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The Reflection Spectra of Würster's Salts

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The reflections of *N*,*N*-dimethyl-*p*-phenylenediamine (WR) perchlorate, bromide, and iodide, and also of *p*-phenylenediamine (PD) perchlorate and bromide were measured over the range from 5000 to 42000 cm^{-1} by Avery's method. The absolute absorption intensity and the refractive index of these solids were obtained by computer analysis. The absorption intensity of the solid was found to be, as a whole, larger than that of the dimer in solution; in particular, the CT band becomes broader and splits in a solid. Further, the anion was found to have a large effect on the electronic structure in the crystal. By taking account of these features of the spectrum and other experimental results, the WR salts were classified into two types according to their way of packing: Type I takes the dimer-unit structure (WRP) and Type II, the equidistantly-overlapped form (WRB and WRI).

It is known that an equilibrium exists between monomer and dimer ions in the solutions of some radical ion salts and that the charge-transfer (abbreviated hereafter to CT) band pertinent to the dimer appears at low temperatures.[1]

In the crystalline state, *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine perchlorate (WBP) shows its phase transition at 186K; below the transition point, the ESR signal due to the triplet exciton[2] appears, and the CT band intensity is sensitive to the temperature. These observations were found to be consistent with the dimerization mechanism of the phase transition,[3] and to contradict the disproportionation mechanism presented by Kommandeur and Pott.[4]

At room temperature, the crystalline spectra of *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (WB) radical salts show only weak CT bands and rather resemble the spectra of the corresponding monomers in solution.[1b,5] The crystals of *N*,*N*-dimethyl-*p*-phenylenediamine (WR) and *p*-phenylenediamine (PD) radical salts, however, show vivid CT bands, and their spectra are similar to those of the corresponding radical dimers in solution.[6] This means that the CT interaction is stronger for the WR and PD crystals than for the WB crystal.

In comparison with the solution spectra of radical dimers, the solid-state spectra were found to be broader; in particular, the CT bands become broad and split into two peaks. The absolute intensities of the crystalline absorption bands, however, were difficult to determine because of the difficulty of measuring the thickness of the very thin crystals. This fact prevents us from making a detailed discussion of the interaction between the radical ions, including the effect of the counter anion. In the present investigation, we measured, at various wavelengths, the reflection intensities of the pressed pellets of WR and PD radical salts and determined the refrative index (n) and the extinction coefficient (k). On the basis of the experimental results of the absolute absorption intensities, we will discuss the electronic structures of these radicals in the solid state.

Experimental

Materials. Würster's red perchlorate (WRP), bromide (WRB), *p*-phenylenediamine perchlorate (PDP), and bromide (PDB) were prepared and purified by the method described in the literature.[7] Würster's red iodide (WRI) was prepared by a method analogous with that used for WRB. (WRI; Calcd: C, 36.52; H, 4.56; N, 10.65; I, 48.27%. Found: C, 36.42; H, 4.59; N, 10.68; I, 48.84%). The radical salts are considerably stable in the air, and the measurements were carried out within a few days after the syntheses.

Measurements. Several methods have been used for the determination of the optical constants of the crystals from the reflection measurements. We constructed the apparatus on the basis of the method of Avery[8] and measured the

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reflections at the incident angles of 50 and 70°. The characteristics of the method are to measure the ratio of the reflecting powers by the use of lights polarized parallel and perpendicular to the incident plane, and to suppress the scattering effect. Kondo[9] showed, taking fuchsine as an example, that this method gives the same refractive index and extinction coefficient for the crystal and the pressed pellet. Therefore, this method is useful for the measurement of Würster's salts, for which it is difficult to obtain a crystal large enough for the reflection measurement.

The light sources were a tungsten lamp for the range of 5000—30000 cm^{-1} and a deuterium-discharged lamp for the range of 25000—42000 cm^{-1}. The polarizers were a Polaroid HR for the range of 5000—11000 cm^{-1} and a Glan-Thompson prism for the visible and ultraviolet regions. A photomultiplier, HTV 7102 or 1P28, was used as a detector. Corrections were made for the polarization of the incident light caused by the optical systems. The samples were ground by means of an agate mortar and were pressed by a KBr disc presser at about 10 kbar.

