The Electronic Spectrum and Structure of the s-Triaminobenzenium Ion

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(Received December 17, 1962)

A quite interesting example of a kind of aromatic carbonium ion seems to be formed in the aqueous solution of *s*-triaminobenzene (TAB). For the equilibrium TAB+$H^+ \rightleftharpoons$ $TABH^+$ (*s*-triaminobenzenium ion), p$K \sim 5.5$[1]. No such protonation on the ring carbon occurs in the case of aniline or *m*-phenylene diamine, where the amino group is protonated[1]. This is a preliminary report on theoretical calculations on the electronic spectra of TAB and $TABH^+$ and on the stabilities of the protonation products of aminobenzenes, which give a basis for interpretation of the observed results[1].

A semi-empirical ASMO CI method[2] was used. The parameters for Hückel MO calculations were the same as given elesewhere[3]. Pyrrole-type nitrogen was assumed, and the valence state ionization potential and electron affinity were obtained from the table[4]. The value of β_{CN}^{core} was taken to be -2.399 eV. All C–C bond distances were assumed to be 1.39 Å, and all C–N distances, 1.36 Å. The hyperconjugation with the CH_2 group in the case of $TABH^+$ was not taken into account. The calculated results are given in Table I, together with the observed values. D_{3h} and C_{2v} symmetries are assumed for TAB and $TABH^+$ respectively.

The calculated spectra are in satisfactory agreement with the observed values. Although the hyperconjugation was excluded in this calculation, it may be taken into account by some approximate method. In the present case, owing to the presence of the three amino groups, the higher occupied orbitals of the local system I (II is the CH_2 group) should be very much elevated compared with the highest occupied orbital of the corresponding local system of the benzenium ion[5]. Therefore, the excitation energies from the higher occupied orbitals of I to the antibonding π-orbital of II may not be so large, and this charge transfer interaction will increase the stability of the protonated aminobenzenes.

Another measure of the stability of the protonated species is the localization energy. The results of calculation by the Hückel MO method are shown in Table II.

In mode A, the destabilization energy of the π-electrons by protonation becomes considerably smaller from aniline to TAB, whereas it is almost constant or even slightly increases in mode B. This result is in accordance with the observed values. The mode A protonation seems to occur also in the case of tri-O^--benzene (TOB) (phloroglucine trianion)[1], for

TABLE I. CALCULATED ELECTRONIC SPECTRA IN COMPARISON WITH THE OBSERVED VALUES

TAB	Calcd.		Obs.		$TABH^+$	Calcd.		Obs.	
	$h\nu$, eV.	f	$h\nu$, eV.	f		$h\nu$, eV.	f	$h\nu$, eV.	$\log \varepsilon_{max}$
$^1A_2'$	4.27	0	4.4	0	$^1B_1$	3.12	0.39	3.4	3.5
$^1A_1'$	5.21	0	5.0	0	$^1A_1$	4.43	0.65	4.5	3.9
$^1E'$	5.79	2.2	5.6	$\log \varepsilon_{max} \sim 4.3$	$^1A_1$	5.57	1.52	?	?
					$^1B_1$	6.07	0.00	?	?

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Table II. Localization energies of some aminobenzenes (in unit of β)[a)]

Mode of protonation	A. Carbon	B. Amino group
Aniline	2.2498[b)]	2.8054
m-Phenylenediamine	1.9562[c)]	2.8058
TAB	1.8294	2.8060

a) The localization energies in this table are given by $(m-m^+)$, where the π energy of the neutral molecule is given by $n\alpha+m\beta$ and that of the protonated system, by $(n-2)\alpha+m^+\beta$.
b) Protonation on para-carbon.
c) Protonation on the carbon at the ortho-position in relation to both amino groups.

which we have calculated the localization energy, assuming suitable Hückel MO parameters ($\delta_{o}\sim 0.8$, $\beta_{co}\sim\beta$) and $(m-m^+)$ being 1.6861.

Mackor et al.[6)] have demonstrated an approximate linear relation between the localization energy and log K in the case of the protonation of many aromatic hydrocarbons. We have observed that the same linear relation holds for TAB and TOB as for aromatic hydrocarbons.

Another possible structure of $TABH^+$ or $TOBH^+$ may be a kind of π-complex in which the proton is situated on the molecular plane. If the proton is situated at the center of the molecule, the lowest energy transition is still forbidden and we cannot interpret the observed strong band. If the proton moves to the periphery of the molecule, the transition becomes possible. This model may finally lead to the localization or hyperconjugation model described above as the most stable equilibrium form.

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