BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2855—2858 (1968)

Polarized Absorption Spectra of Single Crystals of Ion Radical Salts. I. Molecular Compounds of 7,7,8,8-Tetracyano-*p*-quinodimethane with *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine and *N,N*-Dimethyl-*p*-phenylenediamine

Haruo KURODA, Shoji HIROMA and Hideo AKAMATU

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

(Received May 6, 1968)

Polarized absorption spectra in the 10—40 kK region were observed on single crystals of the molecular compounds of tetracyano-*p*-quinodimethane (TCNQ) with tetramethyl-*p*-phenylenediamine (TMPD) and with dimethyl-*p*-phenylenediamine (DMPD). These molecular compounds possess an ionic structure in the ground state. A strong, broad absorption band appears in the near-infrared region of the crystal spectra with a polarization parallel to the crystal axis along which the component ions are alternately stacked making their molecular planes parallel to each other. The absorption maximum of this band is located at 7.7 kK in TMPD·TCNQ and at 8.5 kK in DMPD·TCNQ. These bands are assigned as a one associated with the charge transfer from TCNQ$^-$ ion to the positive ion of the donor. Other absorption bands found in the spectra can be assigned as local excitation bands associated with the intramolecular transitions of the component ions. However, they are found to be considerably broadened and appreciably shifted to higher energy as compared with the solution spectrum of each component ion.

There is a class of solid molecular compounds which possess an ionic structure in the ground state. Such molecular compounds can be formed by the interaction between a strong π-electron donor and a strong π-electron acceptor. The crystal of the 1 : 1 molecular compound involving *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) as the donor and 7,7,8,8,-tetracyano-*p*-quinodimethane (TCNQ) as the acceptor has been suggested to possess a ground state consisting of TMPD monopositive ion and TCNQ mononegative ion.[1,2] This solid molecular compound exhibits a marked electron spin resonance absorption, which has been ascribed to the triplet state arising from the interaction between the radical ions of TMPD and TCNQ.[2] The presence of the visible absorption bands corresponding to the component ions has been reported by Foster and Thomson[1] in the absorption spectrum observed for a Nujol mull of the solid molecular compound. However, no observation has been made on the absorption spectrum of its single crystal, which should provide much informations concerning its electronic structure. In the present investigation, we have studied the polarized absorption spectra of the single crystals of this molecular compound as well as those of the solid molecular compound of *N,N*-dimethyl-*p*-phenylenediamine (DMPD) with TCNQ.

Experimental

The polarized absorption spectra in the 10—40 kK region were measured on very small single crystals by using a microspectrophotometer. The details of the apparatus and the experimental procedures were described in a preceding paper.[3]

The solid molecular compound, TMPD·TCNQ, was prepared by mixing an acetonitrile solution of Würster's blue perchlorate (TMPD·ClO_4) and a methanol solution of Li·TCNQ. The black powder of TMPD·TCNQ precipitated as the solution containing equivalent amounts of TMPD·ClO_4 and Li·TCNQ was concentrated by evaporation of the solvent. The solid thus obtained was recrystallized from an acetonitrile solution. The mole ratio of TMPD to TCNQ was confirmed to be 1 : 1 by the elementary analysis. The DMPD·TCNQ was prepared by mixing a chloroform solution of TCNQ with a chloroform solution of an equimolar amount of DMPD.

Minute crystals freshly prepared from an acetonitrile solution were used for the measurement of spectra. The crystals were found to be frequently twinned, so that the selection was needed to find a single crystal which was not twinned, by examinnig by the polarizing microscope. The absorption spectra of the crystalline powders were also observed by the use of liquid paraffin mulls.

---

[1] R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **59**, 296 (1963).

[2] M. Kinoshita and H. Akamatu, *Nature*, **207**, 291 (1965).

[3] H. Kuroda, T. Kunii, S. Hiroma and H. Akamatu, *J. Mol. Spectry.*, **22**, 61 (1967).

