The Electronic Spectra and Structures of s-Triaminobenzenium and Some Related Ions

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It has been shown by Köhler and Scheibe[1] that *s*-triaminobenzene (TAB), *s*-triaminoanisol, *s*-triaminoxylene, *s*-triaminomesitylene and phloroglucine trianion (TOB) seem to be easily protonated on the ring carbon in an aqueous solution. When *m*-phenylenediamine is singly protonated, the absorption spectrum of the protonation product is almost the same as that of aniline, and the spectrum of singly protonated aniline is very close to that of benzene. However, the spectrum of singly protonated TAB is quite different from that of *m*-phenylenediamine, and intense band appears at a much longer wavelength. This remarkable change in the spectrum has been ascribed[1] to the formathin of $TABH^+$ protonated on the ring carbon.

In the case of the methyl derivatives of TAB, the wavelength of this intense band is a littler larger than in the case of TAB.

These facts are quite interesting from the viewpoint of the conjugation power of the amino group. The study of the electronic structure and spectrum of $TABH^+$ may be somewhat interesting also in view of the recently developed chemistry[2] of the aromatic hydrocarbons protonated in strongly acidic media.

On the other hand, we have been making some theoretical studies of the electronic spectra and electronic structures of such amino-substituted benzenes as aniline, phenylenediamines and TAB and such amino-substituted nitrogen heterocycles as amino pyridines.[3]

Using the results of these studies, we have attempted to interpret theoretically the electronic spectra and structure of $TABH^+$ and also to give a theoretical basis to the observed stability of the protonated TAB and TOB.

In the following, we shall report the results of these theoretical calculations, together with some discussion.

Theoretical Method

The semiempirical ASMO CI method[4] was used for the calculation of the electronic spectra. The necessary Hückel MO's were calculated by assuming appropiate parameters; that is, all resonance integrals were taken to be the same and equal to β, the Coulomb

1) H. Köhler and G. Scheibe, *Z. anorg. u. allgem. Chem.*, **285**, 221 (1956).

2) a) G. Dallinga, A. A. V. Stuart, P. J. Smit and E. L. Mackor, *Z. Elektrochem.*, **61**, 1019 (1957); E. L. Mackor, A. Hofstra and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66. 186 (1958). b) N. Muller, L. W. Pickett and R. S. Mulliken, *J. Chem. Phys.*, **21**, 1400 (1953); *J. Am. Chem. Soc.*, **76**, 4770 (1954). c) T. Morita, *J. Chem. Phys.*, **25**, 1290 (1956); This Bulletin, **31**, 3220 (1958); **32**, 893 (1959); **33**, 1486 (1960).

3) a) N. Mataga, to be published. b) N. Mataga and S. Mataga, This Bulletin, **32**, 600 (1959).

4) a) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); ibid., **23**, 711 (1955). b) R. Pariser, ibid., **24**, 250 (1956). c) N. Mataga, This Bulletin, **31**, 459, 463 (1958); *Z. physik. Chem. N. F.*, **18**, 285 (1958).

parameter for amino nitrogen, to be 1.2,[5] and that for O^- of TOB, 0.8.*

For the protonation products, the localization model was assumed. That is, if there are $2m$ π-electrons in the framework of n cores of the neutral molecule, then there are $2(m-1)$ π-electrons moving in the framework $n-1$ cores in the protonation product.

Thus, the effect of hyperconjugation[2b,e] with the CH_2 group is not explicitly taken into account in the present treatment. However, its effect on the stabilty of the protonation product will be examined, in an approximate way, in the latter part of this paper.

The procedures for the calculation of the electronic spectra of TAB and $TABH^+$ and the stabilities of the protonated aminobenzenes and TOB were as follows.

A) The Stabilities of the Protonation Products.—As a measure of the stabilities of the protonated species, the so-called localization energies[6-9] were calculated.

In the present case, if the π-energy of the neutral molecule is $2m\alpha+M\beta$, that of the localized system is $2(m-1)\alpha+M_r{}^+\beta$ where the proton is attached at position "r."

The localization energy is given by the difference between the π-energies of the neutral molecule and of the localized system, or by $(M-M_r{}^+)$. If all changes in the σ-bond caused by protonation are treated as being effectively constant throughout a series of aminobenzenes, we can anticipate a correlation[2a,c,8,9] between the calculated localization energies and the experimental basicities.

B) The Electronic Spectra.—The orbital energy of the i-th MO, ε_i, may be written formally:

$$\varepsilon_i=\langle\phi_i|F|\phi_i\rangle=\sum_{\mu,\nu}C_{i\mu}C_{i\nu}\langle\phi_\mu|F|\phi_\nu\rangle$$
$$=\sum_{\mu,\nu}C_{i\mu}C_{i\nu}F_{\mu\nu} \qquad (1)$$

where F is the Fock Hamiltonian and ϕ_i is the LCAO MO, for which the Hückel MO's are used in the present calculation:

$$\phi_i=\sum_{\mu}^{n}C_{i\mu}\phi_\mu. \qquad (2)$$

The matrix elements of the Fock Hamiltonian in terms of $2p\pi$ AO's may be written as follows:

$$F_\mu=\langle\phi_\mu|F|\phi_\mu\rangle=-I_\mu+(1/2)\cdot P_{\mu\mu}\gamma_\mu + \sum_{\kappa\neq\mu}(P_{\kappa\kappa}-Z_\kappa)\gamma_{\kappa\mu} \qquad (3)$$

$$F_{\mu\nu}=\langle\phi_\mu|F|\phi_\nu\rangle=\beta_{\mu\nu}-(1/2)\cdot P_{\mu\nu}\gamma_{\mu\nu} \qquad (4)$$

$$\left.\begin{aligned}\gamma_{\mu\nu}&=\langle\phi_\mu(1)\phi_\nu(2)|G_{12}|\phi_\mu(1)\phi_\nu(2)\rangle\\ G_{12}&=e^2/r_{12}\end{aligned}\right\} \qquad (5)$$

$$P_{\mu\nu}=2\sum_{i}^{\text{occ.}}C_{i\mu}C_{i\nu} \qquad (6)$$

In Eqs. 3—5, I_μ is the ionization potential of the μ atom in the appropriate valence state, Z_κ is the core charge of the κ core, $\beta_{\mu\nu}$ is the core resonance integral, and r_{12} in the two electron-operator G_{12} is the inter-electronic distance.

