Effects of Solvents and pH on the Spectral Behavior of 2-(*p*-Aminophenyl)benzimidazole

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The absorption and fluorescence spectra in different solvents and at various pH have indicated that monocation and dication of 2-(*p*-aminophenyl)benzimidazole ($PBNH_2$) are formed by protonating first the tertiary amine nitrogen atom and then the amino group, both in S_0 and S_1, whereas the monoanion in S_0 is obtained by deprotonating the imino group but in S_1, it is formed by deprotonating the amino group. Dianion at H_15 in S_1 is obtained by deprotonating the amino and then imino group.

The spectral shift, shape of the spectral band, Stokes' shift *etc.* depend upon the geometry of the molecule in the ground and excited states, the nature and the position of functional group in the molecule and nature of solvents.[1] In case of biphenyl,[2] S_1 state is relatively more planar than S_0 and large Stokes' shift has been attributed to this change in the geometry on excitation and broad absorption band involving overlapping of two transitions. The presence of groups, like alkyl, amino, vinyl, and phenyl, at the para position shift the long wavelength band towards red and make the molecule a little more planar.[3,4] The presence of these groups at the ortho position shift the spectra towards blue unless the biphenyl molecule along with the substituents form a rigid planar molecule. Similarly in case of 2-phenylnaphthalene,[5] the Stokes' shift of 1770 cm^{-1} is attributed both to the phenyl group rotation and solvent stabilization.

Recently our study on 2-phenylbenzimidazole (PBI)[6] has shown that the Stokes' shift is quite small ($\approx$324 cm^{-1}), indicating that this molecule is planar or nearly planar in S_0 and S_1 states. The presence of amino group in the ortho position of 2-phenyl-substituted benzimidazole leads to a rigid molecule, formed through the intramolecular hydrogen bonding, thus leading to two four-membered ring systems.[7a] The present study of 2-(*p*-aminophenyl)benzimidazole ($PBNH_2$) was carried out to study the above-mentioned effects and the changes observed in the absorption and fluorescence spectra in different solvents and at various pH. The equilibrium constants of various prototropic reactions are calculated both in S_0 and S_1 states.

Experimental

$PBNH_2$ was prepared by heating an equimolar mixture of *o*-phenylenediamine and *p*-aminobenzoic acid at 250 °C, as described in literature[8] and purified further by recrystallization from ethanol. The purity was checked by getting similar fluorescence maxima when excited with different excitation wavelengths. BDH spectrograde methanol, analytical grade sulfuric acid and sodium hydroxide were used as such. Analytical grade acetonitrile (E. Merck), cyclohexane, ether, dioxane, heptane (BDH), and ethanol were further purified by methods described in literature.[9] Triply distilled water was used for the preparation of aqueous solutions. A modified Hammett's acidity scale[10] (H_0) for H_2SO_4–H_2O mixture and Yagil's[11] basicity scale (H_-) for NaOH–H_2O mixture were used for the solutions below pH 1 and above pH 13 respectively.

Absorption spectra were recorded in a Cary 17-D spectrophotometer. Fluorescence spectral measurements were carried out on a recording spectrofluorometer, fabricated in our laboratory and details are described elsewhere.[12] The band width of excitation radiation is 8 mn and both the monochromators are calibrated, from time to time with low pressure mercury lamp. pH in the range 1—13 were measured on a Toshniwal pH meter, model CL-44A. The concentrations of the solutions were of the order of 10^{-5} to 10^{-4} M†. Quinine sulfate in 0.1 M H_2SO_4[13] was taken as the standard for measuring quantum yields, and wavelength used for excitation was 315 nm. The solutions for absorptiometric and fluorimetric titrations were prepared just before the measurements. In fluorimetric titrations, isosbestic wavelengths were used for excitation of different species. The values for dication–monocation, monocation–neutral and neutral–monoanion are 295, 320, and 315 nm respectively.

