

acceptor sites (Fig. 3 and Table 5). While on one side the carboxy O atom is shielded from intermolecular interactions by the crown ether ring, it is involved in relatively short contacts in the opposite direction. Relevant nonbonding distances include: $O(11)\cdots C(5) = 2.936(2)$ and $O(11)\cdots O(4) = 3.098(2)$ within the asymmetric unit, and $O(11)\cdots C(2) = 3.327(2)$ and $O(11)\cdots C(3) = 3.361(2)$ Å between neighboring molecules. It appears that the observed least-energy conformation of the crown ether is well accommodated by inter- as well as intramolecular van der Waals interactions.

The present structure provides a rare example of a non-rigid macrocyclic species whose geometry in the crystal is characterized by a very high organization. Moreover, it suggests that crown ether ligands which are known for their remarkable ability to form complexes with various molecules and ions, may also be useful in hosting and enhancing interactions between other functional moieties.

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The Structure of the 1 : 2 Complex 4,4-Diethylmorpholinium 7,7,8,8-Tetracycanoquinodimethanide, DEM(TCNQ)₂, at 294 K

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Abstract

$C_8H_{18}NO^+ \cdot 2C_{12}H_4N_4^{-1/2}$, DEM(TCNQ)₂, is triclinic, space group $P\bar{1}$, with $a = 7.902(4)$, $b = 28.134(6)$, $c = 7.514(3)$ Å, $\alpha = 91.26(2)$, $\beta = 118.47(4)$, $\gamma = 93.67(2)^\circ$, $U = 1462$ Å³, $Z = 2$; $d_c = 1.255$, $d_m = 1.253$ Mg m⁻³. Final $R_w(F) = 0.077$ for 5460 independent reflections. The structure consists of two

types of TCNQ sheets, *A* and *B*, parallel to (010) with DEM molecules placed between these sheets. In the sheets of type *A*, TCNQ molecules united into dimers form a two-dimensional array. The intradimer separation is 3.41(1) Å; the perpendicular interdimer separation is 3.19(1) Å for units along [101] and [001]. The intradimer overlap is of the shifted ring–ring type. In the type *B* sheets, TCNQ units form dimerized

columns along *c*, with alternating interplanar spacings of 3.14 (1) and 3.36 (1) Å. The overlap in this dimer is of the ring-external-bond type. The presence of more than one preferred orientation of the DEM molecule cannot be excluded, but it is certain that subsidiary orientations, when present, have only a small occupancy.

Introduction

In an earlier paper (Bosch & van Bodegom, 1977) the structure of MEM(TCNQ)₂ at 113 K has been described (MEM = 4-methyl-4-ethylmorpholinium). In this (triclinic) structure dimerized stacks of TCNQ units occur along *c*. An exploration of the magnetic properties of MEM(TCNQ)₂ and DEM(TCNQ)₂ by Kuindersma, Sawatzky, Kommandeur & Schinkel (1975) showed that the electron-spin susceptibility of the two compounds as a function of temperature ($4 < T < 300$ K) is only roughly analogous. Also, in other respects the compounds are different. Temperature-dependent Guinier photographs of DEM(TCNQ)₂, taken in vacuum by Dr G. A. Wieggers (Department of Inorganic Chemistry, Rijksuniversiteit Groningen), revealed the presence of two reversible high-temperature phase transitions, at 415 and 483 K. For MEM(TCNQ)₂ only one reversible high-temperature phase transition was found, at 340 K, from Weissenberg and Guinier photographs and from measurements of its electrical conductivity and its ESR and NMR spectra (Morrow *et al.*, 1980; Sawatzky, Huizinga & Kommandeur, 1978; Huizinga, Kommandeur, Sawatzky, Thole, Kopinga, de Jonge & Roos, 1979). In addition to this high-temperature phase transition which has been assumed to be of first order, MEM(TCNQ)₂ has a second-order phase transition at low temperature (19 K). For DEM(TCNQ)₂ it is not clear yet whether the phase transition shown by the decrease in the magnetic susceptibility around 20 K is of second or first order. Preliminary X-ray diffraction Weissenberg and rotation photographs revealed that the structures of the two compounds are not isomorphous, the (triclinic) unit cell of the DEM compound being twice as large as that of the MEM complex. From the cell dimensions it was deduced that in DEM(TCNQ)₂ alternating sheets of TCNQ columns are not related to each other by translation. A complete structure determination was necessary, however, to determine whether or not the sheets are crystallographically different. As the answer to this question is of vital importance for the interpretation of the physical properties, the X-ray study described in the present paper was undertaken.