The excitation energy of the $i\rightarrow k$ transition, $E(\chi_{ik})=\langle\chi_{ik}|\mathscr{H}|\chi_{ik}\rangle-\langle\chi_0|\mathscr{H}|\chi_0\rangle$, and the interconfigurational matrix element, $\langle\chi_{ik}|\mathscr{H}|\chi_{jl}\rangle$, may be calculated by the following equations:

$$E({}^1\chi_{ik})=(\varepsilon_k-\varepsilon_i) -\langle\phi_i(1)\phi_k(2)|G_{12}|\phi_i(1)\phi_k(2)\rangle +2\langle\phi_i(1)\phi_k(2)|G_{12}|\phi_k(1)\phi_i(2)\rangle \qquad (7)$$

$$\langle{}^1\chi_{ik}|\mathscr{H}|{}^1\chi_0\rangle=\sqrt{2}\langle\phi_k|F|\phi_i\rangle \qquad (8)$$

$$\langle{}^1\chi_{ik}|\mathscr{H}|{}^1\chi_{il}\rangle=\langle\chi_k|F|\chi_l\rangle -\langle\phi_i(1)\phi_k(2)|G_{12}|\phi_i(1)\phi_l(2)\rangle +2\langle\phi_i(1)\phi_k(2)|\underset{k\neq l}{G_{12}}|\phi_l(1)\phi_i(2)\rangle \qquad (9)$$

$$\langle{}^1\chi_{ik}|\mathscr{H}|{}^1\chi_{jk}\rangle=-\langle\phi_j|F|\phi_i\rangle- -\langle\phi_k(1)\phi_j(2)|G_{12}|\phi_k(1)\phi_i(2)\rangle +2\langle\phi_k(1)\phi_j(2)|\underset{i\neq j}{G_{12}}|\phi_i(1)\phi_k(2)\rangle \qquad (10)$$

$$\langle{}^1\chi_{ik}|\mathscr{H}|{}^1\chi_{jl}\rangle= -\langle\phi_j(1)\phi_k(2)|G_{12}|\phi_i(1)\phi_l(2)\rangle +2\langle\phi_j(1)\phi_k(2)|\underset{i\neq j,\ k\neq l}{G_{12}}|\phi_l(1)\phi_i(2)\rangle \qquad (11)$$

For ${}^3\chi$'s, the third terms in Eqs. 7, 9 and 10 and the second term in Eq. 11 vanish.

In the ASMO CI method used here, the wave function Ψ for an electronic state is approximated by a linear combination of χ_0 and χ_{ik}'s.

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5) H. Baba, This Bulletin, **34**, 76 (1961).

* In order to determine the Coulomb parameter for O^-, proportionality between α and the valence state ionization potential was assumed, taking the sp^2 hybridized carbon as a reference; i. e., $\delta_O-/\delta_N=(\alpha_{O^-}-\alpha)/(\alpha_{N^+}-\alpha)=(I^\pi_O\ (tr^2tr^2tr\pi)-I^\pi_C)/(I^\pi_{N^+}\ (tr\ tr\ tr\pi)-I^\pi_C)$, where tr indicates the trigonal hybrid orbital (sp^2).
Using $I^\pi_C=11.16$ eV., $I^\pi_O=17.7$ eV., $I^\pi_{N^+}=28.72$ eV. (J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962)) and $\delta_N=1.2$, δ_{O^-} was calculated to be 0.45. If we use for $I^\pi_{N^+}$ the VESCF value (25.772 eV.) obtained by Brown and Heffernan for pyrrole (Ref. 13), δ_{O^-} can be calculated to be 0.54. Thus, δ_{O^-} seems to be close to 0.5. This value was used at first. However, the electronic spectrum of $TOBH^+$ calculated with this Hückel MO was in poor agreement with the observed data. (S. Mataga and N. Mataga, unpublished.)
Therefore, other values of δ_{O^-} were examined, and it was found that $\delta_{O^-}=0.8$ gave what appeared to be a reasonable result for the spectrum of $TOBH^+$.

6) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

7) K. Higashi and H. Baba, "Quantum Organic Chemistry," Asakura, Tokyo (1956), p. 273.

8) R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry," Interscience, New York (1959), p. 235.

9) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemist," John Wiley & Sons, New York (1961), p. 335.

The oscillator strength, f, is calculated by the method described by Mulliken and Rieke:[10]

$$f=1.085\times10^{11}\omega_{0\alpha}\sum_{r=x,y,z}[M^{r}{}_{0\alpha}]^{2} \qquad (12)$$

where $\omega_{0\alpha}$ is the frequency in cm^{-1} of the transition from the ground state, Ψ_0, to an excited state, Ψ_α. The necessary fromulas for the calculation of $M^{r}{}_{0\alpha}$ are given elsewhere.[4b]

C) The Semiempirical Evaluation of Integrals in the ASMO CI Calculation.—The molecular integrals which arise have been evaluated by a semiempirical procedure.

$Z_\kappa=1$ for the carbon core and $Z_\kappa=2$ for the core of amino nitrogen which contributes two electrons to the π-system. The I_μ value for carbon was taken to be 11.42 eV., and that for the amino nitrogen, 28.85 eV.[11]

$\gamma_{\mu\nu}$'s were evaluated by the same procedure as before,[12,4c,11] using the valence state ionization potential, I_μ, and the electron affinity, A_μ:

$$\gamma_{\mu\nu}=14.3949/(a+R_{\mu\nu})\ \text{(eV.)} \qquad (13)$$

where $R_{\mu\nu}$ is the distance between the μ and ν atom (in Å). In a homonuclear case,

$$\gamma_\mu=14.3949/a=I_\mu-A_\mu \qquad (14)$$

Thus, $a_C=1.328$Å and $a_N=0.868$Å. For the case of heteronuclear two centers, i. e. carbon and nitrogen, the value of a is the harmonic mean of a_C and a_N. Therefore, $a_{CN}=1.049$Å.

The empirical parameter, $\beta_{\mu\nu}$, was taken into account only for the nearest neighbors and neglected for more distant neighbors: $\beta_{CC}=-2.388$ eV.[12,4c] and $\beta_{CN}=-3.6$ eV.[3a] All C–C bond distances were assumed to be 1.39 Å, and C–N distances, 1.36 Å. D_{3h} and C_{2v} symmetries were assumed for TAB and $TABH^+$ respectively.

The values of F_μ's for the amino nitrogens calculated by Eq. 3 using 28.85 eV. for I_μ, which is the ionization potential of the $2p\pi$ electron of N^+ in the trigonal hybrid state, seem to be too large. For a more refined calculation, the VESCF method[13] proposed by Brown and Heffernan may be useful. Actually, we have calculated the electronic spectra and electronic structure of *p*-phenylenediamine[3a] by the VESCF method and have obtained an improved result compared with that obtained by the ASMO CI calculation similar to the one described above.

However, in the present study, we have not attempted such a refined calculation but have used only a simple procedure which gives appropriate values for the F_μ's of amino nitrogen. That is,

$$\langle F_\mu\rangle_N=\langle F_C\rangle_{AV}+\delta_N\cdot\langle F_{CC}\rangle_{AV} \qquad (15)$$

where $\langle F_C\rangle_{AV}$ is the simple arithmetic mean of F_μ's for carbons, $\langle F_{CC}\rangle_{AV}$ is the same quantity of $F_{\mu\nu}$'s for the nearest neighbor carbon-carbon bonds, and δ_N is the Hückel MO parameter for the Coulomb integral of nitrogen, 1.2.

