Properties of simple alkali-tetracyanoquinodimethan (TCNQ) salts. II. Optical properties of M^+TCNQ$^-$ salts

Johan G. Vegter and Jan Kommandeur
Laboratory for Physical Chemistry, The University, Groningen, The Netherlands
(Received 11 June 1973)

The interpretation of properties of (1:1) alkali-tetracyanoquinodimethan (TCNQ) salts on a one-dimensional Bloch model can be extended to optical spectra. Electronic absorptions in the spectral range of 4000–20 000 cm^{-1} are interpreted as band-to-band transitions. These (split) bands are contructed from the ground-state and excited-state wave funcitons of the TCNQ$^-$ ion. A splitting in the absorptions arises from the variable density of states in an energy band. The polarized absorption spectra of KTCNQ were "calculated," using some basic assumptions, and compared with experimental data.

I. INTRODUCTION

Stacks of tetracyanoquinodimethan(TCNQ) ions along the $\vec{a}$ axis, as they occur in the simple (1 : 1) alkali-TCNQ salts,[1,2] can be treated in the one-electron (Bloch) approximation, even though the bandwidths are small. The application of a simple one-dimensional band system is permitted because of the spatial extension of the TCNQ$^-$ ions, reducing the correlation energies. The bands, constructed from the ground-state wave functions φ_1 of the unpaired π electron on each TCNQ$^-$ ion, are symmetry split by structural distortion within each TCNQ$^-$ chain.[2] The temperature dependence of spin susceptibility and lattice distortion leading to phase transitions can be quantitatively understood on this basis, as shown in two recent papers,[3,4] refered to hereafter as I and III, respectively.

It is the purpose of this paper to show that the Bloch model also can explain the optical spectra of crystalline M^+TCNQ$^-$, although other interactions may be important, as considered for instance by Hiroma *et al.* in their exciton treatment of KTCNQ and $Cs_2(TCNQ)_3$.[5]

II. EXPERIMENTAL DATA

For the present, we focus our attention on spectral data of crystalline KTCNQ. We measured its electronic absorption spectrum at room temperature (Fig. 1), as described in Sec. II of Paper I. It strongly resembles Iida's diffuse reflectance spectrum of this salt.[6] The only polarized absorption spectrum of an alkali-TCNQ crystal has been measured by Hiroma *et al.*[5] on KTCNQ and is reproduced in Fig. 2. Peak II was not observed in this polarized spectrum, although there is also some evidence of it in Iida's measurement.[6] For comparison, the TCNQ$^-$ monomer absorbs at 25.3×10^3 and 11.9×10^3 cm^{-1}, whereas the $(TCNQ)_2^=$ dimer exhibits absorption peaks around 27.0×10^3, 15.6×10^3, and 11.5×10^3 cm^{-1}.[7]

III. THEORY

In our treatment we consider band-to-band transitions from the ground-state band system to the excited band system constructed from wave functions φ_i' of an electron bound to the ith TCNQ$^-$ ion in its first excited state. From the Appendix in paper I, we find the tight-binding crystal functions $\psi_k(\pm)$ for the upper and lower ground-state bands derived for a distorted linear chain (Fig. 3) consisting of $\frac{1}{2}N$ unit cells of length a,

$$\psi_k(\pm)=\frac{1}{(2N)^{1/2}}\sum_n e^{ikan}\left[\pm c_k\Phi_{n1}(x)+\Phi_{n2}(x)\right], \quad (3.1)$$

n labels the one-dimensional unit cells, and

$$c_k=\left[h_1+h_2\,e^{-ika}\right]\left[h_1^2+h_2^2+2h_1h_2\cos(ak)\right]^{-1/2}, \quad (3.2)$$

where h_1 and h_2 are transfer integrals between a molecule and its two inequivalent neighbors indicated in Fig. 3, where $|h_1|>|h_2|$. Similar expressions will hold for both excited bands:

$$\psi_k'(\pm)=\frac{1}{(2N)^{1/2}}\sum_n e^{ikan}\left[\pm c_k'\Phi_{n1}'(x)+\Phi_{n2}'(x)\right], \quad (3.3)$$

with

$$c_k'=(h_1'+h_2'\,e^{-ika})\left[h_1'^2+h_2'^2+2h_1'h_2'\cos(ak)\right]^{-1/2}. \quad (3.4)$$

