

- HUIZINGA, S., KOMMANDEUR, J., SAWATZKY, G. A., THOLE, B. T., KOPINGA, K., DE JONGE, W. J. M. & ROOS, J. (1979). *Phys. Rev. B*, **19**, 4723–4732.
- KAMMINGA, P. & VAN BODEGOM, B. (1981). *Acta Cryst.* **B37**, 114–119.
- KUINDERSMA, P. I., HUIZINGA, S., KOMMANDEUR, J. & SAWATZKY, G. A. (1976). *Phys. Rev. B*, **13**, 496–499.
- KUINDERSMA, P. I., SAWATZKY, G. A., KOMMANDEUR, J. & SCHINKEL, C. J. (1975). *J. Phys. Chem.* **8**, 3016–3022.
- MORROW, M., HARDY, W. N., CAROLAN, J. F., BERLINSKY, A. J., JANOSSY, A., HOLCZER, K., MIHÁLY, G., GRÜNER, G., HUIZINGA, S., VERWEIJ, A. B. & SAWATZKY, G. A. (1980). *Can. J. Phys.* In the press.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.
- SAWATZKY, G. A., HUIZINGA, S. & KOMMANDEUR, J. (1978). *Proceedings of the International Conference on Quasi-One-Dimensional Conductors, September 1978, Dubrovnik, Yugoslavia. Lecture Notes in Physics*, pp. 34–44. Berlin: Springer Verlag.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- SUNDARESAN, T. & WALLWORK, S. C. (1972). *Acta Cryst.* **B28**, 491–497.
- XRAY system (1976). Dutch version of the XRAY system. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1981). **B37**, 114–119

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

BY PIET KAMMINGA AND BERT VAN BODEGOM

Laboratorium voor Chemische Fysica, Materials Science Center, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

(Received 16 May 1980; accepted 16 September 1980)

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 $P2_1/m$.

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

Calculated (%)			Found (%)		
H	C	N	H	C	N
4.23	68.69	24.03	4.15	68.68	24.07
			4.22	68.55	24.04

Table 2. *Crystal data of DMM(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.

Monoclinic	
Space group $P2_1/m$ (DMM disordered)	
$a = 7.792$ (7) Å	$(C_6H_{14}NO) \cdot (C_{12}H_4N_4)_2$
$b = 26.814$ (8)	$M_r = 524.6$
$c = 7.594$ (7)	$F(000) = 546$
$\beta = 58.44$ (6)°	$Z = 2$
$U = 1352$ Å ³	$\mu(\text{Mo } K\alpha) = 0.09 \text{ mm}^{-1}$
	$d_c = 1.289 \text{ Mg m}^{-3}$ (294 K)
	$d_m = 1.301$ (294 K)
	(pycnometer)

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 the diffractometer by the θ – 2θ method with Zr-filtered Mo radiation. Two sets of symmetry-related reflections, hkl and $\bar{h}\bar{k}l$, were measured and $I(hkl)$ was calculated as the weighted average of the equivalent reflections. Corrections were applied for Lorentz and polarization effects, but not for absorption [$\mu(\text{Mo } K\alpha) = 0.09 \text{ mm}^{-1}$]. 8046 reflections were measured up to $\theta = 30^\circ$. After averaging, those with net negative intensity were given zero weight. For the remaining 3370 reflections the weight w_c was calculated from $w_c = [\sigma_c(F_o)]^{-2}$, $\sigma_c(F_o)$ being based on counting statistics and errors in the filter factors.

Determination of the structure

In space group $P2_1$ the unit cell contains two independent TCNQ units and one independent DMM group. In $P2_1/m$ there is one independent TCNQ unit, whereas DMM (Fig. 6) lies either at the special position on m or shows disorder. Under the assumption of symmetry $P2_1/m$ for the TCNQ structure, the orientation and location of the TCNQ group were easily recognized from a Patterson map.* After blocked-matrix isotropic least-squares refinement of the heavy atoms of the TCNQ group, in space group $P2_1/m$, a difference map was calculated. This map showed two

DMM molecules symmetrically related by the mirror plane m . Under the assumption of random disorder for the DMM molecule, first a refinement of the structure in space group $P2_1/m$ was carried out. The y coordinates of N(33), C(34) and C(35), lying close to or on the mirror plane at $y = 0.25$, were constrained at 0.25 and the temperature parameters U_{12} and U_{23} of these atoms were set to 0.0. The remaining atoms of the DMM groups were given a population 0.5. After anisotropic refinement of the non-hydrogen atoms, a difference map showed peaks for all H atoms at the

Table 3. *Final positional parameters and equivalent isotropic thermal parameters (Å²) for DMM(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.

