

The Crystal Structures of Free-Radical Salts and Complexes. V.* (Morpholinium⁺)(7,7,8,8-Tetracyanoquinodimethane⁻)

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The 1:1 simple morpholinium salt of tetracyanoquinodimethane (TCNQ) crystallizes as reddish-purple prisms, belonging to the space group $P\bar{1}$, with 2 molecules in the unit cell of dimensions $a=9.54$, $b=8.78$, $c=10.69$ Å, $\alpha=98.4^\circ$, $\beta=122.9^\circ$, $\gamma=93.5^\circ$. The structure was solved by Patterson methods and refined by block-diagonal least squares. The TCNQ ions occur as dimers about an inversion centre with an interplanar spacing of 3.28 Å. Between the dimers there is a gap of 3.61 Å. Each morpholinium ion forms two pairs of bifurcated hydrogen bonds to four TCNQ ions.

Introduction

Many radical ion salts and complexes of 7,7,8,8-tetracyanoquinodimethane (TCNQ) exhibit large specific conductances for organic crystals. The structural investigation of the 1:1 simple salt morpholinium⁺-TCNQ⁻ is described to assist further elucidation of the relationship between the electrical properties and the structures of TCNQ complexes.

Experimental

Crystal data

(C₄H₁₀NO) (C₁₂H₄N₄), M.W. 292.3

Triclinic

$a=9.54 \pm 0.04$, $b=8.78 \pm 0.04$, $c=10.69 \pm 0.04$ Å

$\alpha=98.4 \pm 0.5^\circ$, $\beta=122.9 \pm 0.5^\circ$, $\gamma=93.5 \pm 0.5^\circ$

$U=737.0$ Å³

$D_m=1.312$, $D_c=1.317$ g.cm⁻³, $Z=2$

$F(000)=306$

Cu $K\alpha$ ($\lambda=1.5418$ Å), $\mu=7.2$ cm⁻¹

Space group $P\bar{1}$ (assumed).

Reddish-purple prisms of the salt were obtained when equimolar hot solutions of TCNQ in acetonitrile and morpholine hydroiodide in acetonitrile were mixed and allowed to cool very slowly. The space group and unit-cell dimensions were obtained initially from oscillation and Weissenberg photographs taken with the crystals rotating about all the crystallographic axes. A small uniformly shaped crystal of dimensions 0.7 × 0.5 × 0.3 mm was mounted on a Stoe 2-circle diffractometer and the cell dimensions were refined. Intensity data for the layers $0kl$, $1kl$. . . $5kl$ were collected on the diffractometer using Cu $K\alpha$ radiation. 1669 reflexions were measured, of which 1455 were regarded as observed. In view of the small size of the crystal, no absorption corrections were made. The intensities were corrected for Lorentz and polarization factors.

Structure determination

A three-dimensional sharpened Patterson map was computed using modified $|F_o|^2$ as coefficients. Vectors typical of TCNQ were recognized around the origin and around a large peak at $x=0.275$, $y=0.758$ and $z=0.138$. This peak was taken to represent the combined vectors between the centrosymmetrically related pair of TCNQ ions. The common orientation of the TCNQ ions was derived from the vector pattern round the origin. From this orientation and the known dimensions of TCNQ⁻ the positions of the 16 non-hydrogen atoms of TCNQ⁻ were deduced. Two cycles of block-diagonal least-squares refinement of the TCNQ⁻ coordinates and isotropic thermal parameters with initial values of 3.0 and 4.5 Å² for the temperature factors of carbon and nitrogen atoms respectively, and with unit weights, gave the value of the residual index, $R=0.498$. A three-dimensional Fourier electron-density distribution computed with the signs derived from TCNQ confirmed the atomic positions of the TCNQ ion and also showed all the atoms of the morpholinium ion.

