

The benzene ring is a slightly distorted regular hexagon. The average C–C distance is 1.382 Å. The deviations of the atoms of the ion from the least-squares plane defined by the six carbon atoms are shown in Fig. 6. The carbon ring is not significantly different from planar. The least-squares plane was calculated using a method described by Blow (1960). The orientation of the sulphonate group with respect to the carbon ring is such that atom O(1) is nearly in the plane of the ring. The angle between the least-squares plane and the plane defined by C(1), S and O(1) is 0.7°. The average O–S–O and C–S–O angles in the sulphonate group are 112.1 and 106.2° respectively. These angles are similar to those found in 2,5-dibromobenzenesulphonic acid

trihydrate, 112.5 and 106.2°. The S–O distances found in the present compound 1.448, 1.426 and 1.419 Å are somewhat shorter than the S–O distances in the bromo-compound, 1.463, 1.442 and 1.459 Å. (The distances are not corrected for thermal motion.)

We wish to express our gratitude to Professor I. Olovsson for the facilities he has placed at our disposal. Sincere thanks are also due to him for valuable discussions and suggestions. We are also indebted to H. Karlsson for skilled technical assistance.

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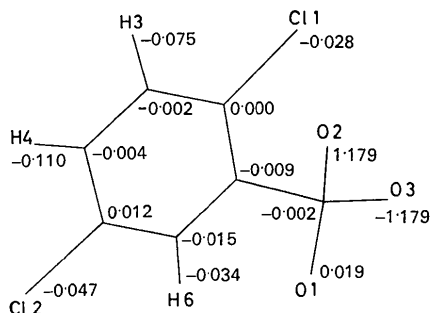


Fig. 6. Deviations of the atoms from the least-squares plane defined by the six carbon atoms of the 2,5-dichlorobenzenesulphonate ion (Å).

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## The Crystal Structures of Free Radical Salts and Complexes.

### I. (Morpholinium<sup>+</sup>)<sub>2</sub>(7,7,8,8-Tetracyanoquinodimethane)<sub>3</sub><sup>2-</sup>

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Crystals of (C<sub>4</sub>H<sub>10</sub>NO<sup>+</sup>)<sub>2</sub>(C<sub>12</sub>H<sub>4</sub>N<sub>4</sub>)<sub>3</sub><sup>2-</sup> are monoclinic, belonging to the space group *P2<sub>1</sub>/c*, with lattice constants *a* = 7.04, *b* = 10.67, *c* = 26.51 Å, *β* = 96.4°, and having *Z* = 2. The structure was solved from a three-dimensional Patterson synthesis and refined by block-diagonal least squares. It consists of columns of TCNQ molecules and anions packed plane-to-plane along the *b* axis. These columns are held together by the morpholinium ions through hydrogen bonding. The characteristic overlap and the short interplanar spacing of 3.25 Å indicate charge-transfer interaction between the TCNQ moieties.

### Introduction

7,7,8,8-Tetracyanoquinodimethane (TCNQ) is a powerful electron acceptor and readily becomes the radical anion TCNQ<sup>-</sup> by accepting an additional electron. As such, it forms salts with cations of many types, inorganic, organic and radical cations. Many of these salts exhibit large specific conductances (Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962)

for organic crystals. In addition, a number of complex salts containing extra molecules of formally neutral TCNQ have even lower resistivities. Crystal structure determinations have already been reported for a number of these simple and complex radical-ion salts but no general picture of the relationship between structure and electrical properties has emerged. To assist in the elucidation of this relationship a number of further structure determinations are being carried

out. The present paper reports the work on the structure of the complex salt (morpholinium<sup>+</sup>)<sub>2</sub>(TCNQ)<sub>3</sub><sup>-</sup>.

### Experimental

#### Crystal data

(C<sub>4</sub>H<sub>10</sub>NO)<sub>2</sub>(C<sub>12</sub>H<sub>4</sub>N<sub>4</sub>)<sub>3</sub>, M.W.788.

Monoclinic

$a = 7.04 \pm 0.02$ ,  $b = 10.67 \pm 0.04$ ,  $c = 26.51 \pm 0.06$  Å,

$\beta = 96.4 \pm 0.2^\circ$ ;

$U = 1979.4$  Å<sup>3</sup>;

$D_m = 1.317$  g.cm<sup>-3</sup>,  $Z = 2$ ,  $D_c = 1.322$  g.cm<sup>-3</sup>.

