Discussion. Projections of the EBM(TCNQ)$_2$ structure are shown in Fig. 3 and projections of EBTM(TCNQ)$_2$ in Fig. 4. The structure data blocks are presented in Tables 3 and 4. Both structures contain tetrameric TCNQ stacks connected to form sheets parallel to the *ac* plane by electrostatically favourable H···N contacts ranging from 2·55 to 2·67 Å in EBTM(TCNQ)$_2$ and from 2·61 to 2·69 Å in EBM(TCNQ)$_2$. The cations are extended along the stacks. The packing of the sheets in the two structures is different. In EBM(TCNQ)$_2$ successive sheets are related by the *c* glide plane at $y = \pm\frac{1}{4}$, whereas in EBTM(TCNQ)$_2$ successive sheets along *y* are translationally equivalent. In both cases the stack contains two, parallel within 1°, independent molecules *A* and *B* in the sequence $[ABB^2A^1][ABB^2A^1]$... *etc.* with inversion centres between molecules of the same kind. The structure data blocks show that the character of the stacks in the two compounds is very different. In EBM(TCNQ)$_2$ the stacks are almost regular with no significant charge difference between *A* and *B*. Three overlaps of type I with practically equal t^c values alternate with an overlap of type II with slightly larger t^c. The stack inclination is 8·1°. In EBTM(TCNQ)$_2$ the stacks are composed of almost isolated tetramers consisting of two distinct equivalent dimers in which most of the (negative) charge is accumulated at the *B* molecules [$\rho^s_B - \rho^s_A = 0{\cdot}34\,(6)$ e for $\rho^s_A + \rho^s_B$ normalized to 1]. The stack inclination, 22·4°, is larger than for EBM(TCNQ)$_2$. The observed charge accumulation on *B* in EBTM(TCNQ)$_2$ agrees with the average $C{\equiv}N\cdots N^+$ distances being shorter for *B* than for *A*.

The present crystal structures reveal that replacement of O by S can have a profound influence on the crystal packing and on the character of the stacks.

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1:2 Complexes of (Thio)Morpholinium Derivatives and the Electron Acceptor 7,7,8,8-Tetracyano-*p*-quinodimethane. Part IV.* *N*,*N*-Dimethylthiomorpholinium Di-7,7,8,8-tetracyano-*p*-quinodimethanide DMTM(TCNQ)$_2$† at Room Temperature and its Phase Transition at 272 K

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Abstract. DMTM(TCNQ)$_2$, $C_6H_{14}NS^+.2C_{12}H_4N_4^{1/2-}$, $M_r = 540{\cdot}6$, monoclinic, $P2_1/m$, $a = 7{\cdot}846\,(3)$, $b = 27{\cdot}051\,(14)$, $c = 7{\cdot}914\,(3)$ Å, $\beta = 55{\cdot}56\,(3)°$, $V = 1385\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}30$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}157$ mm^{-1}, $F(000) = 562$, $T = 294$ K, $R = 0{\cdot}094$ for 2535 observed reflections. Transformation to conventional cell by $(1,0,-1/0,-1,0/-1,0,0)$. The room-temperature structure, which is isomorphous with DMM(TCNQ)$_2$ (I) [Kamminga & van Bodegom (1981). *Acta Cryst.* **B37**, 114–119], contains dimeric stacks connected to form sheets parallel to the *ac* plane. The DMTM cations are disordered around the mirror planes. Disappearance of the mirror symmetry at the phase transition suggests that the cations are ordered in the low-temperature structure.

Introduction. A general introduction to the subject is given in Part I (Visser, Bouwmeester, de Boer & Vos, 1990*a*) of this series. The special interest of

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* Part III: Visser, Bouwmeester, de Boer & Vos (1990*b*).

† 1:2 *N*,*N*-Dimethylthiomorpholinium salt with the radical anion of 2,2′-(2,5-cyclohexadiene-1,4-diylidene)bispropanedinitrile.