At this stage it was not certain which of the six atoms of the morpholinium ion were oxygen and nitrogen, so all were initially assumed to be carbon atoms and were given isotropic temperature factors of 3.00 Å². Three further cycles of refinement of the positional and the isotropic thermal parameters of all the atoms improved the R value to 0.161. In the course of the refinement, two atoms of the morpholinium ion had consistently low temperature factors and the lowest also corresponded to the highest electron-density peak in the Fourier map. It was therefore assumed to be the oxygen atom and the other, on the opposite side of the ring, was assumed to be the nitrogen. This assumption was subsequently confirmed by approximate equalization of all the morpholinium temperature factors and later by four short intermolecular contacts, interpreted as bifurcated hydrogen bonds, made by what had been assumed to be the nitrogen atom.

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Four further cycles of refinement with the weighting scheme:

$$\begin{aligned} \sqrt{w} &= 1 \quad \text{if } |F_o| \leq F^* \quad \text{or} \\ &= F^*/|F_o| \quad \text{if } |F_o| > F^*, \end{aligned}$$

where F^* was given a value of 75 on the scale of Table 2, improved R from 0.161 to 0.126. A difference-Fourier synthesis computed with low-order reflexions showed peaks for all the 14 hydrogen atoms in plausible positions. Four cycles of least-squares refinement of the positional and anisotropic thermal parameters of the non-hydrogen atoms with fixed positional and isotropic thermal parameters for the hydrogen atoms gave a final R value of 0.048. 52 weak reflexions were excluded in the last four cycles of refinement and hydrogen atoms were given temperature factors 0.5 \AA^2 greater than the atoms to which they are attached.

The scattering-factor curves of Cromer & Waber (1965) were used throughout for the carbon, nitrogen and oxygen atoms respectively. The curve for the hydrogen atoms was that quoted in *International Tables for X-ray Crystallography* (1962). The final positional and anisotropic thermal parameters of non-hydrogen atoms, together with their standard deviations, are listed in Table 1. The final calculated structure factors are compared with the observed values in Table 2. A least-squares plane was calculated through the TCNQ ion and the results are summarized in Table 3.

Description and discussion of the structure

Fig. 1 shows a general view of the structure in which the TCNQ ions are stacked in a plane-to-plane manner to form an infinite column of dimers along the b axis. Dimers of TCNQ ions about the inversion centre at

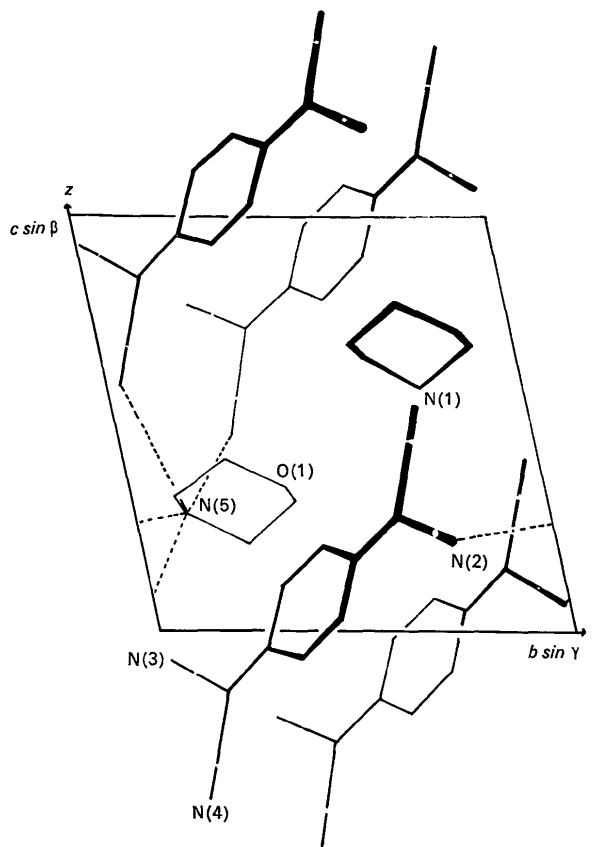


Fig. 1. The structure viewed along the a axis.

