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Charge Transfer Interaction between the Cation Radicals of Some Aromatic Diamines and Triethylamine

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Electronic spectra of the cation radicals of some aromatic diamines in triethylamine were found to differ remarkably from those in other solvents such as ether or alcohol as regards (1) swelling of the absorption at around 25000 cm^{-1}, (2) broadening of the first band system and (3) red shift of the same system. It was concluded that these phenomena are due to the charge transfer interaction between cation radicals and triethylamine.

Dimerization of organic ion radicals in solutions has been extensively studied.[1–6] An anion radical (A$^-$) or a cation radical (D$^+$) dimerizes easily in the solution and a new absorption band due to the charge transfer (CT) between the two half-occupied orbitals of component radicals appears in the long wavelength region. The local excitation bands of the component radicals are also influenced largely by dimerization.

Recently the existence of a complex formed between an organic molecule (D) and its cation radical (D$^+$) has been found and studied extensively by γ radiolysis.[7–10] In this case also, a new absorption band due to charge resonance interaction appears in the visible or near infrared region.

From this D$^+\cdots$D type complex a D$^+\cdots$D$'$ type one would be expected, D$'$ being a different molecule from D. However, no report seems to have been made so far. Since such a complex would be of importance as an intermediate in reactions of cation radicals, we have attempted to find it.

Experimental

Preparation of Materials. Commercial *p*-phenylenediamine(PPD) was recrystallized in benzene and sublimed *in vacuo*. Commercial *N,N*-dimethyl-*p*-phenylenediamine (DMPD) and *N,N*-diethyl-*p*-phenylenediamine(DEPD) were purified by use of the vacuum line technique.

An aqueous solution of commercial *N,N,N',N'*-tetramethyl-*p*-phenylenediamine(TMPD) dihydrochloride was treated with 28% ammonia. The precipitate obtained was dried and sublimed several times *in vacuo*. Triethylamine(TEA), tri-*n*-propylamine(TNPA) and tri-*n*-butylamine(TNBA) were dried over pellets of potassium hydroxide for a day and fractionally distilled in a stream of nitrogen under reduced pressure.

Procedure. Solutions of the aromatic diamines in aliphatic amines, ethanol and EPA were degassed in 15 mm diam. quartz cells by the freeze-pump-thaw technique and sealed. These solutions were cooled in a quartz Dewar with liquid nitrogen and irradiated with a 250 W high pressure mercury lamp through a Toshiba glass filter UV D2, passing 300—400 nm light, to produce the cation radicals of the aromatic diamines. These UV-irradiated samples were then illuminated in the visible and near infrared region, longer than 500 nm, through a Toshiba glass filter V-052 or V-G54 in order to remove absorption due to the solvated electron.[11,12]

The electronic absorption spectra were recorded with a Shimadzu Multipurpose Recording Spectrophotometer MPS-50L.

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Results

Electronic absorption spectra of the cation radicals formed by UV-irradiation of PPD and its derivatives in the rigid glasses of TEA and EPA at 77 K are shown in Figs. 1—4. Curves a and b show the absorption of the irradiated solutions in EPA and TEA, respectively, and curves c give their differences.[13] Change of spectra from EPA solutions to TEA solutions can be characterized as follows.

1. Swelling of the absorption at around 25000 cm^{-1}, attributable to a new band as shown by curve c.
2. Broadening of the first longest wavelength band system of the cation.
3. Red shift of the same system.

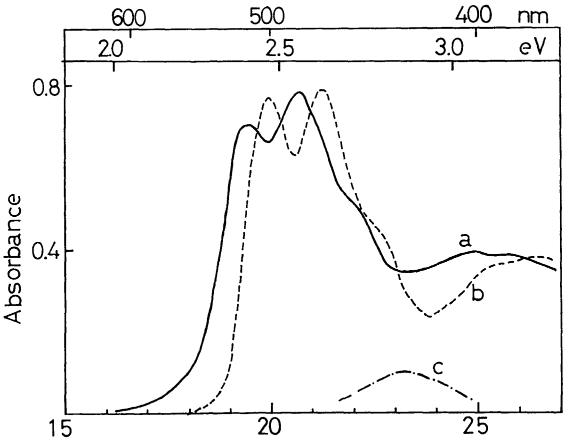

Fig. 1. The visible absorption spectra of the cation radical of *p*-phenylenediamine: a, in TEA; b, in EPA; c, a—b, the difference between a and b.