Let us consider at 0 °K in a stoichiometric crystal the optical transitions from the state $|k\rangle$ in the "valence" band to the empty excited bands. The probability for a direct ("vertical") transition is proportional to $P_k'P_k'$, with

$$P_k'=\langle\psi_k(-)\,|\hat{p}\,|\psi_k'(\pm)\rangle \quad , \quad (3.5)$$

where $\hat{p}$ is the momentum operator.[8] Neglecting terms between non-neighboring ions, one easily finds

$$2P'_k = \mp c_k^* c'_k \langle \Phi_{n_1} | \hat{p} | \Phi'_{n_1} \rangle + \langle \Phi_{n_2} | \hat{p} | \Phi'_{n_2} \rangle - c_k^* \langle \Phi_{n_1} | \hat{p} | \Phi'_{n_2} \rangle + c'_k \langle \Phi_{n_2} | \hat{p} | \Phi'_{n_1} \rangle$$
$$- c_k^* e^{-ika} \langle \Phi_{n_1} | \hat{p} | \Phi'_{(n-1)_2} \rangle \quad \pm c'_k e^{ika} \langle \Phi_{n_2} | \hat{p} | \Phi'_{(n+1)_1} \rangle \ . \tag{3.6}$$

Assuming equivalence of the $TCNQ^-$ ions in the crystal, we can write

$$2P'_k = (1 \mp c_k^* c'_k) P'_0(m) + (-c_k^* \mp c'_k) P'_1(a) + (c_k^* e^{-ika} \pm c'_k e^{ika}) p'_2(a) , \tag{3.7}$$

in which

$$P'_0(m) \equiv \langle \Phi_{n_1} | \hat{p} | \Phi'_{n_1} \rangle ,$$
$$P'_1(a) \equiv \langle \Phi_{n_1} | \hat{p} | \Phi'_{n_2} \rangle , \tag{3.8}$$

and

$$P'_2(a) \equiv \langle \Phi_{n_2} | \hat{p} | \Phi'_{(n+1)_1} \rangle .$$

$P'_0 P'_0$ and $P'_1 P'_1$, $P'_2 P'_2$ are proportional to the probabilities of local transitions and will be polarized in the molecular plane (m) and along the stacking (a) axis (or, in fact, perpendicular to the TCNQ molecular plane), respectively.

A similar expression is obtained for the transitions at $T > 0$ °K from the ground-state "conduction" band to the excited bands; all c_k's in Eq. (3.7) are then provided with a minus sign.

Because the π-electron wave function φ'_i is not known, we cannot evaluate $h'_{1,2}$. Therefore, we simply assume

$$h'_{1,2} = \sigma w h_{1,2} , \tag{3.9}$$

where w is a positive number and $\sigma = +1$ or -1. As will be discussed later, the spectral results require

$$\sigma = -1 . \tag{3.10}$$

Insertion of Eqs. (3.9) and (3.10) into (3.4) leads, with Eq. (3.7), to the following expressions for P'_k at $ak = 0$, $\pm \frac{1}{2}\pi$, and $\pm \pi$, assuming $h_{1,2}$ to be positive:

(a) optical transitions to the lower excited band:

$$P'_{ak=0,\pi} = -P'_1(a) \pm P'_2(a) ,$$
$$P'_{ak=\pi/2} = -[h_1 P'_1(a) - h_2 P'_2(a)] (h_1^2 + h_2^2)^{-1/2} ; \tag{3.11}$$

(b) optical transitions to the upper excited band:

$$P'_{ak=0,\pi} = P'_0(m) , \tag{3.12}$$
$$P'_{ak=\pi/2} = P'_0(m) - i[h_2 P'_1(a) + h_1 P'_2(a)] (h_1^2 + h_2^2)^{-1/2} .$$

Transitions from the ground-state "conduction" band to the excited lower (upper) band have the same transition moments as those from the ground-state "valence" band to the excited upper (lower) band. The possible transitions from the ground-state band system at $ak = 0$, $\pm \frac{1}{2}\pi$ and $\pm \pi$ are drawn in Fig. 4. If $\sigma = +1$, the excited-state bands are interchanged.

