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Electronic Structures of the Ring-Protonated Aromatic Amines

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In order to study the electronic spectra and stabilities of the ring protonated aromatic amines, π-electron structure of nineteen amino-substituted pentadienyl cations were calculated by the composite molecule method. The lower electronic transitions of these ions are assigned to the charge transfer from amino groups to the pentadienyl cation. Stability of the ground state depends on the extent of intramolecular charge transfer, which is determined by the position and number of amino-substitution. The amino group on 1-, 3- or 5-carbon atom greatly stabilizes the ground state while contribution of the amino group on the other position is quite small. Occurrence of the ring or amino protonation for various amino-substituted benzenes is shown to be well predicted by the calculated stabilization energy.

Unlike the ordinary mode of protonation[1] to the aromatic amine, 1,3,5-triaminobenzene in a weakly

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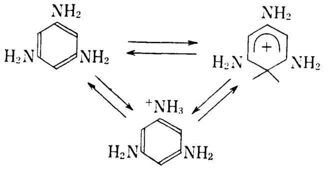
[1] E. M. Arnett, "Progress in Physical Organic Chemistry," Vol. 1, Interscience Publishers, New York (1963), p. 223.

acidic solution is singly protonated to the ring carbon atom as well as to the amino group,2) and the following equilibrium exists among the three components.



In a previous paper,3) we reported that in this equilibrium system, ring protonation is predominant at room temperature while the species protonated on the amino group increases its concentration with decreasing temperature. It was demonstrated spectroscopically that ring protonation of this type also takes place for *N*,*N*-dimethyl-*m*-phenylenediamine in an acidified aqueous solution but not for *N*,*N*-dimethyl-*p*-phenylenediamine.

The mode of protonation seems to be determined by a slight difference in the stability of the protonated species, and therefore very sensitive to the number and position of the amino-substituent. For discussion on this point, the π-electron structures of several ring-protonated aminobenzenes have been calculated by the so called "composite molecule (CM) method." By this method the stabilization energy due to the transfer of π-electrons from amino groups to the benzene ring can be given. The specificity observed with the protonation to various aminobenzenes is discussed on the basis of the calculated stabilization energies.

Method of Calculation

Let us explain the calculation procedure taking 1,3,5-triaminobenzenium ion as an example. The so-called π-electron approximation is adopted and only the singlet states are considered. First the system was divided into two components, *i. e.*, benzenium ion (or pentadienyl cation with 4 π-electrons) and amino groups (with 2 π-electrons per group). The Hückel orbitals (1, 2,···5) of the pentadienyl cation $C_5H_7^+$ were taken as the orbitals for benzenium ion, since they are not appreciably different from the SCF MO by the Pariser-Parr-Pople (PPP) method.4) The three lone-pair orbitals of the amino groups are represented by n_i's where suffix i indicates the position of the carbon atom to which the respective amino groups are attached. Numbering of the atoms and geometry of the molecule are shown in Fig. 1. The bond distances and angles were assumed to be 1.40 Å for C=C bond and 1.47 Å for C–N bond, respectively. All the angles were assumed to be 120°. The two lone-pair orbitals (n_1 and n_5) of the amino groups were combined to give the symmetric n_{s15} and antisymmetric n_{a15} group orbitals

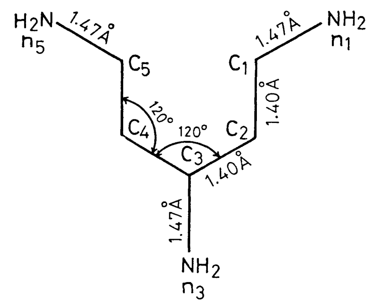


Fig. 1. Geometrical structure and numbering of 1,3,5-triaminopentadienyl cation.

$$n_{s15} = (n_1+n_5)/\sqrt{2}$$
$$n_{a15} = (n_1-n_5)/\sqrt{2}.$$

With the use of the above-mentioned orbitals of the components, ground (G) and several locally-excited (LE's) and charge-transfer (CT's) configurations were constructed, as shown in Fig. 2. The energies of the lowest two locally-excited configurations (LE_1, LE_2) were those estimated from the transition energies of several methylated benzenium ions observed by Hanazaki and Nagakura,5) while the energy of LE_3 was taken from the value calculated by the same authors. The energies of CT configurations were calculated by the relation, $I-A-\Delta C$, where I, A and ΔC stand for the ionization potential of an amino group (10.15 eV),6) the electron affinity of the benzenium ion (estimated to be 7.50 eV[*2]) and the electrostatic interaction energy caused by an electron transfer from an amino group to the benzenium ion, respectively. We adopted the Pariser-Parr approximation8) for evaluating the two-center Coulomb integrals necessary for the calculation of ΔC.

Non-zero off-diagonal matrix elements for the interactions of CT configurations with ground (G)

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2) H. Köhler and G. Scheibe, *Z. Anorg. Allg. Chem.*, **285**, 221 (1956).

3) T. Yamaoka, S. Hosoya and S. Nagakura, *Tetrahedron*, **24**, 6203 (1968).