Analysis. The following relation exists for the isotropic solid with the complex refractive index of $N=n-ik$:

$$I=\frac{r_\mathrm{p}}{r_\mathrm{s}}=\frac{a^2+b^2-2a\sin\beta\tan\beta+\sin^2\beta\tan^2\beta}{a^2+b^2+2a\sin\beta\tan\beta+\sin^2\beta\tan^2\beta}$$

$$a^2+b^2=\{(n^2-k^2-\sin^2\beta)^2+4n^2k^2\}^{1/2}$$

$$a=\left\{\frac{1}{2}(n^2-k^2-\sin^2\beta)+\frac{1}{2}[(n^2-k^2-\sin^2\beta)^2+4n^2k^2]^{1/2}\right\}^{1/2}$$

where r_p and r_s are the reflecting power by the incident light polarized, respectively, parallel and perpendicular to the incident plane, and β is the incident angle. We determined n and k from the I's at $\beta=50$ and 70° by means of the Newtonian approximation for two variables using the electronic computer. The larger the absorption intensity, the smaller the experimental error; when the molar extinction coefficient $\kappa(\nu)$ is larger than 3000 $(\mathrm{mol/l})^{-1}\mathrm{cm}^{-1}$, the error is estimated from repeated measurements to be less than 10%. The following equation represents the relation between $k(\nu)$ and $\kappa(\nu)$:

$$\kappa(\nu)C=\frac{4\pi k(\nu)\nu}{2.303c}$$

where $I(z)=I(0)10^{-\kappa Cz}$, C is the concentration (mol/l), and c is the light velocity. On the other hand, the oscillator strength is calculated from $n(\nu)$ and $k(\nu)$:[10]

$$f=\frac{m}{e^2n_0}\int 4n(\nu)k(\nu)\nu\mathrm{d}\nu$$

where n_0 is the number of molecules in a unit volume.

In order to discuss the difference in the absorption intensity between the solid and the solution, the oscillator strengths must be compared.[11] Here, the $4\pi n(\nu)k(\nu)\nu/2.303Cc$ value will be plotted to show the wave number dependence of the absorption intensity. For the solution, $n(\nu)$ is reasonably approximated as 1.0. Some other physical constants of the solid can be calculated from $k(\nu)$ and $n(\nu)$. The complex dielectric constant, $\varepsilon(\nu)=\varepsilon'(\nu)+i\varepsilon''(\nu)$, is related to $k(\nu)$ and $n(\nu)$ as follows:

$$\varepsilon'(\nu)=n(\nu)^2-k(\nu)^2$$

$$\varepsilon''(\nu)=\frac{2\sigma(\nu)}{\nu}=2n(\nu)k(\nu)$$

$\sigma(\nu)$ is the electric conductivity constant.

Results and Discussion

Figure 1 shows the solid-state spectra of WRP, WRB, and WRI determined from the reflection measurments of pressed pellets, together with the low-temperature spectrum of an ethanol solution of WRP. The low-temperature spectrum of the ethanol solution was assigned to the WR cation dimer.[1b)] The band at 15000 cm^{-1} has mainly the character of the CT band between WR cations (CT band), and the bands at 24500, 27500, 35300, and 39000 cm^{-1} are the locally (within the WR cation)-excited (LE) bands (the LEI, LEII, LEIII, and LEIV bands).[1c)] The solid-state spectra, which are similar to the solution spectrum of the dimer, have the characteristics that the absorption intensity is, as a whole, stronger than that of the solution dimer, and that the CT band becomes remarkably broad and splits in a solid.[5)] Furthermore, the solid-state spectrum is changed by the counter anion, while the solution spectrum is insensitive to it. These characteristics are also seen in PDP and PDB (see Fig. 2).

The Absorption Intensity of the Solid-state Spectrum. The oscillator strengths (f) are listed for the WR and

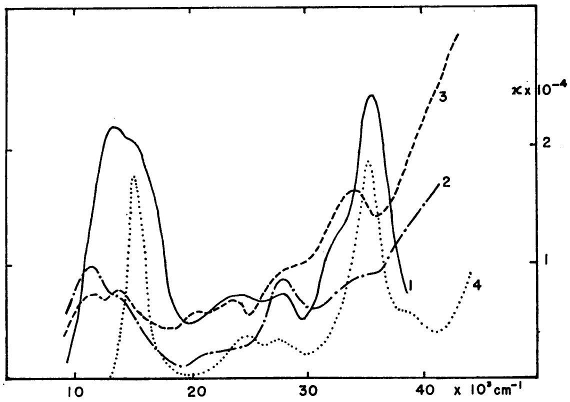

Fig. 1. The absorption spectra of WR salts. Solid (from the reflection measurements): 1 WRP, 2 WRB, 3 WRI; the ethanol solution of WRP at 110 K: 4.

