we have not measured the lifetime of species I*′, for similar cases it has been found that it decreases markedly with increasing solvent polarity [13].

The relatively small increase in $I_{530}/I_{390}$ in *n*-heptane with increase in excitation wavelength (II has a weak absorption and the increase in the above ratio should be greater) could be due to the fast dynamic equilibrium

between the two structures even in the excited state, but definite conclusions cannot be drawn from our results as the absorption spectra of the two structures overlap in this region.

*3.2. Effect of* pH

The absorption spectrum of $OBNH_2$ has been studied in the $H_0$/pH/$H_-$ range —9 - 16. Besides the neutral form, three more new species are observed. The neutral form exists in the pH range 4 - 13. On decrease of pH below 4, all the bands are red shifted, the most prominent being the longest wavelength band and this continues to pH 0.4. On decreasing the pH further, the structure of the band system completely changes. Two instead of three bands appear and this pattern resembles that of benzimidazole compounds (2-phenylbenzimidazole, in particular [3]), the substituent being attached to the 2-position, and the other bands are blue shifted compared with III. However, on increase of pH above 13, red shifts are observed in each band, the three-band system being kept intact. The band maxima are listed in Table 1 and the spectra are shown in Fig. 4.

It has generally been found that for $\pi \rightarrow \pi^*$ (the transition with the longest wavelength) protonation at the tertiary nitrogen atom leads to a red shift, whereas protonation at the amino group leads to a blue shift in the absorption and fluorescence spectra compared with the neutral molecule. Thus the results of Table 1 indicate that the monocation formed in the pH range 0.4 - 4 is due to the protonation at the tertiary nitrogen atom (III)

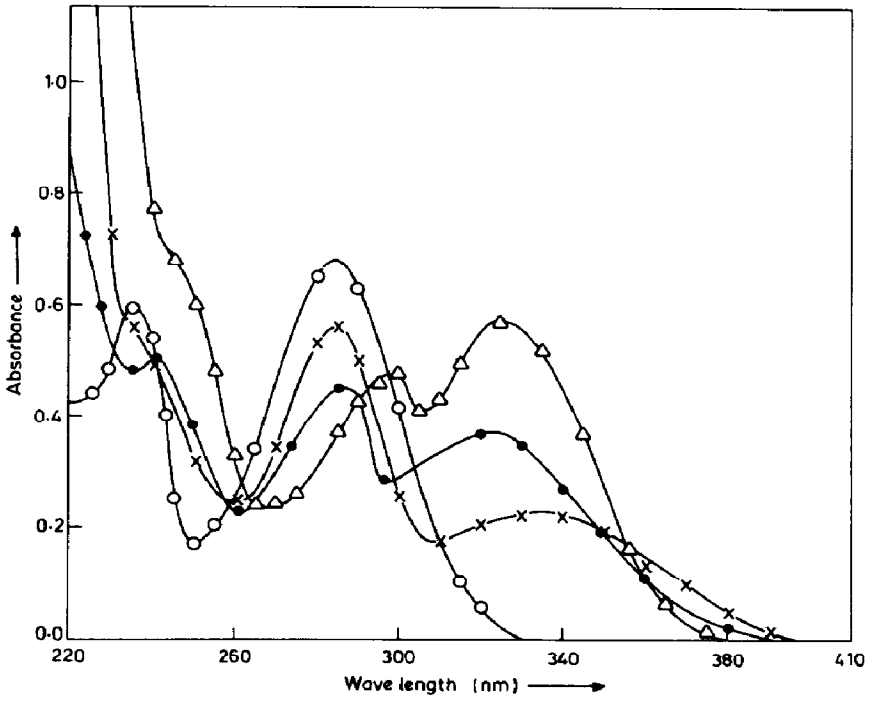



Fig. 4. Absorption spectra of $OBNH_2$ ($2 \times 10^{-5}$ M) at different pH values (298 K): —●—, neutral form; —×—, monocation; —○—, dication; —△—, anion.

and that the dication is formed by the further protonation of the amino group (IV). The formation of the dication can also be envisaged because the three-band system in the absorption is changed into a two-band system which more resembles the spectrum of phenyl-substituted benzimidazole [3]. This is because both the lone pairs at both the nitrogen atoms are blocked by the protons, thus the rings 3 or 4 formed by intramolecular hydrogen bonding are absent. Moreover, the behaviour of the anilinium ion will be similar to that of the phenyl group. Thus the absorption spectrum reverts back to one similar to that of benzimidazole derivatives. The monoanion is formed by deprotonation of the imino nitrogen atom because deprotonation of the amino group is difficult to observe in the $S_0$ state at such a low pH [14].

