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The Structure of the 1:2 Complex 4-Ethylmorpholinium 7,7,8,8-Tetracyanoquinodimethanide, HEM(TCNQ)₂, at 294 K

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Abstract

$C_6H_{14}NO^+ \cdot 2C_{12}H_4N_4^{-1/2}$, HEM(TCNQ)₂, is triclinic, space group $P\bar{1}$, with $a = 14 \cdot 177$ (2), $b = 7 \cdot 558$ (1), $c = 13 \cdot 427$ (2) Å, $\alpha = 92 \cdot 29$ (2), $\beta = 80 \cdot 81$ (1), $\gamma = 105 \cdot 68$ (1)°, $U = 1367$ Å³, $Z = 2$; $d_c = 1 \cdot 275$, $d_m = 1 \cdot 267$ Mg m⁻³. Final $R_w(F) = 0 \cdot 071$ for 5291 independent reflections. The structure consists of sheets of TCNQ molecules parallel to (100), separated by HEM groups. Within the sheet TCNQ molecules, united in tetramers, form columns along **c**. Each tetramer is built up of two dimers related by an inversion centre. The distance between TCNQ molecules within a dimer is $3 \cdot 23$ (1) Å; the intradimer overlap is of the ring–external-bond type. Within a tetramer the separation between the dimers is $3 \cdot 31$ (1) Å, and between successive tetramers $3 \cdot 42$ (1) Å, with overlaps of the shifted ring–ring and ring–external-bond type, respectively. At the HEM positions two randomly disordered molecules are found which differ in orientation. Their main conformational difference is the location of the ethyl CH₃ group with respect to the ring. Owing to Coulomb interaction with the HEM molecules there is a localization of charge on the two symmetrically related inner TCNQ molecules of the tetramers.

Introduction

This paper is one of a series of structural studies of 1:2 complexes of N-substituted morpholinium and TCNQ, carried out to obtain a structural basis for the discussion of the physical properties of these com-

pounds. The compounds investigated so far are MEM(TCNQ)₂ at 113 K (MEM = 4-methyl-4-ethyl-morpholinium; Bosch & van Bodegom, 1977), DEM(TCNQ)₂ at room temperature (DEM = 4,4-diethylmorpholinium; Morssink & van Bodegom, 1981) and DMM(TCNQ)₂ at room temperature (DMM = 4,4-dimethylmorpholinium; Kamminga & van Bodegom, 1981). In the present paper the X-ray study of HEM(TCNQ)₂ at room temperature is described (HEM = 4-ethylmorpholinium). Guinier photographs have shown that HEM(TCNQ)₂ has one phase transition above room temperature ($T_c = 456$ K). Its magnetic behaviour at room temperature shows a strong analogy to that of MEM(TCNQ)₂ below its phase transition at 19 K (Huizinga, 1979).

Experimental work

Dark violet crystals were grown from a mixture of hot solutions of 4-ethylmorpholinium iodide and TCNQ in acetonitrile. Table 1 gives the results of a chemical analysis of the crystals. Room-temperature cell constants were obtained by least squares from the $\sin^2\theta/\lambda^2$ values of 235 reflections obtained from zero-layer

Table 1. *Chemical analysis of HEM(TCNQ)₂*

Calculated (%)			Found (%)		
H	C	N	H	C	N
4·23	68·69	24·03	4·33	68·98	24·06
			4·45	68·92	24·11

Table 2. *Crystal data of HEM(TCNQ)$_2$ at 294 K*

Numbers in parentheses here and elsewhere in this paper (unless stated otherwise) are the e.s.d.'s in the last significant digits.

Triclinic
Space group $P\bar{1}$ (HEM disordered)

$a = 14\cdot177$ (2) Å	$(C_6H_{14}NO).(C_{12}H_4N_4)_2$
$b = 7\cdot558$ (1)	$M_r = 524\cdot6$
$c = 13\cdot427$ (2)	$F(000) = 546$
$\alpha = 92\cdot29$ (2)°	$Z = 2$
$\beta = 80\cdot81$ (1)	μ(Mo $K\bar{\alpha}$) $= 0\cdot09$ mm^{-1}
$\gamma = 105\cdot68$ (1)	$d_c = 1\cdot275$ Mg m^{-3} (294 K)
$U = 1367$ Å^3	$d_m = 1\cdot267$ (294 K)
	(pycnometer)

Weissenberg photographs superimposed with NaCl reflections [λ(Cu $K\alpha_2$) $= 1\cdot54434$, λ(Cu $K\alpha_1$) $= 1\cdot54050$, a(NaCl) $= 5\cdot64006$ Å at 294 K]. Table 2 gives the values obtained. Weissenberg and rotation photographs showed only the symmetry relation $I(hkl) = I(\bar{h}\bar{k}\bar{l})$.