Results and Discussion

The polarized absorption spectra observed of a single crystal of TMPD·TCNQ are shown in Fig. 1. According to the crystal structure analysis by Hanson,[4] the crystal is monoclinic with the lattice constants, $a=9.88$ Å, $b=12.71$ Å, $c=7.72$ Å and $\beta=97.34°$, and belongs to the space group $C2/m$. The unit cell contains two molecules of each component. The donor and acceptor molecules are alternately stacked along the *c*-axis. The absorption spectra shown in Fig. 1, were obtained for a very thin single crystal of a few microns in width, elongated along the *c*-axis, the developed face of which was assigned to (010) plane. The projection of the crystal structure onto the (010) plane along the *b*-axis is reproduced schematically in Fig. 2.

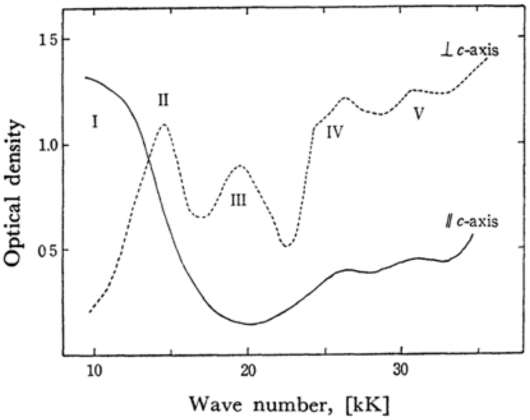

Fig. 1. Polarized absorption spectra of a single crystal of TMPD·TCNQ.

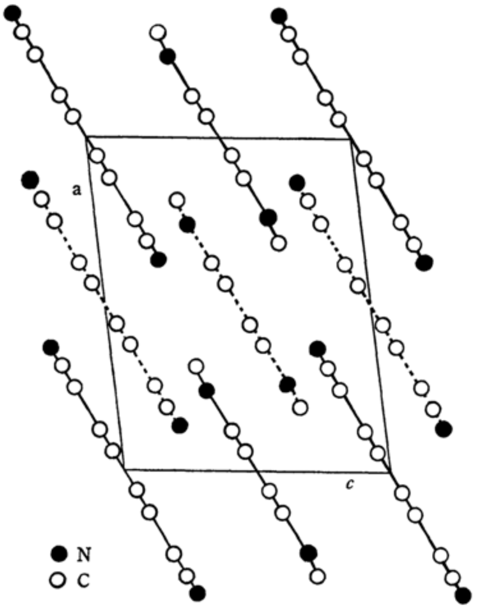

Fig. 2. Crystal structure of TMPD·TCNQ: The short axes of the component ions are parallel to the *b*-axis; the layer of molecules shown with broken line is *b*/2 above that of the molecules shown with solid line.

Evidently there is a strong band in the near-infrared region, which seems to be exclusively polarized in the *c*-axis direction. Unfortunately, our microspectrophotometer could not be applied to the region below 9 kK. Thus the absorption in the low energy region was examined by observing the absorption spectrum of the powder sample. The result is shown in Fig. 3, in which one absorption band with a maximum located at about 7.7 kK is found in the near-infrared region. This must correspond to the low energy band found in the ∥*c* spectrum of the single crystal. The intensities of the absorption bands associated with the long-axis polarized transitions of the component ions should be higher in the ⊥*c* spectrum than in the ∥*c* spectrum, since the oriented-gas model predicts the intensity ratio $I_{\perp c}/_{\parallel c}$ of 2.5 as shown in Table 1, and the short-axis polarized transitions of the component ions should not appear in the ∥*c* spectrum, nor in the ⊥*c* spectrum. Thus we can assign the 7.7 kK band, which we shall denote as "Band I," to the one associated with the charge-transfer between TMPD$^+$ and TCNQ$^-$ ions stacked on each other. Probably it is associated with a transfer of an electron from a TCNQ$^-$ ion to a TMPD$^+$ ion. A similar charge-transfer band has been found in several other molecular compounds having an ionic structure.[5,6]

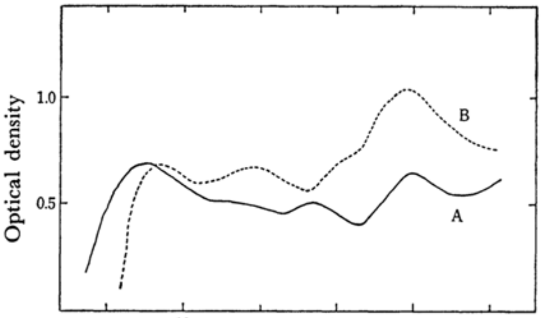

Fig. 3. Absorption spectra of liquid paraffin mulls of the crystalline powders of TMPD·TCNQ (A) and DMPD·TCNQ (B).