$0, \frac{1}{2}, 0$ are found with an interplanar spacing of 3.28 \AA . This distance alternates with a bigger distance of 3.61 \AA between the largely non-overlapping ions related by

Table 1. Final positional and thermal parameters (all $\times 10^4$) of non-hydrogen atoms

(The figures in parentheses indicate the standard deviations.)
Temperature factor = $\exp [-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + hk B_{12} + hl B_{13} + kl B_{23})]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	2464 (3)	4428 (3)	261 (3)	131 (4)	136 (3)	91 (6)	21 (5)	151 (7)	47 (7)
C(2)	2735 (2)	5046 (2)	1688 (3)	108 (3)	109 (3)	78 (6)	52 (5)	127 (6)	64 (6)
C(3)	1657 (3)	4347 (3)	2042 (4)	135 (4)	143 (4)	108 (7)	0 (6)	161 (7)	17 (7)
C(4)	365 (3)	3130 (3)	1009 (3)	132 (4)	141 (3)	98 (6)	0 (6)	164 (7)	17 (7)
C(5)	72 (2)	2540 (2)	-429 (3)	117 (3)	104 (3)	72 (6)	51 (5)	133 (6)	49 (6)
C(6)	1182 (3)	3204 (3)	-763 (4)	134 (4)	129 (3)	103 (6)	19 (5)	145 (7)	44 (6)
C(7)	4054 (3)	6330 (3)	2752 (3)	119 (3)	117 (3)	80 (6)	35 (5)	131 (6)	41 (6)
C(8)	4368 (3)	6865 (3)	4192 (3)	127 (4)	131 (3)	106 (6)	13 (5)	128 (7)	25 (7)
C(9)	5126 (3)	7057 (3)	2401 (3)	121 (3)	107 (3)	113 (6)	11 (5)	123 (7)	25 (6)
C(10)	-1304 (3)	1305 (2)	-1491 (3)	119 (3)	109 (3)	79 (6)	37 (5)	116 (6)	27 (6)
C(11)	-2336 (3)	616 (3)	-1079 (3)	113 (3)	108 (3)	97 (6)	14 (5)	104 (6)	15 (6)
C(12)	-1671 (3)	736 (3)	-2945 (3)	136 (4)	124 (3)	121 (7)	29 (5)	142 (7)	24 (7)
N(1)	4578 (3)	7277 (3)	5360 (3)	209 (4)	202 (4)	137 (6)	-3 (7)	185 (8)	6 (7)
N(2)	5990 (3)	7627 (2)	2113 (3)	185 (4)	146 (3)	168 (6)	-32 (6)	220 (7)	34 (6)
N(3)	-3139 (2)	102 (2)	-700 (3)	142 (3)	159 (3)	139 (6)	-33 (5)	135 (6)	40 (6)
N(4)	-1969 (3)	312 (3)	-4150 (3)	202 (4)	210 (4)	155 (6)	27 (7)	189 (8)	11 (8)
C(13)	-3755 (3)	2624 (3)	2047 (4)	153 (4)	136 (4)	133 (7)	62 (6)	128 (8)	88 (7)
C(14)	-2372 (3)	4030 (3)	3119 (4)	194 (5)	110 (3)	179 (7)	36 (6)	220 (9)	62 (7)
C(15)	-300 (3)	2482 (3)	4208 (4)	128 (4)	136 (4)	144 (7)	-8 (6)	112 (7)	33 (7)
C(16)	-1556 (3)	985 (3)	3204 (3)	130 (4)	122 (3)	114 (7)	27 (5)	134 (7)	48 (6)
O(1)	-782 (2)	3731 (2)	3425 (3)	186 (3)	125 (2)	188 (5)	-23 (4)	249 (6)	39 (5)
N(5)	-3274 (2)	1251 (2)	2789 (3)	123 (3)	113 (3)	84 (5)	-6(4)	110 (5)	24 (5)

Table 2. Comparison of observed and final calculated structure factors (10 x absolute scale)

Table with multiple columns for observed (O) and calculated (C) structure factors across various hkl indices. The table is organized into several groups of columns, each representing a different set of reflections. Each group contains observed values, calculated values, and their differences. The data is presented in a grid-like format with some rows containing multiple values for the same reflection.

