centre d'octaèdres assez réguliers dont les sommets sont constitués par six fluors libres: 2F(5), 2F(6) et 2F(6'), appartenant deux à deux à deux couches successives.

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The Crystal Structures of Free Radical Salts and Complexes.
II. (N-(n-Propyl)quinolinium)$^+$(7,7,8,8-Tetracyanoquinodimethane)$_2^-$

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The 2:1 complex formed between tetracyanoquinodimethane (TCNQ) and N-(n-propyl)-quinolinium (NPQ) crystallizes as brown triclinic crystals, space group $P\bar{1}$, with 2 molecules of the complex in the unit cell of dimensions $a=7\cdot53$, $b=15\cdot15$, $c=14\cdot30$ Å, $\alpha=111\cdot2$, $\beta=88\cdot9$, $\gamma=99\cdot1°$. The structure was solved by Patterson methods and refined by block-diagonal least squares using 2114 independent reflexions measured on a linear diffractometer. The final residual, R, was $0\cdot080$. The TCNQ moieties are packed plane-to-plane to form a column along the c axis. The characteristic overlap and short interplanar spacings indicate charge-transfer interaction between four TCNQ moieties stacked as tetramers.

Introduction

Many molecular complexes of 7,7,8,8-tetracyanoquinodimethane (TCNQ) exhibit large specific conductances for organic crystals. The structural investigation of the complex (N-(n-propyl)-quinolinium)$^+$ (TCNQ)$_2^-$ is described to assist further elucidation of the relationship between the electrical properties and the structures of TCNQ complexes, following the structure of the (morpholinium$^+$)$_2$ (TCNQ)$_3^{2-}$ complex reported in part I (Sundaresan & Wallwork, 1972).

Experimental

Crystal data

(C$_{12}$H$_{14}$N) (C$_{12}$H$_4$N$_4$)$_2$, M.W.580·6,
Triclinic,
$a=7\cdot53\pm0\cdot02$, $b=15\cdot15\pm0\cdot02$, $c=14\cdot30\pm0\cdot04$ Å,
$\alpha=111\cdot2\pm0\cdot1°$, $\beta=88\cdot9\pm0\cdot5°$, $\gamma=99\cdot1\pm0\cdot6°$;
$U=1499\cdot5$ Å^3;
$D_m=1\cdot292$ g.cm^{-3}, $Z=2$, $D_c=1\cdot284$ g.cm^{-3};
$F(000)=602$;
Mo $K\alpha$ ($\lambda=0\cdot7107$Å), $\mu=0\cdot87$ cm^{-1};
Space group $P\bar{1}$.

Crystals of the complex were deposited when boiling solutions of NPQ iodide and TCNQ in acetonitrile were mixed and allowed to cool very slowly. The space group and the cell constants were deduced initially

from oscillation and Weissenberg photographs using Cu $K\alpha$ radiation. The cell dimensions were subsequently refined on a Hilger and Watts linear diffractometer. Intensity data for 7 layers were collected with the crystal rotating about its a axis on the diffractometer using a scintillation counter and Mo $K\alpha$ radiation. A total of 1696 significant counts were recorded out of 3755 reflexions measured on the diffractometer. In view of the small size of the specimen, no absorption corrections were made. The intensities were corrected for Lorentz and polarization factors.

Structure determination

A three-dimensional Patterson map was computed using F_0^2 as coefficients. Vectors typical of TCNQ were recognized round the origin and round peaks at (1) $x=0\cdot086, y=0\cdot033, z=-0\cdot244$; (2) $x=0\cdot141, y=0\cdot067, z=0\cdot489$ and (3) $x=0\cdot227, y=0\cdot122, z=0\cdot233$. These peaks could all be interpreted in terms of a trial structure in which TCNQ moieties were stacked along the z axis, spaced by roughly $c/4$, as shown in Fig. 2. The strong peak at (1) was taken to represent the combined vectors between the two crystallographically independent TCNQ moieties (A and B) and also the centrosymmetrically related pair of TCNQ moieties (A' and A), while the strong peak at (2) was taken to represent the vectors between the TCNQ moieties B' and A. The relatively weaker peak at (3) was taken to represent the

vectors between the other pair (B' and B) of centro-symmetrically related TCNQ moieties. The existence of strong vectors between the two crystallographically independent types of TCNQ suggests that all the TCNQ moieties are packed parallel to each other and thus the common orientation of the TCNQ moieties was derived from the vector pattern around the origin. Using the signs of the structure factors calculated on the basis of this trial structure for the TCNQ moieties, a three-dimensional Fourier electron density distribution was computed. This confirmed the positions of TCNQ moieties and showed 10 of the 13 atoms of the NPQ ion. A second Fourier synthesis based on the signs of the structure factors calculated from the positions of the 42 atoms revealed the other three atoms of the NPQ ion. Further least-squares refinement of

the positional and isotropic thermal parameters of all the atoms gave an R value of 0·201.

The weighting scheme used was:

$$\sqrt{w} = 1 \text{ if } |F_o| \le P_1$$

or

$$\sqrt{w} = P_1/|F_o| \text{ if } |F_o| > P_1,$$

where P_1 was given a value of 200·0 on the scale of Table 2.

