BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3626—3627 (1970)

Polarized Absorption Spectra of the TCNQ Crystal

Shoji HIROMA,*1 Haruo KURODA and Hideo AKAMATU

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

(Received July 23, 1970)

Tetracyano-*p*-quinodimethane (TCNQ) is known to be one of the strongest electron acceptor. A number of radical salts have been prepared from the reaction between TCNQ and an electron donor. Such salts are often organic semiconductors of high conductivity. Although extensive investigations have been carried out on the electrical properties of these salts,[1,2] little has been known on the electronic properties of the crystal of TCNQ itself. Recently we have noticed that the TCNQ crystal exhibits a photoconduction with a relatively high sensitivity in the visible region.*2 In connection with such phenomenon, we have examined the polarized absorption spectra of the single crystal.

Experimental

TCNQ was synthesized by the method described by Acker and Hartler,[3] and purified by recrystallization followed by twice sublimation *in vacuo*. Single crystals of microscopic size, for the measurement of absorption spectra, were prepared from such purified sample by vacuum sublimation onto cotton wool or by crystallization from acetone solution. The crystal spectra were measured with a microspectrophotometer which we have described elsewhere.[4]

Results and Discussions

According to Long *et al.*,[5] the TCNQ crystal is monoclinic, $C2/c$ with the lattice constants, $a=8.906$ Å, $b=7.060$ Å, $c=16.395$ Å, and $\beta=98.54°$, four molecules being contained in the unit cell. We obtained diamond-shaped crystals bounded with{110} with the developed face of (001).

The *a*-axis and *b*-axis polarized spectra were observed from the direction nomal to the (001) plane. The results are given in Fig. 1, and the wavenumbers and polarization ratios are listed in Table 1.

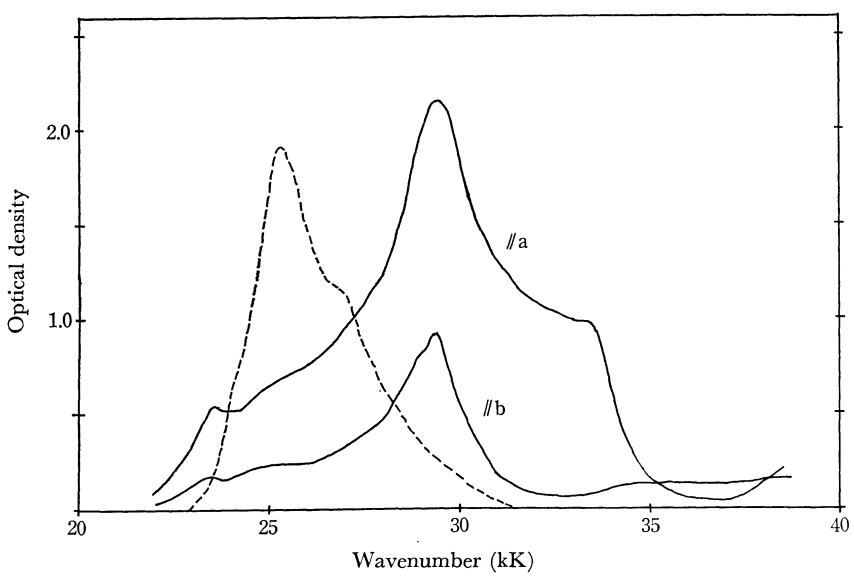

Fig. 1. The polarized absorptions spectra of TCNQ crystal.
(------ solution spectrum)

*1 Present adress: Hitachi Reserch Laboratory, Hitachi, Ltd., Hitachi, Ibaragi.

1) W. J. Siermons, P. E. Bierstedt and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963).

2) N. N. Usov and V. A. Bendershkii, *Phys. Stat. Sol.*, **37**, 535 (1970).

*2 Photo-conductive properties of TCNQ crystal will be reported separately.

3) D. S. Acker and W. R. Hartler, *J. Amer. Chem. Soc.*, **84**, 3370 (1962).

4) H. Kuroda, T. Kunii, S. Hiroma and H. Akamatu, *J. Mol. Spectry.*, **22**, 60 (1967).

5) R. E. Long, R. A. Sparks and K. N. Trueblood, *Acta. Crystallogr*, **18**, 932 (1965).

