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The Crystal Structure of *N*-Methylphenazinium Tetracyanoquinodimethanide*

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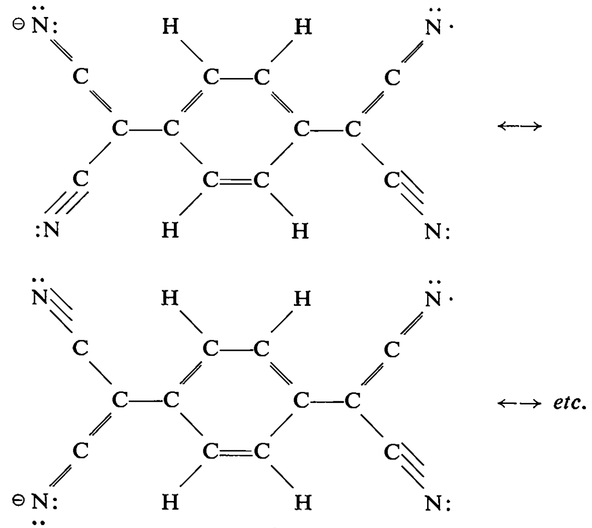
N-Methylphenazinium 7,7,8,8-tetracyanoquinodimethanide, the best known organic electrical conductor, crystallizes with triclinic symmetry $P\bar{1}$, and with a lattice having constants $a=3{\cdot}8682(4)$, $b=7{\cdot}7807(8)$, $c=15{\cdot}735(2)$ Å, $\alpha=91{\cdot}67(1)^\circ$, $\beta=92{\cdot}67(1)^\circ$, $\gamma=95{\cdot}38(1)^\circ$, at 23°C; and $Z=1$. The tetracyanoquinodimethan anion-radicals form a charge-resonance-bonded column parallel to **a** with interplanar spacing 3·26 Å. The van der Waals spacing in the similar column of phenazinium cations is 3·36 Å.

Introduction

Salts of the stable anion-radical, $C_{12}H_4N_4^-$ (I),

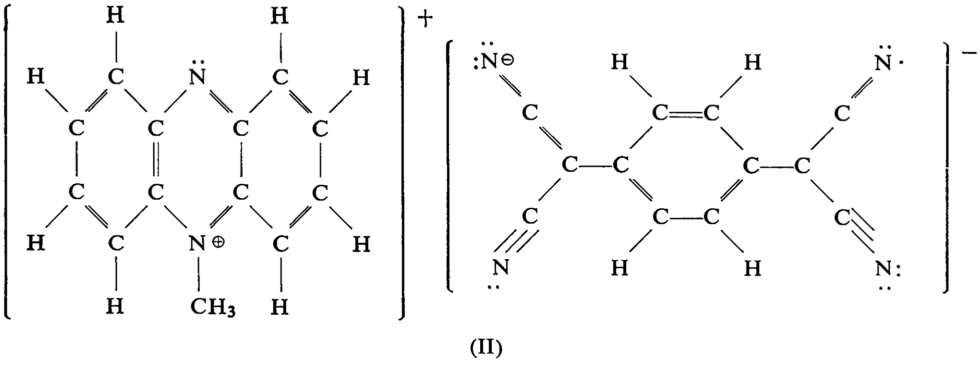


(I)

derived from 7,7,8,8-tetracyanoquinodimethan include some of the best electrically conductive organic compounds known. Furthermore, the range of conductance in these salts is quite large, including values from about 100 ohm^{-1}cm^{-1} to 10^{-12} ohm^{-1}cm^{-1} at room temperature (Acker, Harder, Hertler, Mahler, Melby, Benson & Mochel, 1960; Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962). With few exceptions the more conductive salts are 'complex', containing both formally neutral and formally negative tetracyanoquinodimethan (hereafter TCNQ). Arthur (1964) has shown that the moderately conductive $Cs_2(TCNQ)_3$ salt has a structure based on somewhat irregular columns of TCNQ units stacked face-to-face, in which two-thirds of the interplanar spacings are as short as 3·21 Å. As an aid in understanding the electronic properties of these salts, the crystal structure of one of the exceptional simple salts, *N*-methylphenazinium TCNQ, $(C_{13}H_{11}N_2)^+(C_{12}H_4N_4)^-$ (II) has been determined. This salt has a room temperature specific conductivity of 100 ohm^{-1}cm^{-1}, the highest value known for an organic compound (Melby, 1965).