Table 3. Details of the TCNQ molecular plane

x, y, z are orthogonal atomic coordinates in Å where x is along a , y is in the (a, b) plane and z is along c^* .

(The figures in parentheses indicate the standard deviations.)

Equation to the plane

$$-0.5441x + 0.7526y - 0.3709z + 1.8055 = 0$$

	Distance from the plane
C(1)	-0.072 (3) Å
C(2)	-0.008 (3)
C(3)	0.015 (3)
C(4)	0.006 (3)
C(5)	-0.026 (2)
C(6)	-0.093 (3)
C(7)	0.028 (3)
C(8)	0.011 (3)
C(9)	0.026 (3)
C(10)	0.001 (3)
C(11)	-0.002 (3)
C(12)	0.024 (3)
N(1)	0.005 (3)
N(2)	0.016 (3)
N(3)	0.002 (2)
N(4)	0.073 (3)

the centre at 0, 0, 0. Fig. 2 shows the structure projected along the b axis. It shows the four short contacts involving the nitrogen atom of the morpholinium ion $N(1) \cdots N(5) = 3.042$; $N(2) \cdots N(5) = 3.105$; $N(3) \cdots N(5) = 2.920$ and $N(4) \cdots N(5) = 3.071$ Å which can be interpreted as bifurcated hydrogen bonds. It can readily be seen that all the four nitrogen atoms of the $C-(CN)_2$ groups are hydrogen bonded. The morpholinium ions are arranged in zigzag columns, each of which is surrounded by four columns of TCNQ ions. The hydrogen bonding is quite different from that found in the morpholinium₂.TCNQ₃ structure (Sundaresan & Wallwork, 1972), where each morpholinium NH₂ group is hydrogen-bonded to an oxygen atom of the adjacent

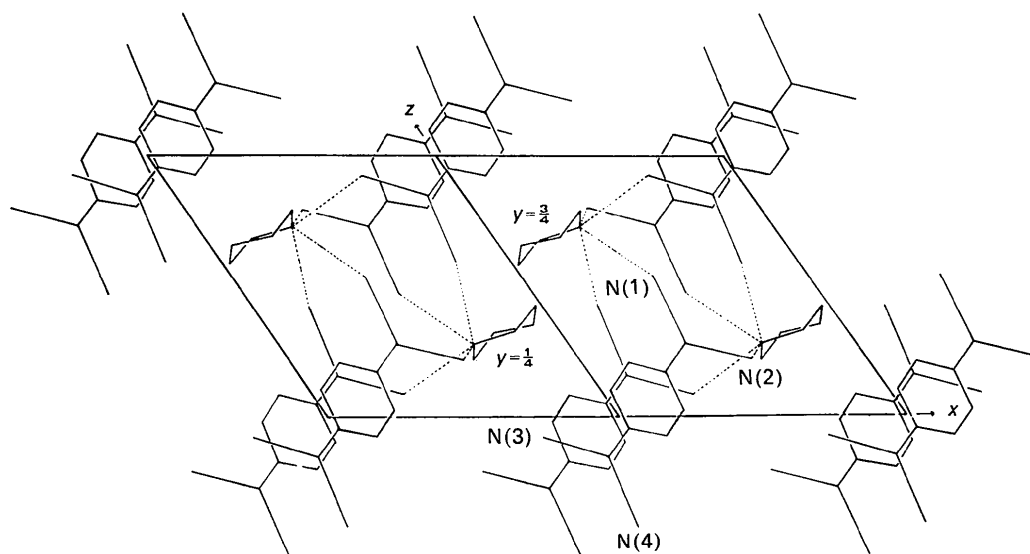


Fig. 2. The structure viewed along the b axis (2 unit cells) showing zigzag columns of morpholinium ions surrounded by columns of TCNQ ions.

morpholinium ion and to one nitrogen atom of a TCNQ ion.