$F(000) = 820$

Mo  $K\alpha$  ( $\lambda = 0.7107$  Å),  $\mu = 0.94$  cm<sup>-1</sup>.

Systematic absences:  $h0l : l = 2n + 1$

$0k0 : k = 2n + 1$

Space group  $P2_1/c$ .

The material was prepared in the form of black lath-shaped crystals by mixing hot solutions in acetonitrile of TCNQ and morpholinium iodide. The space group and cell constants were deduced from oscillation and Weissenberg photographs with Cu  $K\alpha$  radiation. The cell constants were refined subsequently on a Hilger and Watts linear diffractometer. Intensity data for 15 layers were collected with the crystal rotating about the  $b$  axis on the diffractometer with a scintillation counter and molybdenum  $K\alpha$  radiation. Of the

4680 reflexions measured on the diffractometer significant counts were recorded for 2371. In view of the small size of the specimen, absorption corrections were deemed unnecessary. The intensities were corrected for Lorentz and polarization factors.

#### Structure determination

A three-dimensional Patterson map was computed using  $F_o^2$  as coefficients. Vectors typical of a TCNQ molecule were recognized round the origin and round large peaks at  $x = 0.000$ ,  $y = 0.357$ ,  $z = 0.027$  and  $x = 0.000$ ,  $y = 0.280$ ,  $z = -0.055$ . The former was taken to represent the combined vectors from a TCNQ moiety at the origin to one in a general position and the latter to represent combined vectors between a pair of centrosymmetrically related TCNQ moieties. (Two of the six TCNQs in the cell must lie in special positions on related centres of symmetry). The existence of a strong vector between the molecule at the origin and that in the general position suggests that these TCNQ moieties are packed parallel to each other. Thus the TCNQ at each centre of symmetry has a parallel centrosymmetrically related pair, one on either side of it, and the common orientation of the molecules in the group was derived from the vector pattern round the origin. Using the signs of the structure factors calculated from the coordinates of the TCNQ moieties so deduced, a

Table 1. Final positional and thermal parameters of non-hydrogen atoms ( $\times 10^5$ )

The figures in parentheses indicate the standard deviations.

Temperature factor =  $\exp [-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hkB_{13} + k l B_{23})]$