The 19 hydrogen atom positions, other than those of the methyl group, were calculated and a difference Fourier synthesis also confirmed their positions. No attempts were, however, made either to refine their positional parameters or to locate the three methyl hydrogen atoms, since these were not obvious in the dif-

Table 1. *Final positional and thermal parameters of non-hydrogen atoms*

All values are multiplied by 10^4. The figures in parentheses indicate the standard deviations.
Temperature factor $= \exp\left[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})\right]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	2229 (9)	81 (4)	−1467 (5)	183 (16)	54 (4)	63 (5)	1 (12)	−33 (13)	63 (7)
C(2)	1598 (9)	955 (4)	−1365 (5)	226 (17)	54 (4)	49 (4)	7 (13)	−40 (13)	39 (7)
C(3)	−255 (9)	1008 (4)	−1157 (5)	229 (17)	48 (4)	57 (5)	9 (13)	−30 (13)	41 (7)
C(4)	−1415 (9)	262 (5)	−1069 (5)	234 (18)	60 (4)	49 (4)	52 (13)	−14 (13)	47 (7)
C(5)	−784 (9)	−621 (5)	−1172 (5)	183 (16)	62 (4)	49 (4)	10 (13)	−40 (12)	39 (7)
C(6)	1086 (9)	−668 (4)	−1367 (5)	250 (18)	52 (4)	51 (4)	41 (13)	−43 (14)	38 (7)
C(7)	−1963 (9)	−1404 (4)	−1088 (5)	247 (17)	47 (4)	53 (4)	18 (13)	−13 (14)	40 (7)
C(8)	−3817 (9)	−1387 (5)	−908 (5)	199 (17)	68 (5)	81 (6)	−29 (14)	−41 (15)	75 (8)
C(9)	−1352 (10)	−2266 (5)	−1194 (5)	243 (18)	56 (4)	67 (5)	−1 (14)	−14 (15)	44 (8)
C(10)	2798 (9)	1716 (5)	−1469 (5)	244 (18)	53 (4)	60 (5)	16 (13)	−35 (14)	42 (7)
C(11)	2266 (10)	2600 (5)	−1381 (5)	286 (20)	57 (4)	71 (5)	9 (14)	7 (16)	58 (8)
C(12)	4617 (10)	1666 (5)	−1689 (5)	239 (18)	63 (5)	79 (6)	−20 (14)	−1 (15)	59 (8)
C(13)	2912 (9)	456 (5)	−3960 (5)	213 (17)	62 (4)	54 (5)	45 (13)	−11 (13)	43 (7)
C(14)	2207 (10)	1310 (5)	−3884 (5)	250 (18)	60 (4)	48 (4)	44 (14)	−1 (14)	36 (7)
C(15)	337 (10)	1307 (5)	−3717 (5)	265 (19)	65 (5)	54 (5)	45 (14)	−11 (14)	65 (7)
C(16)	−778 (9)	542 (5)	−3611 (5)	225 (18)	60 (4)	54 (5)	21 (13)	−8 (14)	52 (7)
C(17)	−48 (9)	−296 (4)	−3688 (4)	249 (18)	53 (4)	39 (4)	45 (13)	−43 (13)	24 (6)
C(18)	1816 (9)	−305 (5)	−3872 (5)	216 (17)	57 (4)	55 (5)	20 (13)	−24 (13)	33 (7)
C(19)	−1178 (9)	−1081 (5)	−3583 (5)	232 (18)	62 (4)	54 (5)	24 (14)	−58 (14)	34 (7)
C(20)	−3027 (10)	−1074 (5)	−3392 (5)	272 (20)	60 (4)	62 (5)	19 (14)	−44 (15)	43 (8)
C(21)	−515 (10)	−1942 (5)	−3653 (5)	273 (20)	56 (4)	76 (5)	−1 (14)	−74 (16)	53 (8)
C(22)	3303 (9)	2096 (5)	−4005 (5)	232 (18)	65 (5)	54 (5)	60 (14)	2 (14)	46 (7)
C(23)	2627 (10)	2934 (5)	−3941 (5)	264 (19)	62 (4)	59 (5)	6 (14)	−15 (15)	44 (8)
C(24)	5148 (11)	2105 (5)	−4174 (6)	291 (21)	64 (5)	83 (6)	21 (16)	12 (17)	50 (9)
C(25)	7072 (11)	3647 (5)	2814 (6)	303 (22)	56 (4)	90 (6)	24 (15)	−19 (18)	57 (9)
C(26)	6182 (12)	3395 (6)	3561 (6)	345 (24)	76 (6)	101 (7)	29 (18)	15 (20)	86 (10)
C(27)	4647 (12)	3742 (6)	3931 (6)	344 (24)	71 (5)	84 (6)	5 (17)	−3 (18)	61 (9)
C(28)	3928 (10)	4338 (5)	3532 (6)	210 (18)	58 (5)	86 (6)	−22 (14)	−3 (16)	41 (8)
C(29)	2362 (11)	4736 (6)	3912 (6)	314 (23)	77 (6)	84 (6)	33 (17)	38 (18)	32 (9)
C(30)	1757 (12)	5322 (6)	3517 (7)	281 (24)	77 (6)	139 (8)	51 (18)	−9 (21)	42 (11)
C(31)	2638 (12)	5547 (6)	2733 (7)	336 (25)	84 (6)	120 (8)	76 (19)	−48 (22)	50 (11)
C(32)	4171 (11)	5182 (5)	2351 (6)	299 (22)	66 (5)	86 (6)	26 (16)	−43 (17)	42 (9)
C(33)	4820 (10)	4578 (4)	2761 (5)	287 (20)	41 (4)	68 (5)	10 (13)	−48 (15)	20 (7)
C(34)	7441 (11)	4418 (5)	1588 (5)	342 (22)	52 (4)	77 (6)	25 (15)	38 (17)	59 (8)
C(35)	6599 (12)	3784 (6)	567 (6)	409 (26)	73 (5)	75 (6)	−2 (18)	9 (19)	40 (9)
C(36)	7613 (16)	4053 (7)	−266 (7)	635 (38)	102 (7)	74 (7)	−10 (25)	133 (25)	62 (11)
N(1)	−5319 (9)	−1415 (5)	−757 (5)	271 (18)	87 (5)	127 (6)	1 (14)	6 (16)	104 (9)
N(2)	−853 (10)	−2970 (5)	−1270 (5)	368 (20)	66 (4)	110 (6)	36 (14)	−2 (17)	69 (8)
N(3)	6100 (9)	1634 (5)	−1884 (5)	281 (18)	93 (5)	113 (6)	6 (15)	−22 (16)	83 (9)
N(4)	1916 (11)	3322 (5)	−1323 (5)	468 (23)	72 (5)	115 (6)	78 (16)	50 (19)	86 (9)
N(5)	−4529 (9)	−1066 (5)	−3217 (5)	311 (19)	85 (5)	104 (6)	45 (14)	−18 (16)	74 (9)
N(6)	14 (9)	−2615 (4)	−3691 (5)	353 (19)	58 (4)	124 (6)	42 (14)	−53 (17)	66 (8)
N(7)	6675 (10)	2139 (5)	−4314 (6)	314 (19)	80 (5)	122 (6)	32 (14)	61 (17)	55 (9)
N(8)	2138 (9)	3629 (4)	−3900 (5)	358 (19)	60 (4)	97 (5)	27 (13)	−35 (15)	58 (7)
N(9)	6399 (8)	4206 (4)	2411 (4)	271 (16)	48 (3)	82 (4)	16 (11)	−31 (13)	44 (6)

