# The Electronic Absorption Spectra of Würster's Cation Radicals and Their Dimerization in Solution*

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The visible and ultraviolet absorption spectra of the *p*-phenylenediamine cation ($PD^+$), the *N,N*-dimethyl-*p*-phenylenediamine cation ($DMPD^+$), and the *N,N,N',N'*-tetramethyl-*p*-phenylenediamine cation ($TMPD^+$) in the presence and in the absence of an excess counter anion ($X^-=Br^-$, $Cl^-$, and $ClO_4^-$) are studied at low temperatures. Analyses of the data show that these cation radicals are in an equilibrium represented by $2R^+ + X^- \rightleftarrows R^{++}{}_2X^-$ (or, more exactly, $2R^+ + 0.7X^- \rightleftarrows R^{++}{}_2(X^-)_{0.7}$). It is found that the absorption maxima of the dimer and the value of the heat of dimerization are independent of the kind of counter anion. It is concluded that $PD^+$ and $DMPD^+$ form strong dimers (heat of dimerization, $\Delta H=-8.0$ and $-8.2$ kcal/mol respectively) and that $TMPD^+$ forms a relatively weak one ($\Delta H=-5.6$ kcal/mol). The features of the dimer spectra reflect the strength of the interaction of the radical in the dimer. In a strong dimer, the spectrum in the low-frequency region consists of a strong intermolecular charge-transfer band (C band) and a weak local excitation band (R' band), and the frequency shifts of the local excitation bands in the dimer (R' and Y' bands) from corresponding bands in the monomer (R and Y) are large. On the other hand, the spectrum in the weak dimer consists of relatively weak C and strong R' bands, and the shifts of the R' and Y' bands are small. A model of the dimer is proposed in which the two cations are arranged in a parallel manner and are surrounded by the ionic atmosphere of the counter anions.

The half-oxidation products of *p*-phenylenediamine and its *N*-methyl substituted derivatives, which are called Würster's cation radicals, are known as stable organic cation radicals. Michaelis and Granick[1] first suggested that Würster's cation radicals, except for the *N,N,N',N'*-tetramethyl-*p*-phenylenediamine cation ($TMPD^+$ or Würster's blue), are polymerized in crystalline states and in concentrated or cooled solutions. Hausser[2] found that, with lowering of the temperature, a Würster's blue perchlorate solution shows an intense new absorption band in the near-infrared region of the spectrum, a band which appears to increase in intensity as the paramagnetism of the solution decreases. Hausser and Murrell[3] suggested the formation of a radical dimer ($\pi$-complex) and assigned the new band to an intermolecular charge-transfer band in the dimer. In the previous preliminary papers,[4] the present authors experimentally confirmed the suggested solution dimerization by an analysis of the temperature-dependent absorption spectra of several Würster's cation radicals at low temperatures. A similar line of investigation has also been performed by Kimura, Yamada, and Tsubomura.[5]

In these previous works, however, the role of the counter anion in the dimerization was not considered. In the present investigation, spectrophotometric measurements of the solutions of cation radicals of *p*-phenylenediamine ($PD^+$), *N,N*-dimethyl-*p*-phenylenediamine ($DMPD^+$), and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine ($TMPD^+$) were carried out at low temperatures and at various concentrations by using newly-constructed, accurate temperature-control equipment. In order to study the possible contribution of the counter anion to the dimerization, an excess amount of a salt containing a counter anion (ammonium bromide, chloride, or perchlorate) was added to the radical solution and the observed spectrophotometric changes were analyzed on the basis of several monomer-dimer equilibrium models including the counter anion. The nature of dimer interaction was then discussed by using the monomer and the dimer spectra of $PD^+$, $DMPD^+$, and $TMPD^+$ together with the results of other analyses.

## Experimental

*p*-Phenylenediamine bromide (PDBr), *N,N*-dimethyl-*p*-phenylenediamine perchlorate ($DMPDClO_4$) and *N,N,N',N'*-tetramethy-*p*-phenylenediamine perchlorate ($TMPDClO_4$) were used for this study. These radical salts were prepared according to the method described in the literature.[1] For the spectrophotometric solvents, an ethanol–ethyl ether mixture (volume ratio of 2 : 1) was used for $DMPD^+$ and $TMPD^+$, while *n*-propanol was used for $PD^+$, because of the slower decomposition rates of the radicals in the solutions. Each solvent was purified by distillation after desiccation over sodium wire (for ether) or calcium oxide (for alcohols).

