PHYSICAL REVIEW B VOLUME 28, NUMBER 4 15 AUGUST 1983

Determination of the spin-Peierls distortion in N-methyl-N-ethyl-morpholinium ditetracyanoquinodimethanide [MEM(TCNQ)$_2$]: Neutron diffraction study at 6 K

R. J. J. Visser and S. Oostra
Laboratories of Chemical Physics and Physical Chemistry, Materials Science Center,
University of Groningen, Nijenborgh 16, 9747AG Groningen, The Netherlands

C. Vettier
Institut Laue-Langevin, 156X, F-38042 Grenoble Cedex, France

J. Voiron
Laboratoire Louis Néel, Centre National de la Recherche Scientifique,
25 Avenue des Martyrs, 166X, F-38042 Grenoble Cedex, France

(Received 25 March 1983)

We have carried out a crystallographic study of the spin-Peierls distorted phase ($T_c = 17.4$ K) of N-methyl-N-ethyl-morpholinium ditetracyanoquinodimethanide [MEM(TCNQ)$_2$]. Neutron-diffraction data were collected at 6 K from a deuterated sample. At the transition the unit cell axis along the dimerized TCNQ stack is doubled, hence giving rise to tetramers. Refinement of rigid molecules converged to $R = 0.162$ for 340 super-reflections. The structural change consists of a transverse shift $\Delta\vec{v} = 0.17\vec{L} + 0.10\vec{M}$ of every second dimer in the stack. Calculations of transfer integrals confirmed the significance of the distortion.

INTRODUCTION

Since its discovery about a decade ago, the donor-acceptor system N-methyl-N-ethyl-morpholinium ditetracyanoquinodimethanide [MEM(TCNQ)$_2$] has attracted much attention. It shows two phase transitions, a metal-to-semiconductor transition at 335 K and a magnetic-to-nonmagnetic transition at 17.4 K.[1,2] The former has been found to be an electronic Peierls transition, while high magnetic field experiments[3] have implied the latter to be a spin-Peierls transition. Crystal structure determinations at various temperatures[4] have established the presence of pseudo-one-dimensional stacks of TCNQ molecules, which are uniform above and dimerized below 335 K. According to extensive theoretical studies,[5] the rapid decrease of the magnetic susceptibility below 17.4 K is due to a nuclear distortion with wave vector $2k_F$, and requires for this quarter-filled-band system small alternations in the interdimer exchange integrals. Indeed a doubling of the unit cell along the stacking axis was found, but the nature of the distortion still remained ambiguous, although it was thought to be a mainly transverse shift of the TCNQ molecules.[6]

So far, the only structural data available about a spin-Peierls distorted phase were for TTFCuBDT [tetrathiafulvalinium bis-*cis*-(1,2-perfluoromethylethylene-1,2-dithiolato)-copper].[7] At 4.2 K the distortion was found to consist of a slight alternation in the distances between the TTF molecules and a shift of the CuBDT groups towards the TTF chain.[8] Contrary to results on TTFCuBDT,[9] the transition temperature in MEM(TCNQ)$_2$ increases with pressure,[10] which is a theoretical point of interest.[11,12] In view of these facts, we decided to determine the nuclear distortion of the spin-Peierls transition in MEM(TCNQ)$_2$ by neutron diffraction.

EXPERIMENTAL

A crystal of deuterated MEM(TCNQ)$_2$ with approximate dimensions $5\times3\times0.5$ mm^3 was selected for the neutron-diffraction measurements at the D10 four-circle diffractometer located on a thermal beam tube at the high-flux reactor of the Institut Laue Langevin in Grenoble. The incident wavelength was $\lambda = 1.257$ Å [Cu(200) vertically focusing monochromator] with a flux at sample position of about $5\times10^6 n$ cm^{-2} s^{-1} and a $\lambda/2$ contamination fraction less than 2×10^{-4}. The crystal was placed in a special helium flow cryostat mounted on the Eulerian cradle. The cryostat temperature was controlled with a rhodium-iron resistance sensor, and kept constant within 0.4 deg.

Cell dimensions were determined at 33 K and at 6 K (Table I) from the setting angles of 15 optimized reflections with $0.14 < \sin\theta/\lambda < 0.50$. The doubling of the unit

TABLE I. Crystallographic data. e.s.d.'s are given in parentheses.