Results and Discussion

Effect of Solvents on Absorption and Fluorescence Spectra. The absorption and fluorescence spectra of $PBNH_2$ were observed in solvents of different polarity and of hydrogen bond formation tendency. The former is shown in Fig. 1 and the latter in Fig. 2. The absorption maxima, log ε_{max} (except in heptane where the saturated solution was used) are listed in Table 1, whereas the fluorescence maxima and fluorescence quantum yields are listed in Table 2. The two normal band systems of benzimidazole molecule (278, 272 nm, L_b; 243 nm, L_a) are kept intact except that both are red shifted (333, 318 nm, L_b; 277, 268, 258 nm, L_a) and the third band system, λ_{max} (abs) $\approx$207 nm is also observed. The L_b band system is similar to that of benzimidazole, but the structure is lost and is also red shifted as the polarity of the solvent increases except in water, where the broad band is red shifted with respect to heptane but blue shifted with respect to methanol and acetonitrile, the latter being a weakly hydrogen accepting solvent. The behavior of the 207 nm band system is similar to that of L_b one under the similar environments. Whereas the structure of L_a band system also undergoes the similar changes as the L_b one, the band maxima is regularly blue shifted.

The data of Table 2 indicate that the fluorescence spectrum of $PBNH_2$ is nicely structured in less polar solvents and can be explained by the vibrational frequency of $\approx$1450 cm^{-1} in S_0 state. The fluorescence

† 1 M = 1 mol dm^{-3}.

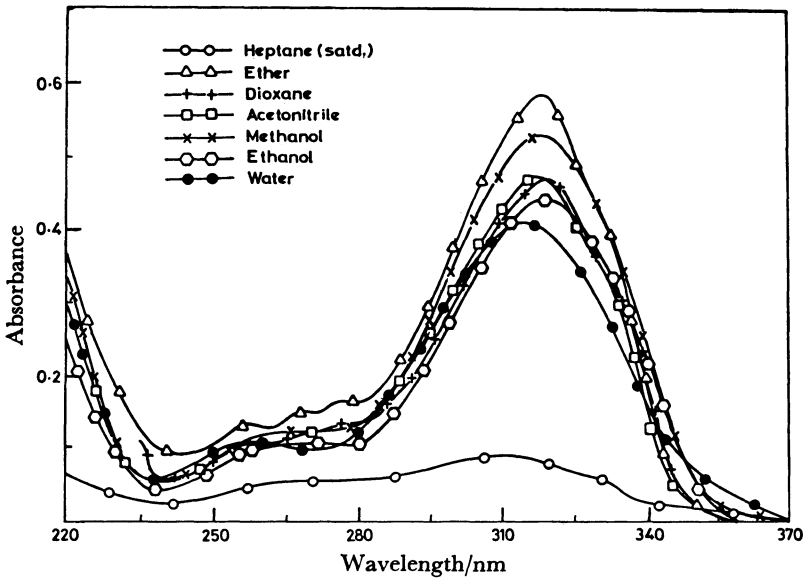

Fig. 1. Absorption spectra of $PBNH_2$ in various solvents at 298 K. (concn 2.5×10^{-5} M)

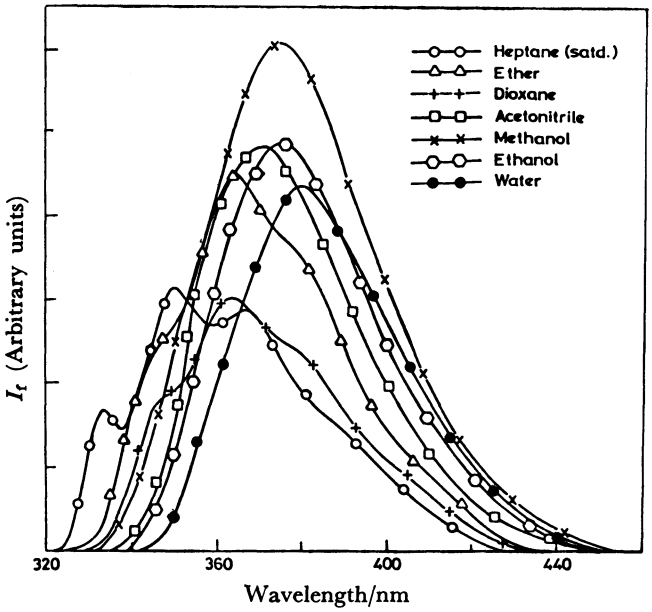

Fig. 2. Fluorescence spectra of $PBNH_2$ in various solvents at 298 K. (concn 2.5×10^{-5} M)