The experimental data

A sample of glistening black, lath-like crystals of *N*-methylphenazinium TCNQ was kindly supplied by Dr L. R. Melby. Several approximately equidimensional specimens were mounted about different axes for Weissenberg photography and the crystal lattice was shown to be triclinic with the shortest translation paralleling the lath axis. Zones [100], [010], and [111] were photographed in an especially accurate Strau-



(II)

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manis-type Weissenberg camera, using crystals about 0·2 mm in average cross-section and Ni-filtered Cu Kα radiation. This camera has been described previously (Fritchie, 1966). The Straumanis design eliminates calibration errors; careful construction (checked with silicon powder from the IUCr lattice-constant project) and careful use eliminates eccentricity errors; and least-squares fitting to $\sin^2\theta$ values of many reflections minimizes small reading errors. Absorption errors can be detected by the trend of fit in the least-squares calculations. Finally, there is a fairly independent check of accuracy if, as is usually the case, several crystals are used in different mountings. For *N*-methylphenazinium TCNQ the lattice constants at 23 ± 1 °C were determined to be $a=3\cdot8682\pm0\cdot0004$, $b=7\cdot7807\pm0\cdot0008$, $c=15\cdot735\pm0\cdot002$ Å, $\alpha=91\cdot67\pm0\cdot01°$, $\beta=92\cdot67\pm0\cdot01°$, and $\gamma=95\cdot38\pm0\cdot01°$. The density of 1·4090 g.cm^{-3} calculated by assuming $Z=1$ agrees fairly well with a value of 1·43 g.cm^{-3} measured by flotation (Melby, 1965). Although the presence of only one asymmetric molecule per unit cell would seem to indicate that $P1$ (C_1) is the correct space group, a disordered structure in space-group $P\bar{1}$ (C_i) is favored. A piezoelectric test, made with an instrument in which hexamethylenetetramine gives an easily detectable effect, was negative.

Intensity data were derived from films prepared by the multiple-film equi-inclination technique. Layers $0kl$ through $3kl$ and $h0l$ through $h6l$ were photographed with Ni-filtered Cu $K\alpha$ radiation, using crystals about 0·2 mm in average diameter. No absorption corrections were made. After application of the Lorentz-polarization factors, F_o data were reduced to a common scale with a computer program that finds self-consistent values of the individual scale factors K_i in the equations

$$K_i=(1/n_i)\sum_{\mathbf{H}}(|\bar{F}_{\mathbf{H}}|/|F_{\mathbf{H}_i}|)$$

subject to the condition that the sum of K_i is constant. In this equation, $|F_{\mathbf{H}_i}|$ is an estimate, within set (or film) i, of reflection **H**; $|\bar{F}_{\mathbf{H}}|$ is the average of all measures of $|F_{\mathbf{H}}|$; and n_i is the number of terms in the ith summation. The summation is taken over all reflections for which estimates are present in the ith set and at least one other. This scale determining procedure, which was pointed out to the author several years ago by Dr B. D. Sharma and whose origin is uncertain in recollection, has the intuitive appeal that it gives each film a scaling factor which is the average of all those obtainable from reflections on the film. Because each reflection must be compared with its 'best value' or average, the procedure is necessarily iterative, at least in direct formulation. In the present case, convergence was fairly slow and of an asymptotic sort. The twenty or so required cycles used only one or two minutes of time on an IBM 7040 computer, however.

The volume of reciprocal space photographed contains 1919 reflections. The intensities of 865 of these are greater than the background intensity.

