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SPECTROSCOPIC STUDIES ON THE PROTONATION OF s-TRIAMINOBENZENE

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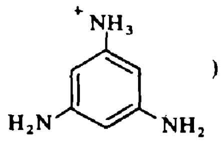
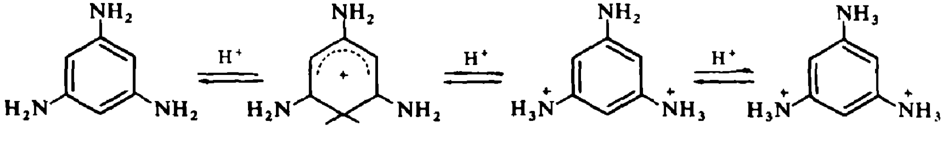
Abstract-The protonation of s-triaminobenzene (TAB) has been studied by measuring IR, UV and NMR spectra, special attention being paid to the structure of the single protonation product ($TABH^+$) of TAB. The IR spectrum at room temperature shows that the N–H stretching vibrations due to the neutral amino groups of TAB remain unaltered in $TABH^+$. Furthermore, in the NMR spectrum of $TABH^+$, the proton signal of the methylene group appears at $\tau = 6 \cdot 7$ ppm. These facts and other supporting evidence, demonstrate that the first protonation at room temperature mainly occurs on the ring C atom and produces the triaminobenzenium ion.

It was further concluded, from the detailed analysis of the temperature dependence of UV spectra, that TAB in aqueous solution of pH 4·3 consists of two components, the triaminobenzenium ion and the amino protonated specimen () which are in equilibrium, and although the former is overwhelmingly predominant at room temperature, the amount of the latter increases with the decreasing temperature. The peaks at 27,400, 36,800 and 45,500 cm^{-1} observed for $TABH^+$ at room temperature have been ascribed to the triaminobenzenium ion, since these peak positions coincide with the transition energies calculated for this ion by the Pariser–Parr–Pople + CI method.

INTRODUCTION

Aromatic amines are generally protonated on the amino groups: for-example, aniline is converted into the anilinium ion in acid solution,[1] but the situation is more complex in the case of s-triaminobenzene.

The shape of the electronic spectrum of s-triaminobenzene in aqueous acid solution, led Köhler[2] to presume that the first protonation occurs on the ring C atom, yielding the substituted benzenium ion (II), whereas protonations by two or three protons occur on the amino groups in the usual way. Mataga[3] calculated the π-electron structure of II by the ASMO-CI method and showed that the calculated transition energies agree with the observed electronic spectrum.



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As the protonation of an aromatic amine usually takes place on the amino group, the ring carbon protonation presumed for TAB may be a special and interesting case. Therefore, we have studied in detail the pH and temperature dependence of the electronic spectrum of TAB* and analysed the equilibrium between TAB and proton. Furthermore, in order to give experimental support to the carbonium ion type structure for $TABH^+$, the IR and NMR spectra of TAB and $TABH^+$ have been measured. Finally, we studied the theoretical aspect of the π-electron structure for $TABH^+$ by means of the Pariser–Parr–Pople + CI method, for the purpose of explaining the observed electronic absorption spectrum and obtaining the fundamental knowledge necessary for the understanding of the protonation mechanism of TAB.

RESULTS AND DISCUSSION

pH Dependence of the absorption spectrum of TAB. These spectra of TAB measured under various conditions are given in Fig. 1. Curves 1, 2, 3 and 4 depict the UV spectra of TAB in distilled water, in buffer solutions of pH 4·3 and 1·2, and in the concentrated sulfuric acid, respectively. Curve 1 is the spectrum of unprotonated TAB and shows the absorption peaks at 35,500 and 45,500 cm^{-1}. Curve 3 is similar to that of aniline in both the peak wavelength and intensity, and as was pointed out by Köhler, this means that two protons are attached to the two amino groups of TAB at pH 1·2 and $TABH_2^{2+}$ (III) is produced. Furthermore, the resemblance of curve 4 to the absorption spectrum of benzene shows that the three amino groups of TAB are converted into the NH_3^+ groups by protonation in concentrated sulfuric acid. Since these details have been described by Köhler,[2] further explanation is omitted.