spectrum of $PBNH_2$ is similar to that of 2-phenylbenzimidazole (PB)[6] and the vibrational frequency in $PBNH_2$ is nearly equal to that observed in PB ($\approx$1500 cm^{-1}). The 0-0 band in the fluorescence spectrum of $PBNH_2$ in heptane can be assigned to the shortest wavelength band of 334 nm. Structure of the band is lost and the band is regularly red-shifted with the increase in the polarity and hydrogen bond formation tendency of solvents, but this effect was not as large as observed for 2-(*m*-aminophenyl)benzimidazole.[7b] The fluorescence quantum yield of $PBNH_2$ increases under the similar conditions in contrast to PB[6] (for this compound the quantum yield remains nearly constant *i.e.* 0.12+0.01 for these solvents), 2-(*m*-aminophenyl)benzimidazole ($MBNH_2$, in this case the quantum yield decreases from 0.146 to 0.08 for solvents ranging from heptane to water) and is even slightly larger than that of benzimidazole in ethanol[14] (0.7). Another fluorescence band is observed at long-wavelength (maximum at 500 nm) and its intensity is much smaller than that of short-wavelength fluorescence band, however the ratio (I_{382}/I_{500}) remains unchanged with the change in the concentration (10^{-5} to 10^{-3} M) of solute, change of solvent and pH of the solution.

It has been shown by Tway and Love[15] that the longwavelength transition in benzimidazole and 2-(4-thiazolyl)benzimidazole is of π-π^* character in non-aqueous polar solvents. Further, the absorption and fluorescence spectra of these compounds are affected by the nature of solvents although the effect is small. Similarly to other amino substituted benzimidazoles or indazoles, $PBNH_2$ also possesses two positions which can accept protons and two sites which can donate protons to the solvents. Thus the spectral shifts observed depend upon the preferential interactions of the solvents with the solute molecule. The high extinction coefficient, red shift in λ_{max} (abs) with increase in the polarity of solvents and high fluorescence yield, all confirm the π—π^* nature of the transition. The small blue shift noticed in water relative to methanol or acetonitrile tells that water is acting as better hydrogen donor solvent to the lone pair of the amino group rather hydrogen acceptor one.

Fluorescence results can also be explained exactly on the same lines. Stokes' shift [ν_{max}(abs)$-\nu_{max}$(fluo)], thought it is large, does not increase significantly with the increase in the polarity of solvents. This indicates that there is no significant change in dipole moment of $PBNH_2$ in S_1 state from that in S_0 and this could be due to the charge migration from carbocyclic ring to the heterocyclic ring, leaving some positive charge

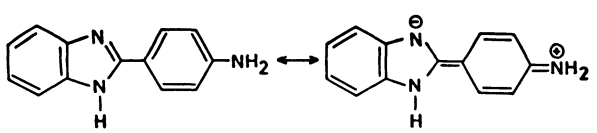

Table 1. Absorption maxima and $\log \varepsilon_{max}$ of $PBNH_2$ in various solvents and at different pH at 298 K

Solvent	λ_{max}(abs)/nm, ($\log \varepsilon_{max}$)					
Heptane	207		270		310	330[a]
Dioxane	—	258 (3.64)	268 (3.70)	277 (3.73)	318 (4.27)	333 (4.09)
Ether	210 (4.35)	257 (3.71)	268 (3.87)	276 (3.82)	316 (4.37)	331 (4.21)
Acetonitrile	211 (4.32)	257 (3.68)	267 (3.64)		316 (4.27)	
Methanol	210 (4.37)	≈260 (3.68)	(broad)		317 (4.32)	
Ethanol	210 (4.38)	260 (3.62)	(broad)		318 (4.27)	
Water (neutral)	207 (4.39)	255 (3.73)	(broad)		313 (4.30)	
10^{-3} M H_2SO_4 (monocation)		230	262		330	
1 M H_2SO_4 (dication)		240	245		295	
pH 12 (monoanion)			260		305 317	332

a) Weak shoulder.