The absorption spectra of the radical solutions at low temperatures were obtained in quartz absorption cells with optical path lengths of 0.1, 0.3, 1.0, and 3.0 cm. The cell was cooled by cold nitrogen gas in a quartz Dewar vessel with optical windows. The cold nitrogen gas was supplied from a liquid nitrogen tank equipped with an electric heater immersed in the liquid nitrogen.

The temperature of the solution in the cell was measured by means of a copper-constantan thermocouple with a standard DC voltage source, a DC amplifier, and an electronic recording millivoltameter with lower and upper limit switches, as is shown in Fig. 1. The rate of the flow of the cold nitrogen gas was controlled automatically by regulating an applied voltage drop across the heater by the use of the switches.

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1) L. Michaelis and S. Granick, *J. Amer. Chem. Soc.*, **65**, 1757 (1943).

2) K. H. Hausser, *Z. Naturforsch.*, **A11**, 20 (1956).

3) K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

4) K. Uemura, S. Nakayama, Y. Seo, K. Suzuki, and Y. Ooshika, This Bulletin, **39**, 1248 (1966). A. Kawamori, A. Honda, N. Joo, K. Suzuki, and Y. Ooshika, *J. Chem. Phys.*, **44**, 463 (1966).

5) K. Kimura, H. Yamada, and H. Tsubomura, *ibid.*, **48**, 480 (1967).

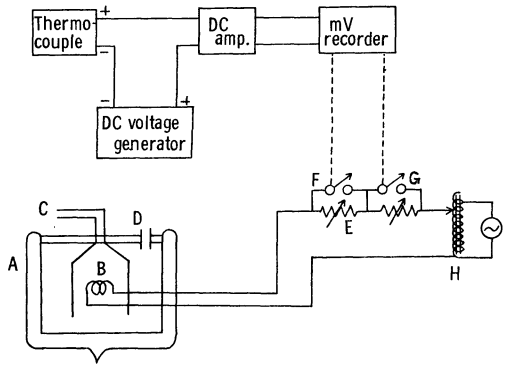


Fig. 1. Apparatus for temperature control.
A: liquid nitrogen tank, B: electric heater, C: cold nitrogen gas outlet, D: liquid nitrogen inlet, E: variable resistor, F: lower limit switch, G: upper limit switch, H: variac.

Thus, the temperature of the cell was kept constant within 0.1 K.

The thermal expansion of the solution was calibrated in each measurement. A Cary recording spectrophotometer, model 14, was used for all the spectrophotometric measurements.

## Results and Discussion

*Electronic Absorption Spectra of PD+, DMPD+, and TMPD+ Solutions and Their Temperature Dependence.* The spectra of PD+, DMPD+, and TMPD+ in dilute solutions at room temperature, *i. e.*, the spectra of radical monomers, all show similar structures, as Figs. 2—4 show. Each spectrum is characterized by an R band with fine vibrational structure in the visible region and by weak X and strong Y bands in the near-ultraviolet region.

At low temperatures, the spectra of these three radicals were significantly changed, as is also indicated in Figs. 2—4: the spectra at low temperatures showed new absorption bands C, R′, and Y′. As the temperature was lowered, it was found that the optical densities of the C, R′, and Y′ bands increased at the expense of those of the R and Y bands. In addition, a similar decrease in the optical density of the X band and the appearance of a new band (X′ band) can be

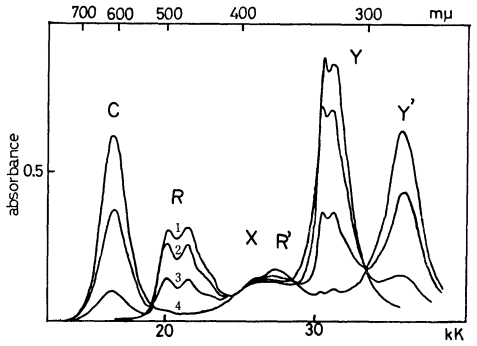


Fig. 2. Temperature dependence of absorption spectra of PD+ in *n*-propanol.
1: room temperature, 2: 195 K, 3: 175 K, 4: 154 K.
Stoichiometric concentration of the solution: $4.05\times10^{-4}$ mol/l, optical path length: 0.1 cm