Fluorescence studies carried out in the $H_0$/pH/$H_-$ range −9 - 16 also confirm the formation of the different cations or anions at various pH values and the spectra are shown in Fig. 5. For example, it has generally been found that the proton-induced quenching of the fluorescence of neutral arylamines is preceded by the formation of ammonium ion at moderate hydrogen ion concentrations [1, 15 - 22]. Thus if the first protonation had occurred at the amino group, the above behaviour would have been observed. However, this is only observed during the second protonation. As stated above, the red shift observed on the first protonation and the blue shift on the second protonation as well as the high p$K_a$ value (the protonation at the amino group generally takes place at a high acid strength) further

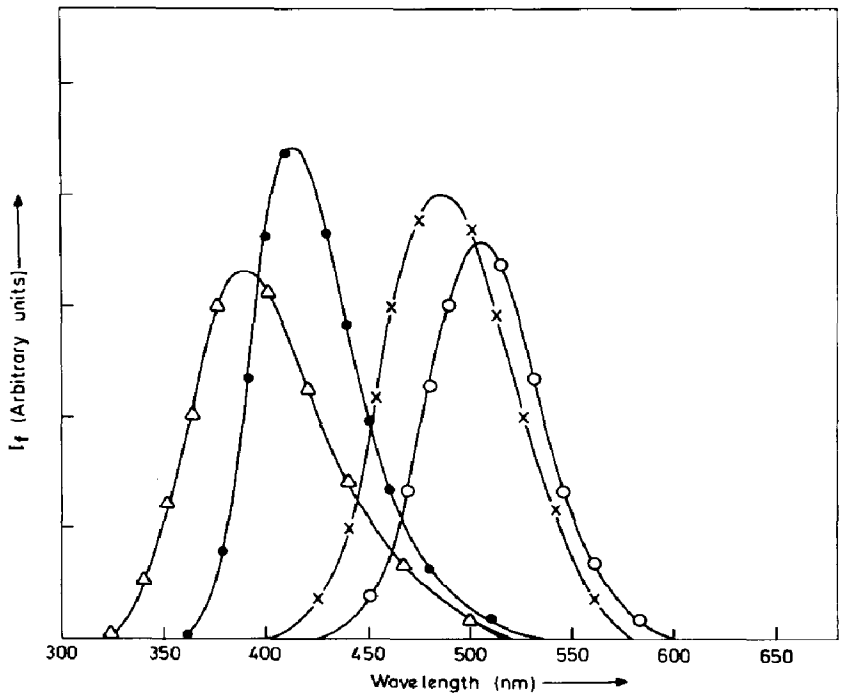



Fig. 5. Fluorescence spectra of $OBNH_2$ ($2 \times 10^{-5}$ M) at different pH values (298 K): —●—, neutral form; —×—, monocation; —○—, dication; —△—, anion.

confirms the above conclusion. The fluorescence observed from the mono-anion also confirms the deprotonation of the pyrrolic nitrogen atom because, in general, the imino anions formed (by deprotonation of the amino group) do not fluoresce, with the exception of 2-naphthylamine [23].

The ground state $pK_a$ values for the various equilibria have been calculated spectrophotometrically and the values are listed in Table 3. The excited state equilibrium constants $pK_a^*$ for the above equilibria have been calculated by using the Förster cycle method [24] and absorption and fluorescence data and the average of the absorption and fluorescence band maxima. The values obtained are also listed in Table 3. The value of $pK_a^*$(I) could not be calculated by this method as the band systems observed for the two species are different. The difference between $pK_a^*$(II) which was calculated using absorption and fluorescence data is not large (*i.e.* 1.6 $pK_a$ units) and this could be due to different solvent relaxation in the two electronic states of the different species or due to using the band maxima instead of the 0–0 transition of the neutral and monocationic species. With the Förster cycle method $pK_a^*$(III) could only be calculated using absorption data, indicating that the imino proton is slightly more acidic in the $S_1$ state than in the $S_0$ state, as expected. The fluorescence data could not be used because after deprotonation of the imino hydrogen atom $OBNH_2$ cannot exist as II, which emits predominantly in polar solvents (water), and the fluorescence which we observe seems to be due to the anion of I, derived from the dynamic equilibrium between I and II.

The fluorometric titrations were carried out for the different equilibria and the fluorescence intensities of the various species as a function of $H_0$/pH/$H_-$ are plotted in Fig. 6. The values of $pK_a^*$(II) and $pK_a^*$(III) obtained are quite close to the ground state values and these confirm further the formation of the different ions predicted earlier, because $pK_a^*$ studies have indicated in general that fluorometric titrations only give ground state $pK_a$ values whenever protonation or deprotonation occurs at the tertiary or imino nitrogen atom respectively [25 - 28]. This behaviour could be due to either the short lifetimes of the species in the $S_1$ state or the small numbers of protons present in solution. Similar behaviour has been observed in the case of molecules whose $pK_a^*$ values lie in the pH range 4 - 10.

