

### V. Conclusion

Nous avons étudié par diffraction de rayons X, à température et à concentration variable, les solutions solides  $\text{Cr}_{1-x}\text{V}_x\text{N}$ . Pour  $x < \frac{1}{3}$ , chacun des composés se déforme au-dessous d'une certaine température  $T_D(x)$  que nous avons pu déterminer. La déformation, brutale dans CrN pur, s'étale sur plusieurs dizaines de K dans les solutions solides sans atteindre tout l'échantillon, même aux températures les plus basses. La fraction déformée de l'échantillon  $p(x, T)$  appartient au groupe d'espace  $Pnmm$ .

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## The Crystal Structure of the 1:2 Complex of *N*-Methyl-*N*-ethylmorpholinium and 7,7,8,8-Tetracyanoquinodimethane, MEM(TCNQ)<sub>2</sub>, at $-160^\circ\text{C}$

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Crystals of MEM(TCNQ)<sub>2</sub> are triclinic, space group  $P1$ ,  $a = 7.824$  (5),  $b = 15.426$  (16),  $c = 6.896$  (5) Å,  $\alpha = 113.59$  (8),  $\beta = 73.27$  (7),  $\gamma = 112.71$  (8)°,  $Z = 1$ . The intensities were collected at  $-160^\circ\text{C}$ . Refinement decreased  $R$  to 0.075 for 4163 independent counter reflexions. The structure consists of TCNQ columns united to form sheets parallel to (010) with MEM ions placed in the holes between the sheets. Within a column interplanar spacings of 3.15 and 3.27 Å alternate, and for successive spacings the overlap between the TCNQ moieties is different, thus giving rise to dimers in the stack. The overlap within the dimer is of the ring-external bond type. The dimerization requires a reconsideration of the electronic and magnetic properties measured earlier.

### Introduction

The TCNQ salts constitute a class of organic solids which are of special interest because of their pseudo one-dimensional nature, reflected in their electronic and magnetic properties, as well as in the phonon spectrum. The magnetic properties are largely determined by the intra-site electron repulsion  $U$  and the inter-site transfer integral  $t$ , the ratio  $U/4t$  determining whether electron-electron repulsion is important in the model.  $U$  is mainly determined by the properties of the TCNQ ion, but  $t$  is critically dependent on the crystal packing.

The physical properties of MEM(TCNQ)<sub>2</sub> were explored by Kuindersma, Sawatzky, Kommandeur & Schinkel (1975) who determined and endeavoured to

explain the magnetic susceptibility of MEM(TCNQ)<sub>2</sub> as a function of temperature. To simplify their problem they implicitly assumed the crystal to contain regular columns of TCNQ ions. It was therefore of interest to determine the crystal structure of MEM(TCNQ)<sub>2</sub>.

### Experimental work

Violet crystals with a metallic lustre were grown from a mixture of hot solutions of TCNQ and morpholinium iodide in acetonitrile. Some were twinned by a rotation of  $180^\circ$  around the needle ( $c$ ) axis. Table 1 shows the results of a chemical analysis of the crystals. Room-temperature cell constants were calculated by a least-

Table 1. *Chemical analysis of MEM(TCNQ)<sub>2</sub>*

Calculated (%)			Found (%)		
C	H	N	C	H	N
69.13	4.49	23.41	69.04	4.48	23.49
			68.81	4.50	23.42

Table 2. *Crystal data of MEM(TCNQ)<sub>2</sub>*

Numbers in parentheses here and elsewhere in this paper are the estimated standard deviations in the last significant digits.

Triclinic Space group <i>P</i> 1	(C <sub>7</sub> H <sub>16</sub> NO)(C <sub>12</sub> H <sub>4</sub> N <sub>4</sub> ) <sub>2</sub> FW 538.6	
	21 °C	-160 °C
<i>a</i> (Å)	7.797 (2)	7.824 (5)
<i>b</i> (Å)	15.312 (19)	15.426 (16)
<i>c</i> (Å)	6.989 (3)	6.896 (5)
$\alpha$ (°)	112.42 (9)	113.59 (8)
$\beta$ (°)	74.38 (6)	73.27 (7)
$\gamma$ (°)	111.82 (8)	112.71 (8)
<i>U</i> (Å <sup>3</sup> )	708.1	694.8
<i>F</i> (000) = 281	<i>d</i> <sub>c</sub> = 1.261 g cm <sup>-3</sup> (21 °C)	
<i>Z</i> = 1	<i>d</i> <sub>m</sub> = 1.254 (21 °C)	
$\mu$ (Mo <i>K</i> $\alpha$ ) = 0.9 cm <sup>-1</sup>	(pycnometer)	
$\lambda$ (Mo <i>K</i> $\alpha$ ) = 0.71069 Å		

squares program from the  $\sin^2 \theta/\lambda^2$  values of 22 reflexions measured on a four-circle automatic Nonius diffractometer. Low-temperature cell constants were calculated from 34 reflexions measured on a three-circle automatic Nonius diffractometer, the crystal being cooled to -160 °C (van Bolhuis, 1971). Table 2 gives the values obtained. Rotation and Weissenberg photographs showed only the symmetry relation  $I(hkl) = I(\bar{h}\bar{k}\bar{l})$ . From the possible space groups, *P*1 and  $P\bar{1}$ , we excluded the latter on the basis of the phonon-echo phenomena found in MEM(TCNQ)<sub>2</sub> by Kuindersma, Huizinga, Kommandeur & Sawatzky (1976), since these phenomena occur only in piezoelectric materials.