Structure factors

A crystal with regular dimensions, 0·4–0·5 mm, was used for the intensity measurements. Intensities were collected at 294 K on an automatic Nonius CAD-3 diffractometer with Zr-filtered Mo radiation and the θ–2θ method. The intensities were corrected for intensity changes of the primary beam, as deduced from reference reflections measured at regular intervals, and for Lorentz and polarization effects. No correction for absorption [μ(Mo $K\bar{\alpha}$) $= 0\cdot09$ mm^{-1}] was applied. 7973 reflections were measured up to $\theta = 30°$. Those with net negative intensity were given zero weight. Four low-order reflections with diffracted beams close to the beam trap and two reflections with strong variation in the measured background were removed from the list. For the remaining 6650 reflections the weight $w_c = [\sigma_c(F_o)]^{-2}$ was calculated, $\sigma_c(F_o)$ being the standard deviation due to counting statistics and errors in the filter factors.

Determination of the structure

In $P\bar{1}$ the cell contains two independent TCNQ moieties and one independent HEM group. From a Patterson map* the orientation of the TCNQ groups and their location were found. After blocked-matrix isotropic least-squares refinement of the non-hydrogen atoms of the TCNQ units a difference map showed a superposition of two HEM molecules, slightly rotated with respect to each other around a point close to the N

* Unless mentioned otherwise the calculations were done with the XRAY system (1976).

atom and mainly differing in the location of the ethyl CH$_3$ group relative to the HEM ring. Under the assumption of random disorder of the HEM group, a structure refinement in $P\bar{1}$ was carried out. After anisotropic least-squares refinement of the non-hydrogen atoms, a difference map showed peaks for all H atoms at the expected positions. H atoms were constrained at 1·08 Å relative to their respective C atoms; only their isotropic temperature parameters were varied. For the non-hydrogen atoms scattering curves were taken from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965). The refinement accounted for corrections for extinction; the largest reduction in intensity was 24% for the strongest, low-order reflection 104. Blocked-matrix least-squares refinement, with anisotropic temperature parameters for the non-hydrogen atoms, decreased $R = \sum \|F_o| - |F_c\|/\sum |F_o|$ to 0·073 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ to 0·071, for the 5291 reflections with $|F_o| > 2\sigma_c(F_o)$. Weights $w = [\sigma_c^2(F_o) + E|F_o|^2]^{-1}$, with $E = 0\cdot0006$, were used. The goodness-of-fit $G = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2} = 1\cdot63$ with $N_o = 5291$ and N_v (number of variables) $= 471$. During the last cycle parameter shifts were all 0·2σ. Final positional parameters are given in Table 3.*

To check whether a better fit to the observed intensities could be obtained for a non-centro-symmetric structure without disorder, the refinement was repeated in $P1$. Four independent TCNQ units and two independent HEM groups were considered. Refinement with the same reflections, weighting scheme and H constraints gave $R = 0\cdot073$, $R_w = 0\cdot073$ and $G = 1\cdot73$ ($N_v = 767$). Correlation coefficients for the atoms of the TCNQ group ranged from 0·66 to 0·76. From the fact that the refinement indices and the difference map did not improve, in spite of the increased number of variables, we conclude that the structure is adequately described in $P\bar{1}$ under the assumption of random disorder of the HEM group. Disorder of the N-substituted morpholinium group has also been found in DMM(TCNQ)$_2$ and, as indicated by extraordinarily large thermal parameters, in DEM(TCNQ)$_2$.

Description of the structure

Packing

The projections of the structure along [001] and [010] are given in Figs. 1 and 2. It is seen that the TCNQ molecules are located in sheets parallel to (100)

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35541 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Final positional parameters and equivalent isotropic thermal parameters* (Å^2) *for HEM(TCNQ)$_2$, at* 294 K ($\times 10^4$)

H atoms were constrained to their respective C atoms. For numbering of atoms, see Figs. 5 and 6. α and β indicate the two disordered HEM groups.