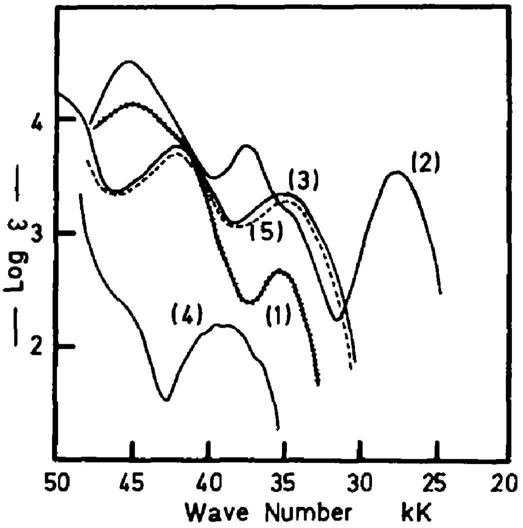

FIG. 1 The electronic spectra of TAB (1) in aqueous solution, (2) in the buffer solution of pH 4·3, (3) in the buffer solution of pH 1·2 and (4) in conc. sulphuric acid. Curve 5 shows the spectrum of aniline.

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* s-Triaminobenzene, unprotonated and protonated by one, two and three protons are abbreviated hereafter to TAB, $TABH^+$, $TABH_2^{2+}$ and $TABH_3^{3+}$, respectively.

Curve 2 of TAB measured at pH 4·3 shows the peaks at 27,400, 36,800 and 45,500 cm^{-1} with molar extinction coefficients of 3300, 9100 and 20,000, respectively. Judging from the pH values of the solution, curve 2 can be ascribed to the singly protonated TAB. As curve 2 is completely different from the absorption spectrum of *m*-phenylenediamine, the protonation may occur on the ring C atom and therefore curve 2 is the absorption spectrum of 2,4,6-triaminobenzenium ion. This is confirmed by the IR and NMR spectra and details are described later.

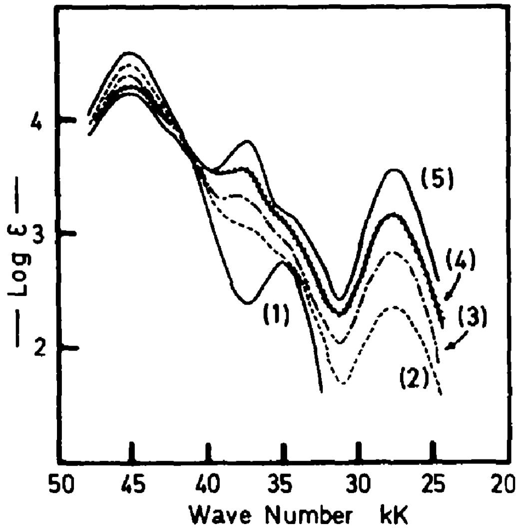

FIG. 2 The pH dependence of the absorption spectrum of TAB. Curves 1, 2, 3, 4 and 5 are measured in the buffer solutions of pH 7·3, 6·6, 6·0, 5·4 and 4·3, respectively.

Fig. 2 shows the spectra of TAB in buffer solutions of pH 7·3, 6·6, 6·0, 5·4 and 4·3. The three peaks of TABH$^+$ and the shoulder at 34,200 cm^{-1} increase in intensity with increasing acidity.