### Structure factors

A regular crystal, 0.4–0.6 mm, was used for the intensity measurements, aligned along *c*. We collected the intensities on a three-circle automatic Nonius diffractometer with Zr-filtered Mo radiation, by the  $\theta$ - $2\theta$  scan method with a counter aperture of 1.9 mm and a scan range of  $(0.85 + 0.50 \tan \theta)^\circ$ . Individual scan speeds were determined by a rapid scan through each Bragg reflexion, and the rate of scanning varied from 10/2 to 10/12 ° min<sup>-1</sup>. We measured the reflexions for one half of reciprocal space up to  $\theta = 34^\circ$ , collecting 5279 reflexions of which 4239 had a net  $I > 0$ . To avoid deviations from linearity of the scintillation counting equipment we used attenuation filters; every 20 reflexions the reference reflexion 053 was measured

so that we could correct for changes in the intensity of the primary beam and possible deterioration of the crystal. The reflexions were also corrected for Lorentz and polarization effects. Corrections for absorption were not made ( $\mu = 0.9 \text{ cm}^{-1}$ ). Reflexions with a net negative intensity were given zero weight. For the remaining reflexions the weight  $w_c$  was calculated from  $w_c = [\sigma_c(F)]^{-2}$ ,  $\sigma_c(F)$  being the standard deviation in  $|F|$  due to counting statistics and errors in the filter factors.

### Determination of the structure

The TCNQ coordinates were found from a Patterson map and refined by the least-squares technique.\* To avoid difficulties due to correlation between the TCNQ moieties by the pseudo inversion centre, we did this refinement in space group  $P\bar{1}$ . Blocked-matrix, isotropic least-squares refinement with 2639 reflexions with  $|F_o| \geq 3\sigma_c(F_o)$  and unit weights decreased  $R = |\Sigma|F_o| - |F_c||/\Sigma|F_o|$  to 0.38. Scattering curves according to Cromer & Mann (1968) were used. An electron density map with the  $|F_o|$ 's as amplitudes and signs derived from the known atomic parameters confirmed the positions of the TCNQ units and showed all the non-hydrogen atoms of the MEM group, as well as their inverted positions. Further refinement with the 2639 reflexions and population parameters 0.5 for the two MEM groups gave  $R = 0.16$ . At this stage we attributed half of the MEM positions to a MEM molecule and adopted the space group *P*1. In the further refinement five blocks were used; TCNQ atoms related by the pseudo-inversion centre were placed in the same block to account for possible correlation effects:  $R = 0.089$ .

Difference syntheses parallel to (001) revealed all the H atoms; sections through the planes of the H atoms of the methyl and ethyl groups showed no indication of disorder. From the maxima in the difference map and geometrical considerations, including C–H = 1.08 Å, the positions of the H atoms were found. During the refinement H atoms were constrained relative to their respective C atoms; only their isotropic temperature parameters were refined.

Refinement with anisotropic temperature parameters for the non-hydrogen atoms gave  $R = 0.061$ , and  $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.075$ ; 4163 reflexions with  $|F_o| \geq 3\sigma(F_o)$  and weights  $w = [\sigma_c(F_o) + E|F_o|^2]^{-1}$  were used;  $E = 0.007$  was chosen such as to make variations in  $\langle w(|F_o| - |F_c|)^2 \rangle$  with  $|F_o|$  and  $\sin^2 \theta/\lambda^2$  as small as possible. The goodness-of-fit  $G = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2} = 4.40$  with  $N_o = 4163$  and  $N_v$  (number of variables) = 395. During the last cycle parameter shifts were all less than 0.8 $\sigma$ .

\* Unless mentioned otherwise, the programs used for the calculations are from the XRAY system (1973) set of programs.

Table 3. Final positional parameters ( $\times 10^4$ )

The positions of the hydrogen atoms were not refined. For numbering of the atoms, see Figs. 5 and 6.

	x	y	z	$U_{iso}$
N(1)	3115 (4)	4325 (2)	3652 (4)	
C(2)	3338 (4)	3583 (2)	3399 (4)	
C(3)	3596 (4)	2663 (2)	3101 (4)	
C(4)	5444 (4)	2693 (2)	3132 (5)	
N(5)	6918 (4)	2702 (2)	3161 (6)	
C(6)	2101 (4)	1782 (2)	2868 (4)	
C(7)	2355 (4)	867 (2)	2655 (4)	
C(8)	885 (4)	16 (2)	2448 (4)	
C(9)	-971 (4)	9 (2)	2468 (4)	
C(10)	-1230 (4)	925 (2)	2714 (4)	
C(11)	240 (4)	1777 (2)	2896 (4)	
N(12)	-5811 (4)	-838 (2)	2387 (5)	
C(13)	-4337 (4)	-864 (2)	2314 (5)	
C(14)	-2484 (4)	-872 (2)	2244 (4)	
C(15)	-2240 (4)	-1787 (2)	2015 (4)	
N(16)	-2016 (4)	-2517 (2)	1838 (4)	
N(17)	-3093 (4)	-4302 (2)	-3564 (5)	
C(18)	-3328 (4)	-3573 (2)	-3400 (5)	
C(19)	-3578 (4)	-2663 (2)	-3197 (4)	
C(20)	-5401 (4)	-2698 (2)	-3368 (5)	
N(21)	-6877 (4)	-2745 (2)	-3520 (5)	
C(22)	-2096 (4)	-1782 (2)	-2889 (4)	
C(23)	-2359 (4)	-863 (2)	-2667 (4)	
C(24)	-888 (4)	-8 (2)	-2447 (4)	
C(25)	956 (4)	-15 (2)	-2440 (4)	
C(26)	1212 (4)	-932 (2)	-2651 (4)	
C(27)	-258 (4)	-1777 (2)	-2855 (4)	
N(28)	5836 (4)	896 (2)	-2322 (5)	
C(29)	4325 (4)	876 (2)	-2281 (5)	
C(30)	2452 (4)	851 (2)	-2226 (4)	
C(31)	2238 (4)	1777 (2)	-1988 (5)	
N(32)	2080 (4)	2528 (2)	-1793 (5)	
N(33)	481 (3)	4923 (2)	33 (4)	
C(34)	2523 (4)	4933 (2)	-470 (4)	
C(35)	3721 (4)	5881 (2)	930 (5)	
C(36)	1748 (4)	6784 (2)	1274 (6)	
C(37)	426 (4)	5874 (2)	-94 (5)	
C(38)	-387 (5)	4809 (3)	2192 (5)	
C(39)	-545 (4)	4029 (2)	-1678 (5)	
C(40)	-2625 (4)	3887 (3)	-1425 (6)	
O	3625 (3)	6728 (2)	642 (4)	
H(C7)	3730	859	2654	179 (79)
H(C8)	1107	-663	2271	206 (83)
H(C10)	-2613	932	2748	337 (103)
H(C11)	19	2455	3064	373 (112)
H(C23)	-3732	-858	-2678	405 (113)
H(C24)	-1093	674	-2277	244 (90)
H(C26)	2586	-940	-2649	317 (99)
H(C27)	-51	-2453	-2987	194 (83)
H(C34)	2593	4302	-216	429 (111)
H'(C34)	3055	4882	-2129	349 (102)
H(C35)	5159	5878	528	248 (85)
H'(C35)	3216	5925	2587	538 (129)
H(C36)	1731	7448	1109	469 (17)
H'(C36)	1282	6822	2931	440 (114)
H(C37)	850	5861	-1738	515 (120)
H'(C37)	-989	5915	447	550 (131)
H(C38)	346	5405	3449	536 (127)
H'(C38)	-1829	4799	2527	416 (110)
H''(C38)	-432	4107	2228	656 (143)
H(C39)	127	4118	-3220	556 (135)
H'(C39)	-409	3366	-1634	644 (143)
H(C40)	-2785	4517	-1598	531 (119)
H'(C40)	-3274	3214	-2623	610 (136)
H''(C40)	-3329	3844	146	1460 (295)