	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	V (Å^3)	Space group
6 K	7.747(15)	15.244(17)	13.626(18)	113.11(8)	73.55(10)	111.77(10)	1356	P_1
33 K	7.752(18)	15.241(18)	6.802(13)	113.04(9)	73.64(11)	111.73(12)	678	P_1

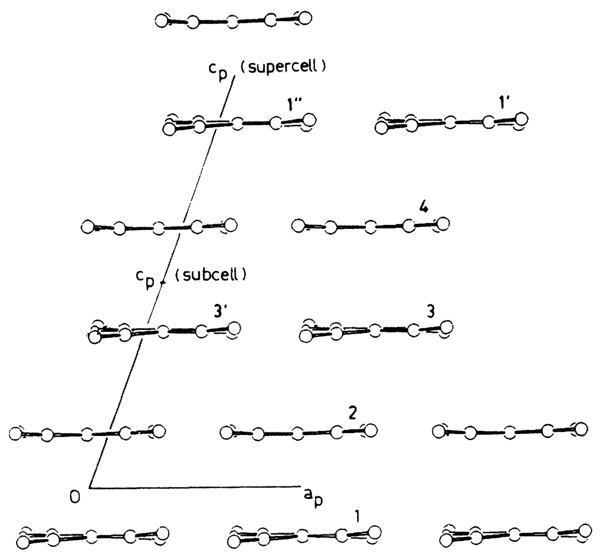

FIG. 1. Projection of the sheet of TCNQ molecules in MEM(TCNQ)$_2$. The longest molecular axis $\vec{L}$ of the TCNQ groups is perpendicular to the paper. Only the C(CN)$_2$ groups are visible.

cell along $\vec{c}$, as found for the low-temperature structure by van Bodegom *et al.*[6] from measurements in the b^*c^* plane, was confirmed. The present experiments did not show a doubling of $\vec{a}$. Within experimental error the (sub) cell does not change at the transition.

At 6 K a total number of 642 reflections, including 33 intensity reference reflections, were collected for $0.0<\sin\theta/\lambda<0.6$ Å^{-1}. For equivalent reflections weighted average intensities were taken. The remaining data set comprised 372 independent (super)reflections with l odd and 206 (subcell) reflections with l even, which in total is approximately 12% of the total number of independent reflections with $\sin\theta/\lambda\leq 0.6$ Å^{-1}.

DETERMINATION OF THE STRUCTURE

In the 6-K supercell with $\vec{c}\simeq 2\vec{c}\,(T>17.4\text{ K})$ the reflections with l odd are weak. Starting from the structure at 113 K (Ref. 4), the molecular shifts responsible for the doubling of the cell were estimated from a Patterson synthesis computed with the l odd reflections only.[13] In agreement with the neutron and x-ray diffuse scattering experiments of van Bodegom *et al.*,[6] displacements along $\vec{b}$ were found. A trial model was set up in which the contents of the lower half of the supercell were shifted with respect to those of the upper half. A shift of $0.01\vec{b}$ gave a reasonable agreement between observed and calculated structure factors. The limited number of reflections did not permit refinement of the individual atoms. Group refinements with all reflections and $w=1$, in which in addition to the scale factor, the positions, orientations, and isotropic temperature factors of rigid molecules with 113-K geometry were varied, decreased

$$R=\sum\,|\,|F_0|-|F_c|\,|\Big/\sum|F_0|$$

to 0.099. Subsequent refinement of the MEM deuterium atoms and the TCNQ nitrogens gave $R=0.079$. Because of large correlations, however, the parameters of these individual atoms are not very accurate (σ's up to 0.06 Å).

To emphasize the molecular displacements in the superstructure, the group refinement was proceeded with the l odd reflections only. R converged from 0.180 to 0.162 for 340 reflections with $w=1$ and $F_0>\sigma(F_0)$, and for 43 variables. (A list of observed and calculated structure factors is available from the authors on request.)

Figure 1 illustrates the TCNQ sheet at 6 K and the numbering of the molecules. Table II gives the final coordinates of the centers of gravity of the molecules at 6 K, the isotropic temperature factors, and the average directions of the axes $\vec{L}$, $\vec{M}$, and $\vec{N}$ of the inertial systems of the TCNQ molecules. Data concerning the orientations and relative shifts of the TCNQ molecules are listed in Tables III and IV. At 6 K the standard deviations in the $\vec{L}$, $\vec{M}$, and $\vec{N}$ components of Table IV, estimated with account of the (large) correlations between the molecular parameters, are 0.02, 0.03 and 0.02 Å, respectively.