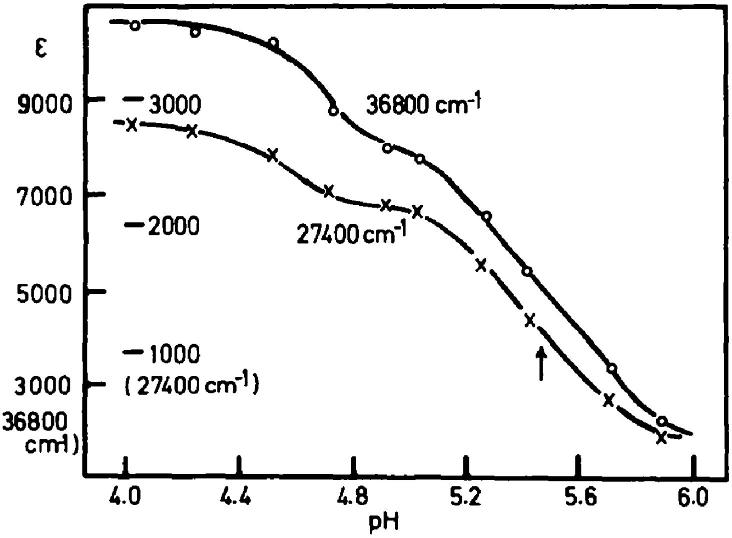

FIG. 3 Plots of the molar extinction coefficients of TAB versus pH.

Fig. 3 gives the plot of the molar extinction coefficients against the pH values of the solution. From the plot, the equilibrium constant pK_B for the reaction TAB + $H^+ \rightleftharpoons TABH^+$, is found to be 5·5.* In the equilibrium curve, a shoulder in the region of pH 4·9, is possibly due to the coexistence of the amino-protonated species or the interaction of TAB with $TABH^+$ like the charge transfer complex.

Structure determination of $TABH^+$. For this purpose, the IR and NMR spectra of $TABH^+$ were taken.

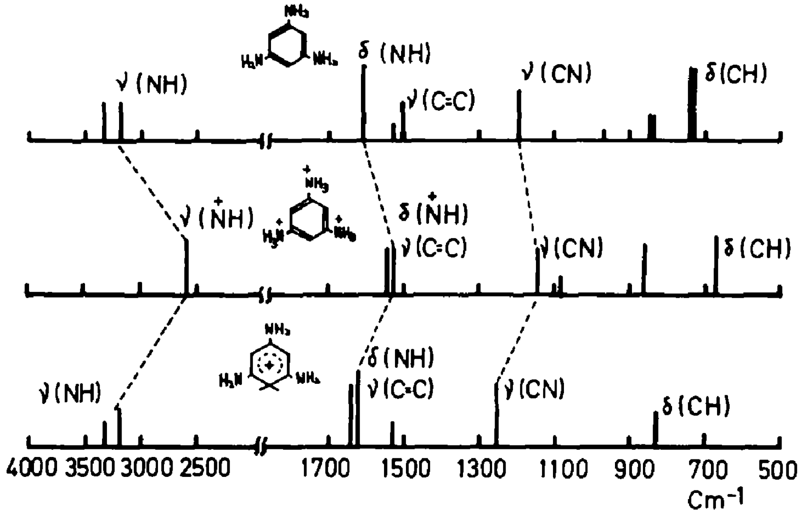

FIG. 4 The IR absorption spectra of TAB, $TABH^+$ and $TABH_3^+$.

The IR spectra of TAB, $TABH^+$ and $TABH_3^{3+}$ are given in Fig. 4. A comparison of the IR spectra of $TABH_3^{3+}$ and TAB reveals that in the spectrum of TAB, the bands assigned to the symmetric and asymmetric NH stretching vibrations of the amino group appear at 3200 and 3380 cm^{-1}; whereas, in the spectrum of $TABH_3^{3+}$, the NH stretching vibration band characteristic of the ammonium salt appears at 2570 cm^{-1}.[4] Further, the NH bending vibration at 1600 cm^{-1} observed for TAB shifts to 1540 cm^{-1} in $TABH_3^{3+}$. As shown in Table 1, a similar tendency is observed with other aromatic amines such as aniline, *p*-phenylenediamine and benzidine which are known to be protonated on the amino group. This information supports the opinion that protonation occurs on the amino groups for $TABH_3^{3+}$.