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Table 1. *Final fractional coordinates* ($\times 10^{-4}$) *and* U_{eq} *values* ($\text{Å}^2 \times 10^{-3}$) *for the non-*H *atoms of* *DMTM*(*TCNQ*)$_2$, *with e.s.d.'s in parentheses*

$U_{eq} = \sum_i U_{ii}/3$ after diagonalization of the **U** tensor.

	x	y	z	U_{eq}
N(1)	1789 (5)	1765 (1)	1323 (6)	100 (2)
C(2)	2313 (4)	1406 (1)	1643 (5)	66 (2)
C(3)	2960 (4)	950 (1)	2008 (4)	51 (1)
C(4)	4801 (4)	964 (1)	1968 (4)	57 (1)
N(5)	6268 (4)	976 (1)	1941 (4)	78 (2)
C(6)	1902 (4)	512 (1)	2275 (3)	48 (1)
C(7)	2630 (4)	45 (1)	2486 (3)	47 (1)
C(8)	1648 (4)	−379 (1)	2663 (3)	48 (1)
C(9)	−174 (4)	−382 (1)	2672 (3)	48 (1)
C(10)	−933 (4)	84 (1)	2505 (4)	51 (1)
C(11)	63 (4)	511 (1)	2303 (4)	51 (1)
N(12)	−4521 (4)	−837 (1)	2960 (4)	82 (2)
C(13)	−3025 (5)	−831 (1)	2890 (4)	60 (2)
C(14)	−1172 (4)	−823 (1)	2822 (4)	51 (1)
C(15)	−379 (4)	−1292 (1)	2886 (4)	62 (2)
N(16)	242 (5)	−1671 (1)	2928 (5)	92 (2)
N(17)	5950 (5)	2500 (0)	5511 (5)	68 (2)
C(18)	3909 (9)	2451 (9)	5808 (11)	116 (6)
C(19)	3762 (10)	2621 (4)	4078 (12)	98 (7)
S(20)	5593 (4)	2337 (1)	1739 (4)	112 (2)
C(21)	7793 (11)	2524 (11)	1686 (11)	130 (6)
C(22)	7681 (10)	2307 (3)	3529 (11)	101 (5)
C(23)	6347 (15)	3069 (3)	5540 (17)	121 (7)
C(24)	5919 (18)	2292 (4)	7228 (17)	158 (9)

DMTM(TCNQ)$_2$ is the unexpected tenfold *increase* in the electrical conductivity and the large drop of ~15% in the magnetic susceptibility observed on *cooling* the compound through the phase transition at 272 K (Oostra, de Boer & de Lange, 1983). Complete determination of the low-temperature structure has not yet been accomplished because of twinning of the crystals.

Experimental. Dark violet, almost black crystals grown by slowly cooling a hot solution of DMTM iodide and neutral TCNQ in acetonitrile. Data taken with Mo $K\alpha$ radiation from a crystal measuring $0{\cdot}12 \times 0{\cdot}20 \times 0{\cdot}35$ mm on a CAD-4F diffractometer provided with graphite monochromator and beam flattener (Helmholdt & Vos, 1977). Cell constants determined from 16 optimized reflections with $0{\cdot}40 < \sin\theta/\lambda < 0{\cdot}48\ \text{Å}^{-1}$; 8606 intensities ($h\ 0 \rightarrow 11$, $k\ -38 \rightarrow 38$, $l\ -11 \rightarrow 11$) measured up to $\theta = 30°$ in a complete hemisphere of reciprocal space, ω–2θ scan, b^* kept as horizontal as possible by use of the modified CAD-4 program developed by de Boer & Duisenberg (1984). Correction for intensity control was within ±1·6%. Equivalent reflections were averaged to give a final set of 4110 independent intensities, 765 of which have $I < 0$. Corrections were applied for Lorentz and polarization effects, but not for absorption.