Experimental work

Dark violet crystals were grown from a mixture of hot solutions of TCNQ and 4,4-diethylmorpholinium io-

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

Calculated (%)			Found (%)		
H	C	N	H	C	N
4.74	69.55	22.81	4.81	69.74	22.75
			4.84	69.76	22.81

Table 2. *Crystal data of DEM(TCNQ)₂ at 294 K*

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

Triclinic	(C ₈ H ₁₈ NO)·(C ₁₂ H ₄ N ₄) ₂
Space group $P\bar{1}$	$M_r = 552.6$
$a = 7.902$ (4) Å	$F(000) = 578$
$b = 28.134$ (6)	$Z = 2$
$c = 7.514$ (3)	$\mu(\text{Mo } K\bar{\alpha}) = 0.09 \text{ mm}^{-1}$
$\alpha = 91.26$ (2)°	$\lambda(\text{Mo } K\bar{\alpha}) = 0.71069$ Å
$\beta = 118.47$ (4)	$d_c = 1.255 \text{ Mg m}^{-3}$ (294 K)
$\gamma = 93.67$ (2)	$d_m = 1.253$ (294 K)
$U = 1462$ Å ³	(pycnometer)

dide in acetonitrile. Table 1 shows the results of a chemical analysis of the crystals. The room-temperature cell constants, listed in Table 2, were obtained by least squares from the $\sin^2 \theta / \lambda^2$ values of 445 reflections obtained from zero-layer-line Weissenberg photographs superimposed with NaCl reflections [$\lambda(\text{Cu } K\alpha_2) = 1.54434$, $\lambda(\text{Cu } K\alpha_1) = 1.54050$, $a(\text{NaCl}) = 5.64006$ Å at 294 K]. Weissenberg and rotation photographs showed only the symmetry relation $I(hkl) = I(h\bar{k}l)$. In contradiction to MEM(TCNQ)₂ (Kuindersma, Huizinga, Kommandeur & Sawatzky, 1976) no phonon-echo phenomena were found. Therefore the space group $P\bar{1}$ was adopted for the structure determination.

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 a three-circle automatic Nonius CAD-3 diffractometer with Zr-filtered Mo radiation. With the ω -scan method, a counter aperture of $0.80 + 1.80 \tan \theta$ mm and a scan range of $(0.68 + 0.86 \times \tan \theta)^\circ$, 8428 independent reflections were measured up to $\theta = 30^\circ$. 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 [$\mu(\text{Mo } K\bar{\alpha}) = 0.09 \text{ mm}^{-1}$] was applied. Reflections with a net negative intensity were given zero weight. For the remaining 5873 reflections the weight $w_c = [\sigma_c(F_o)]^{-2}$ was calculated, $\sigma_c(F_o)$ being the standard deviation in $|F_o|$ due to counting statistics and errors in the filter factors.

Table 3. Final positional parameters and equivalent isotropic thermal parameters (\AA^2) for DEM(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.

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

	x	y	z	U_{eq}
N(1)	-1940 (3)	4150 (1)	7471 (4)	666 (7)
C(2)	-491 (3)	4153 (1)	7460 (3)	474 (7)
C(3)	1305 (3)	4159 (1)	7436 (3)	424 (6)
C(4)	1934 (3)	3704 (1)	7251 (4)	522 (7)
N(5)	2438 (3)	3340 (1)	7089 (4)	774 (8)
C(6)	2343 (3)	4586 (1)	7490 (3)	379 (5)
C(7)	4154 (3)	4583 (1)	7492 (3)	414 (6)
C(8)	5147 (3)	4997 (1)	7504 (3)	408 (6)
C(9)	4416 (3)	5450 (1)	7510 (3)	389 (6)
C(10)	2598 (3)	5450 (1)	7514 (3)	415 (6)
C(11)	1614 (3)	5040 (1)	7511 (3)	416 (6)
N(12)	4108 (4)	6688 (1)	7385 (4)	761 (9)
C(13)	4722 (3)	6327 (1)	7440 (4)	508 (7)
C(14)	5438 (3)	5874 (1)	7477 (3)	420 (6)
C(15)	7191 (3)	5862 (1)	7385 (3)	460 (7)
N(16)	8583 (3)	5834 (1)	7273 (3)	642 (7)
N(17)	4645 (3)	996 (1)	7934 (3)	676 (7)
C(18)	3172 (4)	996 (1)	6509 (4)	492 (7)
C(19)	1322 (3)	994 (1)	4727 (3)	447 (6)
C(20)	451 (4)	1437 (1)	4369 (4)	552 (7)
N(21)	-228 (4)	1795 (1)	4092 (4)	831 (9)
C(22)	459 (3)	584 (1)	3436 (3)	401 (6)
C(23)	-1386 (3)	585 (1)	1659 (3)	423 (6)
C(24)	-2238 (3)	183 (1)	431 (3)	421 (6)
C(25)	-1323 (3)	-255 (1)	880 (3)	385 (6)
C(26)	532 (3)	-257 (1)	2662 (3)	412 (6)
C(27)	1376 (3)	145 (1)	3881 (3)	416 (6)
N(28)	-704 (4)	-1474 (1)	497 (4)	774 (8)
C(29)	-1372 (3)	-1115 (1)	101 (4)	498 (7)
C(30)	-2217 (3)	-672(1)	-377 (3)	418 (6)
C(31)	-4059 (4)	-684 (1)	-2145 (4)	483 (7)
N(32)	-5536 (3)	-699 (1)	-3583 (4)	725 (8)
N(33)	-2887 (3)	2553 (1)	-2070 (3)	544 (6)
C(34)	-1043 (4)	2533 (1)	-2221 (4)	663 (10)
C(35)	729 (4)	2679 (1)	-278 (4)	838 (12)
C(36)	-1003 (4)	3145 (2)	786 (5)	1125 (17)
C(37)	-2817 (4)	3036 (1)	-1122 (5)	875 (13)
C(38)	-4666 (4)	2501 (2)	-4227 (5)	939 (13)
C(39)	-3038 (3)	2151 (1)	-820 (3)	484 (7)
C(40)	-4775 (4)	2154 (1)	-475 (5)	732 (10)
C(41)	-4907 (5)	2029 (2)	-5391 (5)	1147 (17)
O	646 (3)	3143 (1)	444 (5)	1260 (11)
H(C7)	4718	4242	7474	
H(C8)	6544	5000	7549	
H(C10)	2123	5799	7617	
H(C11)	260	5042	7557	
H(C23)	-1948	933	1308	
H(C24)	-3567	197	-987	
H(C26)	1335	-571	2976	
H(C27)	2851	137	5097	
H(C34)	-886	2187	-2765	
H'(C34)	-1261	2763	-3437	
H(C35)	2096	2674	-296	
H'(C35)	954	2487	1042	
H(C36)	-1194	3517	988	
H'(C36)	-556	2930	2092	
H(C37)	-4018	3060	-810	
H'(C37)	-3114	3221	-2478	
H(C38)	-4510	2789	-5090	