When $\langle F\rangle_N$ instead of F_N was used, the most suitable value of the core resonance integral, β_{CN}, was -2.399 eV.[3a] the value of β_{CC} being the same as before. Using $\langle F\rangle_N$ and $\beta_{CN}=-2.399$ eV., we have calculated the electronic spectra of some amino-substituted benzenes such as aniline and phenylenediamines and obtained a very good agreement with the observed.[3a]

Results and Discussion

The Hückel MO's and MO energies of TAB, $TABH^+$ (protonated on carbon), TOB and $TOBH^+$ (protonated on carbon) are given in the appendix. The numbering of the atoms in these compounds is given in Fig. 1.

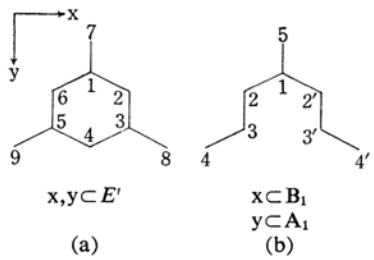

Fig. 1. The numbering of atoms in the base molecule and the corresponding carbonium ion.

A) Comparison of the Calculated Spectra with the Observed.—Using these MO's, the electronic spectra of TAB and $TABH^+$ were calculated by the method described in "Theoretical Method." The calculated spectra are given in Table I together with the observed, and the state functions and energies, taking the energy of the ground configuration, $E(\chi_0)$, as zero, are collected in Table II. The calculated values of such matrix elements as the formal orbital energies, $\langle\psi_i|F|\psi_i\rangle$'s, excitation energies and interconfigurational elements are given in the appendix.

Owing to the D_{3h} symmetry, the transitions to the lowest and the second excited singlet states of TAB respectively are electronically forbidden. These calculated spectra correspond quite well to the very weak absorption bands

10) R. S. Mulliken and C. A. Rieke, *Rep. Progr. Phys.*, **8**, 231 (1941).
11) S. Mataga and N. Mataga, *Z. physik. Chem., N. F.*, **19**, 231 (1959).
12) N. Mataga and K. Nishimoto, ibid., **13**, 140 (1957); N. Mataga, This Bulletin, **31**, 453 (1958); N. Mataga, K. Nishimoto and S. Mataga, ibid., **32**, 395 (1959).
13) R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958); *Australian J. Chem.*, **12**, 319 (1959).

TABLE I. CALCULATED AND OBSERVED SPECTRA OF TAB AND TABH$^+$

TAB	Calcd.		Obs.		TABH$^+$	Calcd.		Obs.	
	$h\nu$, eV.	f	$h\nu$, eV.	f		$h\nu$, eV.	f	$h\nu$, eV.	$\log\varepsilon_{max}$
$^1A'_2$	4.672(4.270)	0	4.4	0	$^1B_1$	3.153(3.121)	0.39	3.4	~3.5
$^1A'_1$	6.016(5.213)	0	5.0	0	$^1A_1$	4.460(4.427)	0.65	4.5	~3.9
$^1E'$	6.191(5.789)	2.2	5.6	$\log\varepsilon_{max}$	$^1A_1$	5.635(5.373)	1.52	?	?
$^3A'_1$	3.341(2.939)	0	?	~4.3	$^1B_1$	6.102(6.070)	0.00	?	?
$^3E'$	4.007(3.605)	0	?	?	$^3B_1$	1.468(1.437)	0	?	?
$^3A'_2$	4.672(4.270)	0	?	?	$^3A_1$	2.096(2.065)	0	?	?
					$^3A_1$	3.774(3.742)	0	?	?
					$^3B_1$	5.237(5.205)	0	?	?

The calculated $h\nu$ values in parentheses are those excluding the ground configuration χ_0 from the configuration interaction. Whether χ_0 was included or not, the calculated f value was almost the same.

TABLE II. THE STATE FUNCTIONS AND ENERGIES FOR TAB AND TABH$^+$

TAB			TABH$^+$		
E, eV.			E, eV.		
−0.4019	$^1A'_1$	$0.9660\chi_0+0.2584(^1\chi_{68}+{}^1\chi_{57})/\sqrt{2}$	−0.0317	$^1A_1$	$0.9972\,\chi_0+0.0338{}^1\chi_{46}-0.0673{}^1\chi_{57}$
4.2705	$^1A'_2$	$(^1\chi_{67}-{}^1\chi_{58})/\sqrt{2}$	3.1215	$^1B_1$	$0.9974{}^1\chi_{56}-0.0714{}^1\chi_{47}$
5.6146	$^1A'_1$	$0.2584\chi_0-0.9660(^1\chi_{68}+{}^1\chi_{57})/\sqrt{2}$	4.4283	$^1A_1$	$0.0145\,\chi_0-0.9633{}^1\chi_{46}-0.2679{}^1\chi_{57}$
5.7891	$^1E'$	$(^1\chi_{67}+{}^1\chi_{58})/\sqrt{2}$ $(^1\chi_{68}-{}^1\chi_{57})/\sqrt{2}$	5.6034	$^1A_1$	$0.0739\,\chi_0-0.2662{}^1\chi_{46}+0.9611{}^1\chi_{57}$
			6.0703	$^1B_1$	$0.0714{}^1\chi_{56}+0.9974{}^1\chi_{47}$
3.3407	$^3A'_1$	$(^3\chi_{68}+{}^3\chi_{57})/\sqrt{2}$	1.4368	$^3B_1$	$0.9787{}^3\chi_{56}-0.2052{}^3\chi_{47}$
4.0072	$^3E'$	$(^3\chi_{67}+{}^3\chi_{58})/\sqrt{2}$ $(^3\chi_{68}-{}^3\chi_{57})/\sqrt{2}$	2.0647	$^3A_1$	$0.8457{}^3\chi_{46}-0.5335{}^3\chi_{57}$
			3.7419	$^3A_1$	$0.5335{}^3\chi_{46}+0.8457{}^3\chi_{57}$
4.6724	$^3A'_2$	$(^3\chi_{67}-{}^3\chi_{58})/\sqrt{2}$	5.2051	$^3B_1$	$0.2052{}^3\chi_{56}+0.9787{}^3\chi_{47}$

in the observed spectra of TAB. Such weak transitions do not exist in the observed spectra of TABH$^+$, and the calculated transition energies are in satisfactory agreement with the observed values. These facts seem to support the assumed structure for TABH$^+$.

B) Calculation of Electronic Spectra with Other Models for TABH$^+$.—Although the results of the calculation described in A agree quite well with the observed spectra of TABH$^+$, we shall examine other models for TABH$^+$.