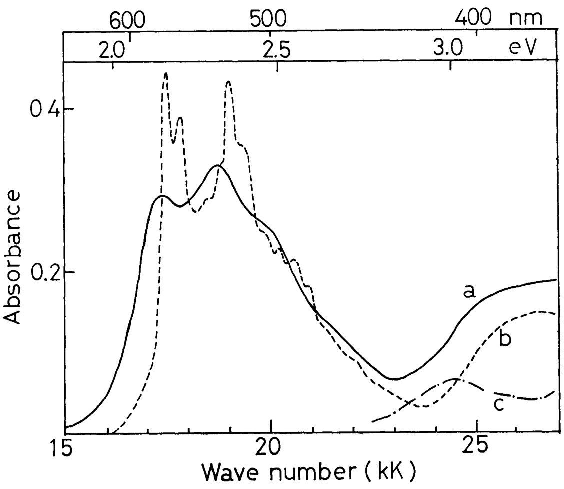

Fig. 2. The visible absorption spectra of the cation radical of *N*,*N*-dimethyl-*p*-phenylenediamine: a, in TEA; b, in EPA; c, a—b.

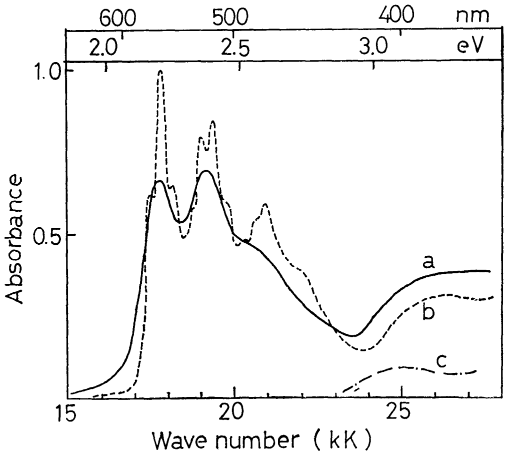

Fig. 3. The visible absorption spectra of the cation radical of *N*,*N*-diethyl-*p*-phenylenediamine: a, in TEA; b, in EPA; c, a—b.

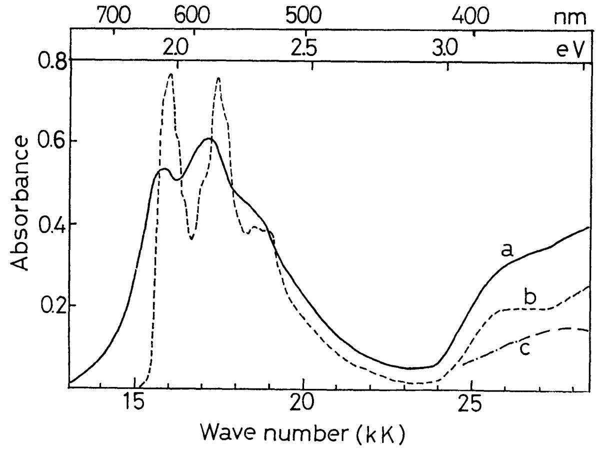

Fig. 4. The visible absorption spectra of the cation radical of *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine: a, in TEA; b, in EPA; c, a—b.

Table 1. Peak positions and half band widths of the first band system of the cation radical of *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine in various solvents at 77 K

Solvent	Width, cm^{-1}	λ_{max}, nm	
TEA	4600	585	635
TNPA	4000	582	632
TNBA	4400	578	632
EtOH	3300	575	625
EA[a]	3300	573	623
EPA[b]	3300	576	620
EP[c]	3100	573	625

a) Ethyl ether (1): Ethyl alcohol (1).
b) Ethyl ether (5): Isopentane (5): Ethyl alcohol (2).
c) Ethyl ether (1): Isopentane (1).

In Table 1, are given the peak positions and the half widths of the first band system for TMPD cation radical in various solvents at 77 K, for the purpose of

Table 2. Peak position of the new band observed in TEA and calculated values of $E_{CT}{}^{v}$ and $E_{CT}{}^{a}$

D	Transition energy at the maximum of the new band, eV	$E_{CT}{}^{v}$, eV	$E_{CT}{}^{a}$, eV
PPD	2.9	2.33	1.46
DMPD	3.0	2.69	1.74
DEPD	3.1	2.79	1.92
TMPD	3.5	2.89	2.00

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[13] As the red shift of the first band system of PPD$^+$ in TEA is especially strong, we obtained curve c for this case by shifting curve b to longer wavelength so that the positions of its vibronic bands agreed with those of curve a, and then subtracting the shifted curve b from a.

relating them with the nature of the solvent. The maximum wavelengths of the observed new absorption (curves c, Figs. 1—4) are summarized in Table 2.