Table 2. Fluorescence maxima and ϕ_f of $PBNH_2$ in various solvents and at different pH at 298 K

Solvent	λ_{max}(flu)/nm				ϕ_f
Heptane	334	350	368	384	0.485
Dioxane		348	363	380	0.453
Ether		348	363	380	0.775
Acetonitrile			370		0.822
Methanol			376		0.900
Ethanol			378		0.836
Water (neutral)			382		0.852
10^{-3} M H_2SO_4 (monocation)			394		0.06
H_0^{-3} H_2SO_4 (dication)			380		0.30
pH 12[a] (monoanion)		352	368	385	—
H_ 16 (dianion)			430		—

a) Fluorescence spectrum recorded at 77K.

on the carbocyclic ring, as shown below. The presence of long-wavelength fluorescence band could not be explained from this study and is still under investigation.

Effect of pH. The absorption (Fig. 3) and fluorescence spectra (Fig. 4) of $PBNH_2$ have been studied in the H_0/pH/H_ range of −9 to 16. The absorption and fluorescence maxima of various forms are reported in Tables 1 and 2 respectively. Starting with H_0= −9, the absorption spectrum shows a long wavelength band at 295 nm. With decreasing hydrogen ion concentration, a red shifted band appears at pH 5 with λ_{max} (abs) at ≈330 nm; at pH ≈8 the absorption band appears at 310 nm; at pH 12 a structured absorption spectrum with λ_{max}(abs) at 317 nm is observed and no further change is noted in absorption spectrum after pH 13. Under the similar conditions upto pH 8, the fluorescence bands observed were at 380, 394, and 382 nm respectively and follows the same trend as observed in absorption. No extra fluorescence band is observed in the pH/H_ range of 8 to 14 besides that at 382 nm. This band is quenched at H_=14. A new red shifted and broad fluorescence band (430 nm) starts appearing at H_=−15 and its formation is not complete even at H_=16, the highest basic concentration used.

Comparing the absorption and fluorescence spectra with the solvent study, 310 and 382 nm (pH 8), 340 and 394 nm (pH≈5), 295 and 380 nm (H_0≈−9) and 317 nm (pH≈12) bands could be assigned to the respective spectra of neutral, monocation, dication, and monoanion species respectively. Since the energy difference between the two observed band maxima corresponding to L_a and L_b of different species either remain nearly the same or increases with the change in hydrogen ion concentration, it can be concluded that no crossing of L_a and L_b occurs, *i.e.* the long-wavelength absorption and fluorescence bands for all of these species belong to the same electronic state (L_b).

The following trend in the absorption and fluorescence spectra is generally observed during protonation or deprotonation of heterocyclic molecules if π-π^* is the lowest energy transition: i) A blue shift in absorption and fluorescence spectra is observed on protonation of amino group and the spectra resembles with the parent molecule.[16] ii) A broad red shifted absorption and fluorescence band is noticed if the tertiary nitrogen atom is protonated[17] and iii) red shift is observed in the spectral behavior if imino or amino group is deprotonated.[18] Further, pK_a for the deprotonation of imino group in benzimidazoles is ≈12±2 whereas that for amino group is >14 and amino group becomes relatively much more acidic in S_1 state as compared to imino group.[16,19,20] The anion formed in the former case is generally fluorescent but that formed in the latter case is nonfluorescent,[19] with the exception of 2-naphtylamine,[21] iv) lastly, proton induced quenching of the fluorescence of neutral amines are generally observed at moderate hydrogen ion concentration before forming ammonium ion in S_1.[22]

With the above points in mind and the spectral behavior as shown in Figs. 3 and 4, it is clear that the monocation is formed by protonating the tertiary nitrogen atom and the dication by protonating both