TABLE 1. THE NH BENDING VIBRATION OF NH_2 AND NH_3^+

	Neutral amine	Protonated amine
Aniline	1620 cm^{-1}	1575 cm^{-1}
p-Phenylenediamine	1638	1573
Benzidine	1605	1560

A comparison of the IR spectra of $TABH^+$ and $TABH_3^{3+}$, shows that a single

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* Köhler[2] also determined spectrophotometrically this equilibrium constant to be 5·5.

band near 2500 cm^{-1} characteristic of the NH_3^+ group cannot be observed in TABH$^+$ (Fig. 4) and that TABH$^+$ has a doublet near 3300 cm^{-1} as in the case of TAB. This means that the protonation occurs on a position other than the amino group and probably on the ring C atom, for TABH$^+$. In this connection, it is to be noted that the CN stretching band at 1180 cm^{-1}* for TAB shifts to 1145, 1110 and 1100 cm^{-1} for TABH$_3^{3+}$, while it shifts to 1260 cm^{-1} for TABH$^+$. This direction of shift observed for TABH$^+$ is the reverse in TABH$_3^{3+}$. This confirms that the positions of protonation for TABH$^+$ and TABH$_3^{3+}$ are different from each other.

Further information was obtained from a comparison of the IR spectra of TAB, TABH$^+$ and TABH$_3^{3+}$ in the region of the lower wave numbers. 1,3,5-Trisubstituted benzenes generally exhibit the characteristic bands due to the CH wagging vibration† in the 865–810 cm^{-1} and 730–675 cm^{-1} regions[5]. In addition, it is evident from the Table 2 that the CH wagging bands of the aromatic amines are not greatly affected by replacing the NH_2 group by the NH_3^+ group. In accordance with these facts, the CH wagging band is observed at 710 cm^{-1} and 690 cm^{-1} for TAB and TABH$_3^{3+}$, respectively, but TABH$^+$ shows no CH wagging band near 700 cm^{-1}. This means that the protonation does not occur on the NH_2 group for TABH$^+$ and further that the aromatic ring of TAB undergoes a considerable change in TABH$^+$.

TABLE 2. WAGGING VIBRATION OF THE RING CH

	Neutral amine	Protonated amine
Aniline	750 cm^{-1} 690	740 cm^{-1} 685
p-Phenylenediamine	840	830
Benzidine	815	810

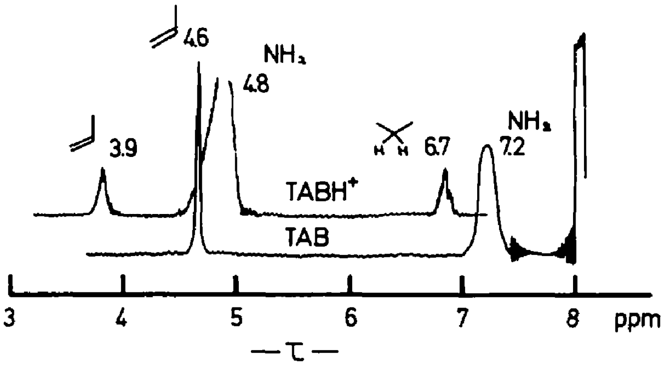

FIG. 5 The NMR spectra of TAB and TABH$^+$. The solvent is dimethyl sulphoxide acidified with hydrochloric acid.

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* The conjugated CN stretching band is generally observed at the wave number region higher than 1200 cm^{-1}; the frequency of 1180 cm^{-1} for TAB is rather low and shows a tolerable localization of π-electrons.

† The NH wagging vibration band is also expected to appear in this region. However, its assignment is not clear. The NH and CH wagging vibration bands may overlap with each other.

The NMR spectra of TAB and $TABH^+$ are given in Fig. 5. The spectrum of TAB shows a couple of proton signals at $\tau = 7{\cdot}2$ and 4·6 ppm. TAB has two different kinds of protons on the ring and the amino group. In view of their τ values and intensities, the signals at 4·6 ppm and 7·2 ppm are attributable to the ring protons and to the amino protons, respectively. The proton on the benzene ring generally shows the signal at $\tau = 2$–3.[6] The aromatic amino proton shows the signal near $\tau = 6$–7,[7] while the amino proton of the aliphatic amine shifts to higher field.[8]