Table 1. *Atomic parameters*

Standard deviations are in parentheses. Temperature factors are of the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$. All hydrogen atoms were given a thermal exponent of 3·0 Å^2.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	−0·0469 (11)	1·1743 (6)	0·0137 (3)	0·0652 (32)	0·0148 (8)	0·0042 (22)	0·0144 (28)	0·0009 (14)	−0·0013 (7)
C(2)	0·1371 (11)	1·0943 (6)	0·0722 (3)	0·0607 (32)	0·0167 (9)	0·0037 (20)	0·0122 (28)	0·0002 (14)	−0·0014 (7)
C(3)	0·1946 (11)	0·9163 (6)	0·0626 (3)	0·0514 (28)	0·0187 (9)	0·0037 (19)	0·0095 (28)	−0·0006 (13)	0·0007 (7)
C(4)	0·3854 (11)	0·8328 (6)	0·1228 (3)	0·0589 (31)	0·0175 (9)	0·0040 (20)	0·0101 (29)	−0·0022 (14)	−0·0002 (7)
C(5)	0·5307 (12)	0·9154 (6)	0·1996 (3)	0·0706 (33)	0·0170 (9)	0·0038 (20)	0·0087 (29)	−0·0012 (14)	0·0004 (7)
C(6)	0·4466 (12)	0·6561 (6)	0·1144 (3)	0·0714 (33)	0·0179 (9)	0·0039 (20)	0·0110 (29)	−0·0011 (14)	0·0000 (7)
C(7)	0·0115 (13)	0·5726 (8)	0·3029 (3)	0·0722 (37)	0·0294 (12)	0·0043 (23)	0·0086 (37)	−0·0006 (16)	0·0022 (9)
C(8)	0·0334 (14)	0·3936 (8)	0·2948 (3)	0·0817 (41)	0·0302 (13)	0·0044 (24)	0·0050 (41)	−0·0015 (17)	−0·0013 (10)
C(9)	0·2011 (13)	0·3118 (7)	0·3574 (3)	0·0778 (37)	0·0215 (10)	0·0050 (24)	0·0060 (35)	0·0038 (17)	−0·0015 (9)
C(10)	0·3558 (11)	0·4034 (7)	0·4304 (3)	0·0612 (33)	0·0220 (10)	0·0038 (20)	0·0110 (31)	0·0020 (15)	−0·0009 (8)
C(11)	0·3332 (12)	0·5855 (7)	0·4372 (3)	0·0625 (31)	0·0211 (10)	0·0038 (20)	0·0059 (31)	0·0019 (14)	−0·0004 (8)
C(12)	0·1610 (13)	0·6658 (7)	0·3720 (3)	0·0730 (36)	0·0249 (11)	0·0047 (24)	0·0077 (36)	0·0026 (16)	0·0033 (9)
N(13)	0·6526 (12)	0·9800 (6)	0·2624 (3)	0·1089 (39)	0·0232 (9)	0·0050 (21)	0·0029 (33)	−0·0086 (16)	−0·0014 (8)
N(14)	0·5007 (12)	0·5127 (6)	0·1102 (3)	0·1081 (38)	0·0214 (9)	0·0052 (21)	0·0193 (31)	−0·0072 (16)	0·0000 (8)
N(15)	0·4795 (11)	0·6786 (5)	0·5069 (3)	0·0831 (32)	0·0208 (8)	0·0042 (18)	0·0119 (28)	−0·0007 (13)	0·0003 (7)
C(16)	0·4672 (44)	0·8750 (15)	0·5145 (10)	0·2149 (169)	0·0159 (23)	0·0088 (85)	0·0217 (104)	0·0189 (64)	−0·0004 (24)
H(17)	−0·0900	1·2991	0·0268						
H(18)	0·2207	1·1635	0·1220						
H(19)	−0·1302	0·6263	0·2553						
H(20)	−0·0702	0·3220	0·2363						
H(21)	0·2260	0·1885	0·3545						
H(22)	0·1324	0·8007	0·3728						

Trial structure and refinement

The short a axis requires that all atoms be resolved in the [100] projection and that each ion lie at least approximately perpendicular to [100]. It was thus expected that comparison of the [100] Patterson function with vector sets constructed from models of the two ions would reveal their orientations and relative positions. This proved to be the case. In the [100] projection, the vector between the centers of the two ions, excluding the *N*-methyl group, was indistinguishable from $(\frac{1}{2}, \frac{1}{2})$. It was concluded that this projection has at least very nearly the symmetry of space group $P\bar{1}$, and this space group was tentatively chosen, subject to confirmation by the behaviour of the non-hydrogen thermal parameters.

Because of the need to use the thermal ellipsoids as the basis of space-group assignment, it seems well to review the logic of this procedure as applied to the present case. In a structure which is at least very nearly centrosymmetrical, one might ask what deviations from centrosymmetry are likely. Because of the asymmetry of packing forces that would be introduced by requiring all methyl groups to fall on one side of the phenazinium nucleus, it is expected that the nucleus as a whole would be displaced away from the methyl group. Ignoring such a displacement by use of a centrosymmetric space group would result in thermal ellipsoids elongated in the direction of displacement. Thus the absence of abnormally elongated ellipsoids implies that the nuclear displacement is at most quite small, that the potential energy of a methyl group would be nearly the same on either side of the phenazine nucleus, and that there is no reason to expect ordering.