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

	x	y	z	U_{eq}
N(1)	1496 (4)	1798 (1)	1347 (4)	946 (10)
C(2)	2057 (4)	1440 (1)	1672 (4)	623 (8)
C(3)	2771 (3)	982 (1)	2017 (3)	489 (6)
C(4)	4642 (4)	1004 (1)	1936 (3)	534 (7)
N(5)	6138 (3)	1022 (1)	1878 (4)	741 (8)
C(6)	1742 (3)	537 (1)	2279 (3)	446 (6)
C(7)	2536 (3)	69 (1)	2448 (3)	457 (6)
C(8)	1578 (3)	–365 (1)	2618 (3)	448 (6)
C(9)	–280 (3)	–375 (1)	2662 (3)	444 (6)
C(10)	–1099 (3)	95 (1)	2531 (3)	485 (6)
C(11)	–133 (3)	527 (1)	2340 (3)	484 (6)
N(12)	–4649 (3)	–846 (1)	3003 (4)	795 (8)
C(13)	–3131 (4)	–837 (1)	2916 (3)	564 (7)
C(14)	–1261 (3)	–822 (1)	2823 (3)	468 (7)
C(15)	–432 (3)	–1291 (1)	2867 (4)	542 (7)
N(16)	214 (3)	–1670 (1)	2928 (4)	792 (8)
N(33)	5751 (4)	2500	5749 (4)	561 (8)
C(34)	3697 (5)	2500	6061 (7)	832 (15)
C(35)	3671 (6)	2500	4162 (7)	850 (17)
C(36)	7090 (8)	2386 (6)	2032 (8)	1068 (51)
C(37)	7295 (7)	2249 (2)	3831 (9)	835 (20)
C(38)	6210 (8)	3060 (2)	5650 (8)	739 (19)
C(39)	5760 (9)	2306 (3)	7587 (9)	970 (27)
O(1)	5136 (7)	2276 (2)	2436 (7)	1040 (17)
H(C7)	3929	63	2434	
H(C8)	2225	–711	2725	
H(C10)	–2517	100	2596	
H(C11)	–768	873	2207	
H(C34)*	2930	2165	6893	
H(C35)	2245	2360	4514	
H'(C35)	3746	2903	3744	
H(C36)	8152	2167	711	
H'(C36)	7428	2778	1693	
H(C37)	7073	1852	4071	
H'(C37)	8775	2346	3518	
H(C38)	6248	3225	4332	
H'(C38)	7660	3106	5496	
H''(C38)	5048	3225	7050	
H(C39)	5444	1911	7752	
H'(C39)	7222	2371	7380	
H''(C39)	4612	2500	8945	

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

* H'(C34) is related to H(C34) by the mirror plane.

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). 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 0.074 and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ to 0.070; 2701 reflections with $|F_o| > 2\sigma_c(F_o)$ and weights $w = [\sigma_c^2(F_o) + E|F_o|^2]^{-1}$ were used; $E = 0.0006$. The goodness-of-fit $G = [\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2} = 1.57$, with $N_o = 2701$ and N_v (number of variables) = 226. During the last cycle parameter shifts were all $< 0.05\sigma$. Final positional parameters are given in Table 3.* To check whether a better fit to the observed intensities could be obtained by omitting the inversion centre and mirror plane, the refinement was repeated in space group $P2_1$. Two independent TCNQ units and one DMM group, without disorder, were considered. Refinement with the same reflections, weighting scheme and H constraints gave $R = 0.085$, $R_w = 0.091$ and $G = 2.12$ ($N_v = 384$). A difference map showed the four highest peaks, from 0.36 to 0.56 $e \text{ \AA}^{-3}$, at positions symmetrically related to those of C(37), C(38), C(39) and O. The e.s.d. of the difference map $\sigma_d = (1/V)[2 \sum_H (F_o - F_c)^2]^{1/2} = 0.07 e \text{ \AA}^{-3}$, with the summation over all reflections corresponding with those included in the refinement (Cruickshank, 1949). Correlation coefficients for the atoms of the TCNQ groups ranged from 0.53 to 0.73. From the fact that the refinement indices and the difference map get worse, in spite of the increasing number of variables, we conclude that the structure has to be described in space group $P2_1/m$ under the assumption of random disorder for the DMM group.