Table 1. Wavenumbers and polarization ratios of absorption peaks (in kK)

$\tilde{\nu}_a$	$\tilde{\nu}_b$	I_a/I_b
23.6	23.6	3.1
24.9	24.9	2.8
29.4	29.4	2.4
33.0	~34	

In the near-ultraviolet region of the solution spectrum, TCNQ exhibits only one strong absorption band at 25.4 kK (f=0.94). By using oriented gas model, the polarization ratio, I_a/I_b, of the absorption band due to this transition ($^1B_{1u}\leftarrow{}^1A_g$) is estimated as 5.9. As we compare the crystal spectra with the solution spectra, we notice, first that the band is markedly broadened in the crystal state, and, second that its shape is quite asymmetric.

From the symmetry of the crystal lattice, we can predict that each intramolecular transition would give two optically-allowed factor group components, namely, A_u and B_u, which give the transitions polarized respectively in the b-axis and a-axis direction. We have carried out a theoretical estimation of the crystal shift and splitting on the 25.4 kK ($^1B_{1u}\leftarrow{}^1A_g$) and 43.9 kK ($^1B_{2u}\leftarrow{}^1A_g$) transitions of TCNQ molecule.*3 The energy levels of exciton states thus estimated are given in Table 2.

Table 2. Estimated energies of optically allowed exciton levels of TCNQ (in kK)

	Molecular transition	
	$^1B_{1u}$ (25.4 kK)*	$^1B_{2u}$ (43.9 kK)*
A_u (b-polarized)	32.3	43.8
B_u (a-polarized)	28.9	44.1
$\Delta\nu$**	3.36	−0.28

* Observed energy for solution spectrum.
** Splitting between the A_u and B_u components.

We could attribute the highest peak at 29.4 kK found in the a-axis spectrum to the B_u component of $^1B_{1u}$ transition. However, a corresponding peak is observed also in the b-axis spectrum. Situation is again puzzling as regards the A_u component, namely, although we can find a peak in the b-axis spectrum at about 34 kK as predicted by the calculation, the corresponding band appears also in the a-axis spectrum. Thus the observed polarization is difficult to be explained on the basis of the above treatment.

The observed spectra suggests the presence of another band in 23—27 kK region. The energy of the charge transfer from a TCNQ molecule to the neighboring one, is estimated as 20.5 kK, if we assume the electron affinity of TCNQ molecule as 2.88 eV and the ionization potential as 7.83 eV.*4 Thus it is likely that the absorption in the 23—27 kK region is associated with the intermolecular charge transfer. This assignment seems to be consistent with the polarization of the absorption in this region, although the observed polarization ratio is appreciably larger than the oriented gas value, 1.6.

Since the interaction between the neighboring molecules is expected to be the most important factor in the case of the TCNQ crystal, we have examined this from another point of view, by calculating the electronic structure of the molecular pair where the two molecules are taking the mutual orientation exactly the same as found for the two molecules closely contacting to each other in the TCNQ crystal. We have applied here a semiempirical SCF·MO·CI method treating the molecular pair as a single π-conjugated system.[5] The results of this calculation are shown in Table 3. It should

Table 3. Transitions predicted by the SCF·MO·CI calculation on the TCNQ molecule and the molecular pair (in eV)

	Monomer		Molecular pair	
	ΔE	f	ΔE	f
(CT)			2.68	0.02
$^1B_{1u}\leftarrow{}^1A_g$	2.68	1.99	3.06	4.65
$^1B_{2u}\leftarrow{}^1A_g$	4.21	0.60	4.36	0.89

be noted that the lowest transition of TCNQ molecule, ($^1B_{1u}\leftarrow A_{1g}$), is predicted to be shifted to higher energy by 3.5 kK in the molecular pair, and that a transition associated with intermolecular charge-transfer interaction is predicted at a lower energy. These results again support our tentative interpretation of the crystal spectra of TCNQ.

The authors are indebted to Mr. T. Ohta in this laboratory for his assistance in the computations presented here.

*3 Since the oscillator strength of this band is large, we treated the problem as a strong coupling case. We have taken the dipole-dipole approximation for the molecular pair separated larger than 30 Å, but estimated the interaction terms directly by use of the molecular wave-function assuming the point-charge model, for the molecular pair within 30 Å.

*4 Excitation energy was estimated by the equation, $\Delta E=I-A-C$, where I was estimated by using the highest occupied SCF MO, A is of electron capture measurement (A. L. Farragher and F. M. Page, *Trans. Faraday. Soc.*, **63**, 2369 (1967)], and the Coulomb attraction energy, C, was estimated by the point charge model.

*5 The details of the method are reported elsewhere (T. Ohta, T. L. Kunii and H. Kuroda, *Theor. Chim. Acta*, to be published).