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1:2 Complexes of (Thio)Morpholinium Derivatives and the Electron Acceptor 7,7,8,8-Tetracyano-*p*-quinodimethane. Part V.† Average Structure of *N*-Butylthiomorpholinium Di-7,7,8,8-tetracyano-*p*-quinodimethanide HBTM(TCNQ)$_2$‡ and Short-Range Ordering

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Abstract. HBTM(TCNQ)$_2$, $C_8H_{18}NS^+.2C_{12}H_4N_4^{1/2-}$, $M_r = 568{\cdot}7$, average structure: triclinic, $P\bar{1}$, $a = 7{\cdot}790\,(1)$, $b = 14{\cdot}760\,(1)$, $c = 6{\cdot}591\,(1)$ Å, $\alpha = 97{\cdot}92\,(1)$, $\beta = 100{\cdot}51\,(1)$, $\gamma = 94{\cdot}65\,(1)°$, $V = 734\,(1)$ Å^3, $Z = 1$, $D_x = 1{\cdot}29$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}152$ mm^{-1}, $F(000) = 297$, $T = 294$ K, $R = 0{\cdot}058$ for 3424 observed reflections. Transformation to conventional cell by (0,0,1/1,0,0/0,1,0). The average structure contains almost regular zigzag stacks consisting of equivalent TCNQ molecules. Overlaps are of type I. The HBTM cations are disordered around inversion centres. Diffuse X-ray scattering reflects short-range ordering which gives rise to a two-dimensionally coupled HBTM superstructure, introducing stacks of type [*ABBA*] where *A* and *B* are independent TCNQ molecules.

Introduction. A general introduction to the subject is given in Part I (Visser, Bouwmeester, de Boer & Vos, 1990). Because of the HBTM disorder discovered during the structure determination, X-ray diffuse scattering experiments were carried out to study the short-range ordering of the compound.

Experimental. Dark violet, almost black, crystals were obtained by slow cooling of a hot solution of HBTM iodide and neutral TCNQ in acetonitrile. All data were collected from a single crystal measuring 0·14 × 0·18 × 0·35 mm, with Mo $K\alpha$ radiation on a CAD-4F diffractometer equipped with graphite monochromator and beam flattener (Helmholdt & Vos, 1977). Cell constants were from 22 optimized reflections with $0{\cdot}64 < \sin\theta/\lambda < 0{\cdot}74$ Å^{-1}; 4255 independent intensities (h $-10 \rightarrow 10$, k $-20 \rightarrow 20$, l $0 \rightarrow 9$), among which there were 408 with $I < 0$, measured with ω–2θ scan up to $\theta = 30°$. Correction for intensity control was within $\pm 1{\cdot}3\%$. Corrections were applied for Lorentz and polarization effects, but not for absorption.

X-ray diffuse scattering was measured at Weissenberg photographs. Cu $K\bar{\alpha}$ radiation, graphite monochromator. Diffuse rods showing a remarkable (as yet unexplained) bumpiness occur at $(h+\frac{1}{2}, \eta, l+\frac{1}{2})$, where η is an arbitrary coordinate value along b^*. Intensities along the rods vary fairly slowly and hardly change upon cooling.

TCNQ molecules were determined from a Patterson map, and HBTM cations from successive difference Fourier syntheses calculated after isotropic refinement of the known part of the structure. In the adopted space group $P\bar{1}$ HBTM lies around an inversion centre and is thus disordered. Space group $P1$ was rejected because short-range order was indicated clearly by the diffuse X-ray scattering and refinement in $P1$, with ordered cations, did not improve the refinement results listed below. Least-squares blocked-matrix refinement on $|F|$, with blocks for each independent molecule. One complete HBTM considered as independent with occupancy 0·5. 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 and 1·00 Å from N). Weights $w = 0$ for $|F_o| < 2\sigma(\text{count};F_o)$; $w = [\sigma^2(\text{count};F_o) + 0{\cdot}0006|F_o|^2]^{-1}$ for remaining reflections. Max. $|\Delta|/\sigma = 0{\cdot}03$, mean $= 0{\cdot}0002$, $R = 0{\cdot}058$, $wR = 0{\cdot}072$, $S = 1{\cdot}91$, $N_o = 3424$, $N_v = 255$. Residual densities $\Delta\rho$ close to molecules: $\Delta\rho_{\max} = 0{\cdot}25$, $\Delta\rho_{\min} = -0{\cdot}18$ e Å^{-3}; remote from molecules $|\Delta\rho_{\max}| = 0{\cdot}19$, $\sigma(\Delta\rho) = 0{\cdot}04$ e Å^{-3}. All computations were carried out on a Cyber 170/760 with the *XRAY* system (1976) and local crystallographic programs. Final coordinates and $U_{\rm eq}$ values of the non-H atoms are listed in Table 1. Fig. 1 shows the bond lengths and atomic numbering for the non-H

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† Part IV: Visser, de Boer & Vos (1990).