Description of the structure

Packing

The projections of the structure along [001] and [100] are given in Figs. 1 and 2. It is seen that the TCNQ molecules are located in sheets parallel to (010) separated by DMM molecules. There is only one type of sheet, successive sheets being related by the 2_1 axis. The disordered DMM groups possess two symmetrically related positions around each of the mirror planes.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35540 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

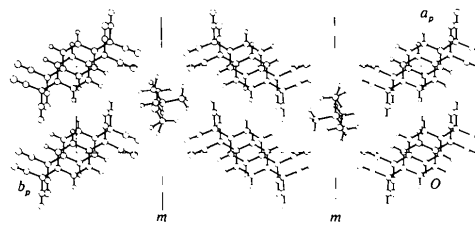


Fig. 1. Projection of the structure of $\text{DMM}(\text{TCNQ})_2$ along [001] onto the plane perpendicular to [001]. The DMM group is disordered. Only one of the two molecules related by the mirror plane m is shown. a_p , b_p and c_p denote projections of axes.

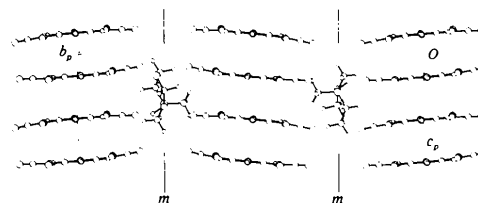


Fig. 2. Projection of the structure of $\text{DMM}(\text{TCNQ})_2$ along [100] onto the plane perpendicular to [100]. The DMM group is disordered. Only one molecule is shown.

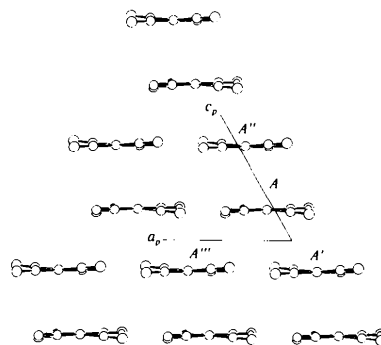


Fig. 3. Normal projection of the sheet of TCNQ molecules in $\text{DMM}(\text{TCNQ})_2$ along the longest molecular axis.

The TCNQ sheet

Fig. 3 gives a drawing of the stacking of the TCNQ units as seen along their longest molecular axes. Fig. 4 shows the different types of overlap between the TCNQ units, while shortest intermolecular distances are given in Table 4. Table 5 lists numerical values for the relative shifts of the molecules parallel to the quinodimethane least-squares plane, along and perpendicular to the longest molecular axis. From Figs. 3 and 4 it is seen that the overlap between A and A'' is much larger than between A and A' and that the overlap between A and A''' is very small. Therefore in the sheet of TCNQ molecules columns can be recognized along c consisting of dimerized TCNQ units. The intradimer overlap is of the shifted ring-ring type. The distances between the quinodimethane planes of the successive TCNQ units in the column are 3.25 (1), within the