Figure 4 also gives the possible optical transitions between both ground-state bands. In a similar treatment, as given above for P'_k, we evaluate

$$P_k = \langle \psi_k(-) | \hat{p} | \psi_k(+) \rangle \tag{3.13}$$

resulting in

$$P_k = -\tfrac{1}{2}(c_k^* + c_k) P_1(a) + \tfrac{1}{2}(c_k^* e^{-ika} + c_k e^{ika}) P_2(a) = -[h_1 + h_2 \cos(ak)]$$
$$\times [h_1^2 + h_2^2 + 2h_1 h_2 \cos(ak)]^{-1/2} P_1(a) + [h_2 + h_1 \cos(ak)] [h_1^2 + h_2^2 + 2h_1 h_2 \cos(ak)]^{-1/2} P_2(a) \quad , \tag{3.14}$$

with

$$P_1(a) \equiv \langle \Phi_{n_1} | \hat{p} | \Phi_{n_2} \rangle$$

and

$$P_2(a) \equiv \langle \Phi_{n_2} | \hat{p} | \Phi_{(n+1)_1} \rangle \quad . \tag{3.15}$$

These transition probabilities vanish in a nonalternating row, whereas $|P_k|$ equals $|P_1(a)|$ in a completely dimerized chain.

IV. COMPARISON WITH EXPERIMENT

In Fig. 5 the calculated optical spectrum is drawn in outline as derived from Fig. 4 with $\sigma = -1$ and $w = 3.5$. For the ground-state band system of KTCNQ we have taken a bandwidth of 0.054 eV for each band and a band gap of 0.182 eV (from Fig. 17 in Paper III). Transitions from the lowest band at $k = 0$ and $\pm \pi/a$ (high density of states) will give rise to absorption peaks. These will be broadened by "impurities" and lattice and molecular vibrations. The intensities of the peaks are arbitrary but it is assumed that $|P'_0| \gg |P'_1| > |P'_2|$. The intensities of the ground-state band-to-band transitions will be small, due to the $\bar{\gamma}$ dependence of the optical density[9] and the partial cancellation of $P_1(a)$ and $P_2(a)$. Furthermore, these transitions will appear as a broad absorption in the region of molecular vibrational transitions. Probably due to these effects, our attempts to detect such a low-lying electronic absorption were in vain.

It is now worthwhile to compare the spectrum obtained by Hiroma[5] with the spectrum calculated on

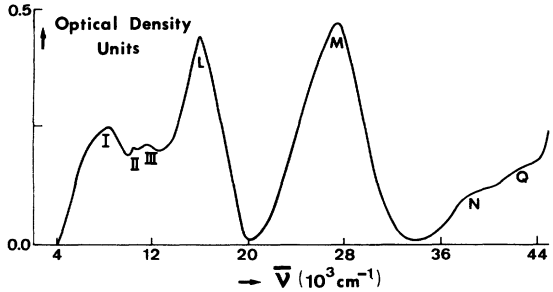

FIG. 1. Electronic absorption spectrum of solid KTCNQ. Absorption peaks arise at 8.3×10^3 cm^{-1} (I), 10.4×10^3 cm^{-1}, (II), 11.8×10^3 cm^{-1} (III), 16.1×10^3 cm^{-1} (L), 27.4×10^3 cm^{-1} (M), 38.2×10^3 cm^{-1} (N) and 43.3 $\times10^3$ cm^{-1} (Q).

the basis of a one-electron band model with $w = 3.5$.

We then come to the assignments as given in Table I. On the whole the agreement between the best experimental data (Hiroma's) and band theory is not bad, particularly in view of the simplifying assumption of Eq. (3.9). The other data are so global that they can almost be fitted to any theory. Particularly satisfying is the agreement with the polarizations, which usually are more reliable.

An uncertainty remains about the peaks at 10.4 $\times10^3$ and 11.8×10^3 cm^{-1} which were clearly observed in our spectrum. It is conceivable that one of them arises from a nondisplaced TCNQ$^-$ absorption, which might occur in a disordered lattice. The most obvious disorder would be imperfections in the alternation of the TCNQ separations. Then, in addition to ions having transfer interactions h_1 and h_2, these would also be ions with either h_1 or h_2 on both sides. The spectrum of these ions would