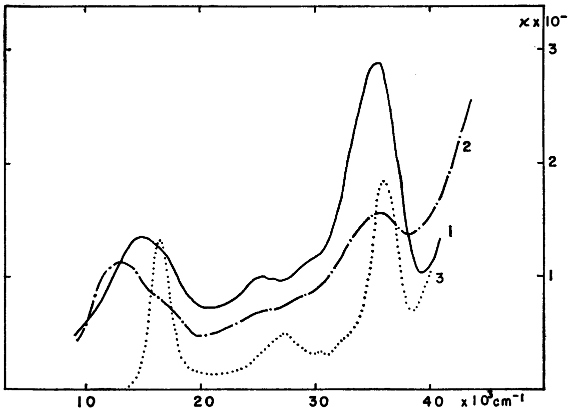

Fig. 2. The absorption spectra of PD salts. Solid (from the reflection measurements): 1 PDP, 2 PDB; the ethanol solution of PDP at 110 K: 3.

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Table 1. The absorption spectra of WR radical salts
(s: shoulder)

	WRP		WRB		WRI		WRP in ethanol at 77 K	
	ν(cm^{-1})	f	ν(cm^{-1})	f	ν(cm^{-1})	f	ν(cm^{-1})	f
CT	13300	0.61	11200	0.25	11400	0.23	14500	0.15
	(15800)^s		(14000)^s		13800			
LEI	24000	0.37	22000	0.19	20000	0.4	25000	0.10
LEII	27800		27800		23500		27500	
	(32000)^s				(28000)^s			
LEIII	35600	0.46	(34000)^s	0.3	34000	0.4	35300	0.28
LEIV							39000	
$\sum f$		1.4		0.7		1.0		0.53

Table 2. The absorption spectra of PD salts

	PDP		PDB		PDP in ethanol at 77 K	
	ν(cm^{-1})	f	ν(cm^{-1})	f	ν(cm^{-1})	f
CT	15000	0.46	13000	0.41	16500	0.12
	(17000)^s		(17000)^s			
LEI	25400	0.4	26000	0.3	27300	0.15
LEIII	(29000)^s		28000		(32500)^s	
LEII	35300	0.64	35500	0.5	36000	0.25
$\sum f$		1.5		1.2		0.52

PD radical salts in Tables 1 and 2 respectively. The value for each CT band was calculated with respect to the broad peak with splittings. The CT band is stronger for the solid radical salts than for the corresponding dimers in solution—4 times for WRP, 1.6 times for WRB and WRI, and 3—4 times for PD salts. Furthermore, the $f_{\text{CT}}/\sum_{\text{I}}^{\text{III}} f_{\text{LE}}$ ratios are 1.9, 1.4, 0.7, 1.5, and 1.9 times larger for the solid WRP, WRB, WRI, PDP, and PDB salts respectively than for the corresponding dimers in solution. Thus, the intensity increase in the solid state is more remarkable for the CT band than for the LE bands except for WRI, for which the tail of the strong absorption above 40000 cm^{-1} makes it difficult to calculate f_{LE} accurately.

The crystal structures of Würster's salts have been reported for WBP,[12] WBB,[6] WBI,[13] and WRB;[14] all of them contain a one-dimentional column of equidistantly-overlapped cation radicals. Theoretically, it was concluded that, in the infinite column, the intensity of the CT band is twice as large as that of the isolated dimer, and that the intensity of the LE band shows no increase, as long as the interaction between the LE states and CT states is negligibly small.[15] The observed increase in the intensity of the CT band for the solid WRB and WRI compared with that for their solutions is of a reasonable magnitude and is caused by the influence of the infinite column.

The intensity of the LE band is influenced by the degree of the mixing of the corresponding LE state with the lowest CT state. As WRB has a very short interplanar distance of the cation radicals (3.105 Å),[14] the interaction between the CT state and the LE state is not completely neglected. Moreover, the higher LE and CT states have complicated effects on the intensity in the crystalline state. On the other hand, WRP has a remarkably strong CT band, and its absorption spectrum as a whole resembles that of the dimer in solution. Taking into consideration the reported experimental results that WBP takes the dimer form in the low-temperature phase[12] and that WR salts show a stronger intercationic interaction than the WB salts in the crystalline state,[5] we can safely anticipate that the WRP radical will take the same molecular packing form as the low-temperature phase of WBP. The zeroth and the first-layer Weissenberg photographs of the WRP single crystal show the extinction rule that $h0l$ and $0kl$ (l=0,1) are absent when h and k are odd[16] (a=10.19, b=13.00, c=7.01 Å, Z=4, orthorhombic). This extinction rule supports the dimer form of WRP because, if the radicals were arranged in the unit cell equidistantly, the resulting interradical distance would become too large compared with those previously reported for Würster's salts. Furthermore, the ESR study of the temperature dependency of WRP powder reported of the triplet signal[17] that its intensity increases as the temperautre increases. From the above-mentioned results, it may be .concluded that WRP takes the dimer form in the crystalline state and that the large increases in the CT band intensity compared with that of the dimer in solution is mainly attributable

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to the increase in the intercationic interaction, accompanied by the change in the molecular configuration. PDP and PDB both show strong CT bands, and the LEIII band is especially strong for PDP. There being no other experimental data, any detailed discussion is now impossible: however, PDP and PDB seem to show the optical properties similar to those of WRP and WRB respectively.