Refinement of the [100] projection, as well as of the complete structure at a later stage, was accomplished by the least-squares procedure described by Hughes (1941), using a modified Gantzel–Sparks–Trueblood block-diagonal program (Gantzel, Sparks & Trueblood, 1962). This least-squares program minimizes $\Sigma\, w\,||F_o|-|F_c||^2$, where $\sqrt{w}$ was first set equal to unity and later to the function $1/(0\cdot4+0\cdot05|F_o|)$. Using only the fifteen ordered non-hydrogen atoms, isotropic refinement proceeded fairly smoothly to $R=18\%$. A difference function calculated at this stage showed no anomalies near the ordered atoms, and did show the *N*-methyl group as a broad, low peak. The thermal parameters of the ordered atoms, ranging from 3·0 to 4·2 Å^2, seemed to confirm the centric nature of the [100] projection. Addition of C(16), the methyl carbon, in disorder between the two sites required by $P\bar{1}$ permitted reduction of R to 13·9%. In contrast to the moderate temperature factors of the ordered atoms, the value of B for C(16) was at this time 6·4 Å^2.

Initial x parameters for all atoms were obtained by examining the foreshortening of the ions in the [100] projection and by use of the [010] Patterson function. Here also, no evidence was found to invalidate the choice of $P\bar{1}$ as space group. The three-dimensional anhydrogenic model was isotropically refined in 10 least-squares cycles from $R=31\cdot2\%$ to $R=16\cdot3\%$. Addition of non-methyl hydrogen atoms in positions indicated by a three-dimensional difference map lowered R to 14·0%; one further cycle of refinement of the carbon and nitrogen atoms reduced R to 13·2%. Seven cycles which the positions and anisotropic thermal parameters of the non-hydrogen atoms and the positions of the hydrogen atoms were refined reduced R to its final value of 9·8%. Hydrogen atoms were given a thermal exponent of 3·0 Å^2 throughout these calculations.

The final atomic parameters are given in Table 1; the calculated and experimental values of the structure factors are in Table 2. Fig. 1 shows final interatomic distances and angles. The average standard deviation in a carbon–carbon or carbon–nitrogen distance [excluding C(16)] is 0·006 Å; angles involving these atoms have standard deviations of about 0·6°. Uncertainty in the position of C(16) is discussed below.

Discussion

Space group

The choice of $P\bar{1}$ as space group is based primarily upon the size and shape of the final thermal ellipsoids of the ordered non-hydrogen atoms. Although not tabulated explicitly, the sizes of the principal axes are very reasonable, ranging from approximately $3\cdot4\times3\cdot9\times4\cdot4$ Å^2 for the inner atoms to about $4\cdot2\times5\cdot0\times6\cdot5$ Å^2 for those near the ends of the ions. The TCNQ$^-$ ion vibrates nearly isotropically except for the two C–N groups, which vibrate principally out-of-plane. The phenazinium nucleus apparently undergoes librational motion roughly in its plane, with average ellipsoid about $4\cdot0\times4\cdot3\times6\cdot1$ Å^2. The ellipsoid of the disordered C(16)

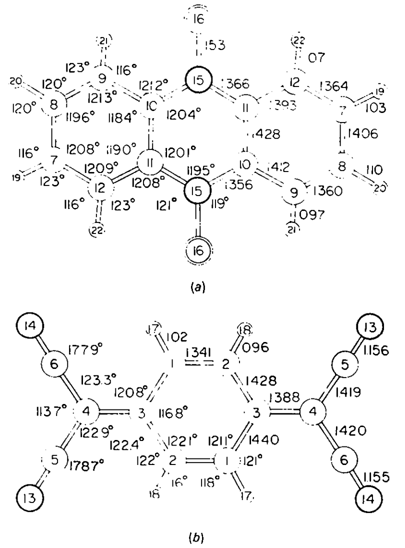

Fig. 1. Interatomic distances and angles. (*a*) *N*-methylphenazinium cation; (*b*) TCNQ anion. Heavy circles are nitrogen; double circles are disorder sites of the *N*-methyl group.

Table 2. *Observed and calculated structure factors*

Each group of three columns contains l, $10|F_o|$, and $10F_c$ respectively, and is headed by the values of h and k common to the group. A negative figure in the $|F_o|$ column gives the observational threshold for an unobserved reflection. An asterisk following the $|F_o|$ column indicates that the reflection was omitted from least-squares and R-value calculations.

