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) | $\rho_A$ = 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)$_2$, $C_5H_{12}NO^+.2C_{12}H_4N_4^{1/2-}$, $M_r = 510{\cdot}5$, tetragonal, $P4_1$, $a = 7{\cdot}032\,(3)$, $c = 52{\cdot}915\,(17)$ Å, $V = 2617\,(3)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}30$ Mg m$^{-3}$, Cu $K\bar{\alpha}$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}70$ mm$^{-1}$, $F(000) = 1060$, $T = 294$ K, $R = 0{\cdot}057$ 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 ($\lambda = 0{\cdot}71069$ Å; graphite monochromator and beam flattener) used for the determination of the cell constants from 11 optimized reflections with $0{\cdot}46 < \sin\theta/\lambda < 0{\cdot}57$ 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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for the intensity measurements because of the long $c$ axis; 3270 intensities collected ($h$ $0\rightarrow8$, $k$ $0\rightarrow8$, $l$ $0\rightarrow67$) with $\omega$–$2\theta$ scan up to $\theta = 78°$; $c^*$ axis kept as horizontal as possible. Intensity control reflections showed irregular fluctuations and did not provide a correction for possible intensity variations of the primary beam. Equivalent $h0l$ and $0kl$ reflections averaged, final set of 2786 independent intensities, including 16 reflections with $I < 0$. Corrections applied for Lorentz and polarization effects, but not for absorption.

The location of the TCNQ molecules was found by hand from a sharpened Patterson map. After isotropic refinement of these molecules the position of the HMM cation was revealed by a difference Fourier synthesis. 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 and

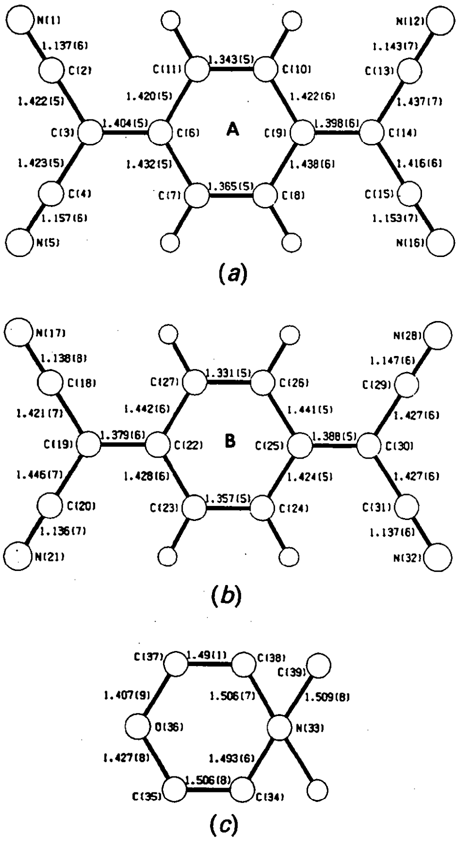

Fig. 1. HMM(TCNQ)₂: bond lengths (Å) and atomic numbering of the non-H atoms.