The spectrum of $TABH^+$ consists of three proton signals with τ values of 3·9, 4·8 and 6·7 ppm. Two signals in the lower field from their position and intensity, can be assigned to the protons of the ring and the amino group. When an aromatic ring is transformed into the corresponding benzenium ion by protonation, the magnetic shielding is modified in two different ways.[9] In the first place, the protonation causes excess positive charges on various C atoms which is reflected in the chemical shift of the adjacent H atoms. Secondly the introduction of a CH_2 group in a conjugated system decreases the ring current due to π-electrons. In the ring protonated TAB, the effect of the positive charge is to shift the ring proton to lower field and the decrement in the ring current would tend to shift it to higher field. The observed lower field shifts of the ring proton and amino proton signals for $TABH^+$ indicate that the former effect is much stronger than the latter.

A new signal appears at 6·7 ppm for $TABH^+$, the intensity of which is almost equal to that of the ring proton signal. This can be assigned to the signal of the methylenic protons produced by the ring protonation. MacLean *et al.*[10] measured the NMR spectra of various substituted benzenium ions. They found that the CH_2 proton

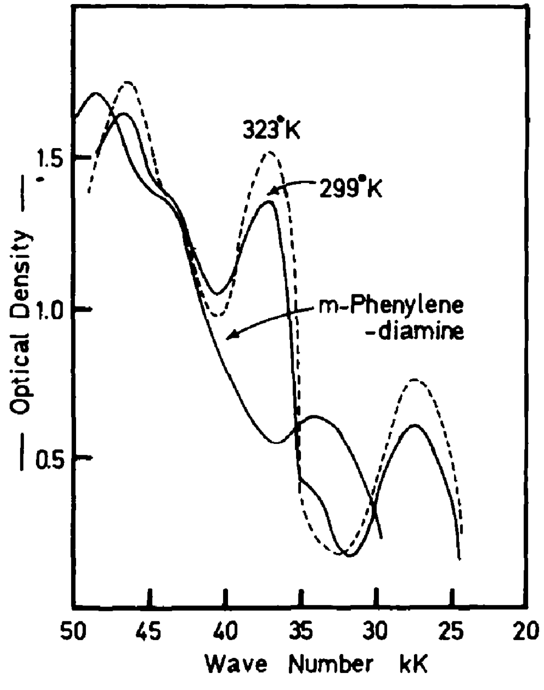

Fig. 6 The temperature dependence of the spectrum of TAB in the buffer solution of pH 4·7 The spectrum of *m*-phenylene-diamine is shown for the purpose of comparison.

signals of substituted benzenium ions appear in the vicinity of $\tau = 6$ ppm and shift to higher field as the basicity of the parent molecule increases. For instance, the CH_2 proton signals appear at 5·72, 5·80 and 6·08 ppm for the benzenium type ions of anisole, pentamethylbenzene and trimethoxybenzene, respectively.[11] In view of this tendency, it is reasonable to assign the signal at $\tau = 6{\cdot}7$ ppm to the CH_2 proton. These results of the IR and NMR spectra confirm that $TABH^+$ takes the benzenium ion type structure.

Temperature dependence of the UV spectrum of TAB in acid solution. The UV spectrum of TAB in acid solution was measured at various temperatures in order to check whether the four bands at 27,400, 34,200, 35,800 and 45,500 cm^{-1} are due to the same species.

Fig. 6 shows the temperature dependence of the spectrum of TAB in a buffer solution of pH 4·7. In this solution, the occurrence of the second equilibrium in which the two protons add to TAB, is almost completely negligible as revealed from its equilibrium constant of 3·9. With rising temperature, the peaks at 27,400, 36,800 and 45,500 cm^{-1} obviously increase their intensity, whereas the intensity of the shoulder at 34,200 cm^{-1} decreases. This suggests that the shoulder is due to a different species from that for the three peaks. The position of this shoulder corresponds to that of *m*-phenylenediamine. Thus, the shoulder at 34,200 cm^{-1} is probably due to $TABH^+$ in which the protonation occurs on the amino group and therefore the spectrum should be similar to *m*-phenylenediamine. The temperature dependence of the absorption spectrum indicates that $TABH^+$ may be protonated on different positions, namely the amino group and the ring carbon, and that both forms may