The major part of the structure was found by direct methods, *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). After isotropic refinement of the located atoms, the remaining heavy atoms could be detected from a difference Fourier synthesis. Each DMTM group occupies two preferred positions related by the mirror plane at $y = +\frac{1}{4}$ or $y = -\frac{1}{4}$. Least-squares blocked-matrix refinement on $|F|$, with blocks for each independent molecule. Scattering factors for non-H atoms from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965). Anisotropic thermal parameters for non-H atoms and isotropic for H atoms (constrained at 1·08 Å from C). Weight $w = 0$ for $|F_o| < 2\sigma(\text{count};F_o)$ and for eight reflections with $w|F_o - F_c| > 8{\cdot}0$; $w = [\sigma^2(\text{count};F_o) + 0{\cdot}0007|F_o|^2]^{-1}$ for remaining reflections. Much effort was spent on finding the best description of the DMTM electron density distribution by superposition of two models with occupancy 0·5. The non-centrosymmetric space group $P2_1$ was rejected as refinement in this space group did not decrease wR in spite of the increase in N_v, nor did it lead to an ordered structure. Refinement criteria: $|\Delta|/\sigma$ max. = 0·02, mean = 0·002, $R = 0{\cdot}094$, $wR = 0{\cdot}083$, $S = 1{\cdot}67$, $N_o = 2535$, $N_v = 228$. Residual density close to molecules $\Delta\rho_{\max} = 0{\cdot}33$, $\Delta\rho_{\min} = -0{\cdot}44\ \text{e Å}^{-3}$; remote from molecules $|\Delta\rho_{\max}| = 0{\cdot}24$, $\sigma(\Delta\rho) = 0{\cdot}06\ \text{e Å}^{-3}$. All computations were carried out on a Cyber 170/760 with the *XRAY* system (1976) and local crystallographic programs. Final coordinates of the non-H atoms and U_{eq} values are given in Table 1. Bond lengths and atomic numbering of the non-H atoms are shown in Fig. 1.* For comparison of R values in similar cases in this series, see remark in the *Introduction* of Part I.

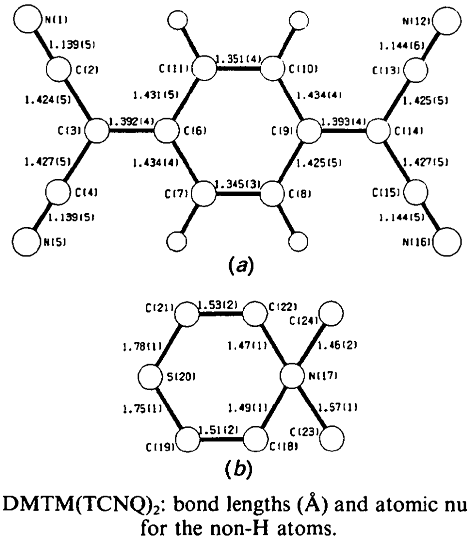

Fig. 1. DMTM(TCNQ)$_2$: bond lengths (Å) and atomic numbering for the non-H atoms.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, and figures giving angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52320 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Crystal structure data block for DMTM(TCNQ)₂*

	TCNQ *A*					
G	0·08656 (37)	0·00648 (10)	0·24668 (35)			
L	0·073333	0·031586	−0·014380			
M	−0·105623	0·018821	−0·006882			
N	−0·085727	0·003831	0·152382			
U	0·0439 (13)					
Charge (e)	$\rho_A = 0{\cdot}55\ (6)$	1·348 (4)	1·431 (4)	1·393 (4)	1·426 (5)	1·141 (5)
Stack	$t(A^{i}–A) = 0{\cdot}032$ eV	$\nu(A^{i}–A) = 1{\cdot}820\mathbf{L} - 3{\cdot}032\mathbf{M} + 3{\cdot}272\mathbf{N}$				
	$t(A–A^{ii}) = 0{\cdot}148$ eV	$\nu(A–A^{ii}) = -0{\cdot}145\mathbf{L} - 1{\cdot}109\mathbf{M} + 3{\cdot}261\mathbf{N}$				

Symmetry code: (i) $\bar{x}, \bar{y}, \bar{z}$; (ii) $\bar{x}, \bar{y}, \bar{z} + 1$.