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

	x	y	z	U_{eq}
N(1)	−1172 (1)	3773 (2)	1965 (2)	721 (7)
C(2)	−1126 (1)	2296 (2)	1852 (1)	473 (6)
C(3)	−1083 (1)	433 (2)	1692 (1)	397 (5)
C(4)	−2016 (1)	−924 (2)	1876 (1)	460 (6)
N(5)	−2764 (1)	−1984 (2)	2026 (1)	704 (7)
C(6)	−198 (1)	−14 (2)	1363 (1)	368 (5)
C(7)	−183 (1)	−1898 (2)	1174 (1)	408 (5)
C(8)	685 (1)	−2320 (2)	841 (1)	415 (5)
C(9)	1611 (1)	−920 (2)	669 (1)	397 (5)
C(10)	1592 (1)	956 (2)	858 (1)	409 (5)
C(11)	728 (1)	1388 (2)	1192 (1)	400 (5)
N(12)	4151 (1)	1182 (3)	48 (2)	814 (8)
C(13)	3422 (1)	43 (3)	170 (2)	555 (7)
C(14)	2501 (1)	−1349 (2)	327 (1)	460 (6)
C(15)	2538 (1)	−3208 (3)	129 (2)	546 (7)
N(16)	2563 (2)	−4690 (3)	−33 (2)	819 (8)
N(17)	−2193 (2)	4011 (3)	4734 (2)	981 (9)
C(18)	−2159 (1)	2519 (3)	4648 (2)	604 (8)
C(19)	−2133 (1)	658 (2)	4533 (1)	465 (6)
C(20)	−3059 (1)	−682 (3)	4767 (1)	538 (7)
N(21)	−3805 (1)	−1760 (3)	4975 (2)	809 (8)
C(22)	−1247 (1)	166 (2)	4178 (1)	407 (5)
C(23)	−1252 (1)	−1709 (2)	3999 (1)	420 (5)
C(24)	−399 (1)	−2192 (2)	3660 (1)	412 (5)
C(25)	538 (1)	−837 (2)	3484 (1)	370 (5)
C(26)	541 (1)	1043 (2)	3667 (1)	406 (5)
C(27)	−317 (1)	1519 (2)	3997 (1)	421 (5)
N(28)	3092 (1)	1113 (2)	2751 (1)	581 (6)
C(29)	2354 (1)	14 (2)	2927 (1)	421 (5)
C(30)	1424 (1)	−1324 (2)	3133 (1)	390 (5)
C(31)	1430 (1)	−3184 (2)	2920 (1)	485 (6)
N(32)	1433 (1)	−4676 (2)	2730 (2)	730 (7)
N(33)α	4877 (11)	4013 (17)	2594 (16)	69 (4)
C(34)α	5101 (5)	5188 (10)	3409 (7)	60 (2)
C(35)α	4265 (5)	6081 (9)	3670 (6)	77 (3)
C(36)α	4062 (6)	6077 (10)	1976 (6)	94 (4)
C(37)α	4943 (13)	4937 (22)	1672 (9)	104 (6)
C(39)α	5750 (3)	3052 (7)	2181 (4)	75 (2)
C(40)α	5772 (15)	1447 (15)	2821 (17)	110 (4)
O(1)α	4234 (3)	7215 (5)	2864 (4)	97 (2)
N(33)β	4972 (10)	4100 (18)	2693 (15)	58 (3)
C(34)β	4774 (6)	5701 (11)	3444 (6)	72 (3)
C(35)β	3934 (5)	6377 (8)	3139 (6)	91 (3)
C(36)β	4207 (6)	5373 (10)	1517 (6)	86 (3)
C(37)β	4975 (11)	4870 (17)	1694 (11)	90 (5)
C(39)β	5773 (3)	3465 (7)	3034 (4)	77 (2)
C(40)β	5781 (15)	1842 (18)	2629 (19)	148 (6)
O(1)β	4126 (8)	6902 (8)	2128 (9)	924 (5)
H(C7)	−867	−2980	1294	
H(C8)	681	−3740	703	
H(C10)	2276	2037	731	
H(C11)	736	2808	1332	
H(C23)	−1944	−2767	4141	
H(C24)	−430	−3620	3513	
H(C26)	1235	2099	3541	
H(C27)	−288	2951	4127	
H(C34)α	5790	6224	3191	
H′(C34)α	5160	4433	4053	

Table 3 (*cont.*)

|	x	y	z
H(C35)α	3578	5007	3783
H′(C35)α	4340	6885	4351
H(C36)α	4079	6965	1360
H′(C36)α	3358	5047	2095
H(C37)α	4858	4050	1023
H′(C37)α	5658	5935	1546
H(C39)α	5627	2380	1470
H′(C39)α	6444	4111	2076
H(C40)α	5079	388	2926
H′(C40)α	5895	2119	3532
H″(C40)α	6371	831	2559
H(N33)α	4114	3210	2763
H(C34)β	5432	6841	3368
H′(C34)β	4580	5241	4220
H(C35)β	3264	5262	3255
H′(C35)β	3826	7536	3596
H(C36)β	4382	5795	735
H′(C36)β	3520	4297	1630
H(C37)β	4975	3667	1232
H′(C37)β	5661	5917	1480
H(C39)β	6484	4436	2812
H′(C39)β	5649	3257	3841
H(C40)β	5905	2050	1822
H′(C40)β	5070	872	2851
H″(C40)β	6354	1295	2833
H(N33)β	4398	2845	2891
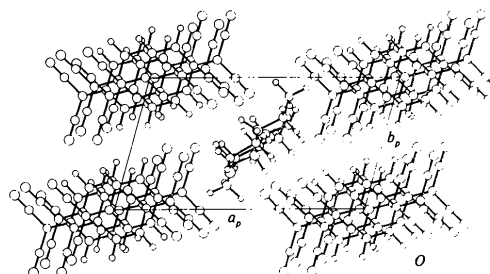
Fig. 1. Projection of the structure of HEM(TCNQ)$_2$ along [001] onto the plane perpendicular to [001]. The HEM group is disordered; only one of the two preferred orientations is shown. a_p, b_p and c_p denote projections of axes.
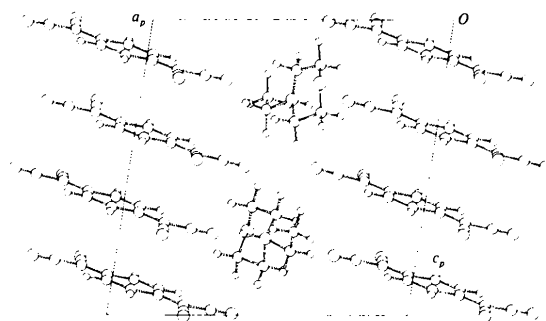