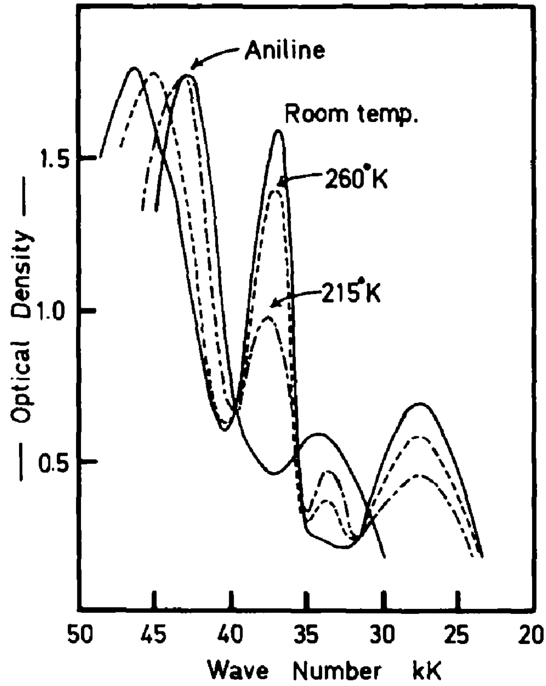

FIG. 7 The temperature dependence of the spectrum of TAB in the alcohol–ether mixed solvent of the pH value where the second protonation just begins.

coexist in a solution of pH 4·7, though the amount of the former type is very small in the temperature range higher than room temperature.

Fig. 7 shows the temperature dependence of the absorption spectrum at the pH value where the second protonation just begins. In this figure, too, with rising temperature, the peaks at 27,400 and 36,800 cm^{-1} increase their intensity and the 34,200 cm^{-1} band becomes weaker. Further, the peak at 45,500 cm^{-1} shifts to lower wave numbers, which means that as the temperature is lowered the observed spectrum approaches that of aniline, that is, the equilibrium $TABH^+ + H^+ \rightleftarrows TABH_2^{2+}$, is inclined to shift to the right.

Calculation of the electronic structure of $TABH^+$ by the Pariser–Parr–Pople + CI method. Since the protonation of aromatic amines usually occurs on the amino group, the carbonium ion structure of $TABH^+$ may be considered as a special case. In order to give theoretical support to the ring carbon protonation of TAB and to interpret the observed electronic spectrum of $TABH^+$ on the basis of its π-electron we applied the Pariser–Parr–Pople + CI type calculation with the aid of the geometrical structure and numbering of the atoms as shown in Fig. 8. The ionization potentials I_p's and the electron affinities E_a's of carbon and nitrogen in the valence states were taken from Pritchard–Skinner's table[12]. The I_p values are 11·42 and 28·85 eV and the E_a values are 0·62 and 15·41 eV for carbon and nitrogen, respectively. The core resonance integrals are considered only for the nearest neighbours and are set equal to $\beta_{CC} = -2{\cdot}40$ eV and $\beta_{CN} = -1{\cdot}50$ eV. The evaluated MO wave functions and energies are listed in Table 3. The actual calculation was made by a Facom 202 electronic computer at our Institute. The configuration interaction calculation was carried out by taking the singly excited configurations corresponding to the electron