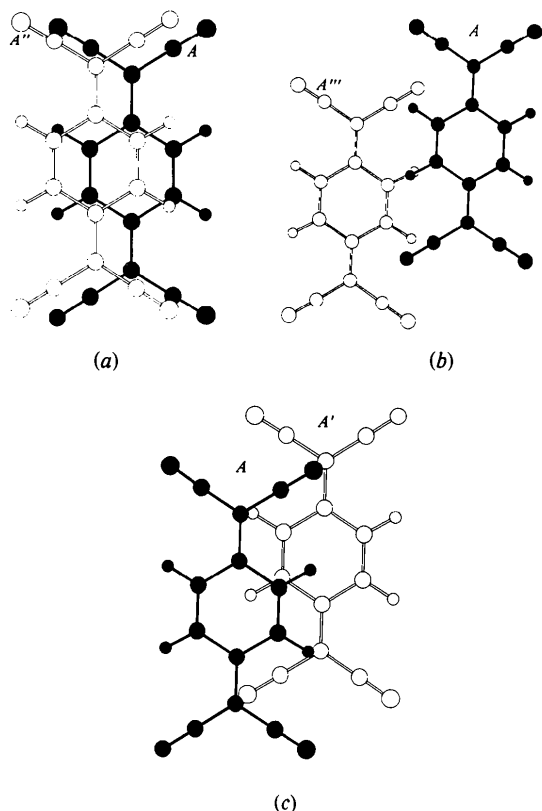


Fig. 4. Projections of two neighbouring TCNQ molecules in $DMM(TCNQ)_2$ along the normal to the quinodimethane least-squares plane. (a) Molecules A and A'' , (b) molecules A and A''' , (c) molecules A and A' .

dimer, and $3.29(1) \text{ \AA}$, between the dimers. Successive molecules A (like A' , A''' etc.) show electrostatic interaction *via* short $N \cdots H$ distances (Table 4).

The TCNQ group

In Fig. 5 the molecular geometry of the TCNQ ion is shown. Within 2σ the group satisfies *mmm* symmetry with respect to its bond lengths; average values for bond lengths are given in Table 6. A least-squares plane was calculated through the eight heavy atoms of the quinodimethane group. Results are given in Table 7. It is seen that the TCNQ molecule as a whole is not planar, and that the cyano groups in particular deviate from the plane. The normal to the quinodimethane plane makes an angle of $30.6(0.5)^\circ$ with c .

The DMM group

The ring of the DMM group is in a chair conformation as has been found for all morpholinium derivatives in complexes with TCNQ whose structures are so far known (Bosch & van Bodegom, 1977; Sundaresan & Wallwork, 1972; Morssink & van

Table 4. Short intermolecular distances (\AA) in $DMM(TCNQ)_2$ at 294 K

All distances smaller than the sum of the relevant van der Waals radii (Pauling, 1960) plus 0.2 \AA are given. Van der Waals radii $r_C = 1.7$, $r_N = 1.5$, $r_O = 1.4$, $r_H = 1.2 \text{ \AA}$.

(a) TCNQ A to TCNQ A' distances

C(2)—C(13 ⁱ)	3.522 (5)	C(11)—C(13 ^h)	3.531 (5)
C(6)—C(13 ⁱ)	3.594 (5)	C(11)—C(14 ^h)	3.567 (5)
C(9)—C(10 ⁱ)	3.582 (5)	C(3)—N(12 ⁱ)	3.312 (5)
C(10)—C(10 ^o)	3.328 (5)		

(b) TCNQ A to TCNQ A'' distances

C(3)—C(14 ^h)	3.478 (5)	C(7)—C(8 ^h)	3.517 (4)
C(3)—C(15 ^h)	3.419 (5)	C(7)—C(9 ^h)	3.275 (4)
C(4)—C(13 ^h)	3.472 (5)	C(7)—C(10 ^h)	3.394 (5)
C(4)—C(14 ^h)	3.471 (5)	C(8)—C(10 ^h)	3.577 (5)
C(6)—C(8 ^h)	3.381 (4)	C(8)—C(11 ^h)	3.407 (5)
C(6)—C(9 ^h)	3.415 (5)		

(c) TCNQ A to TCNQ A''' distances

C(4)—C(8 ^h)	3.594 (4)
-------------------------	-----------

(d) TCNQ A' to TCNQ A''' distances

N(5 ^{iv})—C(11)	3.376 (4)	N(5 ^{iv})—H(C11)	2.582 (3)
N(12)—C(8 ^{iv})	3.360 (4)	N(12)—H(C7 ^{iv})	2.803 (3)
N(5 ^{iv})—H(C10)	2.846 (2)	N(12)—H(C8 ^{iv})	2.578 (3)