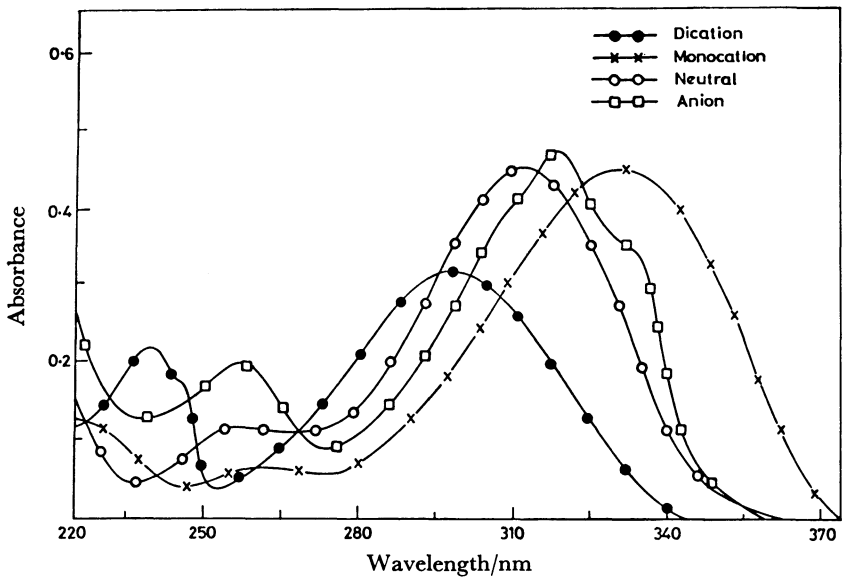

Fig. 3. Absorption spectra of various prototropic forms of $PBNH_2$ at 298 K. (concn 2.5×10^{-5} M)

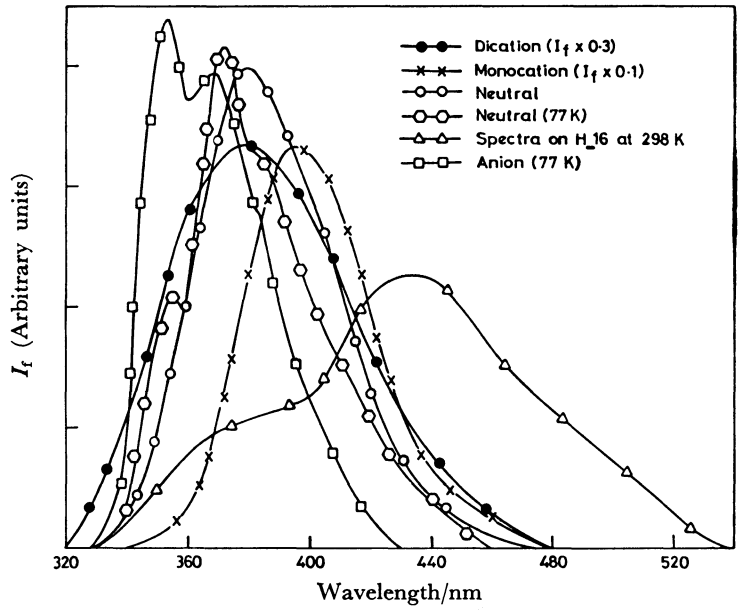

Fig. 4. Fluorescence spectra of various prototropic forms of $PBNH_2$ at 298 K and 77 K.

tertiary and primary amine nitrogen atoms, both in S_0 and S_1 states. This also agrees with the results that the pK_a value for benzimidazole molecule is nearly 5.3 and that for amino group is $\approx$4.0. Further, the λ_{max} (abs), 295 nm, of dication of $PBNH_2$ agrees nicely with the monocation of 2-phenylbenzimidazole.[6] The exact agreement may be accidental but it clearly tells that the effect of anilinium ion is similar to that of phenyl group. The ground state pK_a value for the deprotonation of imino group in benzimidazole is 13.2 and is decreased or increased further if an electron removing or electron donating group, respectively, is substituted in the parent molecule. Similar pK_a value for the deprotonation of aromatic amine is more than 14. The pK_a value of 13.0, observed for above kind of reaction in $PBNH_2$ clearly indicates that monoanion formed in S_0 state is from the deprotonation of the imino group. Further, as mentioned earlier, it has been noticed that increase in the acidity of amino group upon excitation to S_1 state is larger than that of imino group,[16,19,20] the imino anion formed by the deprotonation of amino group is nonfluorescent[19] with the exception of 2-naphthylamine,[21] whereas anion formed by the deprotonation of imino group is generally fluorescent.[18,26,27] With the above results and from our results it is clear that monoanion in S_1 state is formed by the deprotonation of amino group and not imino group as no new fluorescence spectrum was observed with the depletion of neutral $PBNH_2$ in the pH range 8—14. To substantiate this point further, the fluorescence spectrum of $PBNH_2$ at pH 12 is taken at 77 K and is shown in Fig. 4, with the data in Table 2. At