Fig. 2. Projection of the structure of HEM(TCNQ)$_2$ along [010] onto the plane perpendicular to [010]. The HEM group is disordered; only one group is shown.

Table 4. *Short intermolecular distances (Å) in HEM(TCNQ)$_2$ at 294 K*

All distances smaller than the sum of the relevant van der Waals radii (Pauling, 1960) plus 0·2 Å are given. Van der Waals radii $r_C = 1·7, r_N = 1·5, r_O = 1·4, r_H = 1·2$ Å.

(a) TCNQ A to TCNQ A' distances

C(2)–C(8^{ii})	3·569 (3)	C(7)–C(11^{ii})	3·446 (3)
C(3)–C(9^{ii})	3·427 (3)		

(b) TCNQ A to TCNQ B distances

C(2)–C(22^i)	3·529 (3)	C(8)–C(30^i)	3·399 (3)
C(2)–C(27^i)	3·392 (3)	C(8)–C(31^i)	3·286 (3)
C(3)–C(22^i)	3·320 (2)	C(9)–C(29^i)	3·354 (3)
C(3)–C(23^i)	3·497 (3)	C(9)–C(30^i)	3·296 (2)
C(3)–C(27^i)	3·439 (3)	C(9)–C(31^i)	3·473 (3)
C(4)–C(22^i)	3·436 (3)	C(10)–C(29^i)	3·306 (3)
C(4)–C(23^i)	3·335 (3)	C(10)–C(30^i)	3·511 (3)
C(6)–C(24^i)	3·489 (3)	C(11)–C(25^i)	3·504 (3)
C(6)–C(25^i)	3·321 (3)	C(11)–C(26^i)	3·308 (2)
C(6)–C(26^i)	3·420 (3)	C(14)–C(29^i)	3·591 (3)
C(7)–C(24^i)	3·314 (3)		
C(7)–C(25^i)	3·419 (3)		

(c) TCNQ B to TCNQ B' distances

C(18)–C(30^{iii})	3·535 (3)	C(22)–C(25^{iii})	3·424 (2)
C(18)–C(31^{iii})	3·556 (3)	C(22)–C(26^{iii})	3·440 (3)
C(19)–C(29^{iii})	3·420 (3)	C(23)–C(26^{iii})	3·420 (3)
C(19)–C(30^{iii})	3·419 (3)	C(24)–C(27^{iii})	3·435 (3)
C(20)–N(28^{iii})	3·353 (3)	C(25)–C(22^{iii})	3·424 (2)
C(20)–C(29^{iii})	3·381 (3)	C(25)–C(27^{iii})	3·394 (2)

(d) TCNQ A to TCNQ A'' distances

N(1)–C(7^{iv})	3·335 (2)	H(C10)–N(16^{iv})	2·620 (2)
C(10)–N(16^{iv})	3·390 (3)	N(1)–H(C7^{iv})	2·550 (2)

(e) TCNQ B to TCNQ B'' distances

N(17)–C(23^{iv})	3·274 (3)	N(17)–H(C23^{iv})	2·508 (2)
N(32^{iv})–C(26)	3·356 (2)	N(32^{iv})–H(C26)	2·637 (2)

(f) TCNQ A to TCNQ B'' distances

H(C11)–N(32^{iv})	2·722 (2)

(g) TCNQ A to HEM α distances

C(4)–H''(C40)	2·950 (2)	N(5^v)–H'(C39)	2·860 (2)
C(15)–H(C36^{vi})	2·916 (2)	N(5)–H''(C40^{vii})	2·748 (2)
C(15)–H(C39^{viii})	3·036 (2)	N(12)–H(C37^i)	2·537 (2)
N(5^v)–H(C34)	2·475 (2)	N(16)–H'(C39^{viii})	2·868 (2)
N(5^v)–H'(C37)	2·524 (2)		