Table 3 (cont.)

	x	y	z
H'(C38)	-5964	2537	-4093
H(C39)	-2998	1833	-1634
H'(C39)	-1646	2167	547
H(C40)	-4651	2502	243
H'(C40)	-4752	1896	585
H''(C40)	-6026	2095	-1969
H(C41)	-3679	2002	-5656
H'(C41)	-6337	1954	-6687
H''(C41)	-4973	1796	-4291

Determination of the structure

In $P\bar{1}$ the cell contains two independent TCNQ moieties and one independent DEM group. In TCNQ structures the packing of the planar TCNQ groups at distances of ca 3.3 Å from each other often gives rise to characteristic intensity variations in the reflections of different order against the planes parallel to the TCNQ groups. For DEM(TCNQ)₂ two characteristic sets, the reflections 00l and $hh\bar{h}$, turned out to be present. In Patterson sections parallel to (001) and (11 $\bar{1}$) the TCNQ vector diagram was easily recognized, indicating that the structure contains two different TCNQ arrays with different orientations. In $P1$ this can be realized only if each of the arrays contains an inversion centre. From the cell dimensions and consideration of the structural features of other TCNQ compounds, it was concluded that the respective arrays of TCNQ molecules are $\frac{1}{2}\mathbf{b}$ apart. For each of the arrays the location of the TCNQ groups relative to the inversion centre was found by trial and error, with the use of high Patterson peaks which were assumed to correspond with the distances between the parallel TCNQ units. A difference synthesis calculated after isotropic least-squares refinement* of the non-hydrogen atoms of the TCNQ groups showed all non-hydrogen atoms of the DEM molecule. After refinement of the positions and anisotropic temperature parameters of all heavy atoms, peaks for all H atoms were found on their calculated positions in a subsequent difference map. H atoms were constrained at 1.08 Å relative to their respective C atoms; only their isotropic temperature parameters were varied. The refinement accounted for small corrections for extinction; the largest reduction in intensity was calculated at 3.2% for the reflection 22 $\bar{2}$. Reflections with $|F_o| < 2\sigma_c(F_o)$ and 116 weak reflections with $|\sqrt{w} \Delta F| \geq 6$ were excluded from the final cycles. Blocked-matrix least-squares refinement with anisotropic temperature parameters for the non-hydrogen atoms gave $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.072$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.077$ for the 5460 reflections considered. The weighting

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

scheme $w = [\sigma_c^2(F_o) + E|F_o|^2]^{-1}$ with $E = 0.0004$. The goodness-of-fit $G = [\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2} = 2.34$ with $N_o = 5460$ and N_v (number of variables) = 407. During the last cycle parameter shifts were all $< 0.3\sigma$. Final positional parameters are given in Table 3.* For the non-hydrogen atoms scattering curves were taken from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965).

Description of the structure

Packing

Projections of the structure along [001] and [100] are given in Figs. 1 and 2. The TCNQ molecules are located in sheets parallel to (010), sheet *A* around $y = 0.5$ and sheet *B* around $y = 0$, separated by DEM molecules. The TCNQ units of sheet *A* are parallel to (001) and those of sheet *B* parallel to (111) in good approximation.

The TCNQ sheets

Fig. 3 shows a drawing of the stacking of the TCNQ groups in sheets *A* and *B* seen along the longest molecular axes of the units. For each sheet the types of

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35539 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

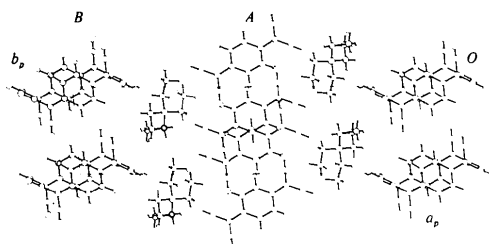


Fig. 1. Projection of the structure of DEM(TCNQ)₂ along [001] onto the plane perpendicular to [001]. a_p , b_p and c_p denote projections of axes.