One of the possible structures of TABH$^+$ is a kind of π-complex,[14] in which the proton is situated on the molecular plane of TAB.

Because of the existence of the proton on the molecular plane, the electronic states of TAB might be considerably changed. The cause of the perturbation in this case will be the electrostatic potential of the proton or the charge-transfer interaction between the π-MO's of TAB and the proton.

We have tried some perturbation calculations using a model in which the proton is situated at the center of and 1.7 Å (half of the interplane distance in graphite) above the molecular plane.

In this model, the perturbing electrostatic potential due to the proton may be written[11] as:

$$\mathscr{H}^p{}_j=-\frac{Z_{H^+}e^2}{r_{pj}} \tag{16}$$

where r_{pj} is the distance between the proton and the j-th electron and $Z_H\cdot e$ is the effective charge of the proton. The formal orbital energy, ε_i, may be modified to ε_i' due to this perturbation.

$$\begin{aligned}\varepsilon_i' &= \varepsilon_i+\langle\phi_i(j)|\mathscr{H}^p{}_j|\phi_i(j)\rangle \\ &\quad+\sum_n\frac{(\langle\underline{i}\underline{\psi}(j)|\mathscr{H}^p{}_j|\psi_n(j)\rangle)^2}{\varepsilon_i-\varepsilon_n} \\ &=\varepsilon_i+\sum_\mu C^2{}_{i\mu}\langle\phi_\mu(j)|\mathscr{H}^p{}_i|\phi_\mu(j)\rangle \\ &\quad+\sum_n\frac{(\sum_\mu C_{i\mu}C_{n\mu}\langle\phi_\mu(j)|\mathscr{H}^p{}_j|\phi_\mu(j)\rangle)^2}{\varepsilon_i-\varepsilon_n}\end{aligned} \tag{17}$$

The integral, $V_\mu=\langle\phi_\mu(j)|\mathscr{H}^p{}_j|\phi_\mu(j)\rangle$, was calculated by a formula[15] using Slater AO's with the values of the orbital exponents, $\zeta_C=1.018$, $\zeta_N=1.212$.[11] The second order terms in Eq. 17 were very small compared with those of the first order and were accordingly disregarded as a first approximation.

Therefore, the values of ε_i' necessary for

14) a) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press (1949); Ref. 7, p. 326; Ref. 9, p. 314. b) S. Nagakura, *Technical Report of ISSP, Ser. A.*, No. 35, Jan., 1962.

TABLE III. STATE FUNCTIONS AND ENERGIES CALCULATED WITH THE ELECTROSTATIC POTENTIAL DUE TO PROTON

E, eV.		
−0.0985	$^1A_1$	$0.9899\chi_0+0.1418(^1\chi_{68}+^1\chi_{57})/\sqrt{2}$
3.7596	$^1A_2$	$(^1\chi_{67}-^1\chi_{58})/\sqrt{2}$
4.7018	$^1A_1$	$0.1418\chi_0-0.9899(^1\chi_{68}+^1\chi_{57})/\sqrt{2}$
5.2782	^1E	$\begin{cases}(^1\chi_{67}+^1\chi_{58})/\sqrt{2}\\(^1\chi_{68}-^1\chi_{57})/\sqrt{2}\end{cases}$

the calculation of the electronic spetra were calculated as follows:

$$\left.\begin{aligned}\varepsilon_6'=\varepsilon_5'=\varepsilon_5+(0.6972)V_C+(0.3026)V_N\\ \varepsilon_8'=\varepsilon_7'=\varepsilon_7+(0.9074)V_C+(0.0926)V_N\end{aligned}\right\} \quad (18)$$

With the V_μ values, $V_C=-6.8649$ eV., $V_N=-4.4321$ eV. and the interconfigurational matrix elements, $\langle\chi_0|\mathscr{H}^p{}_j|^1\chi_{68}\rangle=\langle\chi_0|\mathscr{H}^p{}_j|^1\chi_{57}\rangle=\sqrt{2}(0.4072)$ eV. The state functions and energies were calculated as shown in Table III.

We can obtain a little red shift of the spectrum in this model of $TABH^+$ also. However, the molecular symmetry of this $TABH^+$ is C_{3v}, and in this symmetry the transition to $^1A_2$ is electronically forbidden and that to $^1A_1$ is polarized perpendicular to the molecular plane. Therefore, we cannot interpret the observed strong band at 3.4 eV. by means of this model. Even if we take into account the charge-transfer interaction between the π-MO's of TAB and the proton, the calculated results will be similar to those of the electrostatic model as long as the proton is situated on the principal axis of the C_3 symmetry.

If the proton is moved to the periphery of TAB, the perturbation will become larger and all π-MO's of TAB will be mixed with each other. Thus, the electronic structure is considerably changed, and the electronic spectra will approach the observed data. However, such interactions may finally lead to the localization or to the hyperconjugation model as the most stable equilibrium form.

Accordingly, the theoretical calculation supports the structure of $TABH^+$ protonated on the ring carbon. The structures of $TABH^+$ similar to the π-complex discussed above may probably be realized in the course of the protonation reaction as an intermediate (outer complex), and the system will shifts to the localized one (inner complex).[14b]

Of course, the reaction involving the movement of the proton in an aqueous solution is very rapid, and the equilibrium between TAB and $TABH^+$ will be realized instantaneously.

C) Effect of Methyl Substitution on the Electronic Spectrum of $TABH^+$.—Although we have calculated here only the electronic spectra of TAB and $TABH^+$ from among the compounds examined by Köhler and Scheibe,[1] a similar interpretation will hold also for other compounds.

The transition energies to the lowest excited singlet states of *s*-triaminoxylenium ($TAXH^+$) and *s*-triaminomesitylenium($TAMH^+$) ions are smaller by ca. 0.34 eV.[1] than that of $TABH^+$.

The effects of methyl substitutions on the electronic spectra of protonated benzene[16,17] have been discussed by means of both the localization model and the hyperconjugation model.[2c,16]

Calculations and an interpretation similar to those by Morita[2c] may be possible in the present case also. However, we shall make a more simplified explanation as follows.

The lowest excited singlet state of $TABH^+$ is almost completely contributed by $^1\chi_{56}$, as is shown in Table II; that is, the excitation energy to this state is essentially determined by the transition from the highest occupied to the lowest vacant orbitals.

If we assume an inductive model of methyl substitution by taking the Coulomb integral of the substituted carbon to be $\alpha+\delta\cdot\beta$, the orbital energy differences, $\Delta\varepsilon=\varepsilon_6-\varepsilon_5$, for TAB^+ and $TAXH^+$ may be calculate as follows using the MO's given in appendix.

$$\left.\begin{aligned}&TABH^+ \quad \Delta\varepsilon=-1.0764\,\beta\\ &TAXH^+ \quad \Delta\varepsilon=-1.0764\,\beta+(0.5531)\delta\cdot\beta\end{aligned}\right\} \quad (19)$$

The value of δ averaged for various methyl substituted aromatics seems to be ~-0.5.[9] If we put $0.34=-(0.5531)\delta\cdot\beta$, assuming $\beta\sim-3$ eV., δ is estimated to be ~-0.2. This value is a little different from the ordinary value, -0.5; nevertheless, the observed bathochromic shift by methyl substitution is, at least qualitatively, well understood by means of this simplified calculation.