(e) TCNQ to DMM distances

N(1)—C(37 ^{iv})	3.045 (6)	N(16)—H(C36 ⁱⁱⁱ)	2.712 (3)
N(1)—H'(C37 ^{iv})	2.390 (3)	N(16)—H(C34 ⁱⁱ)	2.728 (3)
N(1)—C(39 ^v)	3.334 (6)	N(16)—H(C35 ⁱⁱ)	2.641 (3)
N(1)—H(C39 ^v)	2.866 (4)	C(15)—H(C34 ⁱⁱ)	2.991 (3)
N(1)—H''(C39 ^v)	2.851 (3)	C(16 ^{vi})—H'(C39)	2.663 (3)
C(2)—H(C39 ^v)	3.033 (3)		

(f) TCNQ to DMM' distances

N(16)—H'(C38 ^{vii})	2.572 (3)	N(12)—H''(C38 ^{viii})	2.484 (3)
C(13)—C(38 ^{viii})	3.600 (5)	H'(C35)—C(2 ^{ix})	3.079 (3)
N(12)—C(38 ^{viii})	3.136 (5)	H(C38)—N(5 ^{ix})	2.781 (3)
C(13)—H''(C38 ^{viii})	2.893 (3)		

Symmetry code

(i)	$-x, -y, -z$	(vi)	$1-x, -y, 1-z$
(ii)	$-x, -y, 1-z$	(vii)	$1-x, y-\frac{1}{2}, 1-z$
(iii)	$1-x, -y, -z$	(viii)	$-x, y-\frac{1}{2}, 1-z$
(iv)	$x-1, y, z$	(ix)	$x, \frac{1}{2}-y, z$
(v)	$x, y, z-1$		

Table 5. Shifts (\AA) of TCNQ molecules A' , A'' and A''' relative to TCNQ molecule A as seen along the normal to the quinodimethane least-squares plane, and distances (\AA) between the 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 $\leq 0.01 \text{ \AA}$.

	A'	A''	A'''
$S(\perp)$	2.54	-1.06	-4.19
$S(\parallel)$	1.64	0.23	-2.27

Distances between quinodimethane least-squares planes

$$A \cdots A' \ 3.29; A \cdots A'' \ 3.25; A \cdots A''' \ 3.10$$

Table 6. Mean bond lengths (Å) for the TCNQ group in $DMM(TCNQ)_2$ 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.

<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
1.350 (2)	1.436 (2)	1.393 (2)	1.452 (2)	1.143 (2)

Table 7. Least-squares plane for the quinodimethane group (C_8) of the TCNQ unit in $DMM(TCNQ)_2$ at 294 K and deviations of atoms from this plane

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

$$\text{Equation of the plane } C(3); C(6)-C(11); C(14) \quad |(\sum \Delta^2)/8|^{1/2} \text{ (Å)} \\ 0.184x + 2.459y + 6.535z = 1.644 \quad 0.018$$

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

N(1)	-29	N(5)	-5	C(9)	0	C(13)	-0
C(2)	-16	C(6)	1	C(10)	1	C(14)	-2
C(3)	-3	C(7)	2	C(11)	1	C(15)	-10
C(4)	-5	C(8)	1	N(12)	3	N(16)	-14

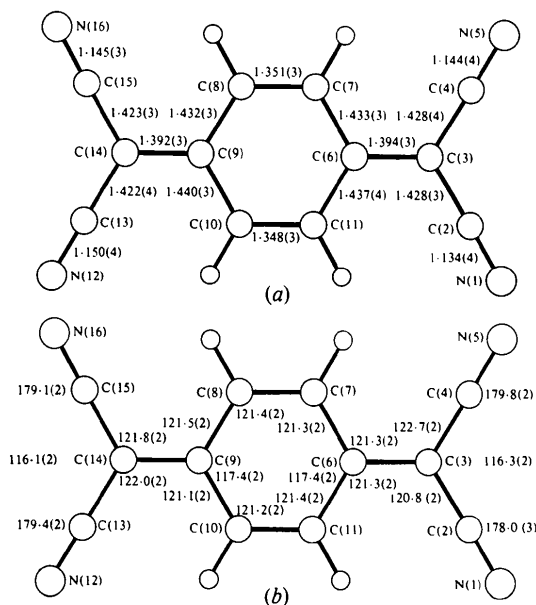


Fig. 5. Molecular geometry of the TCNQ unit in $DMM(TCNQ)_2$. Values for bond lengths (Å) and angles ($^\circ$) are not corrected for libration effects. (a) Bond lengths; (b) bond angles.