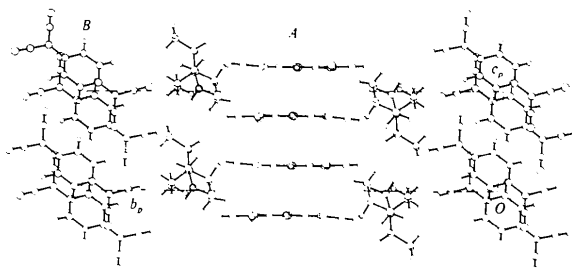


Fig. 2. Projection of the structure of DEM(TCNQ)₂ along [100] onto the plane perpendicular to [100].

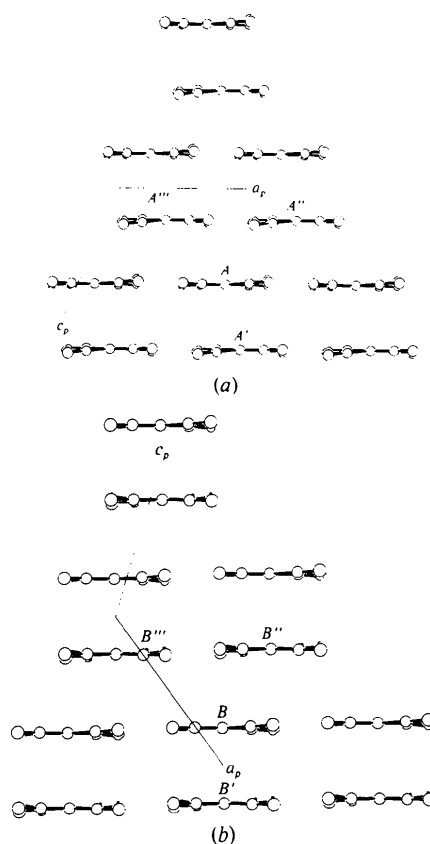


Fig. 3. Normal projection of the sheets of TCNQ molecules in DEM(TCNQ)₂ along the longest molecular axes. (a) Sheet *A*; (b) sheet *B*.

overlap between the units are given in Fig. 4. Table 4 gives short intermolecular distances and Table 5 numerical values for the relative shifts of the molecules parallel to the plane of the quinodimethane group, along and perpendicular to the longest molecular axis.

From Fig. 3(a), Figs. 4(a)–(c) and Table 5 it is seen that molecules *A* and *A'* show a strong overlap of the shifted ring–ring type. The overlaps between *A* and *A''* and between *A* and *A'''* are smaller, but they are not much different from each other. This implies that sheet *A* does not contain one preferred stacking direction of the TCNQ dimers, but has to be considered as a two-dimensional array of TCNQ dimers. For sheet *B* the situation is different. Fig. 3(b), Figs. 4(d)–(f) and Table 5 show that there are again TCNQ dimers, *B*–*B'*, with an overlap of the ring–external-bond type. The overlap between *B* and *B'''* is much smaller, however, than between *B* and *B''*, so that for sheet *B* a preferred stacking direction can be recognized. Sheet *B* thus contains dimerized TCNQ stacks, along *c*, of similar type to that observed in MEM(TCNQ)₂ at 113 K. Both the successive molecules of type *A*, such as *A''* and *A'''*, and *B*, such as *B''* and *B'''*, show electrostatic interaction *via* short N...H distances (Table 4).