(h) TCNQ A to HEM β distances

C(36)–N(16^{iv})	3·354 (10)	N(12)–H(C36^{ix})	2·753 (2)
N(5^v)–H(C34)	2·829 (2)	N(12)–H(C37^i)	2·567 (2)
N(5^v)–H'(C37)	2·561 (2)	N(16)–H(C36^{vi})	2·857 (2)
N(5^v)–H(C39)	2·807 (2)	H(C10)–H'(C36^i)	2·525 (2)

(i) TCNQ B to HEM α distances

C(34)–N(21^i)	3·297 (8)	N(21^v)–H(C34)	2·840 (2)
C(35^x)–N(17)	3·334 (8)	N(21^v)–H'(C35)	2·801 (2)
N(28)–N(33^i)	2·849 (12)	N(28)–H(N33^i)	1·837 (2)
N(17)–H(C35^x)	2·792 (2)	N(32)–H'(C36^{vi})	2·787 (2)
N(21)–H'(C34^{iii})	2·605 (2)		

Table 4 (cont.)

(j) TCNQ B to HEM β distances

C(34)–N(21^v)	3·299 (9)	N(21)–H'(C39^{iii})	2·803 (2)
N(28)–N(33^i)	2·983 (12)	N(28)–H(N33^i)	1·989 (2)
C(29)–H(N33^i)	3·097 (2)	N(28)–H'(C36^i)	2·762 (2)
C(18)–H'(C35^x)	3·054 (2)	N(28)–H'(C40^i)	2·883 (2)
N(21^v)–H(C34)	2·624 (2)	N(32)–H(C35^{vi})	2·809 (2)
N(21)–H'(C34^{iii})	2·754 (2)		

(k) HEM α to HEM α' distances

O–H(C40)	2·378 (4)

(l) HEM α to HEM β distances

C(35)–H(C40^{iv})	3·028 (5)	H'(C34)–H'(C34^{xi})	2·399 (1)
O–H'(C40^{iv})	2·696 (4)	H'(C39)–H'(C35^{xi})	2·437 (1)
H'(C35)–H'(C40^{iv})	2·487 (1)	H(C37)–H(C36^{xi})	2·427 (1)

Symmetry code

(i)	x, y, z	(vii)	$x − 1, y, z$
(ii)	$−x, −y, −z$	(viii)	$1 − x, −y, −z$
(iii)	$−x, −y, 1 − z$	(ix)	$1 − x, 1 − y, −z$
(iv)	$x, 1 + y, z$	(x)	$−x, 1 − y, 1 − z$
(v)	$1 + x, 1 + y, z$	(xi)	$1 − x, 1 − y, 1 − z$
(vi)	$x, y − 1, z$		
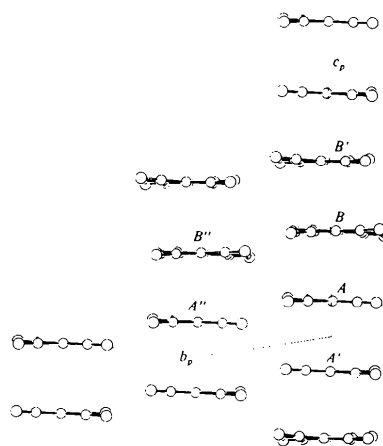
Fig. 3. Normal projection of the sheet of TCNQ molecules in HEM(TCNQ)$_2$ along the longest molecular axis of TCNQ A.

separated by HEM molecules. The HEM groups show random disorder with two preferred orientations of the groups.

The TCNQ sheet

Fig. 3 depicts the stacking of the TCNQ molecules seen along the longest molecular axis of molecule A. Fig. 4 shows the different types of overlap between the TCNQ units; shortest intermolecular distances are given in Table 4. Least-squares planes were calculated for the two TCNQ units, taking only the heavy atoms of the quinodimethane group into account (Table 5). The angle between the normal of the quinodimethane least-squares plane and the c axis is 10·4 (0·5)° for
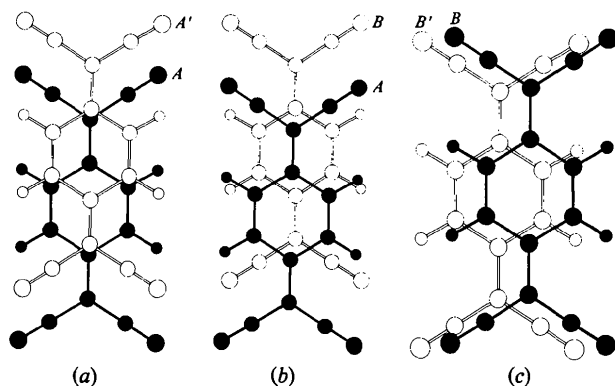
Fig. 4. Projections of two neighbouring TCNQ molecules in HEM(TCNQ)$_2$ along normals to the quinodimethane least-squares planes. (a) Molecules A and A', (b) molecules A and B along the normal to A; (c) molecules B and B' along normal to B.