Table 1. *Final fractional coordinates* ($\times 10^{-5}$) *and* $U_{eq}$ *values* ($Å^2 \times 10^{-4}$) *for the non-*H *atoms of HMM(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) | 22752 (70) | 29969 (66) | 8710 (8) | 743 (14) |
| C(2) | 21870 (58) | 21110 (55) | 6918 (7) | 527 (11) |
| C(3) | 20984 (49) | 10020 (52) | 4674 (7) | 477 (9) |
| C(4) | 27419 (57) | −9066 (55) | 4933 (7) | 528 (11) |
| N(5) | 33225 (73) | −24372 (57) | 5160 (9) | 748 (14) |
| C(6) | 15100 (47) | 17796 (49) | 2358 (7) | 450 (9) |
| C(7) | 15226 (52) | 6399 (55) | 116 (7) | 509 (10) |
| C(8) | 9958 (55) | 13941 (59) | −2156 (7) | 529 (11) |
| C(9) | 3955 (51) | 33426 (56) | −2356 (7) | 504 (10) |
| C(10) | 3868 (54) | 44294 (54) | −90 (8) | 526 (11) |
| C(11) | 9176 (51) | 37043 (52) | 2150 (7) | 485 (10) |
| N(12) | −12557 (87) | 75750 (74) | −5065 (11) | 929 (20) |
| C(13) | −7360 (68) | 60379 (70) | −4925 (9) | 648 (14) |
| C(14) | −1410 (58) | 40899 (65) | −4699 (8) | 570 (12) |
| C(15) | −1544 (65) | 30044 (78) | −6952 (8) | 656 (14) |
| N(16) | −1567 (89) | 21264 (85) | −8792 (9) | 935 (20) |
| N(17) | 75462 (94) | 28371 (100) | 10778 (9) | 1032 (23) |
| C(18) | 74673 (75) | 19457 (80) | 8987 (9) | 699 (15) |
| C(19) | 74058 (54) | 8574 (64) | 6726 (8) | 571 (12) |
| C(20) | 79832 (63) | −11092 (71) | 6939 (10) | 669 (14) |
| N(21) | 83828 (74) | −26700 (70) | 7085 (11) | 882 (18) |
| C(22) | 68456 (50) | 16181 (56) | 4443 (7) | 511 (10) |
| C(23) | 68473 (52) | 5243 (51) | 2169 (8) | 505 (10) |
| C(24) | 63032 (49) | 12582 (53) | −90 (7) | 487 (10) |
| C(25) | 57180 (45) | 31931 (51) | −258 (7) | 454 (9) |
| C(26) | 57000 (51) | 42982 (55) | 2035 (7) | 508 (10) |
| C(27) | 62474 (51) | 35735 (54) | 4241 (7) | 496 (10) |
| N(28) | 40262 (69) | 74326 (55) | −3000 (9) | 732 (14) |
| C(29) | 45117 (62) | 58857 (58) | −2771 (7) | 553 (11) |
| C(30) | 51465 (52) | 39662 (53) | −2548 (7) | 495 (10) |
| C(31) | 50855 (59) | 28765 (61) | −4822 (7) | 543 (11) |
| N(32) | 50294 (75) | 20903 (61) | −6698 (8) | 755 (15) |
| N(33) | 22999 (55) | 47655 (56) | 13585 (7) | 629 (11) |
| C(34) | 9123 (65) | 63668 (63) | 13756 (10) | 696 (14) |
| C(35) | 15198 (94) | 79441 (76) | 12009 (13) | 860 (20) |
| O(36) | 33756 (71) | 85896 (70) | 12682 (10) | 1006 (17) |
| C(37) | 46905 (91) | 71001 (117) | 12375 (15) | 1109 (30) |
| C(38) | 42640 (79) | 55086 (108) | 14140 (12) | 900 (22) |
| C(39) | 16905 (127) | 31122 (99) | 15212 (13) | 996 (26) |

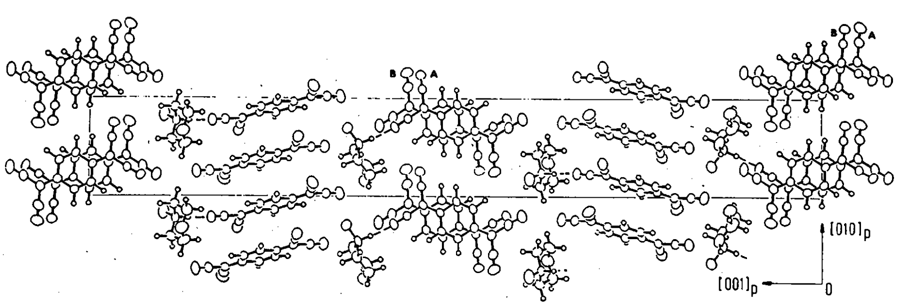

Fig. 2. HMM(TCNQ)₂: projection along [100].

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

| | TCNQ *A* | | | TCNQ *B* | | |
|---|---|---|---|---|---|---|
| *G* | 0·09607 (52) | 0·25477 (55) | 0 (7) | 0·62767 (51) | 0·24111 (55) | 0·02090 (7) |
| **L** | 0·039547 | −0·054646 | 0·016637 | 0·040169 | −0·055014 | 0·016589 |
| **M** | 0·025067 | −0·125215 | −0·008316 | 0·025011 | −0·124954 | −0·008388 |
| **N** | 0·134278 | 0·039469 | −0·003347 | 0·134103 | 0·039784 | −0·003405 |
| *U* | 0·0506 (10) | | | 0·0503 (10) | | |
| Charge (e) | $\rho_A = 0{\cdot}61\ (7)$ | 1·354 (5) | 1·428 (5) | 1·401 (5) | 1·425 (6) | 1·148 (6) |
| | $\rho_B = 0{\cdot}27\ (7)$ | 1·344 (5) | 1·434 (5) | 1·383 (5) | 1·430 (6) | 1·139 (7) |
| Stack | $t^c(A\text{–}B) = 0{\cdot}130$ eV | $\nu(A\text{–}B) = 2{\cdot}057\overline{\mathbf{L}} + 0{\cdot}254\overline{\mathbf{M}} + 3{\cdot}303\overline{\mathbf{N}}$ | | | | |
| | $t^c(B\text{–}A^{\rm i}) = 0{\cdot}141$ eV | $\nu(B\text{–}A^{\rm i}) = -0{\cdot}086\overline{\mathbf{L}} + 0{\cdot}984\overline{\mathbf{M}} + 3{\cdot}332\overline{\mathbf{N}}$ | | | | |