The TCNQ ion is not quite planar and has a somewhat zigzag configuration. The dihedral angles between the mean planes through the quinonoid ring and the two $C-(CN)_2$ groups, $C(5)-C(10)-C(11)-C(12)-N(3)-N(4)$ and $C(2)-C(7)-C(8)-C(9)-N(1)-N(2)$, are 3.5 and 2.4° respectively.

Fig. 3 shows the overlap of the TCNQ ions related by the centre of symmetry $0, \frac{1}{2}, 0$. The overlap is similar to those observed in the crystal structures of Rb^+TCNQ^- (Hoekstra, Spoelder & Vos, 1972) and $(C_6H_5CH_3)_2Cr^+TCNQ^-$ (Shibaeva, Atovmyan & Rozenberg, 1969), although the shifts of molecular centres in those structures are larger than in the present compound. Shifts of this type were also reported in the structures of $Cs_2(TCNQ)^-$ (Fritchie & Arthur, 1966) and $(morpholinium^+)_2(TCNQ)_3^-$ (Sundaresan & Wallwork, 1972) between $TCNQ^-$ ions.

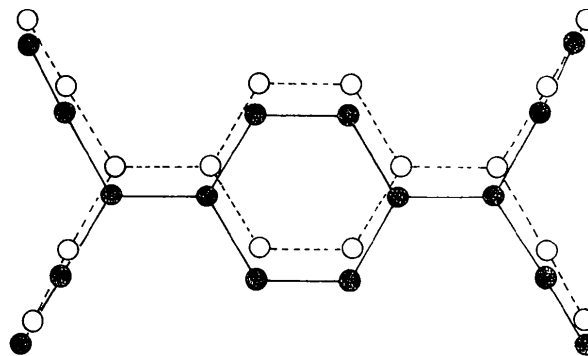


Fig. 3. Nearest neighbour overlap of TCNQ ions related by the centre of symmetry at $0, \frac{1}{2}, 0$.

Fig. 4(a) shows the dimensions of the TCNQ ion. They agree well with the previously established values for TCNQ⁻.

The dimensions of the morpholinium ion are shown in Fig. 4(b). The ion assumes a 'chair' conformation. The bond lengths and bond angles agree very well with those reported for the ion in the 2:3 complex salt (Sundaresan & Wallwork, 1972).

The stacking contacts between the TCNQ's and other short intermolecular contacts are listed in Table 4. The non-stacking contacts N(1)⋯C(13)=3.257; N(2)⋯C(16)=3.273; N(3)⋯C(13)=3.172 and N(4)⋯

C(16)=3.190 Å follow as a direct consequence of the hydrogen bonds. The rest are approximately equal to expected van der Waals distances.

Table 4. *Short intermolecular contacts*

(a) Stacking contacts between TCNQs related by the centre (0, ½, 0)

C(1 ^I)⋯C(4 ^{II})	3.363 Å
C(2 ^I)⋯C(5 ^{II})	3.331
C(3 ^I)⋯C(6 ^{II})	3.374
C(7 ^I)⋯C(10 ^{II})	3.265
C(8 ^I)⋯C(12 ^{II})	3.256
C(9 ^I)⋯C(11 ^{II})	3.270
C(9 ^I)⋯N(3 ^{II})	3.362
C(12 ^I)⋯N(1 ^{II})	3.398
N(1 ^I)⋯N(4 ^{II})	3.210
N(2 ^I)⋯N(3 ^{II})	3.278

(b) Hydrogen bonds

N(1 ^I)⋯N(5 ^{III})	3.042 Å
N(2 ^I)⋯N(5 ^{IV})	3.105
N(3 ^I)⋯N(5 ^V)	2.920
N(4 ^I)⋯N(5 ^{VI})	3.071

(c) Other non-stacking intermolecular contacts

C(4 ^I)⋯O(1 ^I)	3.299
N(1 ^I)⋯C(13 ^{III})	3.257
N(2 ^I)⋯C(16 ^{IV})	3.273
N(3 ^I)⋯C(13 ^V)	3.172
N(4 ^I)⋯C(16 ^{VI})	3.190
N(4 ^I)⋯C(15 ^{VII})	3.385
N(4 ^I)⋯C(16 ^V)	3.277
O(1 ^I)⋯O(1 ^{III})	3.235