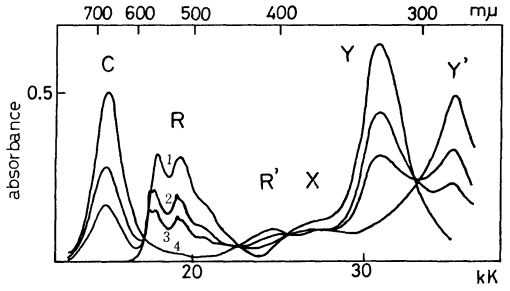


Fig. 3. Temperature dependence of absorption spectra of DMPD+ in ethyl ether-ethanol.
1: room temperature, 2: 160 K, 3: 152 K, 4: 130 K.
Stoichiometric concentration of the solution: $1.16\times10^{-5}$ mol/l, optical path length: 0.1 cm.

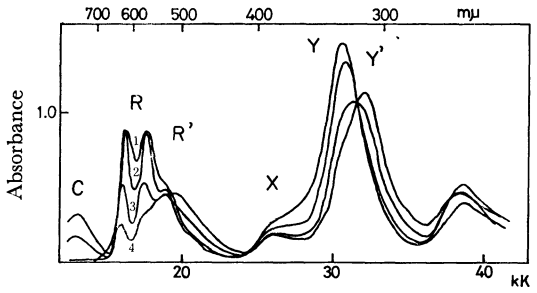


Fig. 4. Temperature dependence of absorption spectra of TMPD+ in ethyl ether-ethanol.
1: room temperature, 2: 148 K, 3: 124 K, 4: 113 K.
Stoichiometric concentration of the solution: $7.58\times10^{-5}$ mol/l, optical path length: 1.0 cm.

expected. However, quantitative measurements in these frequency regions were difficult because of stronger overlapping Y and Y′ bands.

By comparing the temperature dependence of various solutions at different concentrations, we are able to determine that the R and the Y bands can be attributed to the radical monomer, and the C, R′, and Y′ bands, to the radical dimer, as will be shown in the next section.[6]

The frequencies of the absorption maxima ($\nu_{max}$) and oscillator strengths ($f$) of these bands are given in Table 1. The frequency shift of the R′ band from the R band and that of the Y′ band from the Y band are also given in the table. They will be discussed in the last section by comparing them with the heats of dimerization. These spectral properties will be theoretically treated in the next paper.[7]

*Analyses of the Temperature-dependent Spectra.* Up to the present, several investigators have interpreted or analyzed their experimental results[4-6] by assuming a simple dimerization equilibrium:

$$2R^+ \rightleftharpoons (R^+)_2 \qquad (1)$$

or a simple polymerization equilibrium:

$$nR^+ \rightleftharpoons (R^+)_n \qquad (2)$$

6) By analogy with the interpretation of spectra of certain dye solutions (see : E. Rabinowitch and L. F. Epstein, *J. Amer. Chem. Soc.*, **63**, 69 (1941)). R′ and Y′ bands may be assigned to the perturbed excitations in the dimer corresponding to R and Y bands, respectively.

7) To be published elsewhere.

TABLE 1. ABSORPTION MAXIMA ($\nu_{max}$ IN kK) AND OSCILLATOR STRENGTHS ($f$)[a] OF THE ABSORPTION BANDS. BAND SHIFTS OF R' BAND FROM R BAND, AND Y' BAND FROM Y ($\Delta\nu_R$ AND $\Delta\nu_Y$ IN kK). HEATS OF DIMERIZATION ($\Delta H$ IN kcal/mol)