Table 5. Least-squares planes for the quinodimethane group of the TCNQ units in HEM(TCNQ)$_2$ at 294 K and deviations of atoms from these planes

x, y, z are relative coordinates in the axial system **a**, **b** and **c**. The atoms used to define the planes are equally weighted. Δ = distance to the plane. E.s.d.'s are ≤ 0.01 Å.

Equations of the planes

		$[(\sum \Delta^2)/8]^{1/2}$ (Å)
TCNQ A	C(3); C(6)–C(11); C(14)	
$4.399x - 1.289y + 13.205z = 1.710$		0.005
TCNQ B	C(19); C(22)–C(27); C(30)	
$4.452x - 1.303y + 13.196z = 4.941$		0.004

Deviations of all atoms from the plane (Å $\times 10^2$)

TCNQ A				TCNQ B			
N(1)	−12	C(9)	0	N(17)	−19	C(25)	1
C(2)	−6	C(10)	0	C(18)	−10	C(26)	0
C(3)	−1	C(11)	1	C(19)	1	C(27)	−1
C(4)	0	N(12)	3	C(20)	8	N(28)	−8
N(5)	1	C(13)	2	N(21)	16	C(29)	−3
C(6)	0	C(14)	−1	C(22)	−1	C(30)	0
C(7)	0	C(15)	−1	C(23)	0	C(31)	−4
C(8)	0	N(16)	−2	C(24)	0	N(32)	−10

TCNQ A and 10.7 (0.5)° for TCNQ B (Fig. 3), whereas the angle between the normals is 0.2 (0.5)°. Table 6 lists numerical values for separations between the planes and relative shifts along the molecular axes for molecules in neighbouring planes. As measures for the separation between the not strictly parallel planes of TCNQ A and B, we have taken the dot product **n.v** of the vector **n** connecting the two molecular centres and the vector **v** perpendicular to the respective planes. Values of the shifts of A and B relative to each other have been found by projecting B onto the A plane and calculating the shifts along and perpendicular to the longest molecular axis of A, and also by projecting A on B and calculating the shifts relative to B.

Table 6. Shifts (Å) of TCNQ A' and B relative to TCNQ A, and of TCNQ B' relative to TCNQ B (see Fig. 3) as seen along the normal to the quinodimethane least-squares plane of TCNQ A (B), and distances (Å) between these planes

S ($\perp$) is the shift perpendicular to the longest molecular axis; S (‖) is the shift along this axis. E.s.d.'s are ≤ 0.01 Å.

S ($\perp$)		S (‖)	
$A \cdots A'$	−0.03	$A \cdots A'$	−1.70
$B \cdots B'$	0.86	$B \cdots B'$	0.11
$A \cdots B$	−0.08 (−0.01)*	$A \cdots B$	−2.08 (−2.09)*

Distances between the quinodimethane planes

$D(A \cdots A')$	3.42
$D(B \cdots B')$	3.31
$D(A \cdots B)$*	3.24 (3.23)

* Values defined with respect to the normal of TCNQ A, and in parentheses the value defined relative to the normal of B.

Figs. 3 and 4 show that the TCNQ molecules form columns along **c**. Three crystallographically different overlaps are found along the column; two of these overlaps (between A and A' and between A and B) are of the ring–external-bond type, the third (between B and B') is of the shifted ring–ring type.

In contradistinction to the compounds mentioned in the introduction, in HEM(TCNQ)$_2$ differences in overlap connected with differences in relative shifts depicted in Fig. 4 are very small. The separations between the planes as given by Table 6, $A'\overset{3.42}{\cdots}A\overset{3.23}{\cdots}B\overset{3.31}{\cdots}B'\overset{3.23}{\cdots}A\overset{3.42}{\cdots}A$ (distances in Å), show, however, that in the TCNQ columns tetramers may be distinguished which are made up of two identical dimers. As in the other complexes of the present series, there are short N$\cdots$H distances between successive columns in a sheet. For HEM(TCNQ)$_2$ the four independent short N$\cdots$H distances average to 2.579 (2) Å (Table 4).

Individual TCNQ groups

In Fig. 5 the molecular geometry of the two independent TCNQ units is shown. The equations of the planes through the quinodimethane groups are given in Table 5, which shows that the cyano groups are bent out of the planes and that this bending is more pronounced for TCNQ B than for A. Within experimental accuracy the individual TCNQ molecules satisfy mmm symmetry with respect to their bond lengths. Average values for corresponding bond lengths are given in Table 7, in addition to values obtained for some other TCNQ complexes. Comparison of the average bond lengths for TCNQ A and B (Table 7) in HEM(TCNQ)$_2$ shows that for A the alternation in the lengths of bonds a, b and c is stronger than for B. A

Table 7. *Mean bond lengths* (Å) *for the TCNQ groups in HEM(TCNQ)₂ and some other TCNQ complexes at 294 K*