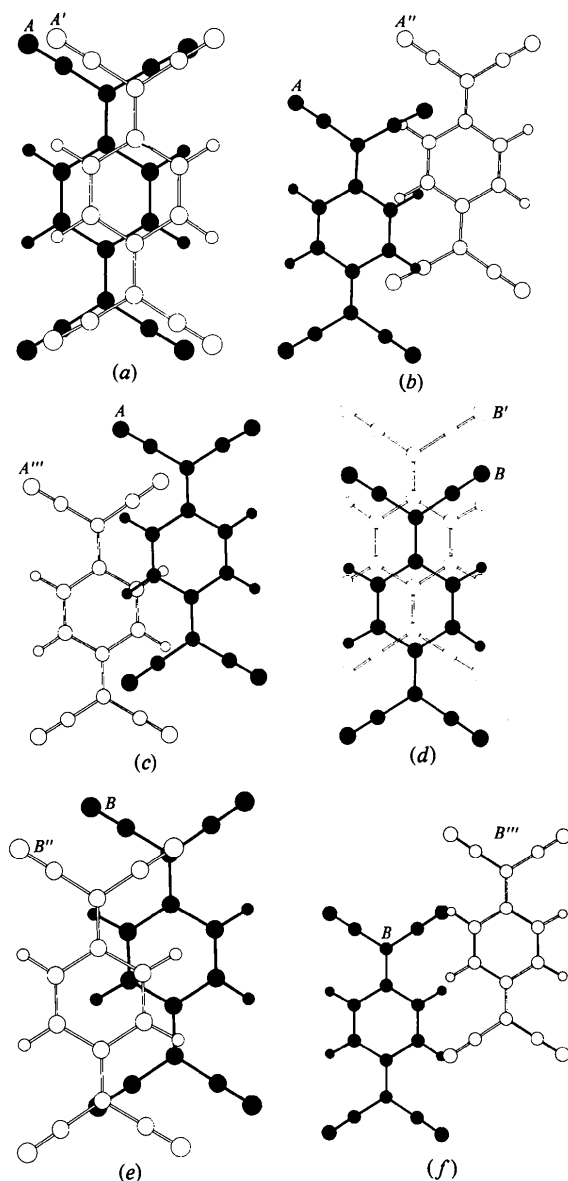


Fig. 4. Projections of two neighbouring TCNQ molecules in $\text{DEM}(\text{TCNQ})_2$ along the normal to the quinodimethane least-squares plane. (a) Molecules *A* and *A'*; (b) molecules *A* and *A''*; (c) molecules *A* and *A'''*; (d) molecules *B* and *B'*; (e) molecules *B* and *B''*; (f) molecules *B* and *B'''*.

Table 4. Short intermolecular distances (Å) in $\text{DEM}(\text{TCNQ})_2$ 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 $r_{\text{C}} = 1.7$, $r_{\text{N}} = 1.5$, $r_{\text{O}} = 1.4$, $r_{\text{H}} = 1.2$ Å.

(a) TCNQ *A* to TCNQ *A'* distances

C(2)—C(15 ⁱ)	3.493 (3)	C(6)—C(9 ⁱ)	3.400 (3)
C(3)—C(14 ⁱ)	3.451 (3)	C(7)—C(9 ⁱ)	3.372 (3)
C(3)—C(15 ⁱ)	3.489 (3)	C(7)—C(10 ⁱ)	3.398 (3)
C(4)—C(13 ⁱ)	3.591 (4)	C(8)—C(11 ⁱ)	3.392 (3)
C(6)—C(8 ⁱ)	3.444 (3)		

Table 4 (cont.)

(b) TCNQ *A* to TCNQ *A''* distances

C(7)—C(15 ⁱⁱ)	3.470 (3)	C(7)—N(16 ⁱⁱ)	3.315 (3)
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(c) TCNQ *A* to TCNQ *A'''* distances

C(2)—C(10 ⁱⁱⁱ)	3.532 (3)	C(11)—C(11 ⁱⁱⁱ)	3.392 (3)
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(d) TCNQ *A''* to TCNQ *A'''* distances

N(1 ^{iv})—C(7)	3.397 (4)	N(1 ^{iv})—H(C8)	2.751 (3)
N(16)—C(10 ^{iv})	3.340 (4)	N(16)—H(C10 ^{iv})	2.692 (3)
N(16)—C(11 ^{iv})	3.324 (3)	N(16)—H(C11 ^{iv})	2.625 (2)
N(1 ^{iv})—H(C7)	2.671 (3)		

(e) TCNQ *B* to TCNQ *B'* distances

C(22)—C(29 ^v)	3.418 (4)	C(24)—C(26 ^v)	3.200 (4)
C(22)—C(30 ^v)	3.210 (4)	C(25)—C(25 ^v)	3.241 (3)
C(22)—C(31 ^v)	3.414 (4)	C(25)—C(26 ^v)	3.344 (3)
C(23)—C(29 ^v)	3.337 (4)	C(25)—C(27 ^v)	3.578 (4)
C(23)—C(30 ^v)	3.410 (4)	C(27)—C(30 ^v)	3.359 (4)
C(24)—C(25 ^v)	3.392 (4)	C(27)—C(31 ^v)	3.287 (4)

(f) TCNQ *B* to TCNQ *B''* distances

C(18)—C(25 ^{vi})	3.586 (4)	C(22)—C(27 ^{vi})	3.600 (3)
C(18)—C(29 ^{vi})	3.479 (4)	C(26)—C(27 ^{vi})	3.588 (4)
C(19)—C(26 ^{vi})	3.581 (3)	C(27)—C(27 ^{vi})	3.398 (4)
C(22)—C(26 ^{vi})	3.503 (4)	C(30)—N(17 ^{vi})	3.330 (4)

(g) TCNQ *B* to TCNQ *B'''* distances

C(23)—N(32 ^{vii})	3.398 (4)
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(h) TCNQ *B''* to TCNQ *B'''* distances

N(17)—C(23 ^{viii})	3.354 (3)	N(32 ^{viii})—C(26)	3.385 (3)
N(17)—C(24 ^{viii})	3.364 (3)	N(32 ^{viii})—H(C26)	2.644 (3)
N(17)—H(C23 ^{viii})	2.698 (3)	N(32 ^{viii})—H(C27)	2.725 (3)

(i) TCNQ *A* to DEM distances

N(5)—H(C37 ^{viii})	2.661 (3)	C(15)—O ⁱⁱ	3.154 (3)
N(5)—H(C35 ^{ix})	2.838 (3)	C(13)—H(C38 ^{xi})	3.050 (2)
N(1 ^x)—H'(C37)	2.725 (2)	H(12)—H(C38 ^{xi})	2.412 (3)
N(16)—H(C36 ⁱⁱ)	2.479 (2)		