D) Similarity of the Electronic Spectrum of $TABH^+$ to Those of Benzenium Ion and Methyl-substituted Benzenium Ions. — As has been discussed in the previous section, the methyl substitution affects the spectrum of $TABH^+$ rather remarkably.

15) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

16) G. Dallinga, E. L. Mackor and A. A. V. Stuart, *Mol. Physics*, **1**, 123 (1958); M. Kilpatrick and H. H. Hyman, *J. Am. Chem. Soc.*, **80**, 77 (1958).

17) J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

TABLE IV. THE CALCULATED ELECTRONIC SPECTRUM OF BENZENIUM ION

E, eV.	State function	f
−0.0107	$^1A_1$ $0.9992\,\chi_0+0.0243{}^1\chi_{13}-0.0310{}^1\chi_{24}$	
3.4941	$^1B_1$ $0.9991{}^1\chi_{23}-0.0419{}^1\chi_{14}$	0.26
5.2930	$^1A_1$ $0.1028\,\chi_0-0.9106{}^1\chi_{13}-0.4002{}^1\chi_{24}$	0.12
7.0331	$^1A_1$ $0.0380\,\chi_0-0.3896{}^1\chi_{13}+0.9202{}^1\chi^{24}$	1.02
8.1188	$^1B_1$ $0.0419{}^1\chi_{23}+0.9991{}^1\chi_{14}$	1.35

In the case of the substitution for the neutral aromatic hydrocarbon molecules, the amino group affects the spectra to a far greater extent than does the methyl group. Therefore, one might expect that the spectrum of $TABH^+$ is very different from that of benzenium ions or methyl-substituted benzenium ions. However, this is not the case for either the observed spectra or for the calculated spectra. The observed excitation energies to the lowest excited singlet states of benzenium, methyl-substituted benzenium, *s*-triaminobenzenium, methyl-substituted *s*-triaminobenzenium ions, and $TOBH^+$ are not very different from one another and lie approximately between 3.0∼3.6 eV. In order to interpret this fact, it will be necessary to compare the MO's and state functions of $TABH^+$ with those of benzenium ion.

The electronic spectrum of benzenium ion has been studied in detail by Morita[2c] using the semiempirical SCF MO CI method. However, for purposes of comparison, the results of theoretical calculations with similar approximations for both compounds may be more reasonable. Accordingly, we have calculated the electronic spectrum of benzenim ion with the same approximations as for $TABH^+$. The calculated energies, state functions and oscillator strengths of transitions from the ground state to the excited states are given in Table IV.

Although the method of calculation used here is less elaborate than that used by Morita, the present results are rather close to Morita's. As is shown in Table IV, the lowest excited singlet state of benzenium ion is almost completely contributed by $^1\chi_{23}$, just as the lowest excited singlet state of $TABH^+$ is almost exclusively contributed by $^1\chi_{56}$. Furthermore, an analogous circumstance holds for other states of both compounds. That is, each excitation energy is essentially determined by the transition from one of the occupied orbitals to one of the vacant orbitals. This may be a remarkable example of the change from the "*round field*" spectra[17] in benzene and TAB (where the configuration interaction is quite strong) to the "*long field*" spectra[17] caused by protonation.

Thus, we have seen the similarity of the state functions of $TABH^+$ to those of benzenium ions, a similarity which corresponds to the resemblance of the observed spectra of these compounds.

Next, we shall show the similarity of the MO's of $TABH^+$ to those of benzenium ions. We can transform the MO's of $TABH^+$ into the following equivalent forms:

$$\left.\begin{aligned}
\phi_4&=0.4084(\phi_2+\phi_{2'})+0.3332(g_3{}^4+g_{3'}{}^4)+0.6665\,g_1{}^4\\
\phi_5&=0.5259(\phi_2-\phi_{2'})+0.4725(g_3{}^5-g_{3'}{}^5)\\
\phi_6&=\qquad\qquad 0.5773(g_3{}^6-g_{3'}{}^6)-0.5773\,g_1{}^6\\
\phi_7&=0.4255(\phi_2-\phi_{2'})-0.5646(g_3{}^7-g_{3'}{}^7)
\end{aligned}\right\} \tag{20}$$

In these MO's, g is the normalized group orbital for $C\text{–}NH_2$, which can be written as:

$$\left.\begin{aligned}
g^4&=0.3418\phi_C-0.9398\phi_N,\quad g^5=0.5678\phi_C-0.8233\phi_N\\
g^6&=0.8702\phi_C-0.4926\phi_N,\quad g^7=0.9247\phi_C-0.3810\phi_N
\end{aligned}\right\} \tag{21}$$

where, in the same ϕ, $g_3=g_{3'}=g_1$.

The corresponding MO's of benzenium ion are given by:

$$\left.\begin{aligned}
\phi_1&=0.5000(\phi_2+\phi_{2'})+0.2887(\phi_3+\phi_{3'})+0.5773\phi_1\\
\phi_2&=0.5000(\phi_2-\phi_{2'})+0.5000(\phi_3+\phi_{3'})\\
\phi_3&=\qquad\qquad 0.5773(\phi_3+\phi_{3'})-0.5773\phi_1\\
\phi_4&=0.5000(\phi_2-\phi_{2'})-0.5000(\phi_3-\phi_{3'})
\end{aligned}\right\} \tag{22}$$

Thus we can see that the transformed MO's of $TABH^+$ are apparently similar to those of benzenium ion. Of course, the two sets of MO's are not exacty the same but are different from each other to some extent. However, we have described the above transformation of the MO's in order to demonstrate the *geometrial* or *topological* nature of the MO's.