Final positional parameters are given in Table 3.\* For numbering of atoms see Figs. 5 and 6.

At positions remote from the atoms the final difference map showed maxima and minima varying from 0.28 to  $-0.26 \text{ e } \text{Å}^{-3}$ . Higher maxima, up to  $0.52 \text{ e } \text{Å}^{-3}$ , were found on most of the TCNQ bonds.

### Thermal motion

A TLS rigid-body motion analysis has been made for the two quinodimethane groups of the TCNQ ions and the MEM ring, taking only heavy atoms into account, with the program *TMA* (Shmueli, 1972). The results are given in Table 4. The r.m.s. discrepancy  $K = [\Sigma (U_o - U_c)^2 / (6N_a - 20)]^{1/2}$  with  $N_a =$  number of atoms is 0.0017, 0.0016, and  $0.0010 \text{ Å}^2$  for quinoid *A* ( $z = 0.27$ ), *B* ( $z = -0.27$ ) and the MEM ring respectively, which values are within twice the mean estimated standard deviations ( $0.0011 \text{ Å}^2$ ) of the anisotropic thermal parameters. Values for *K* taking all heavy atoms of the molecules into account are 0.0021, 0.0024 and  $0.0016 \text{ Å}^2$  respectively, showing that the molecules as a whole are to be regarded as less rigid.

As can be expected from the pseudo-symmetry *mmm* of the quinoid group (Fig. 5) the inertial axes coincide with the pseudo twofold axes of the group. The smallest moment of inertia (inertial axis I) corresponds to the direction C(14)–C(9)···C(6)–C(3) in the TCNQ plane; the largest inertial axis (III) is perpendicular to this plane. Table 4 shows that the librational axes coincide with the inertial axes. The largest libration with  $(\varphi^2)^{1/2} = 3.1^\circ$  is found around (I); for (II) and (III)  $(\varphi^2)^{1/2} = 1.0^\circ$ . A decrease of librational motion with increasing inertial moment has also been found for TCNQ groups in other structures. The translational motions of the quinoid groups and the MEM ring are approximately isotropic (Table 4), the mean eigenvalue for the translation tensor *T* being  $0.13 \text{ Å}^2$ . The screw tensor *S* is approximately zero for the two quinoid groups as is expected from the presence of the pseudo inversion centre in the molecule.

The bond lengths, both uncorrected and corrected for libration, are given in Table 5.

### Description of the structure

#### Packing

The projections of the structure on planes perpendicular to [001] and [100] are given in Figs. 1 and 2. It is seen that the structure contains TCNQ columns along *c*. Table 6 shows that short N···H distances exist

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32606 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *The rigid-body motion for the quinoid groups and the MEM ring in MEM(TCNQ)<sub>2</sub>, at -160 °C*

All values are multiplied by 10<sup>5</sup>, except those for  $T_e^{1/2}$ ,  $L_e^{1/2}$  and  $I$ . An orthogonal system of unit axis is chosen as:  
 $x \parallel [210]$ ,  $y \parallel c^*$ ,  $z = x \times y$ .

(a) Centre of mass referred to the crystal axes

	TCNQ-A (C <sub>8</sub> )	TCNQ-B (C <sub>8</sub> )	MEM (C <sub>4</sub> NO)
$x$	5616	-5700	21251
$y$	8956	-8985	58749
$z$	26741	-26712	3900

(b) Eigenvectors (**L**, **M** and **N**) and eigenvalues ( $I$ ) of the tensor of inertia referred to the above mentioned orthogonal system  $x, y, z$ 

	TCNQ-A (C <sub>8</sub> )			TCNQ-B (C <sub>8</sub> )			MEM (C <sub>4</sub> NO)		
	<b>L</b>	<b>M</b>	<b>N</b>	<b>L</b>	<b>M</b>	<b>N</b>	<b>L</b>	<b>M</b>	<b>N</b>
$x$	99314	7661	8831	99209	7290	10221	96381	4399	26294
$y$	9324	-6327	-99363	10587	-4828	-99321	26608	-9754	-95900
$z$	-7054	99505	-6998	-6747	-99617	-5562	-1653	99426	-10572
$I$ (at. wt Å <sup>2</sup> )	74.0	260.7	334.7	75.0	257.4	332.3	74.6	89.9	156.0

