

Experimental & Theoretical Studies on Electronic Spectra of *o*-, *m*- & *p*- Amino Benzoic Acids & Their Protonated & Deprotonated Species

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Absorption and emission spectra of isomeric aminobenzoic acids in different solvents and at different pH values have been studied. The results have been supplemented by the CNDO/S calculations. The acid-base equilibria in the ground and excited states have also been studied.

There have been several studies¹⁻⁸ on the electronic spectra of aminobenzoic acids. Doub and Vandenberg¹⁻³ recorded the absorption spectra at pH 3.73 and 10.00. Kopylova and coworkers^{6,7} have reported the absorption spectra in aqueous solutions. Tramer⁴ has studied the spectra of *o*-aminobenzoic acid in various solvents and also studied its fluorescence spectra. No emission studies seem to have been made on *m*- and *p*-aminobenzoic acids. Furthermore, the effect of solvent on their spectra has not yet been studied. The present study reports our extensive measurements on the absorption and emission spectra of aminobenzoic acids in different solvents and also under different conditions of acidity. CNDO-S/CI calculations have also been made for these molecules and their protonated species. The theoretical transitions have been correlated with the experimental bands. The lowest excited electronic states have been characterised. Acid-base properties in the excited state are explained in terms of charge distribution in the ground and excited states.

Materials and Methods

Ortho-, *m*- and *p*-aminobenzoic acids (E Merck) were twice crystallised from aqueous ethanol (25%, v/v). Absolute ethanol was twice distilled over sodium metal and stored over molecular sieves. Cyclohexane and methylcyclohexane¹⁰ were stirred with sulphuric acid, washed with water, dried over fused calcium chloride and distilled twice over sodium metal. Acetonitrile was distilled over phosphorus pentoxide, collecting the middle cuts (b.p. 354 K) for use. Methanol (AR) was used as such. Water was triply distilled over potassium dichromate and potassium permanganate solutions.

Absorption spectra were recorded on a UVVIS-NIR Hitachi spectrophotometer and the fluorescence spectra on a Perkin-Elmer MPF-44B spectrofluorimeter. Oscillator strength (f) was calculated using Eq.(1) relationship

$$f = 4.32 \times 10^{-9} \epsilon_{\max} \Delta\bar{\nu} \quad \dots (1)$$

where ϵ_{\max} is the experimental extinction coefficient at band maximum and $\Delta\bar{\nu}$ is the half-band width (in wavenumbers).

Theoretical calculations were carried in the CNDO/S approximation of Del Bene and Jaffe¹¹, using the quantum chemistry program exchange (QCPE 174). The configurations were limited to first 40 singly excited states. Bond lengths and bond angles were taken from literature¹². The molecular axes for the aminobenzoic acids are designated in Fig.1.

The characterization of electronic states have been made on the basis of configurational analysis. In order

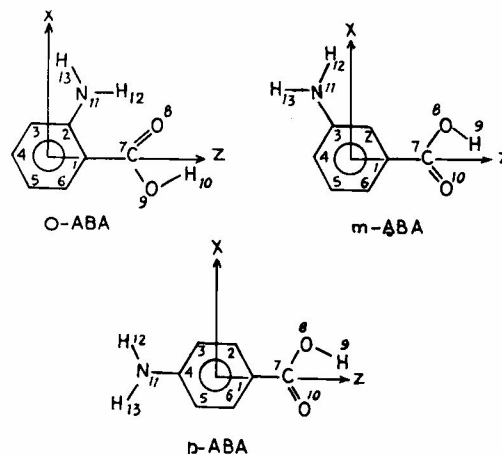


Fig. 1— Molecular axes designations of aminobenzoic acids (Y-Axis is out-of-plane)

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Table 1—Absorption Maxima ($\bar{\nu}/kK$) of Isomeric Aminobenzoic Acids in Various Solvents and at Different pH Values