	$x/a$	$y/b$	$z/c$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
C(1)	-19015 (28)	3830 (17)	253 (7)	1813 (44)	603 (14)	94 (3)	69 (42)	18 (17)	20 (10)
C(2)	-4919 (28)	4806 (16)	4605 (7)	2060 (46)	524 (14)	79 (3)	-173 (40)	34 (17)	48 (9)
C(3)	14087 (27)	833 (17)	4145 (7)	1721 (43)	658 (15)	97 (3)	-271 (40)	-99 (17)	47 (10)
C(4)	-10034 (29)	9673 (17)	9128 (7)	2234 (49)	623 (15)	92 (3)	-58 (44)	83 (18)	25 (10)
C(5)	3329 (33)	11022 (21)	13579 (8)	2773 (58)	872 (20)	93 (3)	27 (56)	36 (21)	-71 (12)
C(6)	-28974 (33)	13540 (19)	9697 (8)	2693 (59)	814 (18)	94 (3)	-216 (52)	247 (21)	-52 (12)
C(7)	-19064 (26)	39628 (17)	2613 (7)	1568 (40)	631 (15)	97 (3)	-60 (41)	57 (17)	-45 (10)
C(8)	-6261 (26)	41191 (15)	7101 (6)	1757 (42)	567 (13)	73 (3)	-348 (39)	26 (16)	10 (9)
C(9)	12874 (27)	37142 (16)	6998 (6)	1855 (43)	614 (15)	66 (3)	-349 (40)	-54 (16)	17 (9)
C(10)	18850 (27)	32182 (16)	2733 (7)	1636 (41)	635 (14)	75 (3)	-69 (41)	-55 (16)	-4 (10)
C(11)	6043 (27)	30861 (15)	-1784 (6)	1805 (42)	498 (13)	66 (2)	-105 (38)	-11 (16)	1 (9)
C(12)	-13110 (26)	34689 (16)	-1639 (6)	1666 (41)	638 (14)	60 (2)	-25 (38)	-61 (15)	-20 (9)
C(13)	12038 (28)	25705 (16)	-6252 (7)	1783 (44)	588 (15)	76 (3)	-62 (40)	-31 (17)	-11 (10)
C(14)	-1203 (29)	23842 (17)	-10635 (7)	2050 (47)	643 (15)	88 (3)	26 (42)	169 (18)	-26 (10)
C(15)	30712 (30)	21325 (18)	-6584 (7)	2050 (48)	763 (17)	74 (3)	88 (44)	95 (18)	18 (10)
C(16)	-12639 (29)	46495 (17)	11514 (7)	2188 (48)	729 (16)	58 (2)	-553 (45)	122 (16)	-82 (10)
C(17)	-167 (30)	48419 (20)	16038 (7)	2016 (48)	917 (20)	95 (3)	-690 (50)	171 (18)	-77 (12)
C(18)	-31792 (29)	49962 (19)	11751 (7)	1924 (44)	844 (18)	85 (3)	-446 (46)	185 (17)	-125 (11)
C(19)	65608 (39)	23767 (26)	23989 (9)	2828 (67)	1343 (28)	127 (4)	690 (70)	252 (25)	191 (16)
C(20)	67961 (37)	37684 (28)	24558 (11)	2545 (64)	1405 (31)	209 (5)	58 (69)	167 (27)	657 (20)
C(21)	38790 (35)	25198 (21)	28911 (9)	2529 (59)	843 (19)	154 (4)	27 (53)	206 (24)	142 (14)
C(22)	42128 (40)	39020 (21)	29240 (9)	3667 (73)	749 (20)	153 (4)	581 (62)	312 (26)	143 (14)
O(1)	50184 (25)	43540 (15)	24936 (7)	2983 (44)	945 (16)	196 (3)	300 (40)	157 (18)	497 (11)
N(1)	-44063 (32)	16700 (22)	10300 (8)	2857 (57)	1443 (26)	166 (4)	370 (62)	406 (23)	-81 (16)
N(2)	13431 (36)	12295 (24)	17204 (8)	4101 (73)	1420 (26)	126 (3)	-232 (68)	-216 (24)	-109 (14)
N(3)	-47285 (28)	52760 (20)	12086 (7)	2416 (48)	1143 (21)	144 (3)	-357 (50)	238 (19)	-252 (13)
N(4)	9259 (31)	50372 (23)	19773 (7)	2749 (52)	1596 (26)	107 (3)	-771 (59)	-7 (19)	-186 (14)
N(5)	45809 (28)	17647 (20)	-6953 (8)	2367 (50)	1220 (21)	156 (3)	551 (52)	207 (20)	20 (13)
N(6)	-11963 (30)	22293 (19)	-14120 (7)	3026 (56)	1116 (20)	102 (3)	-209 (54)	-308 (19)	-114 (12)
N(7)	56942 (26)	18683 (14)	28412 (6)	2468 (44)	620 (13)	106 (3)	-35 (39)	47 (16)	-15 (9)



THE CRYSTAL STRUCTURES OF FREE RADICAL SALTS AND COMPLEXES. I

Description and discussion of the structure

Fig. 1(a) shows the dimensions of the two crystallographically independent types of TCNQ moiety. Average bond lengths of chemically similar bonds of both the TCNQ molecule and ion are summarized in Table 5. Though the averaged dimensions do not compare exactly with the previously published dimensions, a

age bond lengths of chemically similar bonds of both the TCNQ molecule and ion are summarized in Table 5. Though the averaged dimensions do not compare exactly with the previously published dimensions, a

Table 3. Comparison of observed and final calculated structure factors

Table with multiple columns for observed and calculated structure factors, including headers like L, P, O, FC and numerical data for various reflections.



may be compared with C–O distances of 1.388 and 1.428 Å in *trans*-2,5-dichloro-1,4-dioxan (Altona, Knöbler & Romers, 1963) and 1.394 and 1.473 Å in *cis*-2,3-dichloro-1,4-dioxan (Altona & Romers, 1963) and with the C–O–C angles 113.1° and 111.6° in these two compounds respectively. The C–C distances averaging 1.497 Å are a little shorter than the corresponding distances 1.507 Å in piperidinium chloride, 1.527 Å in piperazinium dichloride, 1.513 and 1.528 Å in the *trans*-2,5- and the *cis*-2,3-dichloro-1,4-dioxans, but the angles at the carbon atoms are very similar to those in the compounds cited.

