Absorption Spectra of Cation Radicals Derived from *p*-Phenylenediamine and Its *N*-Methyl Derivatives

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(Received March 9, 1968)

The cation radical salts made by the one-electron oxidation of aromatic diamines have been the subject of interest for many years. Naturally, considerable attention has been paid to their magnetic properties. In connection with our spectroscopic study of the solid salts, we examined the absorption spectra of the cation radicals derived from *p*-phenylenediamine and all the *N*-methyl derivatives in a dilute ethanol solution. The spectra of the same cations were examined by Michaelis *et al.* nearly thirty years ago.[1] Unlike us, however, they oxidized the diamines in a methanol+dilute aqueous solution of acetic acid with bromine and examined the spectra without isolating the salts. Their measurements were very qualitative and covered only the α band. Therefore, we wish to present here a brief summary of our measurements.

The following solid salts were prepared by the methods given in the references[2-4]: *p*-phenylenediamine bromide (I), *N*-methyl-*p*-phenylenediamine bromide (II), *N,N*-dimethyl-*p*-phenylenediamine bromide (III), *N,N'*-dimethyl-*p*-phenylenediamine perchlorate (IV), *N,N,N'*-trimethyl-*p*-phenylenediamine iodide (V), and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine perchlorate (VI).

The measurements were performed at room temperature, using a Beckman DK-2A spectrophotometer, on ethanolic solutions at concentrations of the order of 10^{-5} mol/*l*.

All the spectra bear a close resemblance to each other and show the general features shown schematically in Fig. 1. The positions and molar extinction coefficients (ε) of the three electronic absorption bands, designated as α, β and γ, are summarized in Table 1.

The structures of the α bands are regarded as vibrational.[5] The α band shows a remarkable red-shift upon the introduction of the methyl group (about 1 kK per group), while the other two bands are nearly independent of the number of the substituent.

The agreement between our positions and those reported by Michaelis *et al.*[1] is fair. Accurate measurements of the molar extinction coefficients are much hampered by the instability of the salts. Moreover, in the case of the *p*-phenylenediamine cation the presence of a small amount of the dimeric

TABLE 1. ABSORPTION SPECTRAL DATA FOR THE CATION RADICALS DERIVED FROM *p*-PHENYLENEDIAMINE AND ITS *N*-METHYL DERIVATIVES

Substituent	Color*	α band		β band	γ band	
		$\tilde{\nu}$ (kK)	ε (*l*/mol·cm)	$\tilde{\nu}$ (kK)	$\tilde{\nu}$ (kK)	ε (*l*/mol·cm)
None (I)	Yellow	20.4 21.1	(>4950) (>5120)	~27.6	30.5 doublet	(>13500)
N-Methyl (II)	Pink	19.1 20.4	— —	26.7—27.0	31.0	—
N,N-Dimethyl (III)	Red	18.0 19.4	9100 8960	~26.7	30.7	18800
N,N'-Dimethyl (IV)	Red	18.1 19.6	(7930) (7660)	~26.7	30.8	(15150)
N,N,N'-Trimethyl (V)	Violet	17.2 18.6	— —	~26.7	30.9	—
N,N,N',N'-Tetramethyl (VI)	Blue	16.4 17.8	11100 11100	~26.7	30.6	18800

* In dilute ethanolic solution at room temperature.

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1) L. Michaelis, M. P. Schubert and S. Granick, *J. Am. Chem. Soc.*, **61**, 1981 (1939).

2) L. Michaelis and S. Granick, *ibid.*, **65**, 1747 (1943).

3) J. Piccard, *Ann.*, **381**, 351 (1911).

4) G. K. Hughes and N. S. Hush, *J. Proc. Roy. Soc. N. S. W.*, **81**, 48 (1947).

5) A. C. Albrecht and W. T. Simpson, *J. Am. Chem. Soc.*, **77**, 4454 (1955).

form, indicated by a peak around 16.4 kK, hinders the estimation.[6] The values in parentheses must, therefore, be considered no more than rough estimates.

A simple molecular orbital consideration of the *p*-phenylenediamine cation shows that the odd electron is in the orbital of the b_{3g} symmetry. The transitions associated with the α, β, and γ bands are $^2B_{3g} \rightarrow {}^2B_{1u}$, $^2B_{3g} \rightarrow {}^2A_u$ and $^2B_{3g} \rightarrow {}^2B_{1u}$, respectively. Thus, from symmetry considerations the transition moments in the α and γ bands appear to be along the long axis of the molecular ion, and that in the β band, along the short axis. It is gratifying to see that this prediction agrees well with the results obtained by Albrecht and Simpson, by means of polarized photo-oxidation in a rigid medium, for the *N,N,N',N'*-tetramethyl-*p*-phenylenediamine cation.[5]

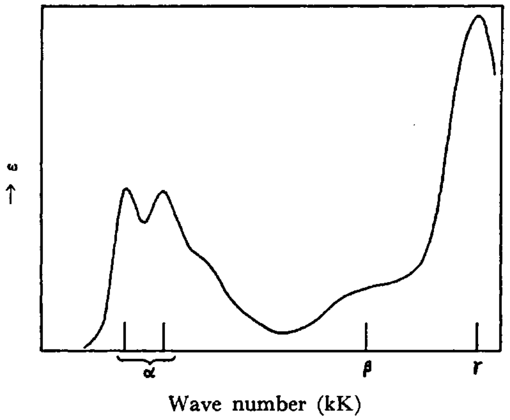

Fig. 1. General feature of the spectra of the cation radicals derived from *p*-phenylenediamine and its *N*-methyl derivatives.

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[6] K. Uemura, S. Nakayama, Y. Seo, K. Suzuki and Y. Ooshika, This Bulletin, **39**, 1348 (1966).