TABLE 3

Values of equilibrium constants of various equilibria in the $S_0$ and $S_1$ states

| *Equilibria* | $pK_a$ | $pK_a^*$ *(Förster cycle)* | | | *Fluorometric titration* |
|---|---|---|---|---|---|
| | | *Absorption* | *Fluorescence* | *Average* | |
| I | 0.4 | — | — | — | −2.4 |
| II | 3.5 | 6.0 | 7.6 | 6.8 | 3.9 |
| III | 12.9 | 12.1 | — | — | 12.7 |

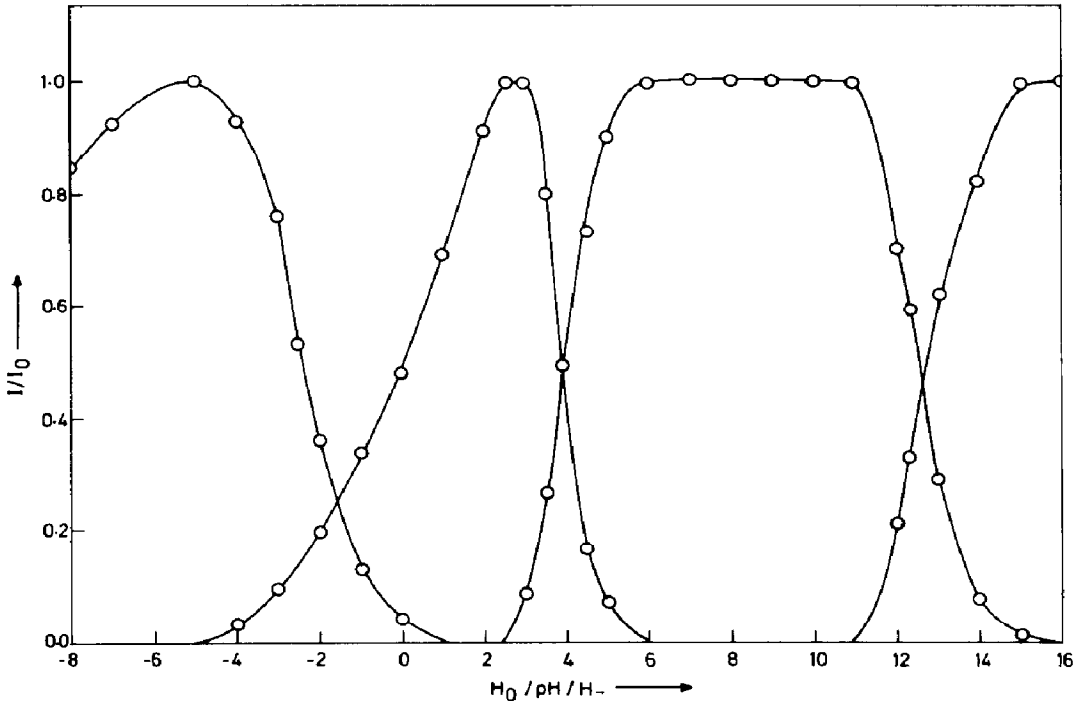



Fig. 6. Plot of $I/I_0$ as a function of pH at 298 K.

The fluorometric titration curves for the dication–monocation equilibrium do not intersect at $I/I_0 = 0.5$. This clearly indicates that this reaction cannot be a simple equilibrium between the conjugate acid–base pair. As observed for similar compounds [15 - 23], this lack of correspondence between the quenching of fluorescence of $OBNH_3^+$ and the appearance of fluorescence of $OBNH_4^{2+}$ could be due to the proton-induced quenching of $OBNH_3^+$ fluorescence at moderate proton concentrations because this process can compete with the proton transfer reaction. Even though under such conditions an accurate value of $pK_a^*(I)$ can only be determined with the help of time-resolved fluorometry, the middle point of the rise of the $OBNH_4^{2+}$ fluorescence curve ($pK_a^*(I) = -2.4$) may not be far from equilibrium.

The various equilibria observed under the different conditions are shown in the scheme in Section 1 (the $pK_a$ values are listed above the arrows).

The following conclusions can be drawn from this study. (i) Intramolecular hydrogen bonding leads to the formation of two species which have different absorption and fluorescence spectra. (ii) The value of $\phi_{flu}$ for the longer wavelength band decreases whereas that of the shorter wavelength band increases with an increase in the tendency of the solvent to form hydrogen bonds. (iii) The protolytic equilibria exhibited by the molecule in the $S_0$ state are the same as those shown in the $S_1$ state.

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