Table 2. *Comparison of observed and final calculated structure factors*

(10 × absolute scale).

Table 2 (*cont.*)

K	FO	FC
H=	4, L=	2
6	69	83
10	53	-60
11	43	-40
-3	77	112
-4	56	-77
-6	56	-64
-8	52	40
-9	97	-106
-10	131	130
-11	106	-113
-12	83	88
-13	104	-115
H=	4, L=	-2
0	127	133
1	137	-142
2	43	-41
3	60	64
4	67	-59
5	257	-246
6	129	-137
7	56	52
8	44	-40
10	86	109
12	64	89
-1	21	19
-5	33	27
-6	43	44
H=	4, L=	3
1	91	95
2	96	-88
4	86	82
5	45	-40
6	30	-30
10	51	-52
11	55	-54
-1	40	-57
-3	62	-64
-4	66	-74
-5	134	141
-7	43	42
-8	40	34
-9	73	-89
-10	61	60
-11	62	-60
-13	130	127
H=	4, L=	-3
0	266	261
1	79	-88
2	133	-139
3	53	49
4	57	-57
7	47	-40
8	65	78
11	63	-48
-1	295	307
-2	187	174
-3	27	30
-4	40	33
-5	122	-136
-6	55	-74
-7	65	-71
H=	4, L=	4
0	51	-51
2	41	44
3	43	39
4	92	-92
5	42	32
-2	79	64
-3	76	72
-4	44	49
-5	88	-79
-6	78	-79
-7	196	-186
-8	81	-63
-9	182	176
-10	53	-50
-13	94	101
H=	4, L=	-4
0	141	-132
1	35	35
2	120	120
3	88	-84
8	43	-48
-3	53	58
-4	46	-34
-5	95	-96
-6	99	-117
-7	157	-173
-8	142	-168
-11	55	-64
H=	4, L=	5
0	289	289
1	41	-37
2	119	-114
3	132	132
6	52	34
7	55	-52
8	63	57
-1	293	242
-2	187	184
-3	190	205
-4	83	83
-5	88	-74
-6	34	-28
-7	43	-36
-8	46	-60
-9	31	-30
-10	61	63
H=	4, L=	-5
3	87	-96
4	100	97
5	62	-51
6	21	-31
10	72	-82
11	101	-115
12	88	-80
-2	37	-34
-5	75	86
-6	62	38
-7	38	32
H=	4, L=	6
0	36	32
1	75	-75
3	52	76
4	92	99
6	52	-41
-3	81	-68
-4	33	35
-5	37	37
-7	46	48
-12	42	55
H=	4, L=	-6
0	61	-60
1	97	91
2	145	149
3	126	-134
4	71	72
5	282	280
6	111	109
7	116	126
8	70	68
10	64	-72
11	62	-51
-1	55	62
-2	85	-89
-3	68	65
-4	72	-54
-6	48	-32
H=	4, L=	7
0	95	95
1	80	-74
2	59	46
4	65	-64
8	69	-50
-1	53	-57
-2	74	82
-4	39	-35
-8	47	44
-13	108	-116
-15	94	-43
-16	47	-41
H=	4, L=	-7
0	78	95
1	46	31
2	117	122
3	49	-51
5	56	40
6	50	-50
8	56	-66
-1	239	-241
-2	74	-65
-3	114	-108
-5	66	72
-6	70	97
-7	56	72
H=	4, L=	8
0	56	41
2	50	-32
4	41	25
-2	90	-94
-4	70	-72
-6	43	51
-8	63	-66
-9	127	-121
-11	120	106
-12	65	-60
-13	47	-44
H=	4, L=	-8
1	45	-38
2	67	-63
3	64	58
5	51	-49
-2	59	49
-3	57	-62
-4	40	43
-6	110	122
-7	146	127
-8	115	127
H=	4, L=	9
0	250	-253
3	43	-30
4	53	-51
-1	129	-123
-2	123	-129
-3	69	-65
-10	69	-72
-12	59	63
H=	4, L=	-9
0	88	-101
1	42	32
7	60	-49
10	127	121
-1	110	122
-2	98	-109
-3	85	104
-4	42	-37
-5	59	-37
-6	54	-39
-7	48	-80
H=	4, L=	10
4	70	-66
-1	66	-70
-2	38	44
-10	54	66
H=	4, L=	-10
0	60	39
1	98	-99
3	58	58
4	88	-89
5	271	-259
6	176	-180
7	109	-105
9	49	62
H=	4, L=	11
-12	54	35
-13	122	109
H=	4, L=	-11
1	49	-42
-2	66	49
-4	52	31
-6	55	-43
-7	64	-51
H=	4, L=	12
-1	52	33
-4	47	39
-6	92	57
-8	72	70
-9	114	89
-10	60	-41
-12	43	28
-13	57	57
H=	4, L=	-12
5	59	31
H=	4, L=	13
1	54	43
-1	77	67
H=	5, L=	0
1	147	-158
2	66	79
-3	20	16
-5	25	-20
-6	135	133
-7	206	216
-8	220	224
-9	90	90
-10	67	-66
-12	67	63
H=	5, L=	1
0	41	-38
1	237	228
2	84	-84
3	40	30
5	60	-59
6	62	-52
8	42	-42
11	51	37
-1	20	-19
-4	35	-35
-5	143	140
-6	230	227
-7	158	164
-8	221	240
-11	50	-72
H=	5, L=	-1
3	44	-30
4	105	-108
6	92	-81
7	54	-56
10	143	135
-5	36	-48
-6	66	-65
-7	112	-134
-8	81	-96
H=	5, L=	2
0	77	82
1	145	152
5	256	268
6	137	137
7	78	73
-1	93	-104
-4	47	-50
-5	73	-77
-6	31	-31
-7	69	-73
-8	40	-51
-9	88	92
-10	99	-101
-11	79	83
H=	5, L=	-2
0	109	-118
4	280	-277
5	387	-391
6	203	-213
7	98	-86
9	39	37
-5	51	68
-6	35	49
-7	81	97