If we transform the base set for the Hückel MO's of $TABH^+$ from $(\phi_1\cdots\phi_8)$ to

$$\left\{\begin{aligned}
&g_1{}^a,\ (g_3{}^a+g_3{}^a)/\sqrt{2},\ g_1{}^b,\ (g_3{}^b+g_{3'}{}^b)/\sqrt{2},\\
&(\phi_2+\phi_{2'})/\sqrt{2},\ (g_3{}^a-g_{3'}{}^a)/\sqrt{2},\\
&(g_3{}^b-g_{3'}{}^b)/\sqrt{2},\ (\phi_2-\phi_{2'}/\sqrt{2}
\end{aligned}\right\}$$

where the group orbitals for $C\text{–}NH_2$ are given by:

$$\begin{aligned}
g^a&=0.870\phi_C-0.493\phi_N\\
g^b&=0.493\phi_C+0.870\phi_N
\end{aligned} \tag{23}$$

then the energy matrix for the Hückel MO's can be written in the following form;

for b_2 species

$$\begin{pmatrix} g_1^a & (g_3^a+g_{3'}^a)/\sqrt{2} & g_1^b & (g_1^b+g_3^b)/\sqrt{2} & (\phi_2+\phi_2)/\sqrt{2} \\ (\alpha-0.5667\beta) & 0 & 0 & 0 & 2(0.87)\beta \\ & (\alpha-0.5667\beta) & 0 & 0 & 2(0.87)\beta \\ & & (\alpha+1.7662\beta) & 0 & 2(0.493)\beta \\ & & & (\alpha+1.7662\beta) & 2(0.493)\beta \\ & & & & \alpha \end{pmatrix}$$

for a_2 species

$$\begin{pmatrix} (g_3^a-g_3^a)/\sqrt{2} & (g_3^b-g_{3'}^b)/\sqrt{2} & (\phi_2-\phi_2)/\sqrt{2} \\ (\alpha-0.5667\beta) & 0 & 2(0.87)\beta \\ & (\alpha+1.7662\beta) & 2(0.493)\beta \\ & & \alpha \end{pmatrix}$$

TABLE V. LOCALIZATION ENERGIES OF SOME AMINOBENZENES AND TOB (in units of β)

Mode of protonation	A. Carbon	B. Amino group
Aniline	2.2498 a)	2.8054
m-Phenylenediamine	1.9562 b)	2.8058
TAB	1.8294	2.8060
TOB	1.6861	—

a) Protonation on para-carbon.
b) Protonation of the carbon atom at ortho-position to both amino groups.

Accordingly, g_a and g_b of each C–NH_2 group are mixed to some extent; that is, the g^i's in (21) can be written as $g^i=c_a{}^i g_a+c_b{}^i g_b$, but $g_1{}^i=g_3{}^i=g^i$ because,

$$\langle g_1^a|\mathscr{H}|(\phi_2+\phi_{2'})/\sqrt{2}\rangle = \langle(g_3^a+g_{3'}^a)/\sqrt{2}|\mathscr{H}|(\phi_2+\phi_{2'})/\sqrt{2}\rangle$$

and

$$\langle g_1^b|\mathscr{H}|(\phi_2+\phi_{2'})/\sqrt{2}\rangle = \langle(g_3^b+g_{3'}^b)/\sqrt{2}|\mathscr{H}|(\phi_2+\phi_{2'})/\sqrt{2}\rangle$$

The calculated spectra of $TABH^+$ and benzenium ion in Tables I and IV respectively indicate that the excitation energy to the lowest excited singlet state of $TABH^+$ is a little smaller than that of benzenium ion. However, this is not the case indeed, the order is just reversed in the observed spectra. This indicates that the present semiempirical ASMO CI method cannot reproduce such a small difference between the observed spectra,** although the calculated excitation energies themselves are close to the observed values.

On the other hand, the difference between the Hückel MO energies of the lowst vacant orbital and the highest occupied orbital can reproduce the observed excitation energy to the lowest excited singlet state quite well, as is described below.

If we assume the inductive parameter for methyl substitution to be ~-0.2, as has already been established, the orbital energy differences may be evaluated as: $-\beta$, -1.0764β, and -1.1β for benzenium ion, $TABH^+$ and mesitylenium ions respectively. The observed excitation energies are 3.1 eV., 3.4 eV. and 3.5 eV. for these ions respectively. Thus, the calculated results agree, at least qualitatively, very well with the observed spectra.

E) The Basicities of TAB and TOB in Comparison with Other Aminobenzenes and Aromatic Hydrocarbons.—As has been described in the "Theoretical Method" section, localization energies due to protonation were calculated as a measure of the stabilities of the protonated species. Calculated results for the protonation of some aminobenzenes and TOB are collected in Table V, where the localization energy is given by $(M-M_r{}^+)$.

As is shown in Table V, the destabilization energy of the π system becomes considerably smaller from aniline to TAB and TOB ($pK\sim9.7$) in mode A, whereas it is almost constant or even slightly increases in mode B. This result is in accordance with the observed data.

Although the effect of hyperconjugation with CH_2 group was not taken into account

** In the present calculation, we have used the same value of the nearest-neighbor core resonance integral for the carbon-carbon bond (β_{CC}) in both $TABH^+$ and benzenium ion. However, there are twice as many π-electrons of $TABH^+$ as those of benzenium ion, whereas the dimension of the core framework of the former is not so large compared with that of the latter. Accordingly, the effective core charge for π-electrons seems to be smaller in $TABH^+$ than in benzenium ion, resulting in the larger overlapping between AO's and, thus, the larger core resonance integrals in the former than in the latter. Moreover, the value of β_{CC} was the same as that used for the neutral aromatic hydrocarbons. Because the effective core charge is larger in benzenium ion than in benzene, a little smaller value of β_{CC} may be more reasonable for benzenium ion.
In general, the calculated spectrum shifts to blue when the values of the core resonance integrals are increased, while a red shift occurs when they are decreased. Therefore, the calculated spectra of $TABH^+$ and benzenium ion will approach the observed values if one adjusts the β_{CC} value in the way described above.

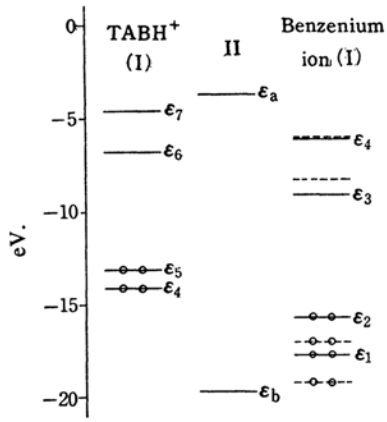

Fig. 2. MO energies for the local systems of $TABH^+$ and benzenium ion, respectively.
In the local system I of benzenium ion, - - - represents the SCF MO energies calculated by Morita.[2c]

either in the calculation of the electronic spectra or in the calculation of the stabilities of the protonated species, it may be examined in some qualitative or semi-quantitative manner.

In the case of $TABH^+$, owing to the presence of the three amino groups, the higher occupied orbitals of the local system I which is indicated in Fig 1b (II is the CH_2 group) may be much more elevated than the highest-occupied orbital of the corresponding local system of benzenium ion.

Actually, this is the case, as is shown in Fig. 2, where the approximate orbital energies for $TABH^+$ and the corresponding quantities for benzenium ion calculated by the present method are indicated, together with the energies of the bonding and antibonding π-orbitals of the CH_2 group as calculated by Morita.[2c] In Fig. 2, the SCF MO energies[2c] for the local system I of benzenium ions are also given for purposes of comparison.