Methyl + cyclohexane	Acetonitrile		Methanol		$10^{-3}M$ HCl ^a		1NHCl ^b		Alkaline soln ^c		
	$\bar{\nu}_{max}$	f	$\bar{\nu}_{max}$	f	$\bar{\nu}_{max}$	f	$\bar{\nu}_{max}$	f	$\bar{\nu}_{max}$	f	
	<i>o</i> -Aminobenzoic acid										
29.35	29.76	0.148	29.85	0.055	30.50	0.039	36.94	0.018	32.24	0.104	
40.32	40.32	0.197	40.49	0.105	41.40	0.077	44.35	0.324	41.84	0.205	
44.90	44.05	0.146	45.66	0.616	46.00	0.449	48.31	0.073	47.17	0.643	
	<i>m</i> -Aminobenzoic acid										
31.64	31.25	0.061	31.85	0.080	32.05	0.013	36.90	0.014	33.20	0.078	
41.32	40.65	0.201	40.82	0.166	36.90	0.008	43.97	0.199	42.84	0.456	
47.96	43.86	0.216	46.30	0.675	45.25	intense	47.95	0.032	47.25	0.636	
	<i>p</i> -Aminobenzoic acid										
36.30	34.96	0.615	34.48	0.268	34.91	0.425	37.55	0.016	37.74	Intense	
46.30	44.25	0.057	45.05	0.127	45.46	0.190	44.05	0.263	47.17	0.378	
							48.08	0.040			

^aNeutral molecule; ^bmonocation; ^canion

to study the intramolecular charge transfer (CT) in these states it is convenient to divide each aminobenzoic acid into the sub-systems $-NH_2$, $-C_6H_4$ - and $-COOH$. Electronic charges on each atom in the ground state and the excited states were calculated from the corresponding wavefunctions.

Results

Absorption spectra: (a) Neutral molecules

The $\bar{\nu}_{max}$ (in kK) together with the oscillator strength (f) for these compounds are given in Table 1. Due to poor solubility of *m*- and *p*-aminobenzoic acids in cyclohexane and methylcyclohexane the spectra were recorded for the saturated solutions of unknown strength and hence only the $\bar{\nu}_{max}$ values have been listed. In the case of *m*- and *p*-aminobenzoic acids all the absorption bands are red shifted with an increase in polarity and hydrogen bonding power of the solvents whereas the trend is reversed for *o*-aminobenzoic acid.

(b) Monocations

It has been found that in 1*N* HCl solution the absorption spectra (Table 1) of aminobenzoic acids correspond to the protonated species, $NH_3^+C_6H_4COOH$. Based on the fact that the spectrum of anilinium ion¹³ is nearly the same as that of benzene, it is expected that spectra of these cations will be similar to that of benzoic acid. It is indeed so, as the 1L_a and 1L_b bands have nearly the same frequencies as those of benzoic acid.

(c) Anions

Carboxylic group of amino acids dissociates in alkaline solutions. Therefore the absorption spectra at $pH \sim 7$ is solely due to $NH_2C_6H_4COO^-$. There is no

Table 2—Fluorescence Maxima ($\bar{\nu}/kK$) of Isomeric Aminobenzoic Acids in Various Solvents

Cyclohexane	Methylcyclohexane	Acetonitrile	Ethanol	$10^{-3}M$ HCl	$10^{-2}M$ KOH
		<i>o</i> -Aminobenzoic acid			
25.98	25.67	25.32	25.87	23.81	25.40
		<i>m</i> -Aminobenzoic acid			
27.25	25.98	25.25	23.36	25.00	24.82
		<i>p</i> -Aminobenzoic acid			
31.85	30.21	29.41	29.59	28.60	29.59

change in the nature of the spectra with increase in pH beyond 7 indicating that deprotonation is already complete.

(d) Bications

The bands at 36 and 42 kK appearing in the spectra in concentrated sulphuric acid (36 *N*) correspond to those of the biprotonated species, $NH_3^+C_6H_4COOH_2^+$. The spectra resemble that of protonated benzoic acid. 1L_a and 1L_b bands corresponding to this biprotonated species are red-shifted by 100-150 cm^{-1} in comparison to those of the protonated benzoic acid.

Emission spectra

It is apparent from the data in Table 2 that, in comparison to the spectra in cyclohexane, significant red shift in fluorescence occurs as the solvent polarity increases indicating increase in the dipole moment upon excitation.

The singly protonated species of these aminobenzoic acids are not fluorescent because $-NH_3^+$ groups in

both ground and excited states provide good routes for degradation of excited states. This behaviour is similar to that of benzoic acid^{14,15}. Only in concentrated sulphuric acid (36 *N*) aminobenzoic acids show fluorescence due to the protonation of carboxyl group in addition to the protonation of amino group. The lowest singlet is observed at ~ 27.00 to 29.00 kK in all the bications and these values compare well with the fluorescence maxima of benzoic acid¹⁶ under acidic conditions.