H=	5, L=	3
0	99	90
1	109	-113
4	117	105
10	54	-70
-5	84	72
-7	209	217
-8	74	-77
-9	76	79
-10	46	-56
H=	5, L=	-3
0	64	-63
2	49	52
5	104	93
6	72	70
-3	113	130
-4	90	95
-5	36	-28
-6	80	-104
-7	171	-197
-8	139	-197
-9	80	-87
H=	5, L=	4
0	107	-108
1	116	112
-5	41	-35
-6	106	-114
-7	224	-217
-8	119	-120
-9	149	-157
-10	143	130
-11	180	-179
H=	5, L=	-4
1	61	62
2	72	-75
4	63	71
8	77	-67
-1	37	34
-4	41	-34
-5	44	34
-7	124	-134
-8	168	-188
-9	111	-129
-10	65	57
H=	5, L=	5
1	42	-47
2	49	-52
3	47	28
6	49	49
-1	192	195
-2	142	123
-3	141	129
-5	166	-155
-6	82	-89
-7	200	-197
-8	58	-72
-9	66	-72
H=	5, L=	-5
0	111	109
1	145	-149
2	113	111
4	92	91
5	127	119
9	90	-75
-1	73	-77
-2	55	41
-4	35	-28
-7	97	117
-8	79	76
-9	44	49
-10	45	-44
H=	5, L=	6
1	62	-68
2	33	-36
3	49	42
4	70	-57
5	126	-125
6	79	-75
-1	68	66
-2	71	60
-4	69	73
-5	39	29
-7	110	102
-8	64	-61
-9	46	41
H=	5, L=	-6
0	41	56
1	49	-51
2	177	-165
3	139	136
4	325	302
5	426	415
6	95	108
-1	67	-71
-2	80	76
-7	89	-78
-8	44	-30
H=	5, L=	7
0	67	-63
1	39	32
2	43	43
-4	46	37
-5	43	-32
-6	70	-63
-7	59	-55
-8	33	-44
-9	46	32
H=	5, L=	-7
0	133	-122
1	77	72
2	111	-106
3	110	99
4	33	-47
5	89	-92
-1	93	79
-2	82	38
-3	39	48
-7	78	67
-8	108	120
H=	5, L=	8
0	50	48
2	44	-41
-6	69	84
-7	134	136
-8	136	132
-11	94	73
-12	43	43
-13	75	-84
-14	59	-42
H=	5, L=	-8
0	58	59
1	49	-43
2	96	100
3	73	-71
5	38	28
6	48	35
-2	46	-47
H=	5, L=	9
-1	152	-146
-2	95	-93
-3	54	-75
-5	53	80
-6	71	77
-7	63	69
-8	86	91
-11	46	-40
-13	46	35
H=	5, L=	-9
0	47	36
1	41	-36
4	66	-72
5	62	-59
-1	50	-37
H=	5, L=	10
1	47	37
3	63	-35
H=	5, L=	-10
0	50	29
1	52	57
3	152	-135
4	265	-239
5	173	-163
H=	5, L=	-10
-1	48	42
H=	5, L=	11
-7	49	56
H=	5, L=	-11
0	57	41
5	66	53
-3	56	-35
H=	5, L=	13
0	65	50
-1	76	83
H=	6, L=	0
-8	69	82
-9	109	127
-10	46	49
-12	56	-38
-13	67	-63
-14	56	-40
H=	6, L=	1
2	32	34
4	101	-104
5	54	-66
-4	18	21
-6	47	-44
-7	57	62
-8	178	191
-9	182	187
-10	54	52
H=	6, L=	-1
2	37	-45
3	120	-109
4	172	-160
5	42	-43
6	53	45
9	54	-48
10	46	-35
-8	66	-73
-9	80	-95
H=	6, L=	2
0	38	-58
1	94	-107
3	120	131
4	321	351
5	155	158
-6	42	-37
-7	74	-64
-8	132	-107
H=	6, L=	-2
0	119	136
1	45	53
2	124	-110
3	243	-225
4	300	-281
5	96	-78
6	83	73
-1	109	126
-3	26	-29
-8	77	102
H=	6, L=	3
3	137	140
4	100	96
5	126	114
-5	57	-54
-6	92	80
-7	41	-33
-8	235	207
-10	47	-30
H=	6, L=	-3
0	46	54
1	37	-37
3	47	-52
4	183	172
-1	48	59
-2	86	68
-3	48	-65
-4	71	-107
-7	59	79
-8	75	-106
-9	57	-81
H=	6, L=	4
-8	235	-201
-9	135	-103
-10	45	-37
-12	51	34
H=	6, L=	-4
3	52	56
4	87	-83
-1	84	-87
-6	33	91
-9	46	-34
H=	6, L=	5
3	44	-65
4	61	76
6	44	39
-1	36	-28
-2	51	-53
-3	39	31
-5	126	119
-6	157	-159
-7	106	-92
-8	363	-312
-9	166	-150
-10	58	-39
H=	6, L=	-5
1	100	96
2	99	-78
3	193	172
6	43	-34
8	137	111
9	60	43
H=	6, L=	6
2	46	80
4	154	-184
5	160	-171
-2	32	-37
-6	106	91
-8	154	139
-9	71	-69
H=	6, L=	-6
0	64	-63
1	60	46
2	128	118
3	86	75
4	199	164
5	106	-85
-1	89	-112
-2	69	-72
H=	6, L=	7
3	84	-85
4	55	-81
-4	54	44
-5	64	-69
-6	31	26
-7	117	-106
-8	102	-87
H=	6, L=	-7
4	61	-82
-2	68	-80
H=	6, L=	8
-7	98	104
-8	131	117
-9	120	110
H=	6, L=	-8
2	41	-32
-1	43	39
H=	6, L=	9
-3	51	-55
-4	52	-52
-6	107	99
-7	201	183
-8	197	172
-9	115	113
H=	6, L=	-9
3	54	-35
7	63	-55
8	89	-68
-1	35	-30
H=	7, L=	1
-6	59	44
H=	7, L=	2
1	99	70
3	97	71
-2	124	-140
-6	59	46
H=	7, L=	3
3	58	78