The labelling is chosen according to Bosch & van Bodegom (1977). Figures in parentheses are the standard deviations of the mean. No libration corrections have been applied.

		a	b	c	d	e	Reference
HEM(TCNQ)₂	A	1·356 (2)	1·439 (1)	1·390 (2)	1·431 (1)	1·141 (2)	(1)
	B	1·362 (2)	1·429 (1)	1·409 (2)	1·422 (1)	1·146 (2)	
	Δ	−0·006	0·010	−0·010	0·009	−0·005	
DEM(TCNQ)₂	A	1·355 (2)	1·435 (2)	1·403 (2)	1·425 (2)	1·148 (2)	(2)
	B	1·358 (2)	1·436 (2)	1·403 (2)	1·430 (2)	1·147 (2)	
	Δ	−0·003	−0·001	0·000	−0·005	0·001	
Cs₂(TCNQ)₃	c*	1·341 (5)	1·444 (4)	1·371 (5)	1·428 (5)	1·140 (4)	(3)
	nc*	1·355 (4)	1·427 (3)	1·410 (4)	1·419 (4)	1·152 (3)	
	Δ	−0·014	0·017	−0·039	0·009	−0·012	
Rb₂(TCNQ)₃	c*	1·340 (9)	1·447 (6)	1·376 (9)	1·439 (9)	1·135 (6)	(4)
	nc*	1·368 (6)	1·430 (4)	1·410 (6)	1·425 (4)	1·142 (4)	
	Δ	−0·028	0·017	−0·034	0·014	−0·007	
(mor)₂(TCNQ)₃	c*	1·348 (3)	1·431 (3)	1·391 (3)	1·426 (3)	1·141 (3)	(5)
	nc*	1·355 (3)	1·419 (3)	1·415 (3)	1·414 (3)	1·145 (3)	
	Δ	−0·007	0·012	−0·024	0·012	−0·004	

References: (1) HEM = 4-ethylmorpholinium, this work; (2) DEM = 4,4-diethylmorpholinium, Morssink & van Bodegom (1981); (3) Fritchie & Arthur (1966); (4) van der Wal & van Bodegom (1978); (5) mor – morpholinium, Sundaresan & Wallwork (1972).
 * c and nc denote a TCNQ group around a centre of symmetry and on a general position respectively.

strong alternation has also been observed in (neutral) TCNQ itself due to its quinoid structure, and in the c-TCNQ's (centrosymmetric) in Cs₂(TCNQ)₃ (Fritchie & Arthur, 1966), Rb₂(TCNQ)₃ (van der Wal & van Bodegom, 1978) and (morpholinium)₂ (TCNQ)₃ (Sundaresan & Wallwork, 1972). For the latter compounds, in which a charge of −1 has been assumed for the nc- (non-centrosymmetric) and a charge of 0 for the c-TCNQ, the difference in alternation between the TCNQ's is stronger than for HEM(TCNQ)₂. The evidence given above and other data from Table 7 indicate that the charge is larger for B than for A. With respect to the charge distribution of $\frac{1}{2} + \delta$ for B and $\frac{1}{2} - \delta$ for A, $0 < \delta < \frac{1}{2}$, HEM(TCNQ)₂ lies in between many of the 1:2 complexes like DEM(TCNQ)₂ for which $\delta = 0$ and the 2:3 complexes like Rb₂(TCNQ)₃ in which $\delta = \frac{1}{2}$ (in this case units with charge $\frac{1}{2} - \delta$ and $\frac{1}{2} + \delta$ occur in the ratio 1:2). As discussed in the literature (*e.g.* Hoekstra, Spoelder & Vos, 1972) the present data show again that the length of bond c, especially, increases with increasing charge, whereas that of b decreases. Flandrois & Chasseau (1977) have used the changes in bond length to calculate charges for TCNQ moieties. For HEM(TCNQ)₂ their method gives a charge of 0·30 e for A and 0·63 e for B. The relatively large charge on TCNQ B may be ascribed to the relatively high electrostatic potential at B in comparison with that at A. From Table 4 we see that the positive N atom of the HEM molecule, N(33)α or N(33)β, lies closer to TCNQ B than to TCNQ A. The distance between N(33)α [N(33)β] and N(28) of TCNQ B is especially small, 2·85 (1) [2·98 (1)] Å.

Small distances between the positive HEM N atom and TCNQ N atoms are favoured by electrostatic interaction, as TCNQ N atoms are known to be slightly negatively charged (Hoekstra, Spoelder & Vos, 1972).

The HEM group

The rings of the two disordered HEM groups have the chair conformation as found for the rings in the N-substituted morpholinium complexes with TCNQ studied before (Kamminga & van Bodegom, 1981, and references therein). Owing to the large correlation between the two disordered groups the molecular geometry could not be determined accurately. In Fig. 6, which shows the bond lengths and angles, the least-squares e.s.d.'s have been omitted as these strongly underestimate the errors in the molecular geometry.