In the ⊥*c* spectrum, there are four absorption bands, which are denoted respectively II, III, IV and V in Fig. 1. All these bands are stronger in the ⊥*c* spectrum than in the ∥*c* spectrum.

---

4) A. W. Hanson, *Acta Cryst.*, **19**, 610 (1965).

5) T. Amano, H. Kuroda and H. Akamatu, This Bulletin, **41**, 83 (1968).

6) B. G. Anex and E. B. Hill, Jr., *J. Am. Chem. Soc.*, **88**, 3648 (1966).

TABLE 1.

	Bands in the crystal spectra		Assignment	Transitions of component ions		Calculated oscillator strength in crystal spectra*		
	$\tilde{\nu}$ [kK]	polarization ratio ($I_{\perp c}/I_{\parallel c}$)		$\tilde{\nu}$ [kK]	$f_{soln.}$	$f_{\perp c}$	$f_{\parallel c}$	$f_{\perp c}/f_{\parallel c}$
I	7.7	~0	CT-Band					
II	14.7	—	$TCNQ^-$ (B_{3u}←B_{2g})	12.0	0.31	0.66	0.26	2.5
III	19.6	~6	$TMPD^+$ (B_{3u}←B_{2g})	18.0	0.25	0.54	0.21	
IV	26.3	2.9	$TCNQ^-$ (B_{3u}←B_{2g})	23.0	0.44	0.92	0.36	
V	31.0	2.8	$TMPD^+$ (B_{3u}←B_{2g})	30.9	0.44	0.92	0.36	

* Oriented-gas values.

In effect, no absorption maximum corresponding to Band II and Band III can not be found in the ∥c spectrum. These four bands seem to be mainly associated with the intramolecular transitions of the component ions. The absorption spectra of $TMPD^+$ and $TCNQ^-$ ions in solution are shown in Fig. 4. The open-shell SCF-LCAO-MO calculations have been carried out recently by Lowitz(7) on the electronic transitions of $TCNQ^-$ ion. According to his result, the first strong absorption band located at about 12 kK is due to π-π^* transition polarized along the long-axis of the molecule and the next band is composed of a strong, long-axis polarized transition and a weak, short-axis polarized transition. The polarizations of the transition in $TMPD^+$ ion have been experimentally studied by Albrecht and Simpson,(8) who have concluded that the 18 kK and 30.9 kK transitions are of the long-axis polarization, while the weak 26.2 kK transition is of the short-axis polarization. These are in agreement with theoretical predictions.(9,10)

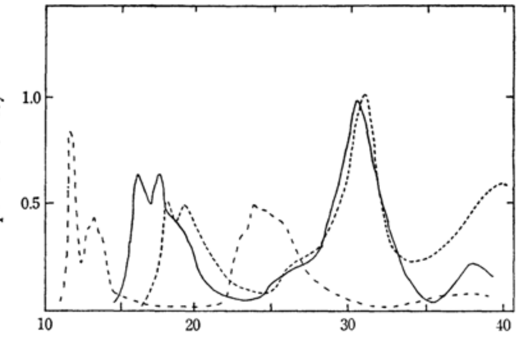

Fig. 4. Absorption spectra of the component ions in acetonitrile: —— $TMPD^+$, - - - $DMPD^+$, —·— $TCNQ^-$.

The probable assignements of the observed bands and the oriented-gas values of the oscillator strength of each intramolecular transition are summarized in Table 1. The observed polarization ratio well agrees with the oriented-gas value in the cases of Band IV and Band V. There seems to be some deviation between the observed and calculated polarization ratios in the cases of Band II and Band III, especially in the last one. From the experiment by Albrecht and Simpson(8) as well as from the reported crystal spectra of the ionic compound formed between TMPD and chloranil,(5,6) there can be no doubt that the 18 kK and 30.9 kK transitions in $TMPD^+$ ion are same as regards the polarization. Thus the difference between their polarization ratios must be associated in someway with the interactions of ions in the crystal lattice. It should be also noticed that the bands II, III and IV in the crystal spectra are shifted to higher energy by about 2 kK compared with the corresponding bands in the solution spectra, and, at the same time, all bands are considerably broadened. A similar effect can be generally found in the crystal spectra of a molecular compound which is composed of positive ions of donor and negative ions of acceptor, when there exists a relatively strong charge-transfer interaction between the component ions.(5)