Therefore, the excitation energies from the higher-occupied orbitals of I to the antibonding π-orbital of II(ϕ_a) may not be very large in the case of $TABH^+$. Employing the Pariser-Parr approximation[4a] for the evaluation of the electron repulsion integrals (γ's) between AO's of I and II, the approximate charge transfer (CT) excitation energies in $TABH^+$ were estimated as follows: $E(^1\chi_{5a})\sim 4.5$ eV. and $E(^1\chi_{4a})\sim 6.4$ eV., where $^1\chi_{5a}\subset B_1$, $^1\chi_{4a}\subset A_1$. Thus, it may be possible that the interactions between these CT configurations and the ground configuration χ_0 stabilize the protonated species.

Mackor et al.[2a] demonstrated an approximate linear relation between the localization energy and log K, where K is the relative basicity constant, in the case of the protonation of many aromatic hydrocarbons.

Although there are only two points for TAB and TOB, the relation between the pK values and the localization eneregies in the present calculation seems to be parallel with that between the values of log K and the localization energies for some aromatic hydrocarbons, as is shown in Fig. 3.

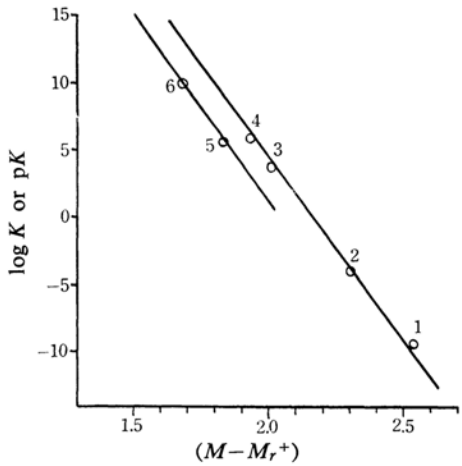

Fig. 3. Relation between the observed basicities and localization enegies.
1. Benzene, 2. Naphthalene, 3. Anthracene, 4. Naphthacene, 5. TAB, 6. TOB.
Localization energies for the polyacene series were taken from Ref. 2a.

Concluding Remarks

The results of the theoretical calculations herein described have revealed that the extraordinarily large proton affinities of TAB and TOB are consistent with the ordinary MO concept of the π-electron system and with the great conjugation power of amino group, and that $TABH^+$ and $TOBH^+$ are carbonium ions similar to the protonation products of benzene and methyl-substituted benzenes. Nevertheless, it is necessary to make a more direct experimental confirmation of the structure of $TABH^+$ by, for example, NMR spectral measurement.

Summary

The electronic spectra and electronic structure of TAB and $TABH^+$ have been studied by the MO method. The calculated spectra agree satisfactorily with the observed values. The stabilities of the protonation products of various aminobenzenes have been studied by Hückel MO calculations. The results of these calculations give an interpretation of the observed facts[1] that TAB in an aqueous solution is easily protonated on the ring

carbon (pK ~5.5), although no such protonation occurs in the case of aniline or *m*-phenylenediamine, where the amino group is protonated. The stability of the protonation product of TOB has also been studied.

It has been pointed out that the spectum of $TABH^+$ is rather similar to that of benzenium ion, although the basicity of the former is much larger than that of the latter. This fact has been explained theoretically.

Further, it has been observed that a relation between the calculated localization energy and the observed basicity constant for the protonation similar to those of many aromatic hydrocarbons approximately holds for TAB and TOB.

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Appendix I.

Hückel MO's and MO energies of TAB, $TABH^+$, TOB and $TOBH^+$.
(MO energies are in units of β)