Symmetry code (i) $x + 1, y, z$.

1·00 Å from N). Maximum isotropic extinction correction 23%, in $|F(210)|$. Weight $w = 0$ for $|F_o| < 8\sigma(\text{count};F_o)$, where it should be noted that for the present case $\sigma(\text{count};F_o)$ is considerably smaller than for the intensities measured with Mo $K\overline{\alpha}$ radiation reported in the previous papers. As the weighting scheme $w = [\sigma^2(\text{count};F_o) + E|F_o|^2]^{-1}$ applied to most of the other TCNQ complexes, failed to make $w|\Delta|^2$ reasonably constant as a function of $|F_o|$, the remaining reflections were weighted according to the analytical scheme $w = [0{\cdot}0072 + 0{\cdot}0787|F_o| - 0{\cdot}00024|F_o|^2]^{-1}$. Max. $|\Delta|/\sigma = 0{\cdot}02$, mean = 0·003; $R = 0{\cdot}057$, $wR = 0{\cdot}088$, $S = 1{\cdot}04$, $N_o = 2697$, $N_v = 371$. Residual density close to molecules $\Delta\rho_{\max} = 0{\cdot}24$, $\Delta\rho_{\min} = -0{\cdot}18$ e Å$^{-3}$; remote from molecules $|\Delta\rho_{\max}| = 0{\cdot}17$, $\sigma(\Delta\rho) = 0{\cdot}05$ 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 for the non-H atoms are given in Table 1. The bond lengths and atomic numbering of the non-H skeletons are given in Fig. 1.*

**Discussion.** Crystals of HMM(TCNQ)₂ belong to the enantiomorphic space group $P4_1$ or $P4_3$ (the absolute configuration has not been determined). Fig. 2 illustrates the well known packing of TCNQ sheets around parallel planes with layers of cations between the sheets.

Successive sheets are equivalent, but rotated over 90° around *c* by the symmetry operation of the $4_1$ axis. The two inequivalent TCNQ molecules *A* and *B* along the stack have the same orientation (stack inclination 19·23°). The structure data block given in Table 2 shows that the overlaps in the stack are alternately of type I and type II with approximately equal $t^c$ values. Layers of cations are hydrogen bonded only to neighbouring sheets with lower *z* coordinates. The hydrogen bonds ($\text{N}^+\text{—H}\cdots\text{N} = 1{\cdot}864$ Å; given by dashed lines in Fig. 2) connect the HMM groups to TCNQ molecules of type *A*. This is accompanied by a larger charge on *A* than on *B* [$\rho^s_A - \rho^s_B = 0{\cdot}39\ (11)$ e for $\rho^s_A + \rho^s_B$ normalized to 1; note however that $\sigma(\rho)$ does not account for the rather large differences between bonds within each molecule which are assumed to be related by *mmm* symmetry during the charge calculation].

Comparison of Table 1 with the analogous tables in Parts I–V, reveals that for HMM(TCNQ)₂ the $U_{\rm eq}$ values are relatively large. This indicates the presence of static or dynamic disorder in addition to the usual thermal motion. Broad diffuse rods at $S = \frac{3}{2}a^* + kb^* + \zeta c^*$ on Weissenberg layers $(\frac{3}{2}, \eta, \zeta)$, $\eta$ and $\zeta$ being arbitrary coordinate values, show that the disorder is not random and that there is no, or at best only little, correlation along *c*. This agrees with the fact that the HMM cations between two neighbouring sheets have strong interaction with only one of the sheets. The decrease in the intensity of the diffuse rods with decreasing temperature makes it reasonable to assume that the disorder is dynamic.

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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 52325 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.