Discussion

We see from Table 1 that the first band system of the cation radical in EA, EPA, and EP shows a tendency to become sharper and shift slightly to shorter wavelength with decreasing polarity of solvents. Since aliphatic amines are less polar than EPA, a sharpening of the band shape along with the blue shift is expected in amine solutions. The results are contrary to this expectation (Table 1 and Figs. 1—4), and it seems most likely that they can only be explained by taking the CT interaction between the cation radical and the aliphatic amine into account. In connection with this, the new absorption bands as shown by curves c, in Figs. 1—4 are most probably assigned to the CT bands, with the cation radical as acceptor and triethylamine as donor. These assignments are quantitatively verified as shown below.

By assuming weak CT interactions, the vertical CT energy (E_{CT}^v) from an aliphatic amine (D′) as an electron donor to a cation radical (D^+) as an electron acceptor can be expressed by

$$E_{CT}^v = I_p^v(D') - E_A^v(D^+) + P(D\cdots D'^+) - P(D^+\cdots D') \qquad (1)$$

where I_p^v and E_A^v are vertical ionization potential and vertical electron affinity, respectively. $P(D^+\cdots D')$ represents the static polarization energy in the ground state of the complex, and $P(D\cdots D'^+)$ the electronic polarization energy in the excited CT state. The polarization energy can be estimated approximately using Born's equation $P = -(1-1/\varepsilon)e^2/2r_0$, where r_0 is the effective radius of an ion and ε the dielectric constant of the medium. The static dielectric constant of triethylamine at 77 K can be estimated to be $\varepsilon_{77K} = 3.6$.[14] The dielectric constant in the visible region is calculated to be $\varepsilon_{op} = 1.96$ using the refractive index $n^{20°C} = 1.40$ at the sodium D-line.[16] When the effective radii for triethylamine and the cation radicals of the aromatic diamines are assumed to be both 3.3 Å, the polarization energy in Eq. (1) is calculated to be

$$P(D\cdots D'^+) - P(D^+\cdots D') = (1/\varepsilon_{op} - 1/\varepsilon)e^2/2r_0 = 0.7\ \text{eV}.$$

The relation between the ionization potential of a neutral molecule and the electron affinity of its cation radical is schematically given in Fig. 5. As a rough approximation, we assume that

$$I_p^v(D) - I_p^a(D) \cong I_p^a(D) - E_A^v(D^+) \qquad (2)$$

Superscripts v and a are abbreviations of "vertical" and "adiabatic", respectively. The I_p^v's and I_p^a's of DMPD and TMPD were measured by Nakato *et al.*[17] The ionization potentials of PPD and DEPD can be estimated from the peak positions of the CT bands of the CT complexes formed between these aromatic diamines and 1,3,5-trinitrobenzene.[18] The results are shown in Table 3.

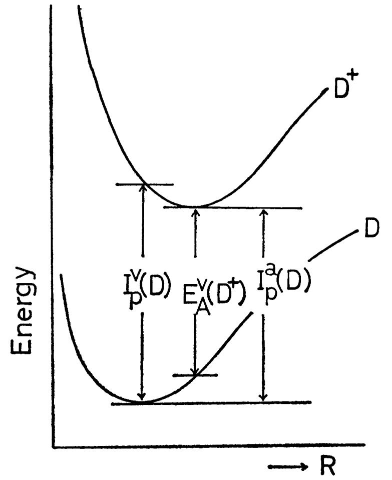

Fig. 5. Schematic energy curves for D and the cation D^+ against a generalized coordinate R for the molecular structure.

The theoretically expected values of E_{CT}, using 7.84 eV as the I_p^v for triethylamine[19] are shown in

TABLE 3. IONIZATION POTENTIALS OF AROMATIC DIAMINES AND ELECTRON AFFINITIES OF THEIR CATION RADICALS

D	I_p^v (D), eV	I_p^a (D), eV	E_A^v (D^+), eV
PPD	7.27	6.74[a]	6.21
DMPD	6.97	6.46	5.95
DEPD	6.81	6.28[a]	5.75
TMPD	6.75	6.20	5.65

a) Estimated by subtracting 0.53 eV from I_p^v. 0.53 eV is the avarage value of $I_p^v - I_p^a$ for DMPD and TMPD.