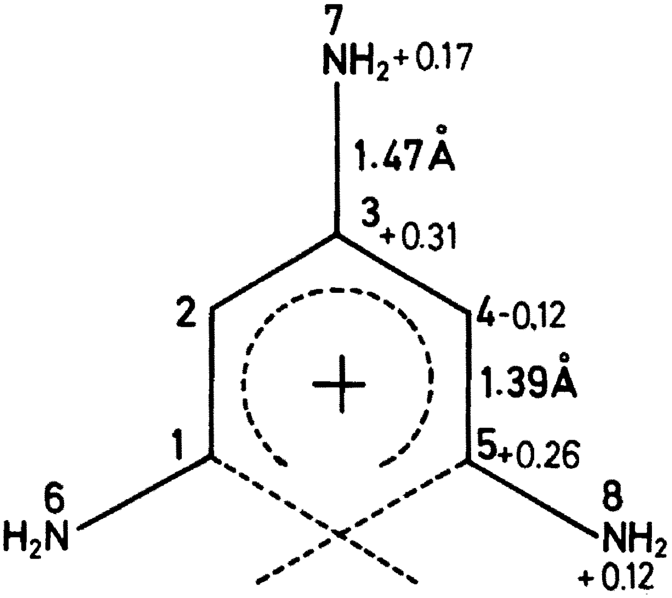

FIG. 8 The geometrical structure, the numbering of atoms and the calculated charge distribution of the triaminobenzenium ion.

excitation from filled orbitals 3, 4 and 5 to vacant orbitals 6, 7 and 8. The calculated result of the 1,3,5-triaminobenzenium ion (II) is schematically shown in Fig. 9. In this figure, the calculated transition energies and oscillator strengths (in parentheses) are given together with the energy of the configuration taken in the present calculation. Further, the observed transition energies and oscillator strengths for $TABH^+$ are also given in this figure for the purpose of comparison. The calculated values are in satisfactory agreement with the observed values. This also supports our opinion that the three absorption bands at 27,400, 36,800 and 45,500 cm^{-1} are due to the ring-protonated $TABH^+$ but that the 34,200 cm^{-1} band is not due to this.

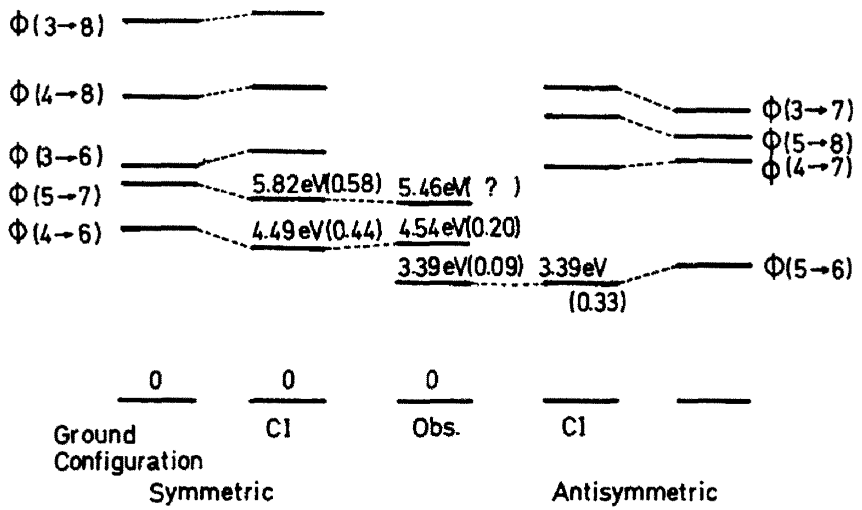

FIG. 9 The calculated and observed transition energies and oscillator strengths (in parentheses) of $TABH^+$ based on the ring protonated structure.

The charge distribution of the ring-protonated $TABH^+$ in the ground state has been evaluated with the result shown in Fig. 8. It is seen from the figure that about 40% of the positive charge of the ring is compensated for by the lone pair electrons of the amino groups.

In order to discuss the method of protonation, the stability of the protonated species should be taken into account. As a measure of this stability, Mataga[3] calculated the localization energy—namely, the destabilization energy due to the protonation on the ring C atom—for aniline, *m*-phenylenediamine and TAB by the simple Hückel method, with the result that it decreases in the order of aniline > *m*-phenylenediamine > TAB. In addition we have also calculated the same quantity for *p*-phenylenediamine and are able to show a decrease of the localization energy in the order of aniline > *p*-phenylenediamine > *m*-phenylenediamine > TAB. On the other hand, the destabilization energy of the π-electron system due to the protonation on the amino group is almost constant for these aromatic amines. These theoretical facts together with the experimental result given in Fig. 7 lead to the conclusion that the energy difference between the protonated specimens on the ring C atom and on the amino group is small for TAB and consequently the two forms can coexist in equilibrium at room temperature. In view of the fact that the band intensity of the ring-protonated $TABH^+$ decreases with lowering of temperature, whereas the peak at 34,200 cm^{-1} assigned to the amino-protonated $TABH^+$ is intensified, the latter is likely to be the stable form. In conclusion, the following equilibrium scheme is proposed for the protonation of TAB.