0 0

2	191	178
3	31	40
4	52	-62
5	332	-305
6	101	-99
7	-9	-2
8	92	85
9	41	35
10	79	80
11	41	39
12	50	-50
13	74	-74
14	77	77
15	25	-31
16	92	95
17	20	17

0 1

0	138	-160
1	451	541
2	164	163
3	29	34
4	174	160
5	27	27
6	88	-87
7	309	-300
8	18	-15
9	137	-138
10	36	-35
11	43	50
12	45	49
13	22	-22
14	25	-26
15	43	41
16	-18	-1
17	22	-22
18	-13	-17
-1	282	297
-2	201	-225
-3	84	-75
-4	266	271
-5	253	238
-6	29	26
-7	41	-38
-8	14	13
-9	86	-85
-10	97	-97
-11	18	-18
-12	36	37
-13	65	63
-14	34	24
-15	196	195
-16	18	-6
-17	-16	3
-18	-13	-3
-19	-11	-3
-20	-7	-17

0 2

0	151	121
1	162	165
2	158	-173
3	180	-172
4	-7	-9
5	74	-83
6	207	-190
7	120	121
8	144	-137
13	34	-37
14	68	-70
-2	173	-168
-3	81	99
-4	163	141
-5	110	-112
-6	257	-248
-7	49	48
-8	205	-171
-9	-13	22
-10	-13	6
-11	32	31
-12	-14	13
-13	34	32
-14	59	58
-15	-18	2
-16	-16	20
-17	-14	-8

0 3

0	117	111
1	173	-140
2	65	-75
3	-5	1
4	59	51
5	-9	-12
6	22	26
7	54	-58
8	-11	13
9	72	-78
10	23	-26
11	34	39
12	36	36
13	41	-41
14	-18	0
15	56	-54
16	-14	12
17	-13	-13
18	-11	-10
-1	442	-403
-2	135	-140
-3	63	65
-4	72	72
-5	16	-16
-6	49	-46
-7	131	-120
-8	68	66
-9	113	-101
-10	52	-52
-11	-14	-4
-12	-16	-11
-13	-18	-8
-14	34	36
-15	-18	-4
-16	-18	5
-17	-14	-20

0 4

0	223	-201
1	43	47
2	65	-61
3	31	-29
4	-7	-11
5	50	50
6	65	66
7	-11	7
8	104	110
9	16	-11
10	18	-23
11	36	32
12	40	44
13	-16	-0
14	45	-49
15	-14	5
16	-13	-10
17	-11	-10
18	-7	-3
-2	129	-125
-3	56	52
-4	31	27
-5	34	-34
-6	101	-95
-7	-9	16
-8	-11	21
-9	-11	6
-10	-13	-16
-11	-14	-0
-12	-14	-6
-13	-14	-7
-14	38	-36
-15	-14	13
-16	52	-52
-17	-11	-7
-18	-9	6

0 5

0	49	-41
1	27	-29
2	84	-90
3	-7	11
4	61	64
5	92	106
6	-9	-11
7	235	240
8	-13	-3
9	27	31
10	27	-30
11	-13	-3
12	-13	2
13	-13	11
14	-13	1
15	-11	-1
16	-9	8
-1	97	-88
-2	20	-22
-3	108	107
-4	45	43
-5	34	-34
-6	32	-33
-7	117	115
-8	27	-32
-9	59	61
-10	-13	-1
-11	-13	10
-12	-13	4
-13	-13	-6
-14	-13	-10
-15	40	-41
-16	-11	-9
-17	-7	-13

0 6

0	40	37
1	32	35
2	11	13
3	-7	-2
4	25	-28
5	27	-30
6	63	66
7	-14	-4
8	178	140
9	56	56
10	-14	-6
13	29	-25
14	56	-44
15	-9	-6
-2	13	15
-3	14	-11
-4	34	-38
-5	40	-40
-6	43	37
-7	18	17
-8	207	183
-9	-13	-4
-10	45	39
-11	-13	19
-12	-13	-6
-13	36	-32
-14	-13	-15

0 7

3	34	32
4	47	46
6	40	-33
-1	83	-84
-6	63	58
-7	90	89

0 8

0	22	-34
6	40	-37
11	27	-21
-5	29	-23

0 9

7	61	-42

1 0

0	149	-175
1	102	-130
2	43	-42
3	120	127
4	22	24
5	149	155
6	41	44
7	25	25
8	56	-65
9	59	-63
10	34	-40
11	59	75
12	-14	-10
13	216	240
14	16	20
15	-16	5
16	-14	7
17	-14	-2
18	43	-39
19	27	-34
-1	239	310
-2	174	-204
-3	690*	1047
-4	129	130
-5	59	59
-6	101	97
-7	16	15
-8	185	-179
-9	135	-129
-10	29	-32
-11	13	-17
-12	-14	5
-13	52	48
-14	50	42
-15	16	-13
-16	54	-50
-17	59	55
-18	22	-19
-19	14	15