The bond lengths and angles involving hydrogen atoms were calculated but are not considered sufficiently accurate to record. Within the rather large experimental error ( $\sigma$  for bond lengths approximately 0.04 Å and for bond angles approximately 2.7°) nearly all were normal.

Fig. 2. shows a general view of the structure in which the TCNQ moieties are seen almost edge-on, stacked very nearly parallel to each other (dihedral

angle 1°28') along the *b* axis, which is 10.67 Å long. Fig. 2 also shows the hydrogen bonding which connects the morpholinium ions along the screw axis by NH...O hydrogen bonds of length 2.852 Å. This chain is also connected sideways to one nitrogen atom of TCNQ<sup>-</sup> by NH...N hydrogen bonds of length 2.945 Å. Both these are normal hydrogen bond distances.

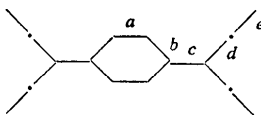
Fig. 3 shows the types of overlap of neutral TCNQ(*A*) projected onto TCNQ<sup>-</sup>(*B*) and for *B'* projected onto *B* (a centrosymmetrically related pair of TCNQ<sup>-</sup> ions). The arrangements are very similar to those previously found (Fritchie & Arthur, 1966) for the only other 2:3 salt to have had its crystal structure determined, (Cs<sup>+</sup>)<sub>2</sub>(TCNQ)<sub>3</sub><sup>-</sup>. Both types of overlap minimize the direct overlap of atoms. These contacts, together with the other short intermolecular contacts, are listed in Table 6. The characteristic overlap and the short interplanar spacings of 3.25 Å (*A*–*B*) and 3.24 Å (*B*–*B'*) indicate that there is charge transfer interaction between the TCNQ moieties.

Table 4. Details of molecular planes

Molecule <i>A</i> (TCNQ <sup>o</sup> )		Molecule <i>B</i> (TCNQ <sup>-</sup> )	
Equation to the plane: 0.2550 <i>X</i> +0.9224 <i>Y</i> -0.2900 <i>Z</i> -0.0000=0		Equation to the plane: 0.2602 <i>X</i> +0.9132 <i>Y</i> -0.3136 <i>Z</i> -3.2502=0	
Atom	Distance from the plane (Å)	Atom	Distance from the plane (Å)
C(1)	0.014	C(7)	0.025
C(2)	-0.002	C(8)	0.007
C(3)	-0.013	C(9)	-0.028
C(4)	0.006	C(10)	-0.016
C(5)	0.005	C(11)	0.029
C(6)	-0.002	C(12)	0.037
N(1)	-0.013	C(13)	0.040
N(2)	0.007	C(14)	0.011
		C(15)	-0.015
		C(16)	0.008
		C(17)	0.016
		C(18)	-0.026
		N(3)	-0.068
		N(4)	0.041
		N(5)	-0.063
		N(6)	-0.022

Table 5. Comparison of mean bond lengths (uncorrected for libration)

Bond	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
* TCNQ <sup>o</sup>	1.346 (4)	1.448 (3)	1.374 (4)	1.440 (3)	1.138 (3)
† TCNQ <sup>1/2-</sup>	1.354 (2)	1.434 (2)	1.396 (2)	1.428 (3)	1.41 (3)
‡ TCNQ <sup>-</sup>	1.356 (6)	1.425 (5)	1.401 (6)	1.417 (5)	1.156 (5)
$\Delta$ (T <sup>-</sup> –T <sup>o</sup> )	+0.010	-0.023	+0.027	-0.023	+0.018
Molecule ( <i>A</i> )	1.348 (3)	1.431 (3)	1.391 (3)	1.426 (3)	1.141 (3)
Molecule ( <i>B</i> )	1.355 (3)	1.419 (3)	1.415 (3)	1.414 (3)	1.145 (3)
$\Delta$ ( <i>B</i> – <i>A</i> )	+0.007	-0.012	+0.024	-0.012	+0.004



\* Long, Sparks & Trueblood (1965).

† Hanson (1968); Goldstein, Seff & Trueblood (1968).