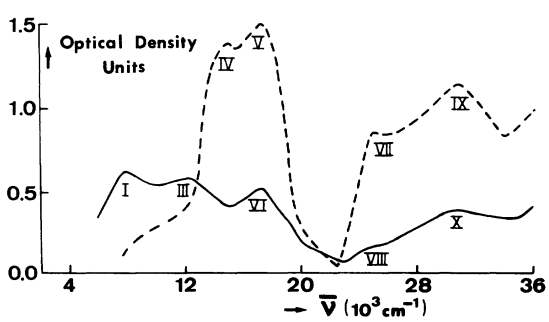

FIG. 2. Polarized crystal absorption spectra of KTCNQ, reproduced with permission from Hiroma *et al.* (Ref. 5). Solid line, $\vec{a}$ spectrum (parallel to the stacking axis); dashed line, $\vec{b}$ spectrum (practically perpendicular to the stacking axis). Absorption peaks: 7.8×10^3 cm^{-1} (I), 12.1×10^3 cm^{-1} (III), 15.0×10^3 cm^{-1} (IV), 17.3×10^3 cm^{-1} (V, VI), 25.0×10^3 cm^{-1} (VII, VIII), and 30.8×10^3 cm^{-1} (IX, X).

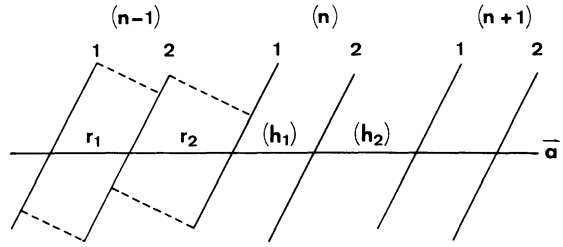

FIG. 3. TCNQ$^-$ ions, stacked in a RbTCNQ crystal (Ref. (2).

not be split in a nearest-neighbor approximation and the TCNQ$^-$ absorption would occur at an energy of 11.9×10^3 cm^{-1}, where it is observed in solution (apart from a crystal shift). It is tempting therefore to assign the 11.8×10^3 cm^{-1} (or 12.1×10^3 cm^{-1} in Hiroma's work) absorption to TCNQ$^-$ ions in special positions.

This assignment is supported by the spectrum of N-methyl-phenazinium-TCNQ (NMP-TCNQ), which crystallographically has only one molecule per one-dimensional unit cell,[10] but nevertheless shows three diffuse absorptions at 4.3×10^3, 11.8×10^3 and 16.4×10^3 cm^{-1}.[6] It is also known[11] that NMP-TCNQ

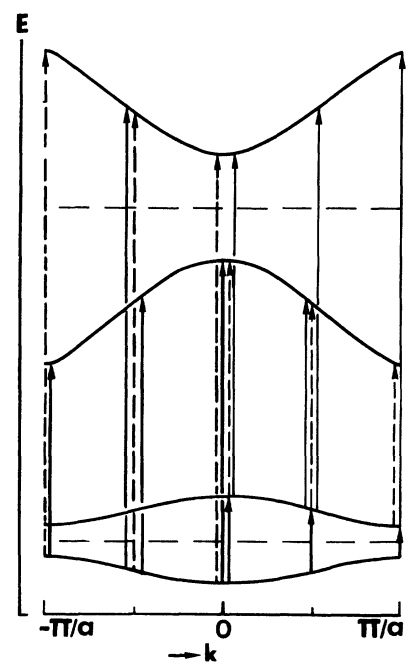

FIG. 4. Band energies $E(k)$ vs the wave vector k for $h'_{1,2}/h_{1,2} = -3.5$. Optical band-to-band transitions from the ground-state "valence" and "conduction" bands are indicated. Solid line: transitions, polarized along the stacking axis (a); dashed line: transitions, polarized in the molecular plane (m).

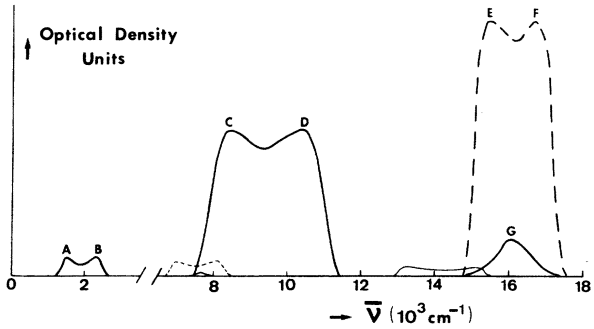

FIG. 5. Electronic absorption spectrum, derived from Fig. 4 ($h'_{1,2}/h_{1,2} = -3.5$) for KTCNQ with a ground-state bandwidth of 0.054 eV and a band gap of 0.182 eV. The crystal shift of the TCNQ$^-$ monomer absorption has been neglected. Solid line: (a) polarized spectrum; dashed line: (m) polarized spectrum. Absorption peaks are "calculated" at 1.5×10^3 cm^{-1} (A), 2.4×10^3 cm^{-1} (B), 8.5×10^3 cm^{-1} (C), 10.5×10^3 cm^{-1} (D), 15.6×10^3 cm^{-1}(E), 16.8×10^3 cm^{-1} (F), and 16.1×10^3 cm^{-1} (G). The other absorptions, denoted by thin lines, arise from transitions from the ground-state "conduction" band.