1 1

0	61	72
1	167	174
2	20	22
3	244	-250
4	349	-333
5	14	15
6	115	-116
7	14	15
8	95	100
9	93	105
10	27	-35
11	54	-62
12	49	48
13	-18	-5
14	-18	10
15	-18	-4
16	-16	8
17	-14	7
18	-11	-10
-1	208	197
-2	909	891
-3	47	-55
-4	52	65
-5	56	-66
-6	45	-46
-7	-11	-8
-8	50	48
-9	43	44
-10	25	28
-11	18	19
-12	-14	0
-13	-16	-20
-14	40	-36
-15	-18	-14
-16	54	55
-17	-14	-6
-18	83	96
-19	-11	9

1 2

0	84	-82
1	11	10
2	13	-10
3	68	-70
4	72	77
5	217	-218
6	-16	7
7	102	-113
8	52	-50
9	-20	27
10	-20	-16
11	58	-68
12	-16	25
13	-18	8
14	-18	11
15	-16	-24
16	-14	-23
17	-13	-4
18	-16	2
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-2	108	107
-3	68	69
-4	40	-36
-5	13	-15
-6	133	135
-7	95	107
-8	22	-22
-9	131	-129
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-11	81	-89
-12	-16	-27
-13	-16	6
-14	-18	29
-15	-18	23
-16	-16	30
-17	75	73
-18	-18	-1
-19	-14	3

1 3

0	36	-36
1	45	-46
2	-9	-11
3	31	-41
4	140	-140
5	34	39
6	88	-88
7	36	-39
8	25	24
9	49	51
10	-14	-15
11	31	-30
12	93	-94
13	34	32
14	23	-24
15	20	-21
16	-13	-1
17	-16	18
18	-11	4
-1	58	59
-2	61	-61
-3	63	69
-4	199	-200
-5	59	-57
-6	56	56
-7	-11	-19
-8	72	-74
-9	-13	9
-10	81	-80
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-12	25	-25
-13	-20	-17
-14	-18	1
-15	-18	4
-16	-16	3
-17	-14	21
-18	-16	-0
-19	-9	1

1 4

0	61	-67
1	16	-21
2	68	69
3	16	14
4	16	13
5	81	92
6	-11	-15
7	45	-50
8	-13	7
9	40	42
10	-14	12
11	61	-54
12	-14	3
13	-22	-26
14	-14	-2
15	-13	-6
16	-11	4
17	-14	10
-1	74	-87
-2	59	66
-3	180	-204
-4	27	-30
-5	-9	-7
-6	50	51
-7	-11	-4
-8	36	-33
-9	49	-51
-10	-14	8
-11	-22	-21
-12	-14	-14
-13	-14	-8
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5	-7	-11
-1	31	-29
-2	22	24
-3	-11	-1
-4	-9	1

has principal axes of 3·8 × 7·2 × 14·3 Å², with the largest value out-of-plane and the second largest nearly parallel to the *b* axis. The somewhat larger apparent thermal motion of the phenazinium nucleus compared with that of the anion could possibly be indicative of an incorrect choice of space group, but seems more likely to be due to the lesser van der Waals forces holding the cations in place.

Packing

A major reason for studying this salt was determination of the mode of packing as a basis for interpreting its unusual electrical behavior. It is thus of great interest to see that the TCNQ⁻ ions pack in a columnar manner (Figs. 2 and 3) generally similar to that found in $Cs_2(TCNQ)_3$ (Arthur, 1964), and that the interplanar spacing within this column is a very short 3·26 ± 0·01 Å, paralleling the short spacing of 3·21 ± 0·01 Å found between two-thirds of the vicinal pairs in the cesium salt. Also interestingly, the nearest-neighbor configuration of a TCNQ⁻ ion, shown in Fig. 4, is very similar to that within the closely-spaced triad of TCNQ units of $Cs_2(TCNQ)_3$. In the latter case, a given ion is related to its more closely-spaced neighbors by a longitudinal displacement essentially identical with that shown in Fig. 4, but with a lateral displacement of about 0·35 Å as well. This distinctive symmetry, together with the short interplanar spacing, seems characteristic of charge-transfer bonding (Mulliken, 1952), in which a 'charge-transfer' or 'supermolecular' orbital is formed between an electropositive 'donor' molecule *D* and an electronegative 'acceptor' molecule *A* by overlap of orbitals of similar energy from the two molecules – the highest occupied orbital of *D* and the lowest unfilled orbital of *A*. In the present case *D* and *A* are identical and, in fact, every molecule in a given anionic column must participate in formation of 'supermolecular' orbitals. In such a case of 'selfcharge-transfer' or 'charge-resonance' involving identical radicals, the occupied and the unfilled orbitals are identical and one would expect the greatest interaction to occur when molecules are directly superimposed. In the case of a pair of TCNQ$^-$ ion-radicals, however, calculation of intermolecular pairing energy (Fritchie, Chesnut & Simmons, 1966) by use of a Hoffman-like procedure (Hoffman, 1963) discloses a second energy minimum with respect to longitudinal translation. This minimum occurs when the center of one ring falls almost exactly over the center of the quinomethan double bond of the adjacent ion, exactly the geometry found in *N*-methylphenazinium TCNQ and very similar to that found in the closely-spaced triad in $Cs_2(TCNQ)_3$.