| Band | PD+ | | DMPD+ | | TMPD+ | |
|---|---|---|---|---|---|---|
| | $f$ | $\nu_{max}$ | $f$ | $\nu_{max}$ | $f$ | $\nu_{max}$ |
| C | 0.068 | 16.53 | 0.066 | 15.04 | 0.016 | 13.07 |
| R' | 0.019 | 25.97 | 0.015 | 24.81 | 0.050 | 19.72 |
| Y' | 0.087 | 35.97 | 0.097 | 35.33 | 0.095 | 32.05 |
| R | 0.027 | 20.08 | 0.033 | 18.76 | 0.038 | 16.26 |
| Y | 0.057 | 31.06 | 0.059 | 30.96 | 0.056 | 30.77 |
| $\Delta\nu_R$ | | 5.89 | | 6.05 | | 3.46 |
| $\Delta\nu_Y$ | | 4.91 | | 4.37 | | 1.28 |
| $\Delta H$ | | −8.0 | | −8.2 | | −5.6 |

a) Calculated as a monomer.

Electrostatic repulsion between the positive charges may retard the process of dimerization (or polymerization) in these models. The electrostatic repulsion energy between two point charges which, are separated by 3.1 Å (obtained from the interplanar separation between the parallel benzene rings in the DMPDBr crystals[8]) amounts to several eV. The energy may be reduced to about a half of the original one if the point charge is distributed over eight atoms of each radical according to the mobile $\pi$-electron densities. The dielectric constant of the medium may also reduce the energy. However, the energy would still be sufficient to retard the dimerization. Thus, a generalized formula is assumed in the present paper.

$$nR^+ + mX^- \rightleftharpoons (R^+)_n(X^-)_m \qquad (3)$$

where $R^+$ is a radical cation, and $X^-$, a counter anion ($Cl^-$, $Br^-$, or $ClO_4^-$). In this model, the contribution of the counter anion may reduce the electrostatic repulsion between the $R^+$'s. The equilibrium constant is given by;

$$K_{nm} = [(R^+)_n(X^-)_m]/([R^+]^n[X^-]^m) \qquad (4)$$

To justify the above assumption, a spectrum of a radical solution was compared with that of another solution containing the same amount of the radical and, in addition, an excess amount of an anion. If the anion plays some role in the polymerization, as is shown in Eq. (3), the concentration of the dimer must be increased by the addition of the excess amount of the anion, thus, the spectrum of the latter solution must show larger dimer bands (C, R', and Y') and smaller monomer bands (R and Y). In fact, such spectral changes were observed experimentally. For example, the optical density of a solution containing $2.3\times10^{-4}$ mol/l PDBr at 176 K and 6050 Å (the absorption maximum of the C band) was 0.79, whereas that of a solution containing approximately the same amount of PDBr and $6.2\times10^{-3}$ mol/l ammonium bromide was 1.00 at the same temperature and wavelength. At the same time, the R' and the Y' bands increased, and the R and the Y bands decreased. Similar spectral changes were also observed upon the addition of excess chloride or perchlorate anion. The assumption is thus justified.

Next, the numerical values of $m$, $n$, and $K_{nm}$ were determined.

*a) Determination of* n: The value of $n$ was determined from a series of temperature-dependent spectrophotometries of a solution containing a very large excess of $X^-$. Under the condition of ($[X^-]\gg[R^+]$), the value of the relative equilibrium constant, $K_n$ is given by;

$$K_n = kK_{nm}[X^-] = I_P/(I_M)^n \qquad k: \text{const.} \qquad (5)$$

where $I_p$ and $I_M$ are the values of the optical densities of a polymer band (C, R', or Y') and a monomer band (R and Y) respectively. Eq. (5) is obtained by assuming that the extinction coefficients of the polymer and the monomer bands do not depend upon the temperature over the temperature region measured. Plots of log $K_n$ against $1/T$ should be linear if the assumed $n$ value is adequate. A series of measurements of a $PD^+$ solution for the cases of $n=1$, 2, 3, and 4 are given in Fig. 5. The linear dependence of log $K_n$ *versus* $1/T$ is obtained if we take $n=2$. The dimerization of the radicals was confirmed from several such series of measurements.