Table 3. The bandwidth and splitting of CT band

	Solid	Solution dimer	Splitting in solid
WRP	6500 cm^{-1}	1800 cm^{-1}	Yes
WRB	6500		Yes
WRI	7500		Yes
PDP	8500	1600	Yes
PDB	8800		Yes
WBP3)	2500a)	2500	No
WBB18)	3000a)		No
WBC18)	3400a)		No
N-EP3)	2700a)	1700	Yes

a) Calculated from the transmission spectra of the quartz plates smeared with the samples at 77 K and 50 K.

The Splitting of the CT Band. Table 3 shows the bandwidths of the CT bands of the solid-state spectra and the low-temperature solution spectra, and the presence of the splitting of the CT band in the solid. The values of the second column show the width of the wave numbers, which correspond to half of the peak-absorption intensity, because a reasonable deconvolution of CT band is impossible. The fact taht the values of PD salts are larger than those of WR salts seems to be due to the larger splitting of the CT band. For comparison, Table 3 also shows the bandwidths of WB salts (P: perchlorate, B: bromide, and C: chloride) and *N*-ethylphenazyl (*N*-EP), which have weak intercationic interaction in the crystalline state. The origin of this splitting has been explained before as being due to the forbidden CT state appearing by means of the intensity borrowing through vibrational or other kinds of perturbations.6) However, as may be seen in Table 3, WR and PD salts, with strong intercationic interaction, have the splittings, while WB salts, with weak interaction, have not. Thereofre, the explanation can not be denied at present that a new absorption occurs due to the long-range interaction between the cation radicals characteristic of the strong intercationic interaction.

The Effect of the Anion Species. The third characteristic of the solid-state spectra of WR and PD salts is the remarkable difference produced by the change of the anion species. In the case of WR salts, the following classification is possible. The conclusion that a salt of Type I has the dimer unit in the crystal is supported by the ESR and X-ray studies. From the characteristics of the salts of Type II (the extroadinary broadning of the solid-state spectra with strong higher energy absorptions, the large red shift of CT band, and the lack of a triplet signal), it is conceivable that the salts of Type II contain a one-dimensional column of equidistantly-overlapped cation radicals in the crystalline state.

Table 4. Classification of WR salts

	Type I (WRP)	Type II (WRB, WRI)
Red shift of CT band from that of dimer in solution	1200 cm^{-1}	3000cm^{-1}
Splitting of CT band	Less clear	Clear
Absorption higher than 40000 cm^{-1}	No tail	Strong tail
ESR	Triplet signal	No signala)

a) Preliminary study by M. Itoh found only the impurity signal.

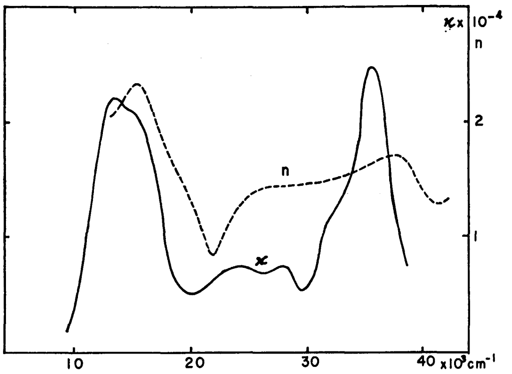

Fig. 3. The molar extinction coefficient and the refractive index of WRP solid determined by the reflection measurement.

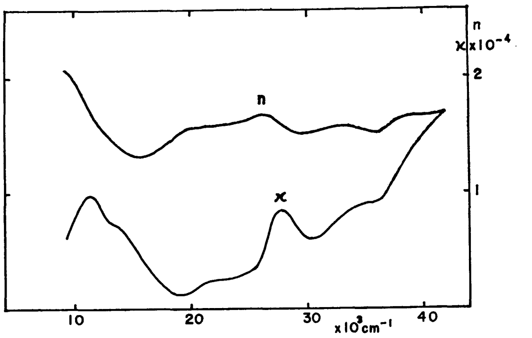

Fig. 4. The molar extinction coefficient and the refractive index of WRB solid determined by the reflection measurement.