One might thus hazard the guess that one of these two favorable configurations – either complete overlap or longitudinal slipping of one-fourth the molecular length – will approximately characterize most TCNQ$^-$ salts. The choice and any distortions are presumably dictated by intercolumnar packing needs. That distortion exists is shown by the potassium TCNQ structure (Anderson & Fritchie, 1964), in which more widely spaced TCNQ$^-$ units ($\sim$3·4 Å) are slipped diagonally from direct superposition by about half the length and in the direction of a quinoid single bond.

In contrast with the closely packed TCNQ$^-$ units, the phenazinium cations maintain a more nearly normal van der Waals interplanar separation of 3·36 Å

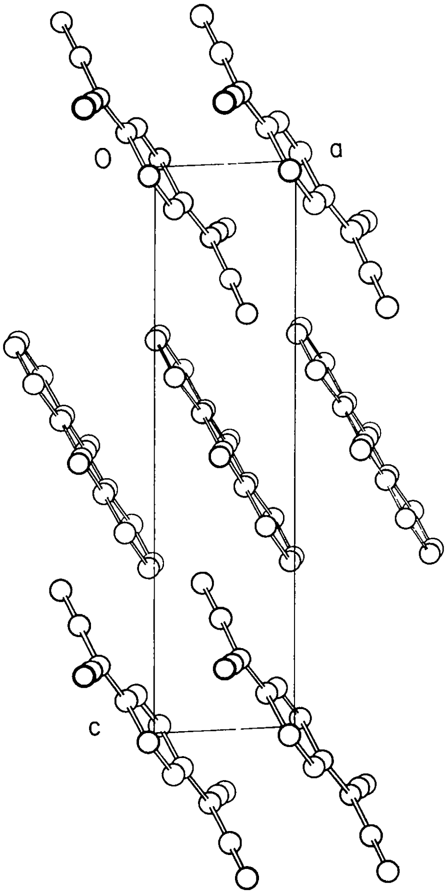

Fig. 2. (010] projection.

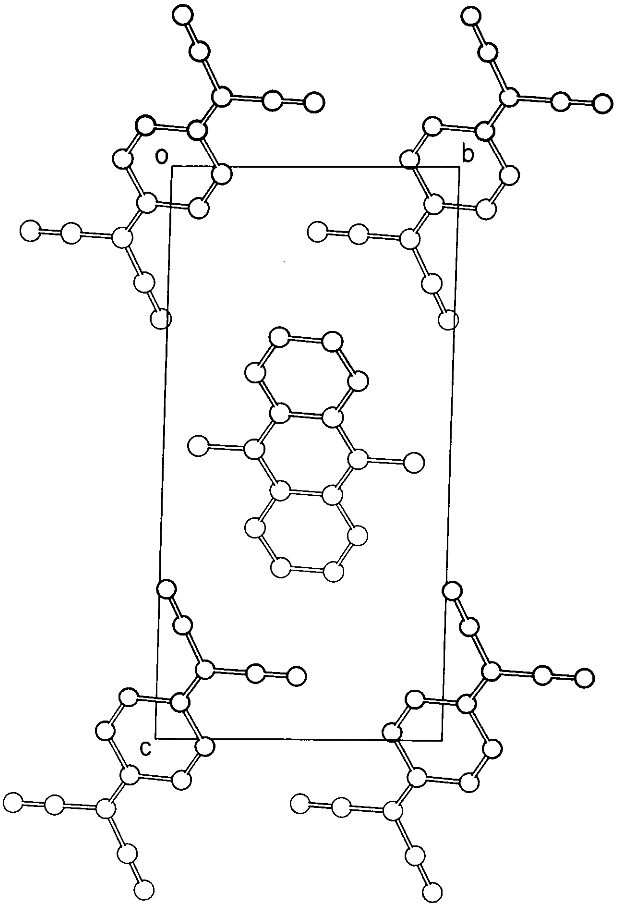

Fig. 3. [100] projection. The disordered *N*-methyl group is shown in both of its alternate sites.