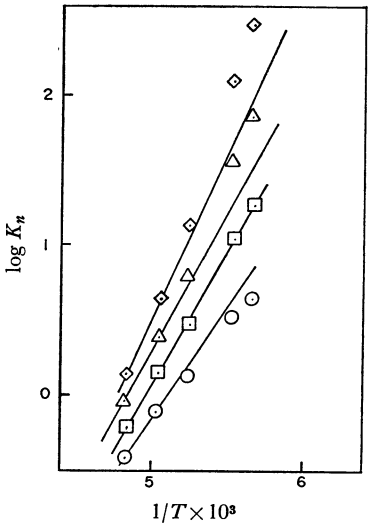


Fig. 5. Plots of log $K_n$ against $1/T$ for a $PD^+$ solution.
○: $n=1$, □: $n=2$, △: $n=3$, ◇: $n=4$.
Stoichiometric concentrations of the radical and the bromide anion are $9.5\times10^{-5}$ and $5.7\times10^{-3}$ mol/l, respectively.

*b) Determination of* m: Two types of absorption spectra were obtained under the conditions of $[X^-]=[R^+]$[9] and of $[X^-]\neq[R^+]$,[10] and the spectrophotometric data were analyzed as follows. It was assumed that the data were accounted for by one of the following three equilibria:

$$2R^+ \rightleftharpoons R_2^{++} \qquad (6)$$

8) J. Tanaka and N. Sakabe, *Acta Crystallogr.*, **B24**, 1345 (1968).

9) A solution containing only a radical salt was used.

10) A mixed solution of a radical salt and an ammonium salt was used.

$$2R^+ + X^- \rightleftharpoons R_2X^+ \quad (7)$$

and

$$2R^+ + 2X^- \rightleftharpoons R_2X_2 \quad (8)$$

The corresponding equilibrium constants are given by:

$$K_{20} = \alpha/\{2c_R(1-\alpha)^2\} \quad (9)$$

$$K_{21} = K_{20}/\{c_X-(\alpha/2)c_R\} \quad (10)$$

and

$$K_{22} = K_{20}/(c_X-\alpha c_R)^2 \quad (11)$$

respectively, where $\alpha$ is the degree of dimerization, and where $c_R$ and $c_X$ are the stoichiometric concentrations of the cation radical and the counter anion respectively. $\alpha$ is estimated from the spectrophotometric data.

The most accurate value of $\alpha$ was obtained from $\alpha = I_C/I_C^0$, where $I_C$ is optical density of the C band at the observed temperature and where $I_C^0$ is that at the lower temperature, where the monomer bands disappear. The values of log $K_{nm}$ of $PD^+$ are plotted against $1/T$ in Fig. 6. The results show that none of the three models (6), (7), and (8) is able to fit the experimental data satisfactorily; *i. e.*, the $R_2$ model fails to explain the increase in the degree of dimerization upon the addition of the excess anion, and the $R_2X$ and the $R_2X_2$ models overestimate the effect of the added salt. These models, the $R_2X$ model is most likely, but it is still not entirely satisfactory. The best fit with the experimental data is obtained if we assume a non-integral $m$ value, $m=0.7$.

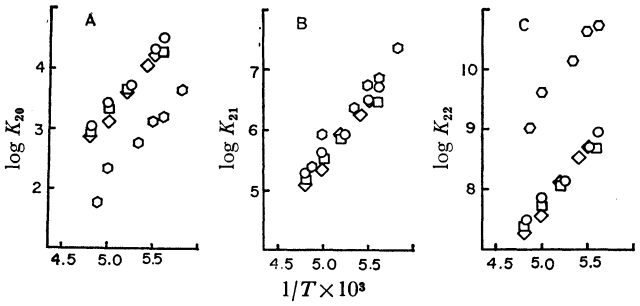


Fig. 6. Plots of log $K_{nm}$ against $1/T$ for $PD^+$ solutions.
(A): $m=0$, (B): $m=1$, (C): $m=2$.
Stoichiometric concentrations of the radical and the anion of each series are:
○: $R^+=9.53\times10^{-5}$ mol/l, $Br^-=5.7\times10^{-3}$ mol/l,
□: $R^+=9.87\times10^{-5}$ mol/l, $Cl^-=5.65\times10^{-3}$ mol/l,
◇: $R^+=9.67\times10^{-5}$ mol/l, $ClO_4^-=5.68\times10^{-3}$ mol/l,
⬡: $R^+=Br^-=2.36\times10^{-4}$ mol/l.