4) H. Hosoya, S. Hosoya and S. Nagakura, *Theoret. Chim. Acta*, **12**, 11, 117 (1968).

5) I. Hanazaki and S. Nagakura, This Bulletin, **38**, 1298 (1965).

6) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

[*2] This value was estimated from the lowest vacant SCF MO energy for the pentadienyl cation after some theoretical corrections presented by Hush and Pople.7) For CT configurations in which the electron is transferred to the second lowest vacant orbital, the A value was taken to be 4.50 eV considering the difference in orbital energies between the first and the second lowest vacant orbitals obtained by Hanazaki and Nagakura.5)

7) N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

8) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).

TABLE 1. ENERGIES, OSCILLATOR STRENGTHS AND DIRECTIONS OF LOWER ELECTRONIC TRANSITIONS OF 1,3,5-TRIAMINOBENZENIUM ION

Energy (eV)			Oscillator strength (f)			Character	Direction of the moment[a]
Calcd		Obsd	Calcd		Obsd		
CM	PPP		CM	PPP			
3.87	3.39	3.39	0.03	0.33	0.09	CT $n_{a_{15}}$→ring	⊥
4.24	4.49	4.54	0.32	0.44	0.20	CT n_3→ring	∥
5.96	5.82	5.46	—	—	—	CT $n_{.5a}$→ring	∥

a) with respect to molecular axis.

TABLE 2. STATE WAVEFUNCTIONS OF 1,3,5-TRIAMINOPENTADIENYL CATION CALCULATED BY THE CM METHOD

Symmetric

Energy (eV)	Coefficient					
	Ψ_G	Ψ_{LE_2}	Ψ_{LE_3}	$\Psi_{CT_3^3}$	$\Psi_{CT^3_{s15}}$	$\Psi_{CT^4_{a15}}$
−2.186	0.8409	−0.0109	−0.0316	−0.2846	0.4020	0.2213
5.206	0.3655	0.5931	0.4142	−0.0774	−0.4412	−0.3774
7.828	−0.2042	0.1268	0.7181	−0.0181	0.1240	0.6410
2.053	0.0027	0.3739	−0.1204	0.7434	0.5409	−0.0219
3.774	−0.2885	0.1722	0.2385	−0.4807	0.5751	−0.5181
6.115	−0.1856	0.6800	−0.4903	−0.3195	−0.0701	0.3590

Antisymmetric

Energy (eV)	Coefficient			
	Ψ_{LE_1}	$\Psi_{CT^3_{a15}}$	$\Psi_{CT_3^4}$	$\Psi_{CT^4_{s24}}$
4.724	0.8262	0.5633	—	—
5.650			1.000	
1.686	−0.5633	0.8262	—	—
5.650	—	—	—	1.000

or *LE* configurations can be represented by the aid of the resonance integral β_{CN} between the neighbouring nitrogen and carbon atoms. The value was determined to be −2.0 eV after several trial calculations.

Results and Discussion

Table 1 shows calculated and observed energies and oscillator strengths for the lower transitions of 1,3,5-triaminobenzenium ion. Results of the Pariser-Parr-Pople type calculation were also cited from the previous paper.[3] The wavefunctions of the ground and excited states are shown in Table 2 to clarify the nature of each transition. As evident from Table 1, the lowest two transitions at 360 mμ and 273 mμ are undoubtedly assigned to the charge-transfer from the amino groups to the ring, the direction of the transition dipoles being perpendicular and parallel to the molecular axis, respectively. The third transition, though not observed, has also a charge-transfer character (parallel band). The results are in good agreement with those obtained previously by the PPP method.

Figure 2 shows the configuration energies used for the present calculation and also the evaluated state energies. The energy of the ground state, 2.186 eV below zero, corresponds to the π-electron stabilization energy (ΔE) caused by the resonance between the ring and amino groups.

In Table 3 the calculated ΔE values of nineteen aminosubstituted benzenium ions are summarized, together with the lower π-electronic transition energies. For some compounds the calculated oscillator strengths are also given. It is apparent that the larger the number of amino groups, the more the ion is stabilized. On close inspection and least-squares calculation, ΔE is found to be additively increased by the amino groups on the ortho, meta and para positions to the protonated carbon with the following values:

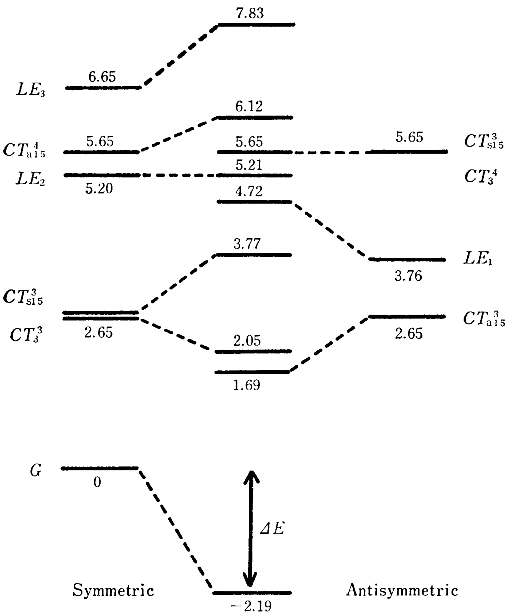


Fig. 2. Configurations used for the CM calculation and the evaluated state energies (eV) of the 1,3,5-triaminopentadienyl cation. Configurations are represented as follows. $G=|1\bar{1}2\bar{2}n_{s15}\bar{n}_{s15}n_{a15}\bar{n}_{a15}n_3\bar{n}_3,|$ $LE_1=\Psi(2—3)$, $LE_2=\{\Psi(2\rightarrow4)-2\Psi(1—3)\}/\sqrt{5}$, $LE_3=\{2\Psi(2\rightarrow4)-\Psi(1—3)\}/\sqrt{5}$, $CT^3{}_{s15}=\Psi(n_{s15}\rightarrow3)$, $CT^3{}_{a15}=\Psi(n_{a15}\rightarrow3)$, $CT_3{}^3=\Psi(n_3\rightarrow3)$, $CT^4{}_{s25}=\Psi(n_{s15}\rightarrow4)$, $CT^4{}_{a15}=\Psi(n_{a15}\rightarrow4)$, $CT_3{}^4=\Psi(n_3\rightarrow4)$, where $\Psi(a\rightarrow b)=\{|\cdots ab\cdots|+|\cdots ba\cdots|\}/\sqrt{2}$ and 1, 2 ⋯ are the Hückel MO's of the pentadienyl cation.

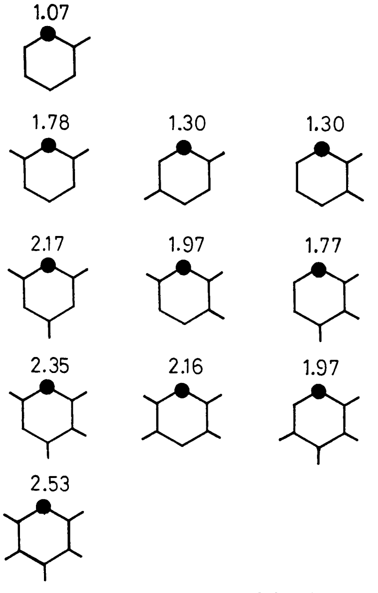


Fig. 3. The most probable sites of the ring-protonation of a series of amino-substituted benzenes are shown by the filled circles. Numbers show the values of ΔE in eV.

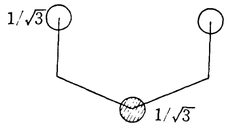
TABLE 3. STABILIZATION ENERGIES, TRANSITION ENERGIES AND OSCILLATOR STRENGTHS CALCULATED FOR VARIOUS AMINO-SUBSTITUTED BENZENIUM IONS

Compound[a]	Stabilization energy (eV)	Transition energy (eV)	Oscillator strength	Direction[b]
2-	−0.34	2.29		
		4.51		
2,4-	−0.64	2.35		
		2.71		
3-	−0.82	2.50	0.554	0°
		3.81	0.253	90°
1-	−1.07	3.60		
		5.39		
2,3-	−1.08	2.87	0.111	90°
		3.93	0.022	0°
2,5-	−1.30	3.01		
		3.94		
4,5-	−1.30	2.94		
		4.27		
2,4,3-	−1.31	1.63	0.011	90°
		3.19	0.016	0°
1,2,4-	−1.52	2.97		
		3.55		
3,5-	−1.58	3.51		
		4.79		
1,2,3-	−1.77	3.18		
		4.37		
1,3,4-	−1.77	1.78		
		1.95		
1,5-	−1.78	3.47	0.039	90°
		5.00	0.320	0°
1,2,5-	−1.97	3.29		
		4.37		
1,2,3,4-	−1.97	3.37		
		3.78		
1,2,4,5-	−2.16	2.48	0.140	90°
		5.47	0.036	0°
1,3,5-	−2.17	3.87		
		4.24		
1,2,3,5-	−2.35	3.64		
		4.40		
1,2,3,4,5-	−2.53	2.85	0.081	90°
		4.02	0.529	0°

a) numbers show the position of substitution of the amino group.
b) with respect to molecular axis.

0.81 eV per *o*-NH_2
0.30 eV per *m*-NH_2
0.62 eV per *p*-NH_2.

This simple relationship can be easily explained on the basis of perturbation treatment, if one recalls the shape of the lowest vacant orbital of the benzenium ion into which the electron migrates from the amino groups. The perturbation of the amino groups on the meta positions might be small because the coefficients of the lowest vacant orbital on these positions are almost zero as shown below.



Here we take 1.7 eV as the borderline value of ΔE between the ring and amino protonations, although it is difficult to determine definitely. The filled circles in Fig. 3 indicate the most probable sites of the ring-protonation of a series of amino-substituted benzenes. The fact that a spectrum of a ring-protonated species could be observed for *N*,*N*-dimethyl-*m*-phenylenediamine (ΔE= 1.78 eV) but not for *N*,*N*-dimethyl-*p*-phenylenediamine(ΔE= 1.30 eV) can be explained by the borderline value of ΔE. The electronic spectra and the mode of amino-substitution do not seem to be correlated with each other by a simple relation.

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