All the aminobenzoic acids show phosphorescence. The lowest triplet in EPA glass is observed at 22.90 kK, 21.86 kK and 23.50 kK in *o*-, *m*- and *p*-aminobenzoic acids, respectively (EPA refers to a 5:5:2 mixture of ethyl ether-isopentane-ethanol).

Theoretical results and their correlation with experimental data

The theoretical values (after configuration interaction) are compared with the experimental results in methanol in Table 3. The $S_0 \rightarrow S_2$ transition in all the isomeric aminobenzoic acids (polarized along the short axis)[†] have been assigned to the lowest observed band. The second experimentally observed bands have been assigned to the theoretically predicted $S_0 \rightarrow S_3$ transition in all the cases, which are polarized along the long axis of the benzene. The strongest absorption bands around 44 kK in *o*- and *m*-aminobenzoic acids have been assigned to the $S_0 \rightarrow S_6$, S_7 and $S_0 \rightarrow S_5$, S_6 theoretical transitions respectively. The theoretical results for the monocations are compared with the experimental results (in 1 *N* HCl) in Table 3. The band at ~ 37 kK is related to the theoretically predicted transition $S_0 \rightarrow S_2$ in all the monocations. This band may be termed as the 1L_b band on the basis of polarization of these transitions. The transitions $S_0 \rightarrow S_3$, S_4 appear as one band at ~ 44.4 kK. It is apparent from Table 3 that there is a fair agreement between the experimental and theoretical transition energies and oscillator strengths.

Nature of the lowest excited state

In benzoic acid the lowest excited state is of $n\pi^*$ nature. However, in aminobenzoic acids the lone pair on nitrogen is in conjugation with the π electrons of benzene and this may lead to the energy of $\pi\pi^*$ transition nearly equal to or slightly lower than $n\pi^*$ transition energy. This may result in lowering of the $\pi\pi^*$ transition frequency vis-a-vis the $n\pi^*$ of all the aminobenzoic acids. Theoretically, this is born out in the case of *p*-aminobenzoic acid where $\pi\pi^*$ state is lower than $n\pi^*$. Experimentally, this is supported by the following facts: (i) the extinction coefficients of all the bands are quite large which cannot be due to $n\pi^*$ transition; (ii) at room temperature fluorescence is

Table 3— Electronic State of Aminobenzoic Acids and Their Cationic Forms

Experimental ^a		Theoretical		Type
$\bar{\nu}/\text{kK}$	f	$\bar{\nu}/\text{kK}$	f	
<i>o</i> -NH ₂ C ₆ H ₄ COOH				
29.85	0.055	29.18	0	$n\pi^*$
(29.35)	—	34.64	0.042	mix
40.49	0.105	42.32	0.052	$\pi\pi^*$
(44.32)	—	46.99	0.001	mix
		48.08	0.001	mix
45.66	0.616	49.31	0.542	mix
(44.90)	—	50.74	0.232	$\pi\pi^*$
<i>m</i> -NH ₂ C ₆ H ₄ COOH				
		29.63	0	$n\pi^*$
31.85	0.080	34.69	0.029	$\pi\pi^*$
(31.64)	—			
40.82	0.166	43.09	0.051	$\pi\pi^*$
(41.32)	—	48.33	0.011	$\pi\pi^*$
46.30	0.675	48.92	0.611	mix
(47.96)	—			
<i>p</i> -NH ₂ C ₆ H ₄ COOH				
		30.79	0	$\pi\pi^*$
34.48	0.268	35.93	0.007	$n\pi^*$
(36.30)	—			
45.05	0.127	41.74	0.224	$\pi\pi^*$
(46.30)	—			
		50.05	0.003	$\pi\pi^*$
		50.33	0.000	$\pi\pi^*$
<i>o</i> -NH ₃ ⁺ C ₆ H ₄ COOH				
31.45	0.018	29.03	0.000	mix
35.71	0.005	36.92	0.007	$\pi\pi^*$
	0.007			
44.40	0.151	44.49	0.055	mix
		44.73	0.007	mix
		48.02	0.000	mix
<i>m</i> -NH ₃ ⁺ C ₆ H ₄ COOH				
32.26	vw	28.15	0.000	$\pi\pi^*$
35.71	0.007	36.98	0.001	mix
		44.43	0.002	$n\pi^*$
44.40	0.272	44.78	0.049	$\pi\pi^*$
		46.44	0.001	$\pi\pi^*$
		50.11	0.361	mix
<i>p</i> -NH ₃ ⁺ C ₆ H ₄ COOH				
33.56	0.042	28.00	0.000	$n\pi^*$
36.10	0.008	37.05	0.007	$\pi\pi^*$
44.25	0.317	43.92	0.143	$\pi\pi^*$
		44.96	0.000	$\pi\pi^*$
		46.66	0.001	$n\pi^*$
		49.71	0.001	mix
		50.89	0.084	mix

^aFor neutral molecules values in parentheses indicate the data in methylcyclohexane. Acidic and basic conditions cannot be created in methylcyclohexane.