(j) TCNQ *B* to DEM distances

C(18)—H''(C41 ^{xiii})	2.838 (3)	C(35)—N(28 ^v)	3.389 (4)
C(40)—N(17 ^{xiii})	3.371 (3)	H(C40)—N(12 ⁱⁱⁱ)	2.744 (2)
N(21)—H(C34 ^{ix})	2.863 (3)	H(C34)—N(28 ^v)	2.635 (2)
H(C36)—H(C10 ⁱⁱⁱ)	2.485 (1)	C(36)—N(12 ⁱⁱⁱ)	3.386 (5)
C(34)—N(28 ^v)	3.384 (3)	N(17)—H(C39 ^{xiii})	2.820 (2)
H(C37)—N(12 ⁱⁱⁱ)	2.690 (3)	H(C39)—N(28 ^v)	2.889 (3)
N(21)—H'(C39 ^{xii})	2.622 (3)		

(k) DEM to DEM distances

H(C35)—C(40 ^{iv})	3.008 (4)	H'(C40)—H(C41 ^{ix})	2.537 (1)
H(C35)—H(C40 ^{iv})	2.487 (1)	C(41)—H'(C40 ^x)	3.100 (4)

Symmetry code

(i) $1 - x, 1 - y, 2 - z$	(vii) $-1 - x, -y, -z$
(ii) $1 - x, 1 - y, 1 - z$	(viii) $1 + x, y, 1 + z$
(iii) $-x, 1 - y, 1 - z$	(ix) $x, y, 1 + z$
(iv) $1 + x, y, z$	(x) $x, y, -1 + z$
(v) $-x, -y, -z$	(xi) $-x, 1 - y, -z$
(vi) $-x, -y, 1 - z$	(xii) x, y, z
	(xiii) $-1 + x, y, -1 + z$

Individual TCNQ groups

In Fig. 5 the molecular geometry of the two independent TCNQ units is shown. Within the experimental accuracy the individual TCNQ units satisfy *mmm* symmetry with respect to their bond lengths; average values for corresponding bond lengths are

Table 5. Shifts (\AA) of TCNQ A' (B'), $A''(B'')$ and $A'''(B''')$ relative to TCNQ $A(B)$ (see Fig. 3) as seen along the normal to the quinodimethane least-squares plane, and distances (\AA) between these planes

$S(\perp)$ is the shift perpendicular to the longest molecular axis; $S(\parallel)$ is the shift along this axis. E.s.d.'s are $<0.01 \text{\AA}$.

$S(\perp)$			
A'	-0.76	B'	0.07
A''	-3.64	B''	2.08
A'''	3.11	B'''	-4.64
$S(\parallel)$			
A'	-0.14	B'	-2.02
A''	-2.31	B''	1.17
A'''	1.81	B'''	-2.96
Distances between the planes			
$D(A \cdots A')$	3.41	$D(B \cdots B')$	3.14
$D(A \cdots A'')$	3.19	$D(B \cdots B'')$	3.36
$D(A \cdots A''')$	3.19	$D(B \cdots B''')$	3.13

Table 6. Mean bond lengths (\AA) for the TCNQ groups in $DEM(TCNQ)_2$, at 294 K

The labelling is chosen according to Table 7 of Bosch & van Bodegom (1977). Figures in parentheses are standard deviations of the mean. No libration corrections have been applied.

	a	b	c	d	e
Molecule A	1.355 (2)	1.435 (2)	1.403 (2)	1.425 (2)	1.148 (2)
Molecule B	1.358 (2)	1.436 (2)	1.403 (2)	1.430 (2)	1.147 (2)

given in Table 6, revealing no significant differences between the molecules. Least-squares planes were calculated for the two TCNQ units with the eight heavy atoms of the quinodimethane group. Results are given in Table 7. As found for most other TCNQ complexes the cyano groups are bent out of the plane of the quinodimethane group, the deviations being more pronounced for TCNQ A (at $y = 0.5$) than for TCNQ B (at $y = 0$). Owing to this both molecules have a shallow boat form. The angle between the normal to the least-squares plane and the c axis is $+28.7 (0.5)^\circ$ for A and $-30.1 (0.5)^\circ$ for B , whereas the angle between the two normals is $57.4 (0.5)^\circ$.

The DEM group

The morpholinium ring of the DEM group has a chair conformation as usually observed for this ring in TCNQ complexes (Bosch & van Bodegom, 1977; Sundaresan & Wallwork, 1972). The bond lengths and angles are listed in Fig. 6 with their e.s.d.'s from the least-squares program. Corresponding bond lengths and angles are not always equal within three times the standard deviation in the difference. We have attributed this to the fact that the density of the DEM group is strongly smeared, especially in the c^* direction as far as the ring is concerned. An indication of this smearing is given by the thermal parameters in Table 8. Whereas