MO energy	Symmetry	MO
TAB		
2.4425	a_2''	$\psi_1=0.3792(\phi_1+\phi_3+\phi_5)+0.3105(\phi_2+\phi_4+\phi_6)+0.3052(\phi_7+\phi_8+\phi_9)$
1.9168	e''	$\psi_2=0.3941(\phi_1-\phi_3)-0.2057(\phi_4-\phi_6)+0.5498(\phi_7-\phi_8)$ $\psi_3=0.2275(\phi_1+\phi_3-2\phi_5)-0.1187(\phi_4+\phi_6-2\phi_2)+0.3175(\phi_7+\phi_8-2\phi_9)$
0.9121	a_2''	$\psi_4=0.1366(\phi_1+\phi_3+\phi_5)+0.2994(\phi_2+\phi_4+\phi_6)-0.4744(\phi_7+\phi_8+\phi_9)$
0.5102	e''	$\psi_5=0.2683(\phi_1-\phi_3)-0.5259(\phi_4-\phi_6)-0.3890(\phi_7-\phi_8)$ $\psi_6=0.1549(\phi_1+\phi_3-2\phi_5)-0.3037(\phi_4+\phi_6-2\phi_2)-0.2246(\phi_7+\phi_8-2\phi_9)$
−1.2271	e''	$\psi_7=0.5221(\phi_1-\phi_3)+0.4255(\phi_4-\phi_6)-0.2152(\phi_7-\phi_8)$ $\psi_8=0.3015(\phi_1+\phi_3-2\phi_5)+0.2457(\phi_4+\phi_6-2\phi_2)-0.1242(\phi_7+\phi_8-2\phi_9)$
−2.1546	a_2''	$\psi_9=0.4134(\phi_1+\phi_3+\phi_5)-0.3838(\phi_2+\phi_4+\phi_6)-0.1233(\phi_7+\phi_8+\phi_9)$
		$P_{11}=0.9308,\quad P_{22}=1.2210,\quad P_{77}=1.8461$
$TABH^+$		
2.2644	b_2	$\psi_1=0.3443(\phi_2+\phi_{2'})+0.2599(\phi_3+\phi_{3'})+0.2441(\phi_4+\phi_{4'})+0.5197\phi_1+0.4883\phi_5$
1.9168	a_2	$\psi_2=0.2056(\phi_2-\phi_{2'})+0.3941(\phi_3-\phi_{3'})+0.5499(\phi_4-\phi_{4'})$
1.7662	b_2	$\psi_3=0.2844(\phi_3+\phi_{3'})+0.5024(\phi_4+\phi_{4'})-0.2844\phi_1-0.5024\phi_5$
0.8363	b_2	$\psi_4=0.4084(\phi_2+\phi_{2'})+0.1139(\phi_3+\phi_{3'})-0.3132(\phi_4+\phi_{4'})+0.2277\phi_1-0.6264\phi_5$
0.5102	a_2	$\psi_5=0.5259(\phi_2-\phi_{2'})+0.2683(\phi_3-\phi_{3'})-0.3890(\phi_4-\phi_{4'})$
−0.5662	b_2	$\psi_6=0.5024(\phi_3+\phi_{3'})-0.2844(\phi_4+\phi_{4'})-0.5024\phi_1+0.2844\phi_5$
−1.2270	a_2	$\psi_7=0.4255(\phi_2-\phi_{2'})-0.5221(\phi_3-\phi_{3'})+0.2151(\phi_4-\phi_{4'})$
−1.9008	b_2	$\psi_8=0.4633(\phi_2+\phi_{2'})-0.2935(\phi_3+\phi_{3'})+0.0946(\phi_4+\phi_{4'})-0.5870\phi_1+0.1893\phi_5$
		$P_{11}=0.8056,\quad P_{22}=1.2083,\quad P_{33}=0.7774,\quad P_{44}=1.7276,\quad P_{55}=1.7664$
TOB		
2.3487	a_2''	$\psi_1=0.3945(\phi_1+\phi_2+\phi_3)+0.3359(\phi_2+\phi_4+\phi_6)+0.2547(\phi_7+\phi_8+\phi_9)$
1.6997	e''	$\psi_2=0.4401(\phi_1-\phi_3)-0.2589(\phi_4-\phi_6)+0.4891(\phi_7-\phi_8)$ $\psi_3=0.2541(\phi_1+\phi_3-2\phi_5)-0.1495(\phi_4+\phi_6-2\phi_2)+0.2824(\phi_7+\phi_8-2\phi_9)$
0.6264	a_2''	$\psi_4=0.0867(\phi_1+\phi_3+\phi_5)+0.2767(\phi_2+\phi_4+\phi_6)-0.4992(\phi_7+\phi_8+\phi_9)$
0.3705	e''	$\psi_5=0.1910(\phi_1-\phi_3)-0.5155(\phi_4-\phi_6)-0.4447(\phi_7-\phi_8)$ $\psi_6=0.1103(\phi_1+\phi_3-2\phi_5)-0.2976(\phi_4+\phi_6-2\phi_2)-0.2567(\phi_7+\phi_8-2\phi_9)$
−1.2703	e''	$\psi_7=0.5194(\phi_1-\phi_3)+0.4089(\phi_4-\phi_6)-0.2509(\phi_7-\phi_8)$ $\psi_8=0.2999(\phi_1+\phi_3-2\phi_5)+0.2361(\phi_4+\phi_6-2\phi_2)-0.1448(\phi_7+\phi_8-2\phi_9)$
−2.1751	a_2''	$\psi_9=0.4125(\phi_1+\phi_3+\phi_5)-0.3793(\phi_2+\phi_4+\phi_6)-0.1387(\phi_7+\phi_8+\phi_9)$
		$P_{11}=0.9400,\quad P_{22}=1.2663,\quad P_{77}=1.7936$
$TOBH^+$		
2.1437	b_2	$\psi_1=0.3846(\phi_2+\phi_{2'})+0.2748(\phi_3+\phi_{3'})+0.2045(\phi_4+\phi_{4'})+0.5496\phi_1+0.4090\phi_5$
1.6997	a_2	$\psi_2=0.2589(\phi_2-\phi_{2'})+0.4401(\phi_3-\phi_{3'})+0.4891(\phi_4-\phi_{4'})$
1.4770	b_2	$\psi_3=0.3237(\phi_3+\phi_{3'})+0.4781(\phi_4+\phi_{4'})-0.3237\phi_1-0.4781\phi_5$
0.5815	b_2	$\psi_4=0.3793(\phi_2+\phi_{2'})+0.0735(\phi_3+\phi_{3'})-0.3366(\phi_4+\phi_{4'})+0.1471\phi_1-0.6732\phi_5$
0.3705	a_2	$\psi_5=0.5155(\phi_2-\phi_{2'})+0.1910(\phi_3-\phi_{3'})-0.4447(\phi_4-\phi_{4'})$
−0.6770	b_2	$\psi_6=0.4781(\phi_3+\phi_{3'})-0.3237(\phi_4+\phi_{4'})-0.4781\phi_1+0.3237\phi_5$
−1.2702	a_2	$\psi_7=0.4089(\phi_2-\phi_{2'})-0.5194(\phi_3-\phi_{3'})+0.2509(\phi_4-\phi_{4'})$
−1.9252	b_2	$\psi_8=0.4672(\phi_2+\phi_{2'})-0.2998(\phi_3+\phi_{3'})+0.1100(\phi_4+\phi_{4'})-0.5996\phi_1+0.2200\phi_5$
		$P_{11}=0.8569,\quad P_{22}=1.2491,\quad P_{33}=0.8317,\quad P_{44}=1.6413,\quad P_{55}=1.6981$

Appendix II.

The calculated values of ε_i's, $E(\chi_{ik})$'s and $\langle\chi_{ik}|\mathscr{H}|\chi_{jl}\rangle$'s for TAB and $TABH^+$ (in units of eV.).

TAB

$\varepsilon_5=\varepsilon_6=-8.7919$, $E(^1\chi_{67})=E(^1\chi_{58})=5.0298$, $E(^1\chi_{68})=E(^1\chi_{57})=5.5001$

$\varepsilon_7=\varepsilon_8=-0.2811$, $E(^3\chi_{67})=E(^3\chi_{58})=3.9379$, $E(^3\chi_{68})=E(^3\chi_{57})=3.2714$

$\langle^1\chi_{67}|\mathscr{H}|^1\chi_{58}\rangle=0.7593$, $\langle^1\chi_{68}|\mathscr{H}|^1\chi_{57}\rangle=-0.2874$, $\langle\chi_0|\mathscr{H}|^1\chi_{68}\rangle=-\sqrt{2}\,(1.3529)$

$\langle^3\chi_{67}|\mathscr{H}|^3\chi_{58}\rangle=-0.3326$, $\langle^3\chi_{68}|\mathscr{H}|^3\chi_{57}\rangle=-0.3326$, $\langle\chi_0|\mathscr{H}|^1\chi_{57}\rangle=-\sqrt{2}\,(0.1493)$

$TABH^+$

$\varepsilon_4=-14.0832$, $E(^1\chi_{46})=4.5065$, $E(^1\chi_{56})=3.1365$, $\langle^1\chi_{46}|\mathscr{H}|^1\chi_{57}\rangle=-0.2905$

$\varepsilon_5=-13.1165$, $E(^3\chi_{46})=2.5422$, $E(^3\chi_{56})=1.5955$, $\langle^3\chi_{46}|\mathscr{H}|^3\chi_{57}\rangle=0.7569$

$\varepsilon_6=-6.7829$, $E(^1\chi_{57})=5.4935$, $E(^1\chi_{47})=6.0553$, $\langle\chi_0|\mathscr{H}|^1\chi_{57}\rangle=0.3826$

$\varepsilon_7=-4.6151$, $E(^3\chi_{57})=3.2645$, $E(^3\chi_{47})=5.0464$, $\langle\chi_0|\mathscr{H}|^1\chi_{46}\rangle=-0.1734$

$\langle^1\chi_{56}|\mathscr{H}|^1\chi_{47}\rangle=0.2099$

$\langle^3\chi_{56}|\mathscr{H}|^3\chi_{47}\rangle=0.7569$