(c) Eigenvectors and eigenvalues of the translation (**T**) and libration (**L<sub>b</sub>**) tensors referred to the inertial system  $L, M, N$ 

	TCNQ-A (C <sub>8</sub> )			TCNQ-B (C <sub>8</sub> )			MEM (C <sub>4</sub> NO)		
	<b>1</b>	<b>2</b>	<b>3</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>1</b>	<b>2</b>	<b>3</b>
<b>L<sub>b</sub></b>									
$L$	98389	17667	2768	-97875	-16482	-12201	94859	31607	1655
$M$	-17778	98306	4467	-18031	40832	89485	31638	-94548	-7730
$N$	-1930	-4888	99862	-9767	89784	-42936	-879	7856	-99687
$L_e$ (rad <sup>2</sup> )	299	57	15	196	52	32	1443	602	105
$L_e^{1/2}$ (°)	3.13	1.37	0.70	2.54	1.31	1.02	6.88	4.45	1.86
<b>T</b>									
$L$	55079	78192	29195	40183	90533	13751	28329	95903	336
$M$	-79406	38317	47186	-84690	31030	43183	85376	-25060	-45639
$N$	25709	-49172	83194	34828	-28997	89141	-43686	13216	-88977
$T_e$ (Å <sup>2</sup> )	2209	1529	1217	2138	1670	1230	2507	1787	995
$T_e^{1/2}$ (Å)	0.15	0.12	0.11	0.15	0.13	0.11	0.16	0.13	0.10

Table 5. *Bond lengths before and after libration correction (Å)*

TCNQ-A	TCNQ-B		TCNQ-B	MEM	
	Uncorrected	Corrected		Uncorrected	Corrected
C(8)–C(7)	1.359 (4)	1.360	C(24)–C(23)	1.362 (4)	1.363
C(11)–C(10)	1.361 (4)	1.361	C(27)–C(26)	1.354 (4)	1.355
C(9)–C(8)	1.444 (5)	1.446	C(25)–C(24)	1.448 (5)	1.450
C(7)–C(6)	1.444 (5)	1.446	C(23)–C(22)	1.451 (5)	1.453
C(6)–C(11)	1.448 (5)	1.450	C(22)–C(27)	1.442 (5)	1.444
C(9)–C(10)	1.441 (5)	1.442	C(25)–C(26)	1.449 (5)	1.451
C(9)–C(14)	1.402 (4)	1.403	C(25)–C(30)	1.382 (5)	1.383
C(6)–C(3)	1.396 (4)	1.396	C(22)–C(19)	1.389 (5)	1.390
C(14)–C(15)	1.437 (5)	1.439	C(30)–C(31)	1.441 (5)	1.443
C(14)–C(13)	1.442 (5)	1.444	C(30)–C(29)	1.441 (5)	1.442
C(3)–C(4)	1.434 (5)	1.436	C(19)–N(20)	1.443 (5)	1.444
C(3)–C(2)	1.436 (5)	1.438	C(19)–C(18)	1.439 (5)	1.440
C(15)–N(16)	1.159 (5)	1.160	C(31)–N(32)	1.162 (5)	1.163
C(4)–N(5)	1.154 (5)	1.156	C(20)–N(21)	1.161 (5)	1.162
C(2)–N(1)	1.161 (5)	1.162	C(18)–N(17)	1.166 (5)	1.167
C(13)–N(12)	1.155 (5)	1.157	C(29)–N(28)	1.163 (5)	1.164
MEM					
	Uncorrected	Corrected		Uncorrected	Corrected
C(34)–C(35)	1.511 (4)	1.518	N(33)–C(34)	1.529 (4)	1.538
C(36)–C(37)	1.520 (4)	1.527	N(33)–C(37)	1.523 (5)	1.534
C(36)–O	1.433 (4)	1.442	N(33)–C(38)	1.498 (5)	1.513
C(35)–O	1.429 (5)	1.440	N(33)–C(39)	1.525 (4)	1.553
C(39)–C(40)	1.523 (5)	1.531			

between successive TCNQ columns in the [100] direction. Four distances with an average value of 2.76 Å are approximately equal to the sum of the van der Waals radii [ $r(\text{N}) = 1.5$ ,  $r(\text{H}) = 1.1$  Å; Pauling

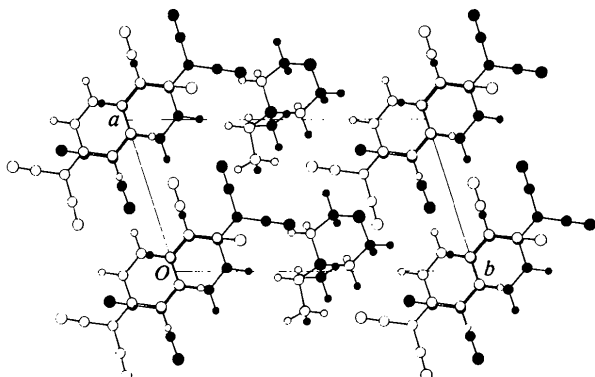


Fig. 1. Projection of the structure on the plane perpendicular to [001].

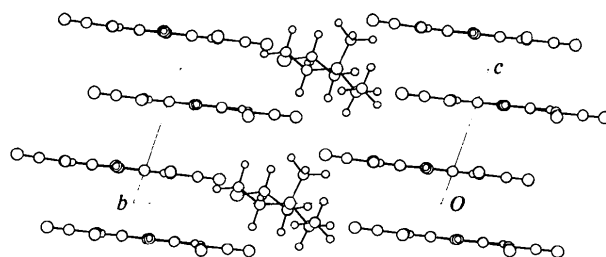


Fig. 2. Projection of the structure on the plane perpendicular to [100].