is disordered, and then again we have symmetrically and asymmetrically surrounded TCNQ$^-$ ions with (in a nearest-neighbor approximation) correspondingly split and nonsplit TCNQ$^-$ absorptions. The absorption at 11.8×10^3 cm^{-1} would again be the transition arising from symmetrically surrounded TCNQ$^-$ ions.

The foregoing treatment can also account qualitatively for the electronic spectrum of $Cs_2(TCNQ)_3$, exhibiting an extra absorption peak at about 10 000–11 000 cm^{-1}.[5,12] In this complex, the TCNQ's form columns, with a unique grouping of $(TCNQ)_3^{=}$ triads.[13] Accordingly, a one-dimensional band model predicts optical transitions to three excited bands, leading to three absorptions. The available spectral data reveal absorptions at 16 000–17 000, 10 000–11 000 cm^{-1}, and a low-energy absorption below 5×10^3 cm^{-1}.[5,12]

So far, we have interpreted the KTCNQ spectrum on the basis of a one-electron theory. The variable density of states in the bands then leads to a splitting. This does not mean that other interactions can be neglected.

For instance, the crystallographic inequivalence of the TCNQ$^-$ ions leads to a Davydov splitting, a clear two-electron effect, as for instance considered by Hiroma.[5] It was the purpose of this paper, however, to show that elementary band theory can go quite a way in explaining the electronic spectra, thus bringing these in line with previous models for the magnetic susceptibility behavior and phase transitions of the simple alkali-TCNQ salts.

The pressure dependence of the electronic absorption spectra of among others LiTCNQ Ref. (14) and KTCNQ (Ref. 15) reveals a blue shift of the absorption L in Fig. 1, which is in agreement with the band picture of Fig. 4. An increase in the pressure leads to an increase in the absolute values of the transfer integrals, which predominantly affects the excited-state band system, due to our assumption $|h'_{1,2}| > |h_{1,2}|$. Neglecting the pressure shift of γ_0, it can be seen directly from Fig. 4, that absorption L undergoes a blue shift, whereas the low-energy absorption I should exhibit a red pressure shift. Although the latter shift has not been measured on LiTCNQ and KTCNQ, these low-lying absorptions generally do show a red shift at high pressures, as for instance observed in Na^+ Chloranil^{-1}.[16]

The spectra of the other alkali-TCNQ salts are similar to the KTCNQ spectrum in Fig. 1, except for the location of the low-energy absorption and the presence of peak III at about 11.8×10^3 cm^{-1}. Absorption peaks always appear at $(7.4\pm1.4)\times10^3$ cm^{-1} (I), $(10.3\pm0.1)\times10^3$ cm^{-1} (II), $(16.1\pm0.2)\times10^3$ cm^{-1}(L), $(26.9\pm0.6)\times10^3$ cm^{-1} (M), and $(38.5\pm0.8)\times10^3$ cm^{-1} (N). The exact location depends somewhat upon the nature of the alkali ion in the M^+TCNQ$^-$ crystal.

It appears then, that the interpretation of these spectra as band-to-band transitions is quite general and successful.

TABLE I. Comparison of "calculated" and experimental spectra of KTCNQ.

Peak	Iida (Ref. 6) Energy 10^3 cm^{-1}	This work Energy 10^3 cm^{-1}	Hiroma *et al.* (Ref. 5) Energy 10^3 cm^{-1}	Pol.	Band theory Energy 10^3 cm^{-1}	Pol.	$ak \to ak'$
I	8.5	8.3	7.8	(a)	8.5	(a)	$\pi \to \pi$
II	10–11	10.4			10.5	(a)	$0 \to 0$
III		11.8	12.1	(a)			
L IV			15.0	(m)	15.6	(m)	$0 \to 0$
L V	16.4	16.1	17.3	(a)	16.1	(a)	$\frac{1}{2}\pi \to \frac{1}{2}\pi$
L VI			17.3	(m)	16.8	(m)	$\pi \to \pi$