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

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skeletons.* For comparison of R values in similar cases in this series, see remark in the *Introduction* of Part I.

Table 1. *Final fractional coordinates* ($\times 10^{-4}$) *and* U_{eq} *values* ($Å^2 \times 10^{-4}$) *for the non-*H *atoms of HBTM(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)	2108 (2)	3754 (1)	4399 (4)	952 (9)
C(2)	2597 (2)	3048 (1)	4194 (3)	583 (6)
C(3)	3198 (2)	2159 (1)	3944 (2)	425 (5)
C(4)	5054 (2)	2134 (1)	4274 (3)	518 (5)
N(5)	6544 (2)	2112 (1)	4543 (3)	729 (6)
C(6)	2026 (2)	1360 (1)	3416 (2)	348 (4)
C(7)	2647 (2)	471 (1)	3170 (2)	362 (4)
C(8)	1514 (2)	−310 (1)	2650 (2)	355 (4)
C(9)	−343 (2)	−270 (1)	2305 (2)	332 (4)
C(10)	−968 (2)	621 (1)	2544 (2)	350 (4)
C(11)	169 (2)	1399 (1)	3090 (2)	355 (4)
N(12)	−4863 (2)	−1026 (1)	1141 (3)	606 (5)
C(13)	−3372 (2)	−1039 (1)	1411 (2)	411 (5)
C(14)	−1522 (2)	−1064 (1)	1754 (2)	360 (4)
C(15)	−964 (2)	−1963 (1)	1477 (2)	439 (5)
N(16)	−555 (2)	−2686 (1)	1228 (3)	682 (6)
N(17)	−1036 (4)	4398 (2)	−180 (6)	435 (10)
C(18)	−2727 (5)	4023 (3)	−1751 (5)	613 (13)
C(19)	−3845 (5)	3312 (3)	−981 (7)	659 (15)
S(20)	−4611 (1)	3783 (1)	1311 (2)	579 (3)
C(21)	−2471 (5)	4184 (2)	2872 (6)	560 (12)
C(22)	−1423 (4)	4839 (2)	1851 (5)	525 (11)
C(23)	16 (5)	5040 (2)	−1173 (5)	570 (12)
C(24)	1773 (5)	5429 (3)	177 (9)	614 (17)
C(25)	2871 (6)	5959 (3)	−1080 (7)	791 (18)
C(26)	4560 (7)	6423 (4)	303 (9)	896 (23)

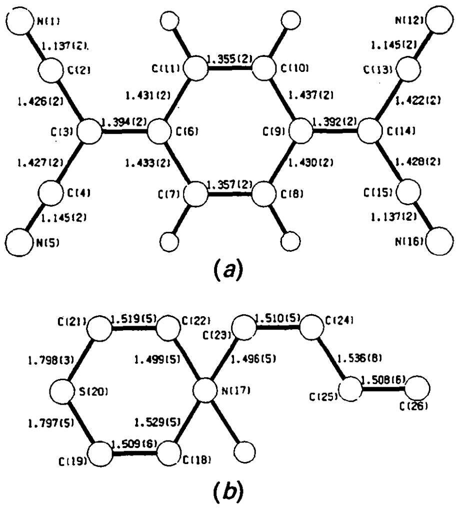

Fig. 1. Bond lengths (Å) and atomic numbering for the non-H atoms.

Discussion. Projections of the average structure are given in Fig. 2 and the structure data block in Table 2. The TCNQ molecules, which are all symmetrically related by inversion centres, form almost regular zigzag stacks. Overlaps are all of type I and the stack inclination is 2·7°. Electrostatically favourable H···N contacts of $\simeq$2·71 (1) Å connect the stacks along a to form sheets parallel to the ac plane. Each HBTM cation is disordered over two orientations related by the inversion centre of its special position. The cation, with half occupancy, forms an N^+—H···N bond of 2·163 Å with a TCNQ molecule (dashed line in Fig. 2a).

The occurrence of pronounced continuous rods on the diffuse X-ray pictures shows that the HBTM disorder is not random. The smooth variation of the intensity along the rods agrees with the assumption that the rods are primarily due to the HBTM molecules, with a smoothly varying Fourier transform, in the structure. The locations ($h+\frac{1}{2}$, η, $l+\frac{1}{2}$) of the rods and their small intensity change with temperature reflect a static two-dimensionally coupled (HBTM) superstructure with centred $2a$,$2c$ planes.