‡ Hanson (1965); Fritchie & Arthur (1966); Fritchie (1966).

Table 6. *Short intermolecular contacts*(a) Molecule *A* to Molecule *B* (stacking contacts of 3.400 Å or less)

C(1 <sup>i</sup> )—C(12 <sup>ii</sup> )	3.363 Å
C(1 <sup>i</sup> )—C(15 <sup>iii</sup> )	3.318
C(2 <sup>i</sup> )—C(11 <sup>iv</sup> )	3.389
C(2 <sup>i</sup> )—C(13 <sup>iv</sup> )	3.330
C(2 <sup>i</sup> )—C(15 <sup>iii</sup> )	3.400
C(3 <sup>i</sup> )—C(10 <sup>iv</sup> )	3.386
C(3 <sup>i</sup> )—C(14 <sup>iv</sup> )	3.326
C(5 <sup>i</sup> )—C(9 <sup>i</sup> )	3.395

(b) Molecule *B* to molecule *B'* (stacking contacts less than 3.300 Å)

C(7 <sup>i</sup> )—C(11 <sup>iii</sup> )	3.294 Å
C(8 <sup>i</sup> )—C(11 <sup>iii</sup> )	3.299
C(13 <sup>i</sup> )—C(16 <sup>iii</sup> )	3.280
C(14 <sup>i</sup> )—C(17 <sup>iii</sup> )	3.294
C(17 <sup>i</sup> )—N(6 <sup>iii</sup> )	3.294
N(4 <sup>i</sup> )—N(6 <sup>iii</sup> )	3.294

(c) Hydrogen bonds

O(1 <sup>i</sup> )—N(7 <sup>iv</sup> )	2.852 Å
N(7 <sup>i</sup> )—N(6 <sup>v</sup> )	2.945

(d) Other non-stacking intermolecular contacts less than 3.400 Å.

C(1 <sup>i</sup> )—N(5 <sup>viii</sup> )	3.302 Å
C(19 <sup>i</sup> )—N(4 <sup>vi</sup> )	3.383
C(19 <sup>i</sup> )—N(6 <sup>v</sup> )	3.390
C(20 <sup>i</sup> )—N(6 <sup>v</sup> )	3.345
C(21 <sup>i</sup> )—N(3 <sup>ix</sup> )	3.386
O(1 <sup>i</sup> )—N(4 <sup>i</sup> )	3.135
N(3 <sup>i</sup> )—N(7 <sup>vi</sup> )	3.174
N(4 <sup>i</sup> )—N(7 <sup>iv</sup> )	3.075

Superscripts indicate equivalent positions as follows:—

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

Standard deviations are all within the range 0.002 to 0.003 Å

Confirmation of the fact that the TCNQ molecule and ion retain their separate identities in the complex salt is found in the solid state infrared spectrum which is virtually the superposition of bands due to TCNQ<sup>0</sup>, TCNQ<sup>-</sup> and the morpholinium ion. The electronic spectrum also shows peaks characteristic of each of the TCNQ species as well as a charge-transfer band centred at about 8500 cm<sup>-1</sup> due to donor-acceptor interaction between TCNQ<sup>-</sup> and TCNQ<sup>0</sup>.

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## Structure Moléculaire et Cristalline du Tétraphényl-1,4,5,8 Naphtalène

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(Reçu le 17 mars 1971)

The structure of 1,4,5,8-tetraphenylnaphthalene has been determined by X-ray analysis. Space group *P2<sub>1</sub>/c*, *Z* = 2, *a* = 6.455, *b* = 24.333, *c* = 8.017 Å,  $\beta = 114^\circ 3'$ . The molecule has *2/m* point group symmetry. The naphthalene nucleus has a boat-like conformation. The maximum angle between the mean planes of the phenyl groups and that of the central naphthalene molecule is 58°.

## Introduction

Ce travail fait partie d'un ensemble d'études expérimentales sur l'encombrement stérique intramoléculaire.

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Il fait suite à deux recherches publiées d'autre part (Evrard, Piret, Germain & Van Meerssche, 1971; Evrard, Piret & Van Meerssche, 1971) sur les structures du tétraphényl-1,2,3,4 cyclopentadiène et du bromo-5 tétraphényl-1,2,3,4 cyclopentadiène.

La détermination de la structure du tétraphényl-