Table 3. *Details of molecular planes*

x, y, z are orthogonal atomic coordinates in Å where x is along **a**; y is in the (**ab**) plane and z is along **c***. The figures in parentheses indicate the standard deviations.

Molecule *A*
Equation to the plane:
$-0{\cdot}1895x+0{\cdot}0053y-0{\cdot}9819z-1{\cdot}6371=0$

Molecule *B*
Equation to the plane:
$-0{\cdot}1686x-0{\cdot}0256y-0{\cdot}9853z-4{\cdot}8061=0$

	Distance from the plane		Distance from the plane
C(1)	−0·020 (6) Å	C(13)	−0·010 (6) Å
C(2)	−0·018 (6)	C(14)	−0·017 (6)
C(3)	−0·025 (6)	C(15)	0·003 (6)
C(4)	−0·015 (6)	C(16)	0·005 (6)
C(5)	−0·016 (6)	C(17)	0·010 (6)
C(6)	−0·029 (6)	C(18)	0·013 (6)
C(7)	−0·000 (6)	C(19)	0·014 (6)
C(8)	0·028 (7)	C(20)	−0·001 (7)
C(9)	0·007 (7)	C(21)	0·019 (7)
C(10)	−0·011 (6)	C(22)	0·003 (6)
C(11)	−0·003 (7)	C(23)	0·008 (7)
C(12)	0·017 (7)	C(24)	−0·010 (8)
N(1)	0·042 (7)	N(5)	−0·038 (7)
N(2)	−0·003 (7)	N(6)	0·001 (7)
N(3)	0·060 (7)	N(7)	−0·022 (7)
N(4)	0·009 (7)	N(8)	0·018 (6)