The polarized absorption spectra of the DMPD·TCNQ are shown in Fig. 5. The crystal structure has not been determined for this molecular compound. The spectra were observed, on a thin single crystal elongated along one direction, for the two polarizations of light parallel and perpendicular to the elongated axis, which we shall denote here as the "*l-axis*" of the crystal.

The observed spectra are quite similar to the

---

7) D. A. Lowitz, *J. Chem. Phys.*, **46**, 4698 (1967).

8) A. C. Albrecht and W. T. Simpson, *J. Am. Chem. Soc.*, **77**, 4458 (1955).

9) M. Geoppert-Mayer and K. J. McCallum, *Rev. Mod. Phys.*, **14**, 248 (1942).

10) H. J. Monkhorst and J. Kommandeur, *J. Chem. Phys.*, **47**, 391 (1967). They assigned the 13 and 31 kK band to the transitions, polarized along the "*x-axis*", which corresponds to the short-axis according to the notation of molecular axes given in their paper. However, they have recently informed us that this notation is incorrect, and the "*x-axis*" is the long-axis of molecule.

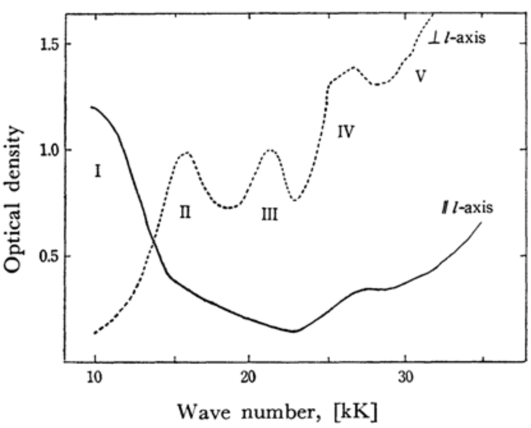

Fig. 5. Polarized absorption spectra of a single crystal of DMPD·TCNQ.

spectra of TMPD·TCNQ: namely, the first absorption band in the near-infrared region is exclusively polarized in the *l-axis* derection while the bands in the 12—35 kK region are stronger in the $\perp l$ spectrum than in the $\| l$ spectrum. The absorption maximum of the first band is located at about 8.5 kK according to the absorption spectrum of the liquid paraffin mull of the powder already shown in Fig. 3. We shall assign this low energy band to the charge-transfer from a TCNQ$^-$ ion to the neighboring DMPD$^+$ ion. We can assign the other bands in Fig. 5 to the bands mainly associated with the intramolecular transitions of the component ions: Bands, II and IV, are due to the long-axis polarized transitions of TCNQ$^-$ ions, and Bands, III and V to the long-axis polarized transitions of DMPD$^+$ ion. Band III of DMPD·TCNQ is located at a wave number higher by 1.7 kK than the corresponding band of TMPD·TCNQ. This difference is nearly equal to the difference between the enrgy of the lowest transition of TMPD$^+$ ion and that of DMPD$^+$ ion.

The similarity found between the polarized spectra of TMPD·TCNQ and those of DMPD·TCNQ seems to suggest the resemblance between their crystal structures. Thus we may consider that, in the crystal of DMPD·TCNQ, the ions of the two components are alternately stacked on each other along one crystal axis making their long molecular axes parallel to each other as in the crystal of TMPD·TCNQ.

Finally it should be noted that the intensity of the charge-transfer band is considerably strong in the crystal spectrum of TMPD·TCNQ as well as in that of DMPD·TCNQ. Although we have not carried out the absolute measurement of the intensity of absorption, the fact that the charge-transfer band is observed in the crystal spectra of these molecular compounds with an intensity comparable to or higher than the absorption bands associated with strong intramolecular transitions of the component ions, evidently indicates that the intensity of the charge-transfer band is fairly strong. This phenomenon seems to suggest the presence of a strong charge-transfer interaction between the neighboring ions in the crystal lattice.