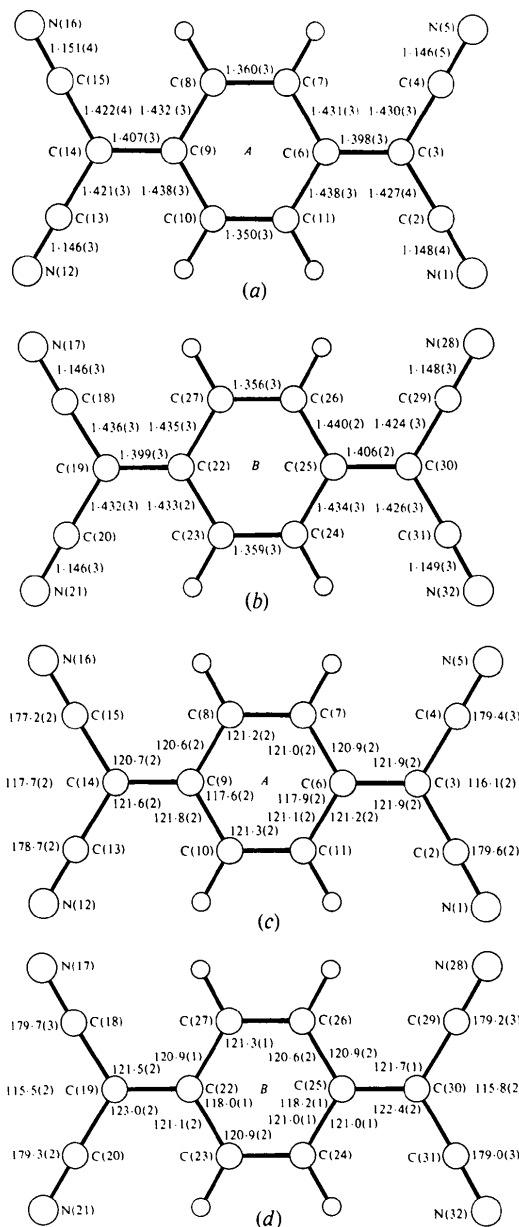


Fig. 5. Molecular geometry of the TCNQ units in $DEM(TCNQ)_2$. Values for bond lengths (\AA) and angles ($^\circ$) are not corrected for libration effects. Bond lengths: (a) molecule A ; (b) molecule B . Bond angles: (c) molecule A ; (d) molecule B .

U_{11} and U_{22} for DEM are comparable with the values observed for the quinodimethane group, U_{33} are extraordinarily large. For O a U_{33} as large as 0.24\AA^2 was found. Further large values are $U_{22}[\text{C}(38)] = 0.13$ and $U_{22}[\text{C}(41)] = 0.17 \text{\AA}^2$. In view of the strong smearing the usual model with linear harmonic vibrations is not adequate and it is therefore not surprising that in the final difference map some maxima, ranging from 0.20 to 0.33 e \AA^{-3} , are observed in the region of the DEM molecule. The e.s.d. of the difference map, $\sigma_d = (1/V)[2 \sum_H (F_o - F_c)^2]^{1/2}$, is 0.05 e \AA^{-3} , with the

Table 7. *Least-squares planes for the quinodimethane (C₈) groups of the TCNQ units in DEM(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* = deviation from the plane. E.s.d.'s are ≤ 0.01 Å.

Equations of the planes <i>A</i> : C(3), C(6)–C(11), C(14);	[($\sum \Delta^2$)/8] ^{1/2} (Å)
<i>B</i> : C(19), C(22)–C(27), C(30)	
TCNQ <i>A</i> 0.007 <i>x</i> – 1.699 <i>y</i> + 6.592 <i>z</i> = 4.856	0.014
TCNQ <i>B</i> 6.274 <i>x</i> + 6.559 <i>y</i> – 6.498 <i>z</i> = –1.571	0.011

Deviations of all atoms from the plane for TCNQ <i>A</i> (Å × 10 ²)							
N(1)	–0	N(5)	–24	C(9)	1	C(13)	–6
C(2)	–1	C(6)	1	C(10)	1	C(14)	–2
C(3)	–2	C(7)	1	C(11)	1	C(15)	–8
C(4)	–14	C(8)	1	N(12)	–10	N(16)	–15

Deviations of all atoms from the plane for TCNQ <i>B</i> (Å × 10 ²)							
N(17)	–2	N(21)	–6	C(25)	0	C(29)	–9
C(18)	–2	C(22)	1	C(26)	1	C(30)	–2
C(19)	–2	C(23)	1	C(27)	1	C(31)	–3
C(20)	–4	C(24)	1	N(28)	–16	N(32)	–4

Table 8. *Indication of the strong smearing of the DEM density from the thermal parameters*

Averages are in 10^{–2} Å²; only non-hydrogen atoms are considered. *Q* stands for quinodimethane groups.

	Average		Average
<i>U</i> ₁₁ (DEM)	7.8 (1)	<i>U</i> ₁₁ (<i>Q</i>)	4.2 (1)
<i>U</i> ₂₂ (DEM)	5.7 (1)	<i>U</i> ₂₂ (<i>Q</i>)	4.0 (1)
<i>U</i> ₃₃ (DEM)	16.1 (1)*	<i>U</i> ₃₃ (<i>Q</i>)	4.4 (1)

* Variation from 8.3 for N to 24.1 for O.