ference map. Further least-squares refinement of all the non-hydrogen atoms with isotropic thermal parameters and 19 hydrogens in fixed positions gave the value of $R=0{\cdot}123$. At this stage it was observed that the value of R increased sharply from zero to higher layers. The F_{obs} values for some of the strong reflexions in higher layers were very low compared with the F_{calc} values. This was considered to be due to the combined effects of the missetting of the crystal and inaccurate determination of the layer offsets. Another crystal was therefore mounted, rotating about the a axis, and intensity data were collected on the linear diffractometer. 1783 significant counts were recorded and the intensities were converted into $|F_o|$ values. 4 cycles of least-squares refinement of the previous positional parameters and isotropic thermal parameters with the new $|F_o|$ values gave $R=0{\cdot}136$. Owing to the second crystal being smaller than the first, it was observed that many of the weaker reflexions, especially in lower layers, which were observed in the first set of data were below the threshold

for significant intensity in the second set of data. It was therefore decided to include these weaker reflexions from the first set of data in with the second set of data

A

B

(a)

(b)

Fig. 1. Bond lengths (Å) and bond angles (°), with their standard deviations (in parentheses), for (a) the two independent TCNQ moieties (b) the NPQ ion.

Fig. 2. The molecular arrangement, viewed along the a axis.

scaled appropriately by the overall scale factor. A total of 331 such reflexions were included and further least-squares refinement using the augmented second set of data (2114 reflexions) of the non-hydrogen atoms with anisotropic temperature factors gave the final R value of 0·0804. Hydrogen atoms were included in the structure factor calculation for this refinement in fixed positions with fixed isotropic temperature factors. The scattering factor curves of Cromer & Waber (1965) were used throughout. The final positional and thermal parameters of all the 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. Least-squares planes were calculated through each of the TCNQ moieties and are listed in Table 3.
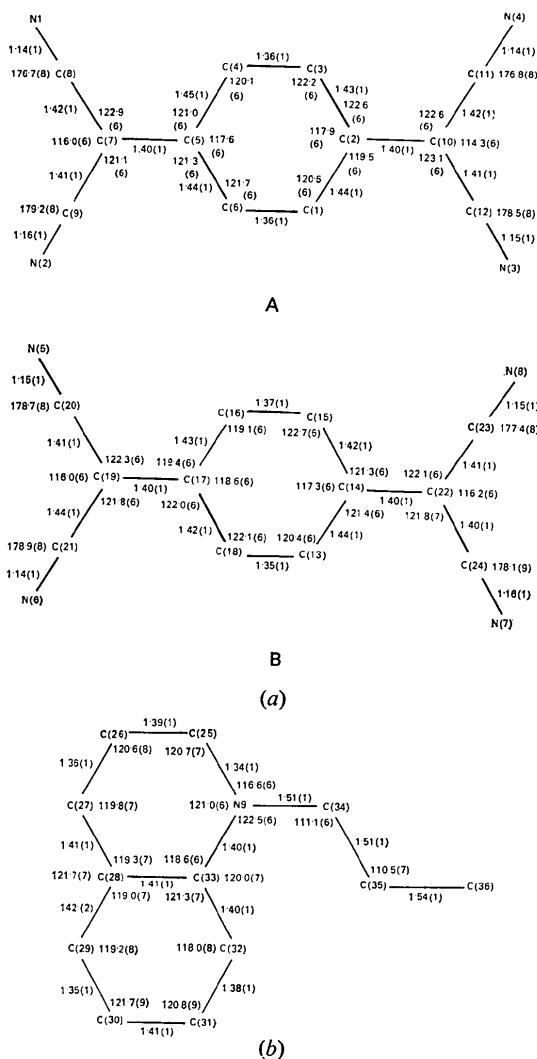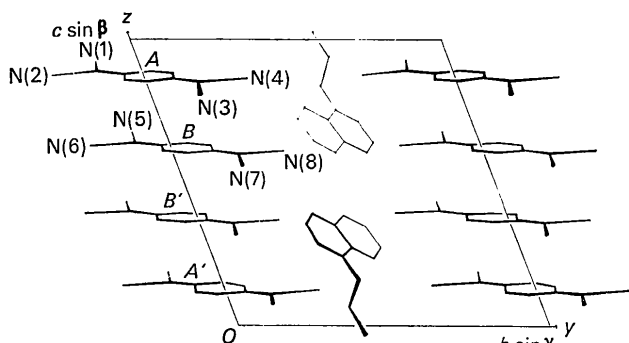
Description and discussion of the structure

Fig. 1(a) shows the dimensions of the two crystallographically independent types of TCNQ moiety. Averaged bond lengths of chemically similar bonds of both the TCNQ moieties are summarized in Table 4. Most of the averaged dimensions are intermediate between the previously published dimensions for TCNQ$^-$ and TCNQ^0. A multivariate significance test (Cruickshank & Robertson, 1953) of the differences in dimensions between the two TCNQ moieties gives a value of $T^2 = 1·36$ which is not significant for five degrees of freedom. This suggests that the two TCNQ moieties are indistinguishable. This may be due to either delocalization of charge or the disordered arrangement of TCNQ^0 and TCNQ$^-$. In view of the lack of other evidence for disorder, the former explanation is preferred. The molecules are not quite planar, the C–(CN)$_2$ groups being bent slightly out of the planes of the quinonoid rings as well as being slightly twisted. Molecule A has a bowed configuration with both C–(CN)$_2$ groups nearer to the origin than the quinonoid ring whereas molecule B has a tendency towards a zigzag configuration, though N(5) is the only atom significantly out of the mean plane. The dihedral angle between the mean planes of the molecules A and B is 2·1°. The C–CN groups C(7)–C(8)–N(1), C(10)–C(11)–N(4) and C(22)–C(23)–N(8) are significantly non-linear, but the bends are mainly in the planes of the molecules, in each case in such a direction as to reduce the distance between the nitrogen atoms of a C–(CN)$_2$ group.