(1960)], whereas four others, averaging to 2.57 Å, are slightly shorter than this sum. We assume that the short distances are indicative of a Coulomb attraction between N and H atoms of successive columns. As has been pointed out by several authors (*e.g.* Hoekstra, Spoelder & Vos, 1972) the N atoms of TCNQ units bear a small negative charge, and it seems reasonable to assume that the H atoms attached to the conjugated

Table 6. Short intermolecular distances (Å)

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:  $r_{\text{C}} = 1.7$ ,  $r_{\text{N}} = 1.5$ ,  $r_{\text{O}} = 1.4$ ,  $r_{\text{H}} = 1.2$  Å.

(a) Molecule A to molecule B distances

C(3)—C(31)	3.535 (6)	C(7)—C(30)	3.335 (5)	C(9)—C(26)	3.438 (3)	C(13)—C(23)	3.337 (4)
C(6)—C(29)	3.455 (6)	C(8)—C(25)	3.337 (5)	C(10)—C(24)	3.234 (4)	C(14)—C(22)	3.213 (4)
C(6)—C(30)	3.192 (4)	C(8)—C(26)	3.197 (4)	C(10)—C(25)	3.456 (5)	C(14)—C(23)	3.365 (5)
C(6)—C(31)	3.316 (5)	C(9)—C(23)	3.577 (5)	C(11)—C(30)	3.444 (4)	C(14)—C(27)	3.430 (5)
C(7)—C(25)	3.554 (5)	C(9)—C(24)	3.361 (5)	C(11)—C(31)	3.280 (4)	C(15)—C(22)	3.355 (5)
C(7)—C(29)	3.311 (4)	C(9)—C(25)	3.276 (4)	C(13)—C(22)	3.490 (5)	C(15)—C(27)	3.272 (4)

(b) Molecule A to molecule B' distances

C(6)—C(31 <sup>vii</sup> )	3.583 (6)	C(7)—C(31 <sup>vii</sup> )	3.374 (4)	C(9)—C(24 <sup>vii</sup> )	3.537 (5)	C(15)—C(23 <sup>vii</sup> )	3.349 (4)
C(6)—N(32 <sup>vii</sup> )	3.387 (4)	C(8)—C(24 <sup>vii</sup> )	3.402 (4)	C(14)—C(23 <sup>vii</sup> )	3.533 (5)	N(16)—C(19 <sup>vii</sup> )	3.356 (4)
C(7)—C(30 <sup>vii</sup> )	3.563 (5)	C(8)—C(25 <sup>vii</sup> )	3.561 (5)	C(15)—C(22 <sup>vii</sup> )	3.545 (5)	N(16)—C(22 <sup>vii</sup> )	3.337 (4)

(c) Interchain distances

H(C7)—N(12 <sup>iv</sup> )	2.706 (4)	H(C26)—N(21 <sup>iv</sup> )	2.776 (4)	N(5)—H(C10 <sup>iv</sup> )	2.786 (4)	N(28)—H(C23 <sup>iv</sup> )	2.761 (4)
H(C8)—N(12 <sup>iv</sup> )	2.555 (4)	H(C27)—N(21 <sup>iv</sup> )	2.590 (3)	N(5)—H(C11 <sup>iv</sup> )	2.575 (4)	N(28)—H(C24 <sup>iv</sup> )	2.565 (4)

(d) MEM—TCNQ distances

N(1)—H(C34)	2.796 (4)	N(21 <sup>ii</sup> )—H(C37)	2.658 (3)	C(36)—N(16 <sup>vi</sup> )	3.382 (6)
N(1)—H'(C34 <sup>vii</sup> )	2.676 (3)	N(32)—H(C34)	2.420 (3)	C(37)—N(16 <sup>vi</sup> )	3.336 (6)
N(1)—H'(C35)	2.811 (4)	N(32)—H'(C39)	2.681 (4)	C(38 <sup>iv</sup> )—N(5)	3.331 (5)
N(1)—H(C39 <sup>vii</sup> )	2.700 (3)	O—C(13 <sup>ii</sup> )	3.275 (3)	C(38)—N(17)	3.223 (4)
N(5)—H''(C38 <sup>iv</sup> )	2.508 (3)	O—C(18 <sup>ii</sup> )	3.109 (3)	C(2)—H(C34 <sup>vii</sup> )	2.929 (3)
N(5)—H'(C40 <sup>iii</sup> )	2.664 (4)	O—C(19 <sup>ii</sup> )	3.123 (4)	C(2)—H(C39 <sup>vii</sup> )	3.019 (3)
N(12)—H(C36)	2.579 (2)	O—C(20 <sup>ii</sup> )	3.040 (5)	C(2)—H''(C40 <sup>iv</sup> )	2.923 (3)
N(16 <sup>ii</sup> )—H(C35)	2.639 (2)	C(35)—C(18 <sup>ii</sup> )	3.391 (4)	C(4)—H''(40 <sup>iv</sup> )	2.965 (4)
N(17 <sup>ii</sup> )—H'(C34)	2.829 (3)	C(36)—C(20 <sup>ii</sup> )	3.524 (5)	C(4)—H'(40 <sup>iii</sup> )	3.067 (4)
N(17 <sup>ii</sup> )—H(C35)	2.712 (3)	C(34)—N(32)	3.347 (6)	C(18 <sup>ii</sup> )—H'(C34)	3.082 (3)
N(17 <sup>iv</sup> )—H'(C38)	2.588 (3)	C(35)—N(16 <sup>ii</sup> )	3.350 (4)	C(18 <sup>ii</sup> )—H(C35)	2.945 (3)
N(17 <sup>vi</sup> )—H(C40)	2.778 (4)	C(35)—N(17 <sup>ii</sup> )	3.361 (4)	C(20 <sup>iv</sup> )—H'(C35)	2.947 (3)
N(21 <sup>i</sup> )—H'(C35)	2.649 (3)	C(36)—N(12 <sup>ii</sup> )	3.297 (4)	C(27 <sup>v</sup> )—H'(C36)	3.088 (3)

Symmetry code

(i)	$x + 1, y + 1, z + 1$	(iv)	$x + 1, y, z$	(vi)	$x, y + 1, z$
(ii)	$x + 1, y + 1, z$	(v)	$x, y + 1, z + 1$	(vii)	$x, y, z + 1$
(iii)	$x + 1, y, z + 1$				

TCNQ system have a small positive charge. According to Table 6 no short distances are present between successive MEM groups. The structure can thus be described as consisting of TCNQ columns united to form sheets parallel to (010) with MEM molecules placed in holes between the sheets.