Table 3. *Comparison of bond lengths*

Bond	$C_{13}H_{11}N_2^+$	$C_{12}H_8N_2$*	Bond	TCNQ$^-$	TCNQ^0†
C(7)—C(8)	1·406 (6)	1·412 (13)	C(1)–C(2)	1·341 (6)	1·346 (4)
C(8)—C(9)	1·362 (5)	1·374 (9)	C(2)–C(3)	1·434 (5)	1·448 (3)
C(9)—C(10)	1·402 (5)	1·408 (9)	C(3)–C(4)	1·388 (6)	1·374 (4)
C(10)–C(11)	1·428 (6)	1·433 (13)	C(4)–C(5)	1·420 (5)	1·440 (3)
C(10)–N(15)	1·361 (5)	1·345 (9)	C(5)–N(13)	1·156 (5)	1·140 (3)

* Herbstein & Schmidt (1955).
† Long, Sparks & Trueblood (1965).

(Pauling, 1960). It is thus likely that no unusual interaction is present among these ions and that the electrical conductivity is a property solely of the $TCNQ^-$ columns.

Molecular dimensions

The bond lengths in the cation and in the anion provide an interesting comparison with those found in the corresponding neutral molecular species (phenazine: Herbstein & Schmidt, 1955; TCNQ: Long, Sparks & Trueblood, 1965). Averages of the bond lengths in the two neutral materials and the two ions, assuming *mmm* symmetry in all cases, are summarized in Table 3. Differences between phenazine and the phenazinium cation, both of which in valence bond theory are described by many similar resonance structures, are negligible. Comparison of $TCNQ^\circ$ with $TCNQ^-$, however, shows that the quinoid valence structure which explains fairly well the bond lengths of neutral TCNQ is apparently only the predominant form in the anion, where a number of canonical forms of similar energy must be considered.

No great faith can be placed in the $N\text{–}C_{\text{methyl}}$ bond length of 1·53 Å. This value is considerably greater than the C–N average bond length of 1·48 Å given by Sutton (1957), but because of the disorder between two equivalent sites and extreme thermal motion (or further masked disorder) it should be considered only an order-of-magnitude estimate. Final F_o maps through the site of C(16), in sections at constant x and at constant y, showed no unusual features (*i.e.*, no double maximum or unusual shape). It is concluded either that the potential in which this methyl group moves is very broad, or that close approaches between methyl groups which happen to occupy adjacent cells force a variety of mean positions upon these atoms.

Both the anion and the cation are planar, with a maximum deviation from planarity for the non-hydrogen atoms of 0·010 Å in the case of the phenazinium plane and of 0·013 Å in the case of the $TCNQ^-$ plane.

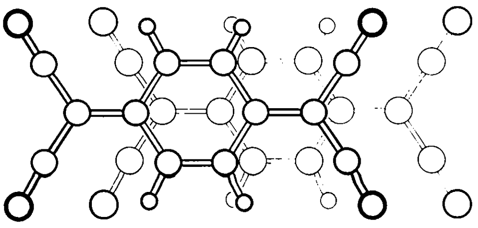

Fig. 4. Nearest-neighbor packing within the $TCNQ^-$ column. Direction of view is perpendicular to the molecular planes.

Equations of the least-squares planes (Blow, 1960) and displacements of atoms from these planes are given in Table 4.

Table 4. *Least-squares planes*

An orthonormal axial system {**m, n, p**} with **n**||**b** and **p**||**c*** is used to describe the planes. Contributing weights w and deviations δ are given.

Plane 1: $0{\cdot}88112m+0{\cdot}09189n-0{\cdot}46387p=-1{\cdot}9702$ (phenazine)

Plane 2: $0{\cdot}86461m+0{\cdot}19829n-0{\cdot}46166p=\ 1{\cdot}5430$ (TCNQ)

Plane 3: $0{\cdot}86164m+0{\cdot}19401n-0{\cdot}46898p=\ 1{\cdot}5095$ (TCNQ)

Atom	w_1	$\delta_1\times10^3$(Å)	Atom	w_2	$\delta_2\times10^3$(Å)	w_3	$\delta_3\times10^3$(Å)
C(7)	6	−10	C(1)	6	6	6	−1
C(8)	6	1	C(2)	6	13	6	1
C(9)	6	4	C(3)	6	3	6	−3
C(10)	6	4	C(4)	6	13	6	1
C(11)	6	4	C(5)	6	−2		−26
C(12)	6	6	C(6)	6	7		2
N(15)	7	3	N(13)	7	−9		−44
C(16)		41	N(14)	7	−4		−4
H(19)		−66	H(17)		−46		−58
H(20)		70	H(18)				−28
H(21)		22					
H(22)		−1					

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