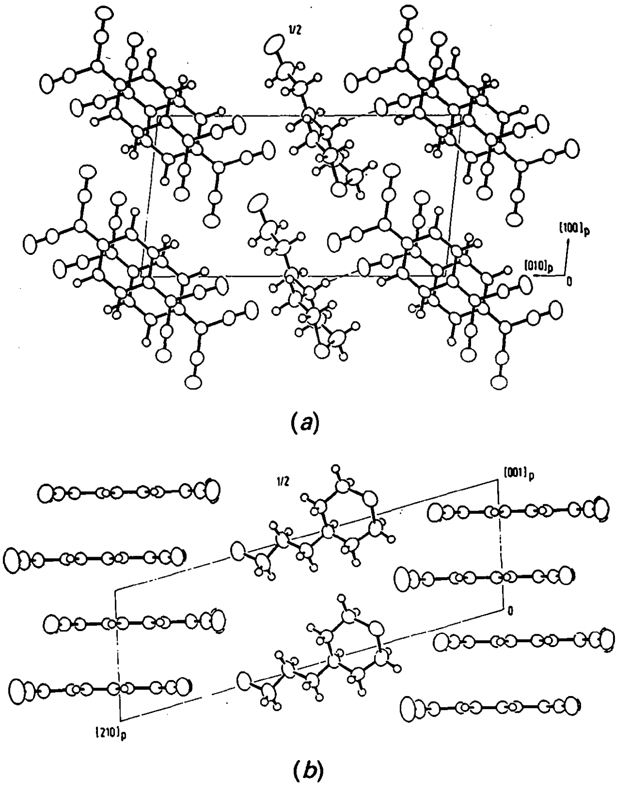

Fig. 2. Projections of the average HBTM(TCNQ)$_2$ structure: (a) along [001]; (b) along the molecular axis **M** (see Table 1 in Part I) of one layer of TCNQ and HBTM groups. Only one of the two HBTM groups, with half occupancy, is given.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, and figures showing angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52322 (18 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 HBTM(TCNQ)$_2$*

		TCNQ *A*				
G	0·08400 (7)	0·05458 (9)	0·028590 (21)			
L	0·083896	0·057403	0·039059			
M	−0·101029	0·037845	−0·003774			
N	0·002415	−0·002815	0·151207			
U	0·0365 (4)					
Charge (e)	ρ_A = 0·45 (3)	1·356 (2)	1·433 (2)	1·393 (2)	1·426 (2)	1·141 (2)
Stack	$t^c(A^i–A)$ = 0·141 eV	$\nu(A^i–A)$ = 2·007L + 0·082M + 3·265N				
	$t^c(A–A^{ii})$ = 0·118 eV	$\nu(A–A^{ii})$ = −1·866L + 0·193M + 3·319N				

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

These conclusions are consistent with the crystal structure, in which the HBTM molecules are closely connected in the $y = \frac{1}{2}$ plane, whereas they are well separated along *b* by the TCNQ sheets at $y = 0$. In the 2*a*,2*c* superstructure neighbouring HBTM molecules are assumed to have antiparallel orientation. A parallel arrangement of neighbouring HBTM molecules would imply parallel dipole moments and intermolecular distances up to ≃0·3 Å shorter than the sum of the relevant van der Waals radii. As a consequence of the antiparallel arrangement of the HBTM molecules along *c* and the resulting doubling of the *c* axis, the stacks along *c* tend to have tetrameric [ABB^iA^i] character, with *A* and *B* independent TCNQ molecules and A^i and B^i obtained by inversion.

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1:2 Complexes of (Thio)Morpholinium Derivatives and the Electron Acceptor 7,7,8,8-Tetracyano-*p*-quinodimethane. Part VI.* *N*-Methylmorpholinium Di-7,7,8,8-tetracyano-*p*-quinodimethanide HMM(TCNQ)$_2$†

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Abstract. HMM(TCNQ)$_2$, $C_5H_{12}NO^+.2C_{12}H_4N_4^{1/2-}$, $M_r = 510·5$, tetragonal, $P4_1$, $a = 7·032$ (3), $c = 52·915$ (17) Å, $V = 2617$ (3) Å^3, $Z = 4$, $D_x = 1·30$ Mg m^{-3}, Cu $K\bar{\alpha}$, $\lambda = 1·5418$ Å, $\mu = 0·70$ mm^{-1}, $F(000) = 1060$, $T = 294$ K, $R = 0·057$ for 2697 observed reflections. The crystals contain rather regular TCNQ stacks with overlaps of type I and type II alternating. The stacks are connected to form sheets parallel to *ab* and successive sheets along *c* are rotated over 90°.

Introduction. A general introduction to this series is given by Visser, Bouwmeester, de Boer & Vos (1990).

Experimental. Blue-black often pyramid-shaped crystals were obtained by slowly cooling a hot solution of HMM iodide and neutral TCNQ in acetonitrile. All data were collected from a single crystal of 0·50 × 0·75 × 0·75 mm on a CAD-4F diffractometer. Mo $K\bar{\alpha}$ radiation ($\lambda = 0·71069$ Å; graphite monochromator and beam flattener) used for the determination of the cell constants from 11 optimized reflections with $0·46 < \sin\theta/\lambda < 0·57$ Å^{-1}. Ni-filtered Cu $K\bar{\alpha}$ radiation, passing the beam flattener, applied

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* Part V: Visser, van Smaalen, de Boer & Vos (1990).

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

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