#### The TCNQ columns

Fig. 3 gives a schematic drawing of the stacking of the TCNQ units in a column, as seen along the largest molecular axis. The planes of the molecules are approximately parallel to (001), with the centres of the coordinate centroids at  $z = 0.27$  (molecule *A*) and  $z = -0.27$  (molecule *B*). Perpendicular distances of 3.15 and 3.27 Å, between the best least-squares planes of the quinodimethane groups, alternate along the column. Fig. 4(a) and (b) show the projections of (*B*) (at  $-0.27$ ) and (*B'*) (at 0.73), respectively, on (*A*). The figure shows that the planes of (*B*) and (*B'*) are shifted in different ways relative to that of (*A*). The plane of (*B*) is shifted by 0.12 Å perpendicular to the largest molecular axis and by 1.97 Å along this axis. For (*B'*)

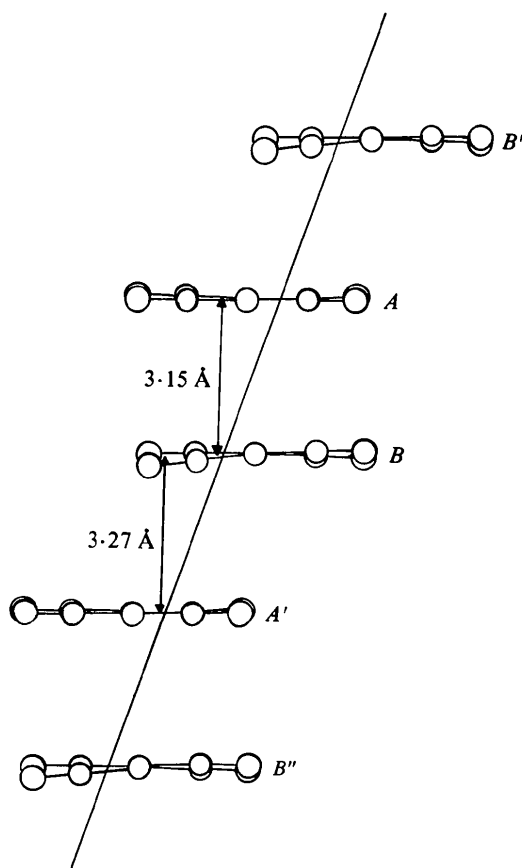


Fig. 3. Molecules seen along the average direction of the longest axes.

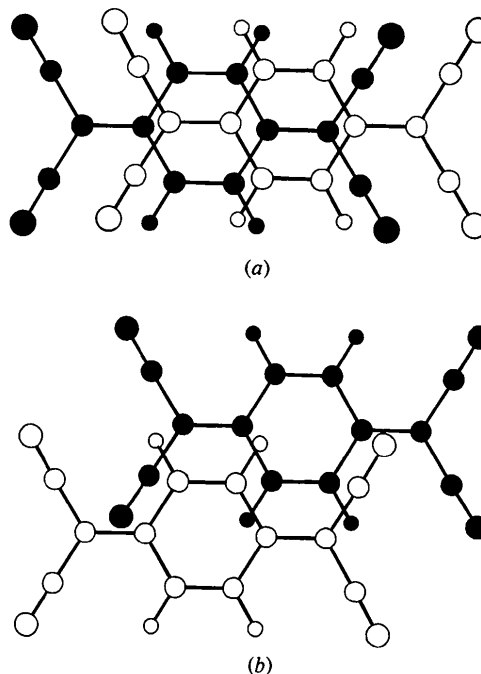


Fig. 4. (a) Projection of molecule *B* on the least-squares plane of the quinoid group of (*A*). (b) Projection of molecule *B'* on the least-squares plane of the quinoid group of (*A*).

these shifts are 2.57 and 2.21 Å respectively. From Fig. 4 and Table 6, where the short distances between successive TCNQ molecules in a column are listed, we see that the overlap between (*A*) and (*B*) is considerably larger than between (*A*) and (*B'*), thus indicating the presence of (*A*)–(*B*) dimers in the stack. This dimerization can also be seen from Fig. 3 and from Fig. 2. The overlap between (*A*) and (*B*) is of the ring-external bond type and has been observed in many other TCNQ compounds.

#### Individual TCNQ groups within a column

In Fig. 5 the molecular geometries of the two independent TCNQ units are shown. Within the standard deviations the individual TCNQ units satisfy *mmm* symmetry with respect to their bond lengths; average values for corresponding bond lengths are given in Table 7.