Discussion. Projections of the DMTM(TCNQ)₂ structure are shown in Fig. 2 and the structure data block is given in Table 2. The structure is isomorphous with the room-temperature DMM(TCNQ)₂ (I) structure (Kamminga & van Bodegom, 1981). The crystals contain strongly dimerized stacks, with intradimer overlap of type I and a stack inclination of 34·4°. All molecules in the stack are related by inversion centres. Successive stacks along *a* are connected to form sheets by electrostatically favourable H···N contacts of ~2·63 (1) Å. Successive sheets in the *b* direction are related by mirror planes at $y = \pm\frac{1}{4}$. The cations are disordered around the mirror planes.

Upon cooling, the crystals show a phase transition at 272 K. At this transition the symmetry changes to $P\bar{1}$ or $P1$ [$a = 7{\cdot}853\ (1)$, $b = 27{\cdot}293\ (4)$, $c = 7{\cdot}924\ (1)$ Å, $\alpha = 80{\cdot}44\ (2)$, $\beta = 55{\cdot}24\ (1)$, $\gamma = 80{\cdot}52\ (1)$°, transformation to conventional cell by $(-1,0,1/1,0,0/0,1,-1)$, $V = 1371$ Å^3 at 264 K, this volume being 6 Å^3 smaller than the cell volume above T_c measured at 273 K], and the crystals become twinned. The changes in symmetry and cell dimensions suggest an ordering of the DMTM cations and a shift of the sheets relative to each other at the phase transition. The structural changes within the sheet are expected to be small, because of the small changes in *a*, *c* and *β*. Successive sheets along *b* are no longer equivalent, however, but alternately surrounded by DMTM in a different way. The resulting difference in crystal potential at the sheets has been used as a tentative explanation of the observed anomalous physical behaviour, by Visser, van Smaalen, de Boer & Vos (1984).

Ordering of the cations has been proved to occur during the phase transition of DMM(TCNQ)₂ (I) at 260 K by a complete X-ray analysis of the low-temperature modification DMM(TCNQ)₂ (I*a*) ($P2_1/c$, $Z = 8$; Middeldorp, Visser & de Boer, 1985). Crystals of this modification contain octameric stacks composed of four independent molecules. The isomorphism of the room-temperature phases of DMTM(TCNQ)₂ and DMM(TCNQ)₂ (I) is thus not retained by the low-temperature phases.

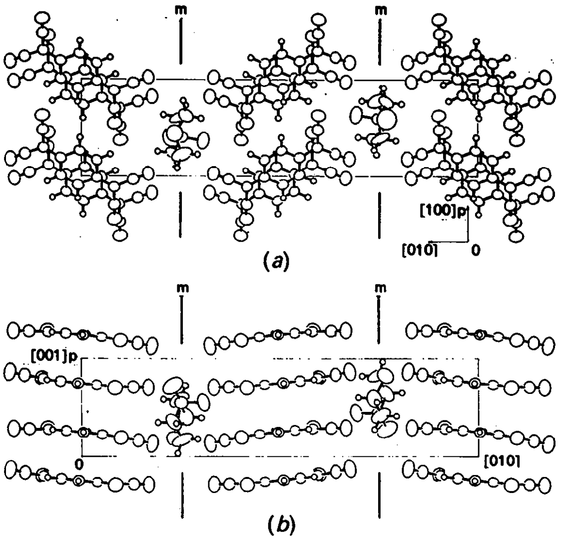

Fig. 2. Projections of DMTM(TCNQ)₂: (*a*) along [001]; (*b*) along [100].

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