Discussion

In contradistinction to MEM(TCNQ)₂ at 113 K and to DEM(TCNQ)₂ and DMM(TCNQ)₂ at room temperature, which all contain TCNQ dimers, the TCNQ stacks in HEM(TCNQ)₂ at room temperature have a tetrameric character. A tetramerization is also expected for MEM(TCNQ)₂ below 19 K from the strong drop in its magnetic susceptibility at 19 K and from the doubling of the unit cell along the stack direction observed below 19 K (van Bodegom, Larson & Mook, 1981). The similarity between HEM(TCNQ)₂ at room temperature and MEM(TCNQ)₂ below 19 K is in
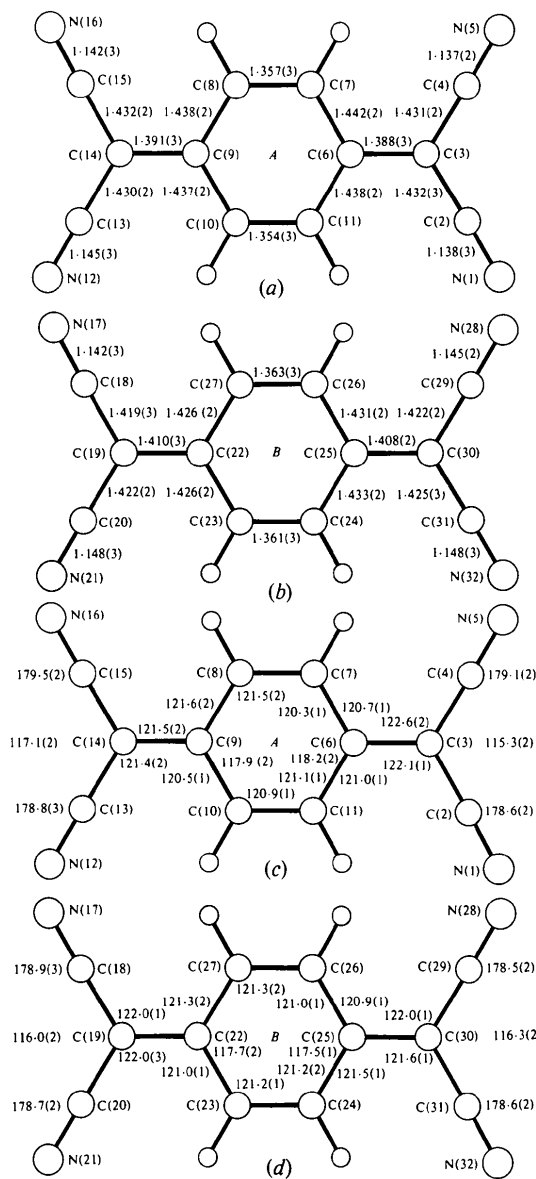
Fig. 5. Molecular geometry of the TCNQ units in HEM(TCNQ)₂.
Values for bond lengths (Å) and angles (°) are not corrected for
libration effects. Bond lengths: (a) molecule A, (b) molecule B.
Bond angles: (c) molecule A, (d) molecule B.

Fig. 6. Molecular geometry for the HEM molecule (disordered) in
HEM(TCNQ)₂. Bond lengths in Å, bond angles in °. (a) HEMα.
(b) HEM β. The angle C(37)—N(33)—C(39) is 95 and 128° for
α and β respectively.

accordance with the analogy between their magnetic
properties at these temperatures. This similarity in
physical behaviour does not, however, answer the
question why in HEM(TCNQ)₂ the stacks have tetra-
meric character at relatively high temperatures. We
have tentatively assumed that in HEM(TCNQ)₂ the
stack character is influenced strongly by the short
$N^+(HEM)—H\cdots N^{-\delta}[TCNQ,N(28)]$ distance of ap-
proximately 2·9 Å. A definite answer requires further
physical measurements and theoretical calculations.

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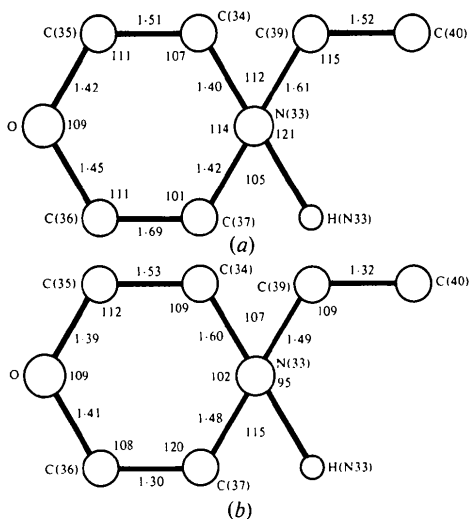interest, Dr G. A. Wiegers of the Department of

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