These values reveal no significant differences between (*A*) and (*B*), with the exception of bond *c* for which the difference is possibly significant. Hoekstra, Spoelder & Vos (1972) noticed that bond *c* has a relatively large increase in length with increasing charge. It is therefore noteworthy that in this study it is bond *c* for which the possibly significant difference has been found, as this may indicate that the charge on (*A*) is slightly larger than on (*B*). Comparison of the mean values of corresponding bond lengths of our study with those for  $\text{TCNQ}^{1/2-}$  (Ashwell, Wallwork, Baker &

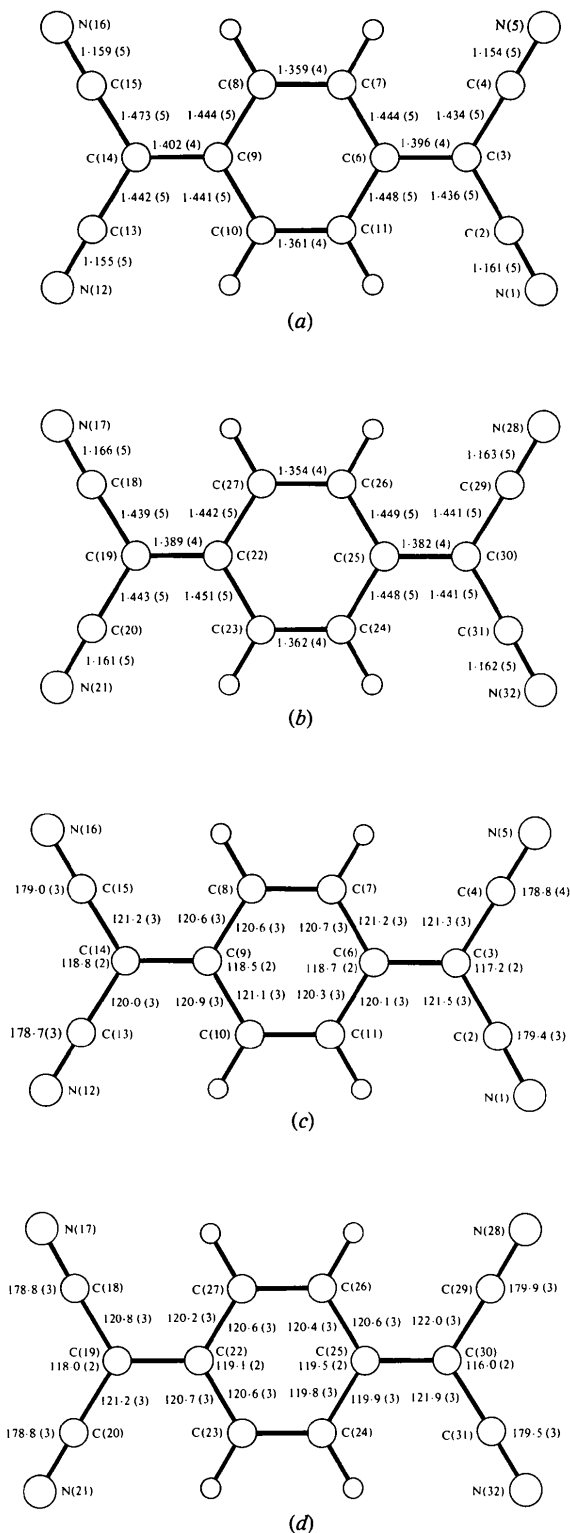


Fig. 5. Molecular geometry of the TCNQ units in MEM(TCNQ)<sub>2</sub>, at  $-160^{\circ}\text{C}$ . Values for bond lengths ( $\text{\AA}$ ) are not corrected for libration effects. Bond lengths: (a) molecule A, (b) molecule B. Bond angles: (c) molecule A, (d) molecule B.

Berthier, 1975) (Table 7) shows that the values given there tend to be shorter. We have attributed this to the difference in temperature of the measurements.

Least-squares planes were calculated for the two TCNQ units with the eight heavy atoms of the quinodimethane groups. Results are given in Table 8. The TCNQ units are not planar. Fig. 3 shows that both molecules have a slight boat form which resembles the situation found in Rb-TCNQ-I (Hoekstra, Spoelder & Vos, 1972; Fig. 6). The angles the normals to the planes make with  $c$  are  $20.5$  and  $21.3^{\circ}$  for (A) and (B) respectively. The distances between the least-squares planes of the quinodimethane groups are  $3.15$  and  $3.27$   $\text{\AA}$ . Values for these distances for least-squares planes calculated with all heavy atoms of the TCNQ units are  $3.20$  and  $3.21$   $\text{\AA}$ . The angle between the normals to the planes (A) and (B) is  $1.15^{\circ}$  with eight atoms per TCNQ unit and  $1.81^{\circ}$  with all the heavy atoms.

### The MEM group

Bond lengths and angles are given in Table 5 and Fig. 6. The ring is in the chair conformation, which has also been found in the morpholinium groups in MOR(TCNQ) (Sundaresan & Wallwork, 1972), in tris(morpholinocarbodithioato) complexes (Butcher & Sinn, 1976) and morpholine biguanide hydrobromide (Handa & Saha, 1973).

In the following discussion the bond lengths are uncorrected for thermal motion. The angles around N(33) point to a somewhat distorted tetrahedral geometry. The lengths of the two C-O bonds, mean  $1.431$  (3)  $\text{\AA}$ , may be compared with the C-O lengths in dioxane [ $1.423$  (3)  $\text{\AA}$ , Davis & Hassel, 1963]. The two ring C-C lengths, mean  $1.516$  (3)  $\text{\AA}$ , tend to be slightly shorter than the bonds, determined by electron diffraction, in cyclohexane [ $1.528$  (5)  $\text{\AA}$ , Davis & Hassel, 1963]. The C-CH<sub>3</sub> length is equal to the C-CH<sub>3</sub> lengths in 2,5-dimethylhexane-2,5-diol [mean  $1.524$  (2)  $\text{\AA}$ ; Helmholdt, 1975]. The N-CH<sub>3</sub> bond,  $1.498$  (5)  $\text{\AA}$ , is shorter than the N-CH<sub>2</sub> bonds, mean  $1.526$  (2)  $\text{\AA}$ . This phenomenon also occurs in the hydrocarbons where the bond lengths tend to increase

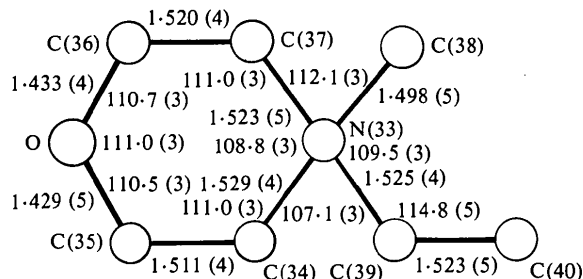
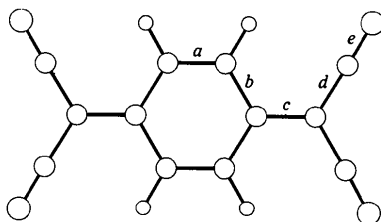


Fig. 6. Molecular geometry of MEM in MEM(TCNQ)<sub>2</sub>, at  $-160^{\circ}\text{C}$ . Values for bond lengths ( $\text{\AA}$ ) are not corrected for libration effects. The angles C(37)-N(33)-C(39) and C(38)-N(33)-C(34) are  $109.5$  (3) and  $109.8$  (3) $^{\circ}$  respectively.