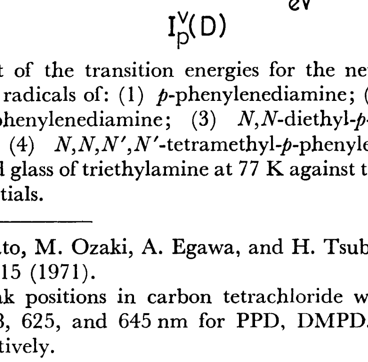

Fig. 6. Plot of the transition energies for the new bands of the cation radicals of: (1) *p*-phenylenediamine; (2) *N*,*N*-dimethyl-*p*-phenylenediamine; (3) *N*,*N*-diethyl-*p*-phenylenediamine; (4) *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine, in the rigid glass of triethylamine at 77 K against their ionization potentials.

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[14] Assuming an approximate equation $\varepsilon_{T'} = \varepsilon_T - \alpha(T'-T)$ with $\alpha = 5.2\times10^{-3}$ deg^{-1} and $\varepsilon_{298\,K} = 2.42$, we obtain 3.6 as $\varepsilon_{77\,K}$[15]. Here, the value of α for triethylamine is taken to be equal to that for trimethylamine, since the former is not known.[15]

[15] A. A. Maryott and E. R. Smith, Table of Dielectric Constants of Pure Liquids, National Bureau of Standards Circular 514 (Issued Aug. 10, 1951).

[16] J.A. Riddick and W.B. Bunger, "Organic Solvents," third edition, John Wiley & Sons, New York (1970), p. 439.

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[18] The peak positions in carbon tetrachloride were measured to be 505, 578, 625, and 645 nm for PPD, DMPD, DEPD, and TMPD, respectively.

[19] a) M. I. Al-Joboury and D.W. Turner, *J. Chem. Soc.*, **1964**, 4434. b) D. W. Turner, *Advan. Mass. Spectrom.*, **4**, 755 (1968).

Table 2, together with the observed values for the new bands. The agreement between calculated and observed values is fairly good. Taking account of errors in the calculation, the measured new bands can be ascribed to the CT bands.

The relation between the ionization potentials of the aromatic diamines and the peak positions of the new bands is shown in Fig. 6. The solid line in this figure is drawn with a gradient of -1, in accordance with Eq. (1). Four measured points are seen to lie fairly well on this line.

Table 4. Peak position of the new band for TMPD$^+$ in three aliphatic amines and ionization potentials of the amines

D′	Energy at the maximum of the new band, eV	I_p^v (D′), eV	I_p^a (D′), eV
TEA	3.49	7.84	7.50[a]
TNPA	3.44		7.23[a]
TNBA	3.26		

a) K. Watanabe and J. R. Mottle, *J. Chem. Phys.*, **26**, 1773 (1957).

The behavior of the new band for TMPD$^+$ in some aliphatic amines was examined, the result being given in Table 4. The energy at the maximum of the new band was found to become lower, the lower the ionization potential of the aliphatic amines, as expected theoretically from Eq. (1). The magnitude of the shift seems reasonable, although the exact data of ionization potential of these aliphatic amines are not available. These results strongly support our assertion that the new bands originate from charge transfer from triethylamine to the cation radicals.

The remarkable broadening of the first band system of the cation in TEA compared with that in EPA may be explained as follows. The minimum charge transfer energy, that is, the adiabatic charge transfer energy E_{CT}^a, can be obtained by substituting $I_p^a(D')$ and $E_A^a(D^+)$ for $I_p^v(D')$ and $E_A^v(D^+)$, respectively, in Eq. (1). The result is shown in Table 2. Here 7.50 eV was used as the value of I_p^v for TEA.[20] As is seen in this table, E_{CT}^a is smaller than E_{CT}^v by 6000—7000 cm^{-1}. Accordingly, it is most probable that the first band system of the cation radicals lies entirely in the region of the lower vibronic part of the CT state. These lower vibronic CT states may be considered to be pseudocontinuous and optically forbidden. They interact with the vibronic states of the first system of D$^+$ to broaden their band shape.[21,22] Similarly the red shift of the absorption peak of the first system of the cation radicals might be explained by the interaction with the CT states.

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