Bodegom, 1981). Owing to a 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 they strongly underestimate the errors in the molecular geometry.

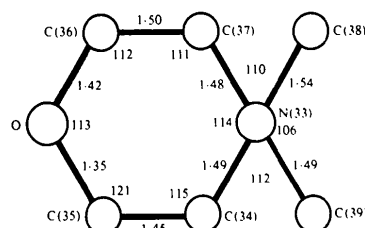


Fig. 6. Molecular geometry of the DMM molecule (disordered) in $DMM(TCNQ)_2$. Bond lengths in Å, bond angles in $^\circ$. The angles $C(37)-N(33)-C(39)$ and $C(38)-N(33)-C(34)$ are 111 and 102° respectively.

Discussion

In $MEM(TCNQ)_2$ at 113 K all TCNQ sheets are translationally equivalent. In both $DMM(TCNQ)_2$ and $DEM(TCNQ)_2$ alternating sheets along the **b** direction are not translationally equivalent. In $DMM(TCNQ)_2$ the sheets are related, however, by the twofold screw axis along **b**, whereas in $DEM(TCNQ)_2$ the two sheets have a different character. The sheet in $DMM(TCNQ)_2$ is analogous to that in $MEM(TCNQ)_2$ in that both sheets contain pseudo-one-dimensional dimerized TCNQ stacks. The intradimer overlap in the two stacks is different, however, being of the shifted ring-ring type in $DMM(TCNQ)_2$ and of the ring-external-bond type in $MEM(TCNQ)_2$. The $DMM(TCNQ)_2$ sheet is not analogous with either of the two sheets in $DEM(TCNQ)_2$. One of the sheets in $DEM(TCNQ)_2$ has its pseudo-one-dimensional character, but not its intradimer overlap mode, in common with the $DMM(TCNQ)_2$ sheet, whereas the second sheet in $DEM(TCNQ)_2$ shares its intradimer overlap with the $DMM(TCNQ)_2$ sheet, but not its pseudo-one-dimensional character. Further studies of the physical properties of the TCNQ compounds are necessary to obtain a clear insight into the impact of their sheet structures on their physical behaviour.

The authors thank Dr J. L. de Boer for his help during the collection of the data, Dr G. A. Wiegers of the Department of Inorganic Chemistry, for taking the Guinier photographs, and Mr A. B. Verweij, who grew the crystals. The current interest and advice of Professor Dr A. Vos were very stimulating. The investigations were supported (in part) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). The computations were carried out at the Computing Center of the University of Groningen.

References

- BOSCH, A. & VAN BODEGOM, B. (1977). *Acta Cryst.* B33, 3013-3021.

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65–82.
- MORSSINK, H. & VAN BODEGOM, B. (1981). *Acta Cryst.* **B37**, 107–114.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- SUNDARESAN, T. & WALLWORK, S. C. (1972). *Acta Cryst.* **B28**, 491–497.
- XRAY system (1976). Dutch version of the XRAY system. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1981), **B37**, 119–125

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

BY BERT VAN BODEGOM AND JAN L. DE BOER

*Laboratorium voor Chemische Fysica, Materials Science Center, Rijksuniversiteit Groningen, Nijenborgh 16,
9747 AG Groningen, The Netherlands*

(Received 17 May 1980; accepted 16 September 1980)

Abstract

$C_6H_{14}NO^+ \cdot 2C_{12}H_4N_4^{-1/2}$, HEM(TCNQ)₂, is triclinic, space group *P1*, with $a = 14.177$ (2), $b = 7.558$ (1), $c = 13.427$ (2) Å, $\alpha = 92.29$ (2), $\beta = 80.81$ (1), $\gamma = 105.68$ (1)°, $U = 1367$ Å³, $Z = 2$; $d_c = 1.275$, $d_m = 1.267$ Mg m⁻³. Final $R_w(F) = 0.071$ 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 3.23 (1) Å; the intradimer overlap is of the ring-external-bond type. Within a tetramer the separation between the dimers is 3.31 (1) Å, and between successive tetramers 3.42 (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-ethylmorpholinium; 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