The NPQ ion shows no abnormal dimensions in so far as it can be compared with other related species.

Fig. 2 shows a general view of the structure in which the four TCNQ moieties are stacked along the c axis which is 14·30 Å long. The A and B molecules are nearly parallel and the average interplanar spacing $A\cdots B$ is 3·24 Å. The $A\cdots A'$ perpendicular distance is 3·28 Å but the $B\cdots B'$ separation is 3·43 Å indicating no appreciable molecular interaction.

Fig. 3 shows the three types of overlap that occur, A on B and A' on A being virtually identical and very

Table 4. *Comparison of mean bond lengths (uncorrected for libration)*

Bond	Reference	a	b	c	d	e
TCNQ⁰	1	1·346 (4)	1·448 (3)	1·374 (4)	1·440 (3)	1·138 (3)
TCNQ⁻	2, 3, 4, 5, 6	1·360 (15)	1·425 (9)	1·405 (10)	1·414 (6)	1·150 (7)
TCNQ¹ᐟ²⁻	7, 8, 9	1·355 (4)	1·434 (8)	1·390 (9)	1·426 (4)	1·144 (5)
Molecule A		1·359 (7)	1·437 (5)	1·401 (7)	1·413 (5)	1·146 (5)
Molecule B		1·361 (7)	1·429 (5)	1·401 (7)	1·417 (5)	1·149 (5)

1. Long, Sparks & Trueblood (1965).
2. Hanson (1965).
3. Fritchie & Arthur (1966).
4. Fritchie (1966).
5. Kobayashi, Ohashi, Marumo & Saito (1970).
6. Sundaresan & Wallwork (1972)
7. Hanson (1968).
8. Goldstein, Seff & Trueblood (1968).
9. Kobayashi, Marumo & Saito (1971).
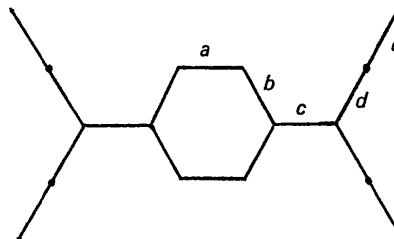
similar to that found in most of the TCNQ complexes. But the overlap B' on B is a new and less favourable overlap involving a diagonal shift of centres. These different types of overlap, combined with the different interplanar spacings suggest that, in the structure, the TCNQ moieties are grouped as tetramers $BAA'B'$ with a gap between the B' and the next B. A and B seem to be particularly close, however, indicating a tendency towards dimer formation. This is very similar to the situation found by Kobayashi, Ohashi, Marumo & Saito (1970) for triethylammonium 2TCNQ. The short intermolecular contacts are listed in Table 5.

Table 5. *Short intermolecular contacts*

(a) Molecule A to molecule B

C(1ⁱ)—C(18ⁱ)	3·29 Å		C(6ⁱ)—C(21ⁱ)	3·28 Å
C(2ⁱ)—C(17ⁱ)	3·32		C(10ⁱ)–C(13ⁱ)	3·39
C(3ⁱ)—C(16ⁱ)	3·34		C(10ⁱ)–C(14ⁱ)	3·31
C(4ⁱ)—C(20ⁱ)	3·34		C(11ⁱ)–C(14ⁱ)	3·40
C(5ⁱ)—C(19ⁱ)	3·27		C(12ⁱ)–C(13ⁱ)	3·27

(b) Molecule A to molecule A'

C(1ⁱ)—C(8ⁱⁱ)	3·38		C(4ⁱ)—C(6ⁱⁱ)	3·32
C(2ⁱ)—C(7ⁱⁱ)	3·33		C(5ⁱ)—C(5ⁱⁱ)	3·33
C(3ⁱ)—C(9ⁱⁱ)	3·35			

(c) Other intermolecular contacts

C(3ⁱ)—N(3ⁱⁱⁱ)	3·34		C(29ⁱ)–N(6ⁱⁱ)	3·33
C(6ⁱ)—N(1ⁱᵛ)	3·34		C(31ⁱ)–N(7ᵛⁱⁱ)	3·38
C(18ⁱ)–N(7ᵛ)	3·38		C(33ⁱ)–N(8ᵛⁱⁱ)	3·20
C(25ⁱ)–N(6ᵛⁱ)	3·38		N(9ⁱ)—N(8ᵛⁱⁱ)	3·23
C(26ⁱ)–N(6ᵛⁱ)	3·30			