TABLE II. Centers of gravity of MEM and TCNQ, isotropic temperature factors, and average directions of the inertial axes $\vec{L}$, $\vec{M}$ and $\vec{N}$ of the TCNQ molecules. The temperature factor is of the form $\exp-[8\pi^2U_{\text{iso}}(\sin\theta/\lambda)^2]$. For TCNQ the data are based on the quinodimethane group. e.s.d.'s are given in parentheses.

	x	y	z	U_{iso}
TCNQ1	−0.0445(33)	−0.0786(18)	−0.1262(28)	0.0078(50)
TNCQ2	0.0712(26)	0.0984(8)	0.1413(27)	0.0048(19)
TCNQ3	−0.0389(33)	−0.0718(19)	0.3724(29)	0.0071(49)
TCNQ4	0.0749(23)	0.1046(10)	0.6416(25)	0.0044(20)
MEM1	0.1147(34)	0.5460(19)	0.0159(28)	0.0247(43)
MEM2	0.1211(34)	0.5528(20)	0.5154(28)	0.0220(42)

Average directions: $\vec{L}=0.108\,12\vec{a}+0.062\,54\vec{b}+0.008\,10\vec{c}$
$\vec{M}=-0.085\,25\vec{a}+0.037\,40\vec{b}+0.003\,88\vec{c}$
$\vec{N}=-0.029\,61\vec{a}+0.016\,12\vec{b}+0.080\,32\vec{c}$

σ (directions $\vec{L},\vec{M},\vec{N}$)$\simeq 1°$

TABLE III. Angles of the normals of the quinodimethane planes with each other, and with the $\vec{c}$ axis; 6-K values in the lower left and 113-K values (Ref. 4) in the upper right part of the table. Standard deviations of the 6-K values are approximately 1°.

	TCNQ1	TCNQ2	TCNQ3	TCNQ4	$\vec{c}$ axis
TCNQ1	0.0	1.2	0.0	1.2	21.3
TCNQ2	1.7	0.0	1.2	0.0	20.5
TCNQ3	0.3	1.9	0.0	1.2	21.3
TCNQ4	1.3	0.5	1.6	0.0	20.5
$\vec{c}$ axis	20.3	22.0	20.1	21.6	0.0

COMPARISON OF THE 6- AND 113-K STRUCTURES

Comparison of Fig. 1 with the TCNQ sheet of the 113-K structure[4] and the numerical values of Table III, shows that the orientations of the TCNQ molecules at the two temperatures are virtually the same.

From Table IV and Fig. 1 it can be seen that at 113 K the TCNQ stack is dimerized with alternating intra- and interdimer overlap vectors $\vec{v}_{1\text{-}2}$ and $\vec{v}_{2\text{-}3}$. In the 6-K structure dimers, with intradimer separations $\vec{v}_{1\text{-}2}$ and $\vec{v}_{3\text{-}4'}$, are still present. The average vector

$$\vec{v}_{\text{intra}} = 1.95\vec{L} + 0.07\vec{M} + 3.14\vec{N}$$

is not significantly different from the intradimer overlap at 113 K. For the interdimer vectors $\vec{v}_{2\text{-}3}$ and $\vec{v}_{4\text{-}1'}$ at 6 K (Table IV), the (mutually equal) $\vec{N}$ components are smaller than at 113 K. As between 113 and 6 K the orientations of the TCNQ groups remain virtually the same, and as $2\vec{c}$ does not change significantly between 33 and 6 K, it can be assumed that the decrease in interdimer distance already occurs above the phase transition due to the anisotropic shrinkage of the lattice between 113 and 33 K.[14]

The only change which does occur at the phase transitions is in the $\vec{L}$ and $\vec{M}$ components of the interdimer vectors. For $\vec{v}_{4\text{-}1'}$ at 6 K these coordinates are still equal to those at 113 K, but $\vec{v}_{2\text{-}3}$ differs from $\vec{v}_{4\text{-}1'}$ by

$$\Delta\vec{v} = 0.17\vec{L} + 0.10\vec{M} .$$

This shift vector is parallel to the TCNQ planes, and hence transverse. Its length is $0.20(\sigma \simeq 0.03)$ Å, the angle with the $\vec{b}$ axis amounts to $23(\sigma \simeq 8)$ deg. Figure 2 illustrates the difference between the two interdimer overlaps.

To evaluate the physical significance of $\Delta\vec{v}$, the transfer integrals t_{ij} for the TCNQ molecules associated with $\vec{v}_{2\text{-}3}$ and $\vec{v}_{4\text{-}1'}$ were calculated according to Janssen *et al.*[15] In spite of uncertainties in the absolute values of t_{ij}, due to the inevitable approximations of their method, the calculated ratio $t_{2\text{-}3}/t_{4\text{-}1'} = 1.4$ is thought to be quite reliable. This implies that at the phase transition the tetramerization is indeed accompanied by the creation of a gap in the spin-wave spectrum, thus leading to the decrease in spin susceptibility observed.