Table 7. Mean bond lengths of the TCNQ molecules in MEM(TCNQ)<sub>2</sub>, at -160 °C

The labelling system is illustrated below. Figures in parentheses are standard deviations of the mean. No libration corrections have been applied.



	a	b	c	d	e
*TCNQ <sup>1/2-</sup>	1.355	1.433	1.396	1.424	1.145
Molecule A	1.360 (3)	1.444 (3)	1.399 (3)	1.437 (3)	1.157 (3)
Molecule B	1.358 (3)	1.448 (3)	1.386 (3)	1.441 (3)	1.163 (3)

\* Ashwell, Waliwork, Baker & Berthier (1975).

Table 8. Least-squares planes for the quinodimethane groups of the TCNQ units and deviations of atoms from these planes (Å)

In the equations of the planes  $x$ ,  $y$  and  $z$  are relative coordinates referring to the axes  $a$ ,  $b$  and  $c$ . The atoms used to define the planes are equally weighted.

(a) Equations of the planes	R.m.s. deviation from the plane (Å)		$\chi^2$				
TCNQ-A: $0.06358x - 1.64765y + 6.45982z = 1.58344$	0.007		26				
TCNQ-B: $0.09050x - 1.57879y + 6.42543z = 1.56933$	0.017		177				
(b) Deviations of the atoms from the plane for TCNQ-A (Å × 10 <sup>3</sup> )							
N(1)	83	N(5)	58	C(9)	3	C(13)	26
C(2)	43	C(6)	-11	C(10)	9	C(14)	-6
C(3)	4	C(7)	4	C(11)	-4	C(15)	-1
C(4)	31	C(8)	1	N(12)	60	N(16)	6
(c) Deviations of the atoms from the plane for TCNQ-B (Å × 10 <sup>3</sup> )							
N(17)	-13	N(21)	-197	C(25)	-4	C(29)	-73
C(18)	-21	C(22)	13	C(26)	2	C(30)	-17
C(19)	-32	C(23)	14	C(27)	18	C(31)	-9
C(20)	-120	C(24)	7	N(28)	-117	N(32)	-1

with the number of C atoms attached to the bond considered, *viz* 1.545 Å in diamond (Sutton, 1958) and 1.525 (2) Å for isobutane (Lide, 1960). A tentative explanation is that the non-bonded N...C (or C...C) repulsions across the bond are stronger than the N...H (or C...H) repulsions.

The N-C bonds of the quaternary ammonium group in MEM are longer than 1.472 (8) Å, observed for the N-C lengths in trimethylamine (Lide & Mann, 1958).

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## Crystallographic Studies of Addition Compounds of Hexafluorobenzene. Crystal Structure of the 1:1 Adduct with *N,N*-Dimethylaniline

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The 1:1 addition compound between *N,N*-dimethylaniline and hexafluorobenzene crystallizes at room temperature in a monoclinic cell. A lattice with space group  $I2/m$  and  $a = 6.927$  (1),  $b = 14.833$  (2),  $c = 7.071$  (1) Å,  $\beta = 103.67$  (1)° was chosen rather than a Bravais lattice with space group  $C2/m$ . The structure was refined to  $R = 0.060$  for 280 counter data. The structure is disordered with the *N,N*-dimethylaniline molecule in two different orientations. The partner molecules are stacked alternately in infinite columns, and the mean separation between the molecular planes is 3.52 Å. The benzene rings of the partner molecules overlap in a way which is often found in charge-transfer complexes.

### Introduction

The structures of the addition compounds between hexafluorobenzene (HFB) and the symmetrically methylated benzenes *p*-xylene, mesitylene, durene and hexamethylbenzene have been reported (Dahl, 1975 and references therein). In all these compounds the molecules are stacked alternately in infinite columns. With regard to interplanar distances (Table 1) and overlap (Fig. 1) a clear trend is observed: The *p*-xylene and mesitylene compounds have the largest interplanar

distances, and overlap with the benzene rings twisted 30° relative to each other. Further increase in the number of methyl groups gradually shortens the interplanar distance and alters the relative orientation of the benzene rings towards parallelism.

No charge-transfer bands have been observed in spectra of addition compounds between HFB and aromatic hydrocarbons in solution (Beaumont & Davis, 1967; Swinton, 1974). However, a short interplanar distance and an overlap like that of the hexamethylbenzene compound may be considered as typical features of charge-transfer complexes. As methyl groups are known to increase the donor strength of an aromatic hydrocarbon (Herbstein, 1971), the observed trend has been interpreted as being due to charge-transfer forces in the compounds with more than three methyl groups (Dahl, 1975).

As distinct from the compounds mentioned above, addition compounds between HFB and aromatic amines in solution show charge-transfer bands (Beau-

Table 1. Mean interplanar distance in addition compounds between HFB and methylated benzenes

	Temperature (°C)	Distance (Å)
<i>p</i> -Xylene–HFB	20	3.55
Mesitylene–HFB	–35	3.56
Durene–HFB	20	3.51
Hexamethylbenzene–HFB	–40	3.43