The concentration-dependent optical densities of the C bands of $PD^+$, $DMPD^+$, and $TMPD^+$ without an excess anion were analyzed by the use of Eqs. (9)—(11). The results lead to the conclusion that the $R_2$ model underestimates the concentration dependence, while the $R_2X$ and the $R_2X_2$ models overestimate it.

The spectrophotometric data of the other bands were also analyzed in similar manners. The results lead to the same conclusion as the above one within the limits of experimental error.

The heat of dimerization derived from the slopes of the log $K_{21}$ *versus* $1/T$ plots are $\Delta H=-8.0$, $-8.2$, and $-5.6$ kcal/mol for the $PD^+$, $DMPD^+$, and $TMPD^+$ dimers respectively. The $\Delta H$ values are found to be independent of the kind of counter anion added.

Finally, we must add our important observations that the values of $\nu_{max}$'s are also found to be independent of either the kind or amount of anion added. The only change observed upon the addition is in the degree of dimerization of the radical.

*Structure of the Dimer.* The structure of the $R_2X$ dimer (or, more exactly, $R_2X_{0.7}$) suggested by the above results is one in which the dimer is surrounded by an ionic atmosphere of the counter anions, $X^-$'s. The ionic atmosphere may reduce the electrostatic repulsions between the $R^+$'s. The non-integral $m$ value ($m=0.7$), which is best accounts for the experimental data, is perhaps due to averaged effective contribution of the various ionic atmospheres. The model is supported by the independence of the values of $\nu_{max}$'s and $\Delta H$'s of the kind of anion added, $X^-$.

Another model, a sandwich-type model, in which an anion, $X^-$, is sandwiched by the two cation radicals, may also explain the fact that $m=1$. However, this model asserts a strong dependence of $\nu_{max}$'s and $\Delta H$'s on the kind of anion; this conflicts with the experimental results.

The origin of the attractive force between the cation radicals in the present dimer model is the direct (partly covalent and partly ionic) interaction of the $\pi$-electron systems of the $R^+$'s, while that between the cation radical and the anion in the ionic atmosphere is mainly electrostatic.

The proposed model is supported by the crystal structures of Würster's radical salts. In Würster's blue ($TMPD^+$) perchlorate crystal,[11] the radical monomer are packed in a parallel manner, forming a column of radicals which is surrounded by perchlorate anions. In Würster's red ($DMPD^+$) bromide crystal,[8] a radical dimer is formed by placing two radicals in a parallel manner, and the dimers are packed together, forming a column of dimers. The column is surrounded by bromide anions.

The present model for the solution dimer is considered to be a fragment of the column of cation radicals in the crystal. The interaction between the two cation radicals and that between the cation and the anion in the model are, in principle, the same as those in the crystals. It is reasonable that the crystal and the solution dimer have similar structures and similar interactions.

*The Strong Dimer and the Weak Dimer, and Their Spectral Features.* The heat of dimerization obtained in the present work is a measure of the strength of the $\pi$-electronic interaction in the dimer. Therefore, it may reasonably be concluded that the interactions in the $PD^+$ and the $DMPD^+$ dimers are stronger than that in the $TMPD^+$ dimer. The weaker interaction in the $TMPD^+$ dimer may be accounted for by the increased steric repulsions between the crowded methyl groups in the two $TMPD^+$ radicals.

11) J. D. Turner and A. C. Albrecht, unpublished data, see : *J. Chem. Phys.*, **39**, 2321 (1964).

These two types of dimers show different spectral features. The strong dimer have strong C and the weak R′ bands, whereas the weak dimer has weak C and strong R′ bands, as Table 1 shows. The shifts of the $\nu_{max}$'s of the local excitation bands by the dimerization ($\Delta\nu_R$, and $\Delta\nu_Y$, in the table) also show different trends; *i. e.*, they are larger for the strong dimer and smaller for the weak one. These interesting properties will be theoretically treated in the next paper.[7]

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