Superscripts indicate the following equivalent positions:

I	x	y	z	V	-1-x	ȳ	z̄
II	x̄	1-y	z̄	VI	x	y	z-1
III	x̄	1-y	1-z	VII	x̄	ȳ	z̄
IV	1+x	1+y	z				

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References

- CROMER, T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
 FRITCHIE, C. J. JR & ARTHUR, P. JR (1966). *Acta Cryst.* **21**, 139.
 HOEKSTRA, A., SPOELDER, T. & VOS, A. (1972). *Acta Cryst.* **B28**, 14.
International Tables for X-ray Crystallography. (1962). Vol. II. Birmingham: Kynoch Press.
 SHIBAEVA, R. P., ATOVMIYAN, L. O. & ROZENBERG, L. P. (1969). *Chem. Comm.* p. 649.
 SUNDARESAN, T. & WALLWORK, S. C. (1972). *Acta Cryst.* **B28**, 491.

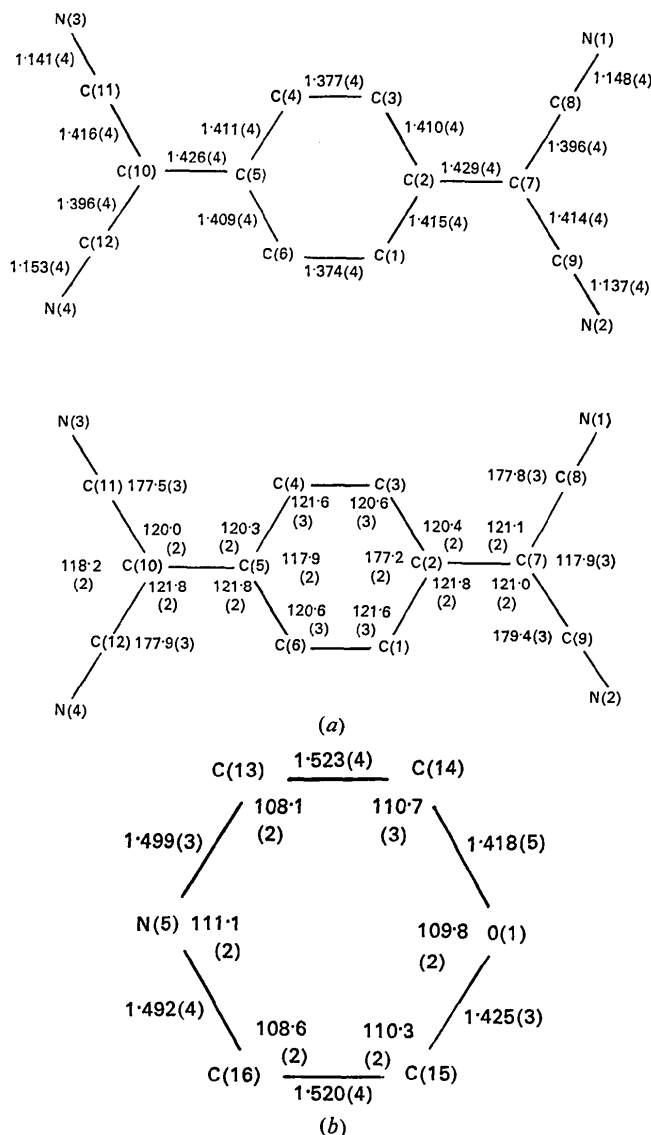


Fig. 4. Bond lengths (Å) and bond angles (°), (with their standard deviations in parentheses), for (a) the TCNQ ion and (b) the morpholinium ion.