In Table V we give a compilation of the ratios of the various transfer integrals at the different temperatures at which the crystal structures have been determined. Although the phase transitions need not be governed completely by the pseudo-one-dimensional stacks (see, e.g.,

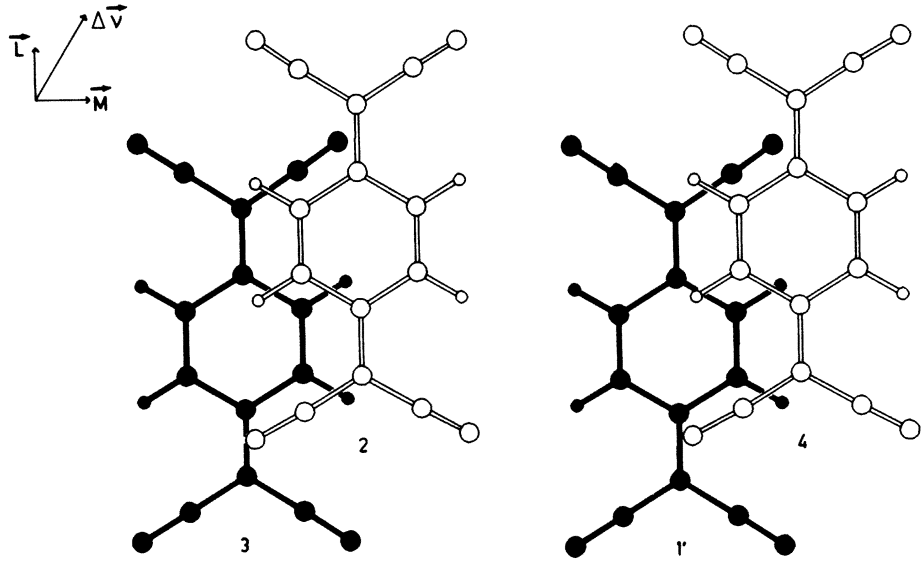

FIG. 2. Interdimer overlaps of MEM(TCNQ)$_2$ at 6 K along $\vec{N}$, which is perpendicular to the molecular planes. The inset gives the shift $\Delta\vec{v}$ on 10 times its scale.

TABLE IV. Vectors $\vec{v}_{p\text{-}q}$ between the centers of the quinodimethane groups of molecules p and q, averaged over the inertial systems $\vec{\mathrm{L}}$, $\vec{\mathrm{M}}$ and $\vec{\mathrm{N}}$ of the constituent molecules.

	113 K (Ref. 4)
Intradimer:	$\vec{v}_{1\text{-}2}=\vec{v}_{3\text{-}4}=\ \ 1.97\vec{\mathrm{L}}+0.13\vec{\mathrm{M}}+3.15\vec{\mathrm{N}}$
Interdimer:	$\vec{v}_{2\text{-}3}=\vec{v}_{4\text{-}1'}=-2.22\vec{\mathrm{L}}-2.57\vec{\mathrm{M}}+3.29\vec{\mathrm{N}}$
Interchain:	$\vec{v}_{2\text{-}3'}=\vec{v}_{4\text{-}1''}=-6.14\vec{\mathrm{L}}+4.20\vec{\mathrm{M}}+3.30\vec{\mathrm{N}}$
	6 K
Intradimer:	$\vec{v}_{1\text{-}2}=\ \ 1.98\vec{\mathrm{L}}+0.06\vec{\mathrm{M}}+3.13\vec{\mathrm{N}}$
	$\vec{v}_{3\text{-}4}=\ \ 1.92\vec{\mathrm{L}}+0.08\vec{\mathrm{M}}+3.15\vec{\mathrm{N}}$
Interdimer:	$\vec{v}_{2\text{-}3}=-2.07\vec{\mathrm{L}}-2.46\vec{\mathrm{M}}+3.21\vec{\mathrm{N}}$
	$\vec{v}_{4\text{-}1'}=-2.24\vec{\mathrm{L}}-2.56\vec{\mathrm{M}}+3.24\vec{\mathrm{N}}$
Interchain:	$\vec{v}_{2\text{-}3'}=-6.07\vec{\mathrm{L}}+4.18\vec{\mathrm{M}}+3.30\vec{\mathrm{N}}$
	$\vec{v}_{4\text{-}1''}=-6.23\vec{\mathrm{L}}+4.09\vec{\mathrm{M}}+3.30\vec{\mathrm{N}}$

Ref. 16), MEM(TCNQ)$_2$ now appears to be the first quarter-filled-band system for which the crystal structures of the three predicted[17] phases (regular, dimerized, and tetramerized) are known.