[†]The transition polarized along the long axis of benzene ring is termed 1L_a band while that polarized along the short axis of benzene ring is termed 1L_b band.

Table 4— Values of pK_a s and pK_a^* for Aminobenzoic Acids (ABA)

Equilibrium	Acid	$pK(S_0)$	$pK(S_1)$ determined from	
			Absorption	Fluorescence
${}^+H_3NC_6H_4COOH \rightleftharpoons H_2NC_6H_4COOH + H^+$	<i>o</i> -ABA	2.55	-11.0	—
	<i>m</i> -ABA	3.12	-7.1	—
	<i>p</i> -ABA	2.14	-3.4	—
$H_2NC_6H_4COOH \rightleftharpoons H_2NC_6H_4COO^- + H^+$	<i>o</i> -ABA	4.80	8.5	8.1
	<i>m</i> -ABA	4.74	7.2	4.4
	<i>p</i> -ABA	4.85	10.8	6.9

Table 5— Ground and Excited State Charge Densities in Aminobenzoic Acids

Subsystem	State		
	S_0	1L_b	1L_a
<i>o</i> -Aminobenzoic acid			
-NH ₂	0.008	0.306	0.132
-COOH	-0.102	0.091	-0.063
-C ₆ H ₄	0.094	-0.397	-0.069
<i>m</i> -Aminobenzoic acid			
-NH ₂	-0.009	0.098	0.097
-COOH	-0.092	-0.176	-0.143
-C ₆ H ₄	0.101	0.078	0.046
<i>p</i> -Aminobenzoic acid			
-NH ₂	-0.005	0.099	0.072
-COOH	-0.113	-0.154	-0.115
-C ₆ H ₄	0.118	0.055	0.043

generally observed if S_1 is a $\pi^* \rightarrow \pi$ and phosphorescence if S_1 is $\pi^* \rightarrow n$ transition; and (iii) the observed solvent effect (both absorption and fluorescence) also support the nature of the transition to be $\pi\pi^*$. It is possible that $n\pi^*$ transition in all the cases be buried under the strong $\pi\pi^*$ band.

Acid-base equilibria

The ground state pK_a values for the equilibria (2) and (3)



determined potentiometrically are given in Table 4. The excited state pK_a^* values at room temperature were calculated using Eq.(4) based on Förster¹⁷ cycle;

$$pK_a^* - pK_a = 2.1 \times 10^{-3} (\bar{\nu}_{HA} - \bar{\nu}_A) \quad \dots (4)$$

where $\bar{\nu}_{HA}$ and $\bar{\nu}_A$ are the band maxima (in cm^{-1}) of the acid and the conjugate base respectively. The values obtained are listed in Table 4. The Förster cycle

calculations are based on the assumptions that (i) the vibrations are equally spaced, (ii) reorientation of solvent molecules surrounding a dissolved molecule in an excited state does not take place and (iii) there is no geometrical change due to transition between the S_0 and S_1 states of the species involved in the equilibrium. The difference between pK_a^* values for equilibrium (3), calculated using the absorption and fluorescence data, may be due to the different solvent orientations in the ground and excited states. The ground state pK_a values for equilibrium(3) indicate that the *ortho* effect is very small in the ground state but develops on excitation.

pK_a^* values for equilibrium (2) are determined only from absorption data as the monocation is nonfluorescent. The pK_a^* (2) is much lower compared to pK_a (2) in the ground state. This is in agreement with the pK_a^* values reported for this type of equilibrium¹⁸. It is evident from Table 5 that excitation to a singlet state decreases the electronic charge density (q_{NH_2}) on the amino group and a qualitative correlation exists between q_{NH_2} and pK_a^* . Excitation produces a larger decrease in the acidity of *ortho*- and *para*-aminobenzoic acids than that of *meta*- isomer.

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