Table 3. Ground and excited state equilibrium constants of $PBNH_2$ at 298 K

Equilibrium	pK_a	pK_a^*			
		F.C. (abs)[a]	F.C.[a] (flu)	F.C.[a] (ave)	(F.T.)[b]
Dication–monocation	1.40	−7.92	−0.42	−4.18	−1.6
		7.50			
Monocation–neutral	5.05	11.03	6.58	8.80	5.00
		4.45			
Neutral–anion	13.00[c]	—	—	—	12.18[d]

a) Förster cycle method. b) Fluorimetric titration. c) Deprotonation of pyrrolic group. d) Deprotonation of amino group.

such a low temperature and in frozen state, the geometry of the species and the nature of the environments in S_1 state corresponds to that of ground state *i.e.* the species present in S_1 is the monoanion formed by the deprotonation of imino group. Though the absorption spectra of the monoanion at 77 K is not observed but the nature of vibrational mode interacting with the electronic mode obtained from the absorption spectrum at 298 K seems to be the smae as observed from the fluorescence spectrum of monoanion of $PBNH_2$ at 77 K. This will give a support to our assignment of monoanion species in S_0 and S_1 states.

The 430 nm fluorescence band, observed at 298 K and at H_15 and 16, could be assigned to the formation of dianion. This species is formed by the deprotonation of imino nitrogen atom, and is consistent with the above-mentioned conclusions. The dianion could have also been obtained by the second deprotonation of amino group but this has been rejected on the ground that the fluorescence observed from the dianion, formed by the double deprotonation of amino group in case of 9-phenanthrylamine,[23] 1- and 2-naphthylamines[28] is blue shifted, both in comparison to neutral and monoanion species whereas this one is red shifted with respect to neutral one.

The values of pK_a for various equilibria calculated spectrophotometrically are listed in Table 3. The values of pK_a^* obtained by fluorimetric titration curves (Fig. 5) as well as by Förster cycle method,[25] wherever applicable, are also listed in Table 3. These values depict the general behavior of the benzimidazoles and prove the assignment of the various species as mentioned earlier. pK^* values for monocation–neutral and neutral–monoanion equilibria are nearly equal to that for benzimidazole molecule, indicating that the presence of electron-donating amino group at the proper position of the phenyl group does not allow the phenyl group to behave as electron-withdrawing group. The results of fluorimetric titration curves (Fig. 5) are also consistent with the earlier findings *i.e.* arylammonium ions are stronger acids in S_1 state, the value of dissociation constant obtained for monocation–neutral equilibrium agrees with that of ground state value (this behavior is common for the protonation of tertiary nitrogen atom[26,27] and the relative increase in the acidity of amino group upon excitation to S_1 state is more than that of imino group. The large difference between the pK_a^* values obtained by Förster cycle method, using absorption or fluorescence data, for the dication–monocation equilibrium (7.50 pK_a units) and monocation–neutral equilibrium (4.45 pK_a units) could be due to the unequal solvent relaxation or it may however, be due to use of band maxima in stead of 0-0 band.

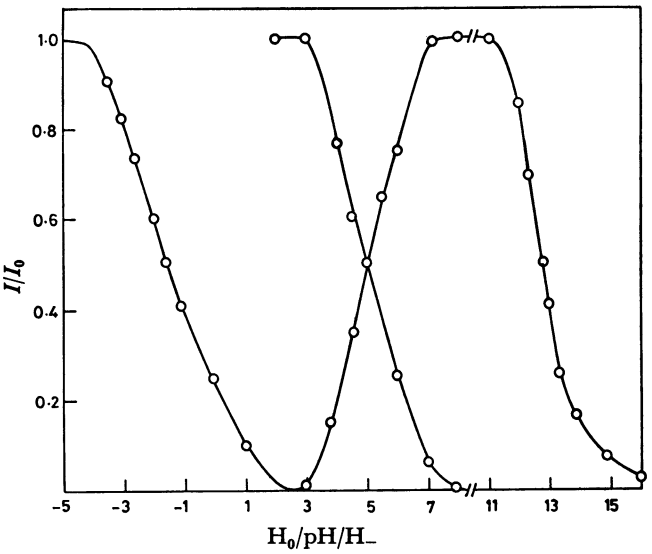

Fig. 5. Plot of relative fluorescence intesity(I/I_0) of different species as a function of H_0/pH/H_.
I/I_0 of dication in the range $H_0 = -9$ to pH=3; I/I_0 of monocation or neutral molecule in the pH range of 3 to 9; I/I_0 of neutral molecule in the pH range 11 to H_=16.

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