TABLE V. Ratios of the transfer integrals along the TCNQ stack in MEM(TCNQ)$_2$. The numbering of the molecules is according to this paper.

Uniform	348 K[a,b]	$t_{1\text{-}2}:t_{2\text{-}3}=t_{3\text{-}4}:t_{4\text{-}1'}=1:0.94$
Dimerized	323 K[a]	$t_{1\text{-}2}:t_{2\text{-}3}=t_{3\text{-}4}:t_{4\text{-}1'}=1:0.24$
	294 K[a]	$t_{1\text{-}2}:t_{2\text{-}3}=t_{3\text{-}4}:t_{4\text{-}1'}=1:0.23$
	113 K[a]	$t_{1\text{-}2}:t_{2\text{-}3}=t_{3\text{-}4}:t_{4\text{-}1'}=1:0.20$
Tetramerized	6 K	$t_{1\text{-}2}:t_{2\text{-}3}:t_{3\text{-}4}:t_{4\text{-}1'}=1:0.30:0.93:0.21$

[a] Calculated with parameters from Ref. 4.

[b] Stack is not crystallographically uniform.

ACKNOWLEDGMENTS

The authors are indebted to Professor Dr. A. Vos and Professor Dr. J. Kommandeur for their stimulating interest and helpful suggestions. B. H. Kwant and A. Verwey are acknowledged for preparing and crystallizing the deuterated compound. This investigation was supported in part by the Netherlands Foundation for Chemical Research Scheikundig Onderzoek Nederland (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek).

---

[1] S. Huizinga, J. Kommandeur, G. A. Sawatzky, B. T. Thole, K. Kopenga, W. J. M. de Jonge, and D. Roos, Phys. Rev. B 19, 4723 (1979).

[2] The previously reported value of $T_c=19$ K appears to be inaccurate (see Ref. 10).

[3] D. Bloch, J. Voiron, J. W. Bray, I. S. Jacobs, J. C. Bonner, and J. Kommandeur, Phys. Lett. 82A, 21 (1981).

[4] A. Bosch and B. van Bodegom, Acta Crystallogr. Sect. B 33, 3013 (1977); B. van Bodegom, *ibid.* 37, 857 (1981); B. van Bodegom, and A. Bosch, *ibid.* 37, 863 (1981).

[5] See review of J. W. Bray, L. V. Interrante, I. S. Jacobs, and J. C. Bonner, in Extended Linear Chain Materials, edited by J. S. Miller (Plenum, New York, in press), Vol. IV.

[6] B. van Bodegom, B. C. Larson, and H. A. Mook, Phys. Rev. B 24, 1520 (1981).

[7] D. E. Moncton, R. J. Birgeneau, L. V. Interrante, and F. Wudl, Phys. Rev. Lett. 39, 507 (1977).

[8] J. S. Kasper and D. E. Moncton Phys. Rev. B 20, 2341 (1979).

[9] I. S. Jacobs, J. W. Bray, L. V. Interrante, D. Block, J. Voiron, and J. C. Bonner, in *Physics in One Dimension,* edited by J. Bernasconi and T. Schneider (Springer, New York, 1981), p. 173.

[10] D. Bloch, J. Voiron, C. Vettier, J. W. Bray, and S. Oostra (unpublished).

[11] J. W. Bray, Solid State Commun. 35, 853 (1980).

[12] H. T. Jonkman, S. Huizinga, and J. Kommandeur, Mol. Cryst. Liq. Cryst. (in press).

[13] For all calculations the XRAY 1976 set of crystallographic programs was used.

[14] R. J. J. Visser and J. L. de Boer, J. Phys. (Paris) (in press).

[15] G. J. M. Janssen, H. T. Jonkman, R. J. J. Visser, J. L. de Boer, and J. Kommandeur, J. Phys. (Paris) (in press).

[16] S. Oostra, B. van Bodegom, S. Huizinga, G. A. Sawatzky, G. Grüner, and J. P. Travers, Phys. Rev. B 24, 5004 (1981).

[17] S. Huizinga, J. Kommandeur, H. T. Jonkman, and C. Haas, Phys. Rev. B 25, 1717 (1982).