Superscripts indicate equivalent positions as follows:

	x	y	z
i	x	y	z
ii	$\bar{x}$	$\bar{y}$	$\bar{z}$
iii	$x-1$	y	z
iv	$x+1$	y	z
v	$1-x$	$\bar{y}$	$\bar{z}-1$
vi	$1-x$	$\bar{y}$	$\bar{z}$
vii	$1-x$	$1-y$	$\bar{z}$

visible and near infrared spectra of KBr discs of the crystals show not only low-energy charge transfer bands at about 11400 and 10400 cm⁻¹ but an extra very low energy band at about 3500 cm⁻¹. The latter has been
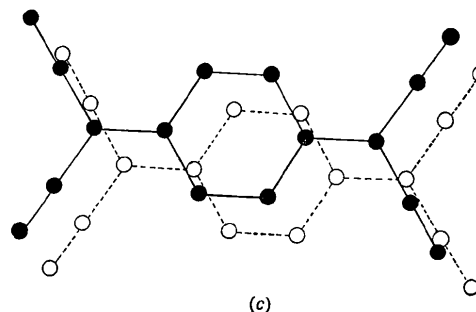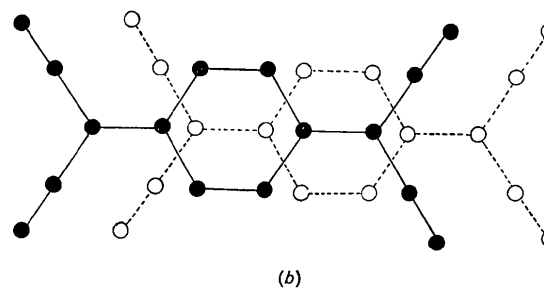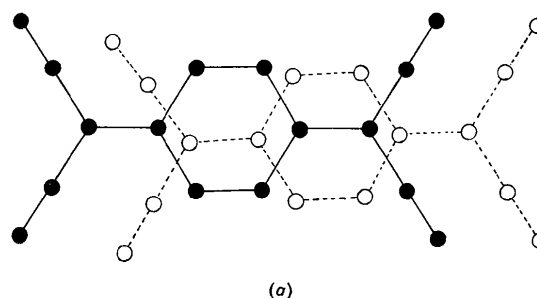

(a)

(b)

(c)

Fig. 3. Nearest neighbour overlap. (a) molecules A (———) and B (· · · ·) (b) molecules A (———) and A' (· · · ·) (c) molecules B (———) and B' (· · · ·).

Spectroscopically, the NPQ complex shows some distinctive features which appear to be characteristic of TCNQ complex salts of high conductivity. Firstly the

attributed (Iida, 1969) to an electron transition from a valence band to a conduction band. Secondly the vibrational bands in the infrared range from 2500 to 700 cm^{-1} in the solid (KBr discs) are nearly all broadened and those that probably represent skeletal vibrational modes have peaks at frequencies intermediate between those in neutral TCNQ and TCNQ$^-$ as shown in Table 6. This provides further evidence for delocalization of charge between the formally neutral TCNQ and TCNQ$^-$ in the complex.

Table 6. *Positions of main peaks in the solid state infrared spectra* (KBr *discs*)

Probable assignment	v in complex (cm^{-1})	v in TCNQ (cm^{-1})	v in TCNQ$^-$ (cm^{-1})
C≡N str.	2199+2167	2228	2195
C=C ring str.	1566	1545	1581
C=C *exo* str.	1528	1545	1509
C–H bend	1328	1353	1329
C–CN str. (b_1u)	1134	1126+1114	1186

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The Crystal and Molecular Structure of Trichlorotris-(3-sulphanilamido-6-methoxypyridazine)bismuth(III)

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Trichlorotris-(3-sulphanilamido-6-methoxypyridazine)bismuth(III), BiCl$_3$(C$_{11}$H$_{12}$O$_3$N$_4$S)$_3$, is trigonal (*R*3) with cell parameters: $a = 18·79(1)$, $c = 10·31(1)$ Å, $Z = 3$. A three-dimensional X-ray analysis, carried out using Patterson and Fourier methods and refined by least-squares methods with photographic data collected at room temperature (Cu $K\alpha$), shows the Bi to be on a threefold axis surrounded by three chlorine ions [Bi–Cl = 2·529(8) Å] and by three nitrogen atoms [Bi–N = 2·90(1) Å] and three oxygen atoms [Bi–O = 3·09(2) Å] of three sulphamido groups from three different organic molecules. The values of the distances in these contacts indicate that the chlorine atoms are much more strongly bonded to bismuth than the organic molecules.

Introduction

Trichlorotris-(3-sulphanilamido-6-methoxypyridazine)-bismuth(III) was prepared by Adami, Piccinini & Marazzi-Uberti (1961) and introduced in therapy because of its useful pharmaceutical properties, that it is absorbed by the organism more rapidly and completely than the simple mixture of its components. This property could be related to its nature as a coordination compound. The composition, deduced from conventional chemical analysis, corresponds to the formula

$$BiCl_3(H_2N-\!\!\langle\ \rangle\!\!-SO_2NH-\!\!\langle\ \rangle\!\!-OCH_3)_3$$
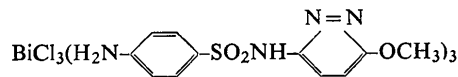
in which the stoichiometric ratio is BiCl$_3$: organic molecule = 1 : 3. But this piece of information is not enough to foresee the coordination around the metal, nor the behaviour of chlorine and of the organic ligand in which more than one possible coordination site is present. These points have been determined from a three-dimensional X-ray crystal analysis which is now reported.