V. DISCUSSION

In earlier work[5,6,14,15] the lowest-energy absorption has usually been interpreted as a charge-transfer absorption as it appears, mainly on the basis of its polarization. It should be pointed out, that the present interpretation, apart from explaining many more polarizations, also contains a large amount of charge transfer, be it to the excited orbital of the neighboring ion [cf. Eq. (3.11)]. The charge-transfer to the ground-state orbital is in this theory deplaced towards the very low energies of the ground-state "valence"–to–"conduction-band" transitions. The relative success of this theory, therefore, implies that the quantity U (the "energy of the doubly ionized state"), which is of the utmost importance in the interpretation of solid state magnetic susceptibility or transport data, is zero or at least very small in the alkali-TCNQ salts. This conclusion is in direct contrast to that of Hiroma *et al.*,[5] who derive a value of about 1 eV for U, when they interpret the spectra as charge-transfer spectra.

A few final remarks may be of use about the utilization of one-electron theory in this case. It is clear, that it cannot be the final answer. After all, electron-electron interaction is always present. We have tried to explain in I,[3] why it may probably be neglected in the $TCNQ^-$ chains. We have recently[17] obtained results on other TCNQ salts, where it is clear that one-electron theory is insufficient to explain all the solid state phenomena. Even then, though, the one-electron theory appears to give the best starting point. When, however, the quantity U is of the order of or greater than the total bandwidth in the ground state, strong deviations from one electron theory will occur. Recent results obtained in this laboratory have shown, that this may be the case for a number of TCNQ salts with organic counter ions. It should be noted, however, that a nonzero U will not affect the spectra in the visible part of the spectrum very strongly, since it will still be small compared to the energies involved in these transitions. It may therefore be expected that the band-to-band interpretation of these spectra may still hold, even when transport or magnetic susceptibility data can no longer be interpreted within a one-electron scheme.

Finally, dc photoconductivity might be expected on the basis of band-to-band transitions. Apparently, this is not observed. Since it is a transport phenomenon, it will be affected by the same problems of disorder, as discussed in an earlier paper paper,[3] and this would decrease its magnitude considerably, and even render its observation impossible. Some hope may be retained for ac photoconductivity at high frequency, such experiments are presently being set up in our laboratory.

[1]G. R. Anderson and C. J. Fritchie, Proceedings of the Society for Applied Spectry, San Diego, October, 1963 (unpublished).

[2]A. Hoekstra, T. Spoelder, and A. Vos, Acta Crystallogr. B 28, 14 (1972).

[3]J. G. Vegter, J. Kommandeur, and P. A. Fedders, Phys. Rev. B 7, 2929 (1973).

[4]J. G. Vegter and J. Kommandeur, Mol. Cryst. (to be published).

[5]S. Hiroma, H. Kuroda, and H. Akamatu, Bull. Chem. Soc. Jap. 44, 9 (1971).

[6]Y. Iida, Bull. Chem. Soc. Jap. 42, 71 (1969).

[7]R. H. Boyd and W. D. Phillips, J. Chem. Phys. 43, 2927 (1965).

[8]H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (Wiley, New York, 1944), Sec. 8c.

[9]G. M. Barrow, *Introduction to Molecular Spectroscopy* (McGraw-Hill, Kōgakusha, 1962), Sec. 4.4.

[10]C. J. Fritchie, Acta Crystallogr. 20, 892 (1966).

[11]A. N. Bloch, R. B. Weisman, and C. M. Varma, Phys. Rev. Lett. 28, 753 (1972); H. R. Zeller, *ibid.* 28, 1452 (1972).

[12]Y. Iida, Bull. Chem. Soc. Jap. 42, 637 (1969).

[13]C. J. Fritchie and P. Arthur, Acta Crystallogr. 21, 139 (1966).

[14]I. Shirotani, N. Sakai, H. Inokuchi, and S. Minomura, Bull. Chem. Soc. Jap. 42, 2087 (1969).

[15]N. Sakai, I. Shirotani, and S. Minomura, Bull. Chem. Soc. Jap. 43, 57 (1970).

[16]N. Sakai, I. Shirotani, and S. Minomura, Bull. Chem. Soc. Jap. 44, 675 (1971).

[17]T. Hibma, P. Dupuis, and J. Kommandeur, Chem. Phys. Lett. 15, 17 (1972).