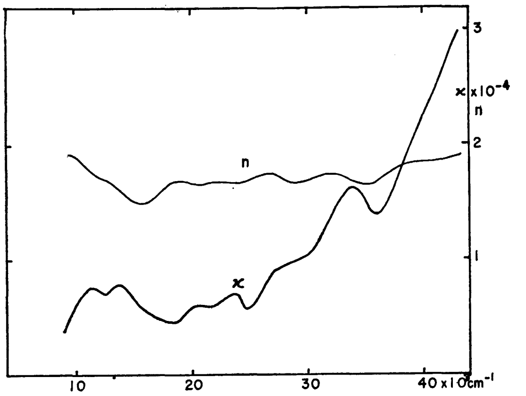

Fig. 5. The molar extinction coefficient and the refractive index of WRI solid determined by the reflection measurement.

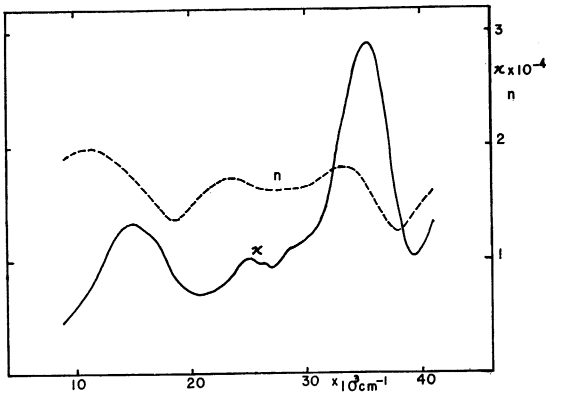

Fig. 6. The molar extinction coefficient and the refractive index of PDP solid determined by the reflection measurement.

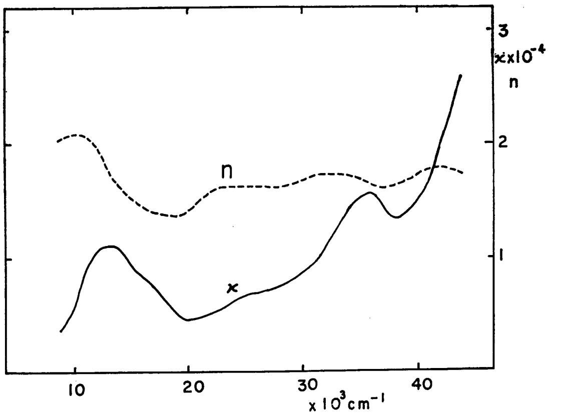

Fig. 7. The molar extinction coefficient and the refractive index of PDB solid determined by the reflection measurement.

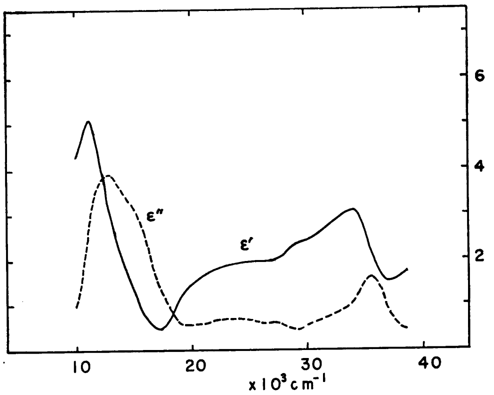

Fig. 8. The real and imaginary parts of the dielectric constant of WRP solid.

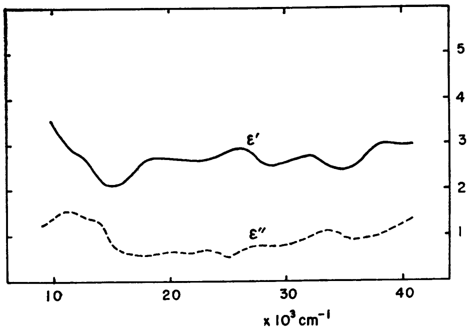

Fig. 9. The real and imaginary parts of the dielectric constant of WRI solid.

The Determinations of the Optical Constants. Figures 3, 4, 5, 6, and 7 show the wave number dependence of the refractive index, $n(\nu)$, together with the molar extinction coefficients of WR and PD salts. At the wave number near the CT band, $k(\nu)$ takes the maximum value, and the wave number dependence of $n(\nu)$ is especially large. This suggests that the absorption maximum determined by the transmission measurement must be modified by taking the reflection effect into account. Figures 8 and 9 show the real and imaginary parts of the dielectric constant. The very small value of the real part of WRP near 17000 cm^{-1} causes the remarkably strong reflection.

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