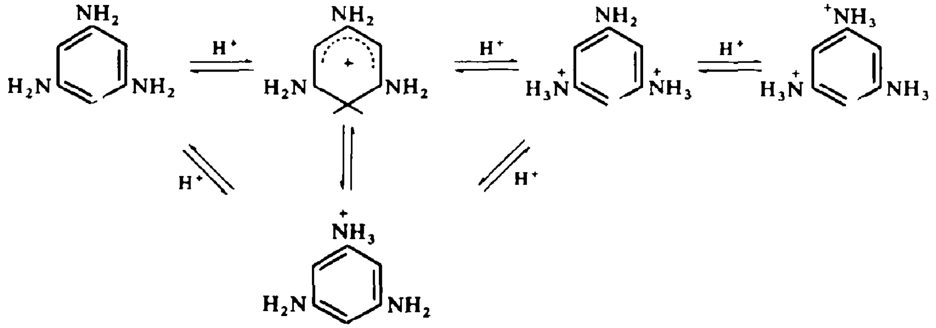

TABLE 3. MO ENERGIES AND WAVE FUNCTIONS OF THE RING-PROTONATED $TABH^+$ CALCULATED BY THE PARISER–PARR–POPLE METHOD

	MO wave function							
ε, eV	1	2	3	4	5	6	7	8
−20·6769	0·2927	0·3841	0·4921	0·3841	0·2927	0·2746	0·3748	0·2746
−19·8238	0·3501	0·2128	0	−0·2128	−0·3501	0·5762	0	−0·5762
−19·2118	0·1538	−0·0847	−0·2923	−0·0847	0·1538	0·5523	−0·4925	0·5523
−17·3275	−0·1604	−0·3444	−0·1406	−0·3444	−0·1604	0·2804	0·7308	0·2804
−16·6596	−0·3336	−0·4909	0	0·4909	0·3336	0·3841	0	−0·3841
− 8·3331	0·5199	−0·0162	−0·5714	−0·0162	0·5199	−0·1882	0·2474	−0·1882
− 5·7216	−0·5157	0·4621	0	−0·4621	0·5157	0·1426	0	−0·1426
− 3·6160	0·3074	−0·4757	0·5709	−0·4757	0·3074	−0·0732	−0·1474	−0·0732

EXPERIMENTAL

Materials. s-TAB was produced by the reduction of s-trinitrobenzene. s-Trinitrobenzene (4 g) in EtOAc (48 cc) was catalytically reduced using Pd-C and after the calculated volume of H_2 was absorbed, the soln was filtered. White needle crystals of TAB were obtained on cooling the filtrate. Purification was carried out by repeated sublimation at 60°, 10^{-5} mm Hg. TAB thus obtained was stored *in vacuo* because of its instability in air.

Aniline, *p*-phenylenediamine, benzidine and their hydrochlorides were purchased from Tokyo Chemical Industry Co., Ltd. Aniline was distilled under the reduced press before use. *p*-Phenylenediamine was recrystallized from ethyl ether. Their hydrochlorides were purified by recrystallization from dil HCl.

Measurements. A Cary model 14M recording spectrophotometer was used to measure the UV spectra of TAB in AcOH–NaOAc buffer solns of various acidities. All measurements were carried out at room temp except in the determination of the equilibrium constant, when the measurements were made at a constant temp, 25° ± 0·5°.

The absorption spectra at low temps were measured by using Clio-Tip supplied by Air Product and Chemicals Co. Ltd.

The IR spectra of TAB and TABH$^+$ were measured with a Hitachi EPI-2 recording spectrophotometer. NMR spectra were measured with a Japan Electron Optics Laboratory NMR spectrometer 3H-60 located at the Institute of Industrial Science, the University of Tokyo.*

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