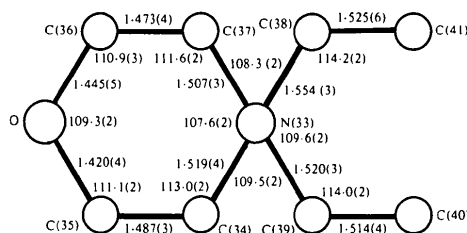


Fig. 6. Molecular geometry of the DEM molecule in DEM(TCNQ)₂. Bond lengths in Å, bond angles in °. The angles C(37)–N(33)–C(39) and C(38)–N(33)–C(34) are 111.9 (2) and 109.8 (2)° respectively.

summation over all independent reflections included in the refinement (Cruickshank, 1949). The strong smearing indicates disorder for the DEM group, but we have not been able to deduce to what extent the disorder has a dynamic or a static character. In this respect it is noteworthy that, for the morpholinium-type groups, disorder with two preferred orientations of the molecule has been observed for the room-temperature structures of MEM(TCNQ)₂, HEM(TCNQ)₂ and DMM(TCNQ)₂ [HEM = 4-ethylmorpholinium (van

Bodegom & de Boer, 1981); DMM = 4,4-dimethylmorpholinium (Kammaing & van Bodegom, 1981)]. No such disorder was found for the 113 K structure of MEM(TCNQ)₂ (Bosch & van Bodegom, 1977). It cannot be excluded that DEM(TCNQ)₂ has, in analogy to the above compounds, more than one preferred orientation for the DEM group, but if this is the case the occupancy for the subsidiary orientation(s) is smaller than for the cases mentioned above. For MEM(TCNQ)₂ the disorder as a function of temperature, and its possible influence on the phase transition, will be discussed in a following paper.

Discussion

In DEM(TCNQ)₂ two different types of TCNQ sheets alternate along **b**. One sheet is strongly analogous to the sheet in MEM(TCNQ)₂ at 113 K and contains pseudo-one-dimensional dimerized TCNQ stacks with the TCNQ molecules approximately parallel to (001). The other sheet is described best as a two-dimensional array of TCNQ dimers having the TCNQ planes approximately parallel to (111). The impact of the presence of these two different sheets on the electric and magnetic properties is being studied in the Department of Physical Chemistry of the University of Groningen.

TCNQ complexes containing dimerized TCNQ stacks generally have a phase transition on heating where the dimerized stacks transform into (nearly) uniform stacks (Sawatzky, Huizinga & Kommandeur, 1978). It is tempting to relate the occurrence of two high-temperature phase transitions in DEM(TCNQ)₂ to the fact that there are two types of sheet, the dimers in which may transform to monomeric stacks at different temperatures.

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

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Abstract

$C_6H_{14}NO^+ \cdot 2C_{12}H_4N_4^{-1/2}$, DMM(TCNQ)₂, is monoclinic, space group $P2_1/m$ (with disorder of DMM), $a = 7.792$ (7), $b = 26.814$ (8), $c = 7.594$ (7) Å, $\beta = 58.44$ (6)°, $U = 1352$ Å³, $Z = 2$; $d_c = 1.289$, $d_m = 1.301$ Mg m⁻³. Final $R_w(F) = 0.070$ for 2701 independent reflections. The structure contains columns of TCNQ units located in sheets parallel to (010) separated by DMM molecules. Each column consists of TCNQ dimers with an interplanar spacing of 3.25 (1) Å and a considerable overlap of the shifted ring-ring type. The interplanar spacing between the dimers is only slightly larger, 3.29 (1) Å, but here large shifts parallel to the TCNQ plane make the overlap small. The DMM molecule is disordered, possessing two positions related by the mirror plane in the structure.

Introduction

Earlier structural studies of the 1:2 complexes of TCNQ with 4-methyl-4-ethylmorpholinium (MEM) at 113 K and 4,4-diethylmorpholinium (DEM) at 294 K (Bosch & van Bodegom, 1977; Morssink & van Bodegom, 1981) showed that the TCNQ packing modes in the two compounds are not the same. In the

triclinic DEM(TCNQ)₂ structure there are two types of sheets, only one of which is similar to the sheet in MEM(TCNQ)₂. As the sheet structure of TCNQ complexes influences their physical behaviour, the differences found stimulated us to study the structures of further 1:2 *N*-substituted morpholinium–TCNQ complexes. In the present paper the X-ray diffraction study of DMM(TCNQ)₂ is described (DMM = 4,4-dimethylmorpholinium). Not much is known yet of its physical properties, apart from the fact that it has one phase transition above room temperature [475 K; Guinier photographs; Dr G. A. Wiegers, Department of Inorganic Chemistry, Rijksuniversiteit Groningen].

Experimental work

Dark violet crystals were grown from a mixture of hot solutions of 4,4-dimethylmorpholinium 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 θ , χ and ϕ values of 77 reflections measured on an automatic Nonius CAD-3 diffractometer. Table 2. Weissenberg and rotation photographs gave the symmetry relation $I(hkl) = I(h\bar{k}l) = I(h\bar{k}l)$ and the systematic absences $0k0$ for k odd, thus giving as possible space groups $P2_1$ and $P2_1/m$.