The Crystal Structure of Triethylammonium Bis-7,7,8,8-tetracyanoquinodimethanide, (TEA)$^+$(TCNQ)$_2^-$

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The crystal is triclinic with space group $P\bar{1}$ and $a = 13\cdot22$, $b = 14\cdot44$, $c = 7\cdot89$ Å, $\alpha = 108\cdot1$, $\beta = 103\cdot6$, $\gamma = 87\cdot3°$, $Z = 2$. The structure was deduced from a three-dimensional Patterson synthesis and refined by the block-diagonal least-squares method to an R value of $0\cdot123$ for 2308 observed reflexions. The planar TCNQ molecules are stacked face-to-face to form a column along [101]; there are two different modes of overlapping of the molecules. Four molecules form a repeating unit in the column. The interplanar distances within the TCNQ column are $3\cdot32$, $3\cdot30$ and $3\cdot24$ Å. The bond lengths of the two independent TCNQ molecules indicate that they are in the states TCNQ^0 and TCNQ$^-$ respectively. By the use of appropriate force constants and observed bond lengths, the activation energy for an electron to 'hop' from TCNQ$^-$ to TCNQ^0 is calculated to be at least $0\cdot06$ eV. Triethylammonium ions are arranged in the space between the columns. High values of the thermal factors of the atoms of TEA$^+$ together with diffuseness in the electron-density distribution are certainly related to some positional freedom.

Introduction

The salts containing the anion radical TCNQ$^-$† include some of the best electrically conductive organic compounds ever known. Recent structure analysis of these salts revealed that the structures are based on TCNQ columns in which the molecules are stacked face-to-face (Goldstein, Seff & Trueblood, 1968; Hanson, 1968; Fritchie, 1966; Fritchie & Arthur, 1966; Hanson 1965; Long, Sparks & Trueblood, 1965; Anderson & Fritchie, 1963). In crystals of Cs$_2$(TCNQ)$_3$ the electrons within the TCNQ columns were found to be localized on specific molecules, whose geometries differ from those of other neutral molecules (Fritchie & Arthur, 1966). The observed dependence of molecular dimensions on formal charge is consistent with the result of bond order calculations (Goldstein, Seff & Trueblood 1968; Lowitz, 1967; Menefee & Pao, 1962). The present study of the crystal and molecular structure of TEA-(TCNQ)$_2^-$‡ was undertaken to compare the structure with those of other TCNQ salts and to propose a plausible mechanism for electrical conduction in these crystals.

Experimental

The opaque black crystals of TEA$^+$(TCNQ)$_2^-$ were kindly supplied by Dr T. Kondow. The cell dimensions were determined from Weissenberg photographs. The crystals used for the collection of the intensity data were approximate parallelepipeds and had a maximum dimension of 0·3 mm. Equi-inclination Weissenberg pho-

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† TCNQ = 7,7,8,8-tetracyanoquinodimethane.
‡ TEA = triethylammonium.

tographs were taken around the c axis up [to [the [fifth layer and the b axis up to the ninth layer with Cu $K\alpha$ radiation ($\lambda = 1\cdot5418$ Å); the multiple-film technique was used. In all 2308 reflexions were observed. The intensities were estimated visually with a standard film strip and were converted to $|F(hkl)|$ by applying the usual Lorentz, polarization and shape corrections. No correction was made for absorption in view of the small sizes of the crystals.

The crystal data are: C$_6$NH$_{16}$·(C$_{12}$ N$_4$H$_4$)$_2$, F.W. 506, triclinic, $a = 13\cdot222 \pm 0\cdot020$, $b = 14\cdot440 \pm 0\cdot010$, $c = 7\cdot885 \pm 0\cdot010$ Å, $\alpha = 108\cdot07 \pm 0\cdot07$, $\beta = 103\cdot59 \pm 0\cdot04$, $\gamma = 87\cdot33 \pm 0\cdot04°$, $U = 1390\cdot3$ Å^3, $D_m = 1\cdot222$ g.cm^{-3}, $Z = 2$, $D_x = 1\cdot218$ g.cm^{-3}, space group $P\bar{1}$ (C_i^1 No.2), $F(000) = 526$, linear absorption coefficient for Cu $K\alpha$, $\mu = 6\cdot24$ cm^{-1}.

Determination of the structure

The space group $P\bar{1}$ was assumed tentatively and this was verified at a later stage by calculation of the structure factors. The trial atomic coordinates of the TCNQ molecules could be readily deduced from sharpened three-dimensional Patterson maps. The three-dimensional electron density distribution was calculated with phases based on the deduced coordinates of the TCNQ molecules. Approximate positions of the atoms of the TEA ions were found on this and successive three-dimensional Fourier syntheses. Block-diagonal least-squares refinement was performed using the program of T. Ashida. Isotropic refinement proceeded fairly smoothly to $R = 0\cdot19$. At this stage, the electron density maps, however, showed broader and slightly lower peaks at the atomic positions of the TEA ion than those at the atomic positions of the TCNQ molecule. Moreover, the thermal parameters of these atoms were found

to be very large. The possibility of the space group $P1$ was therefore considered. According to the symmetry of the space group $P1$, attempts were made to pack the TEA ions into the region suggested by the electron density maps. Atomic coordinates of the TEA ions deduced from these trial structures were tested by calculating structure factors and comparing them with the observed values. Attempts were also made to refine these coordinates by the least-squares method. No improvement was achieved however. Thus $P1$ was rejec-

ted. Considerable peaks were found around the atomic positions of TEA$^+$ in three-dimensional difference maps, but it was not possible systematically to assign individual atoms to these peaks and they were reduced markedly after subsequent anisotropic refinement. The nitrogen atom has the smallest temperature factor and corresponds to the highest electron density peak among the atoms of the TEA$^+$ ion. Positions of the carbon atoms were ill-defined on the electron density maps and their parameter values obtained by the least-squares
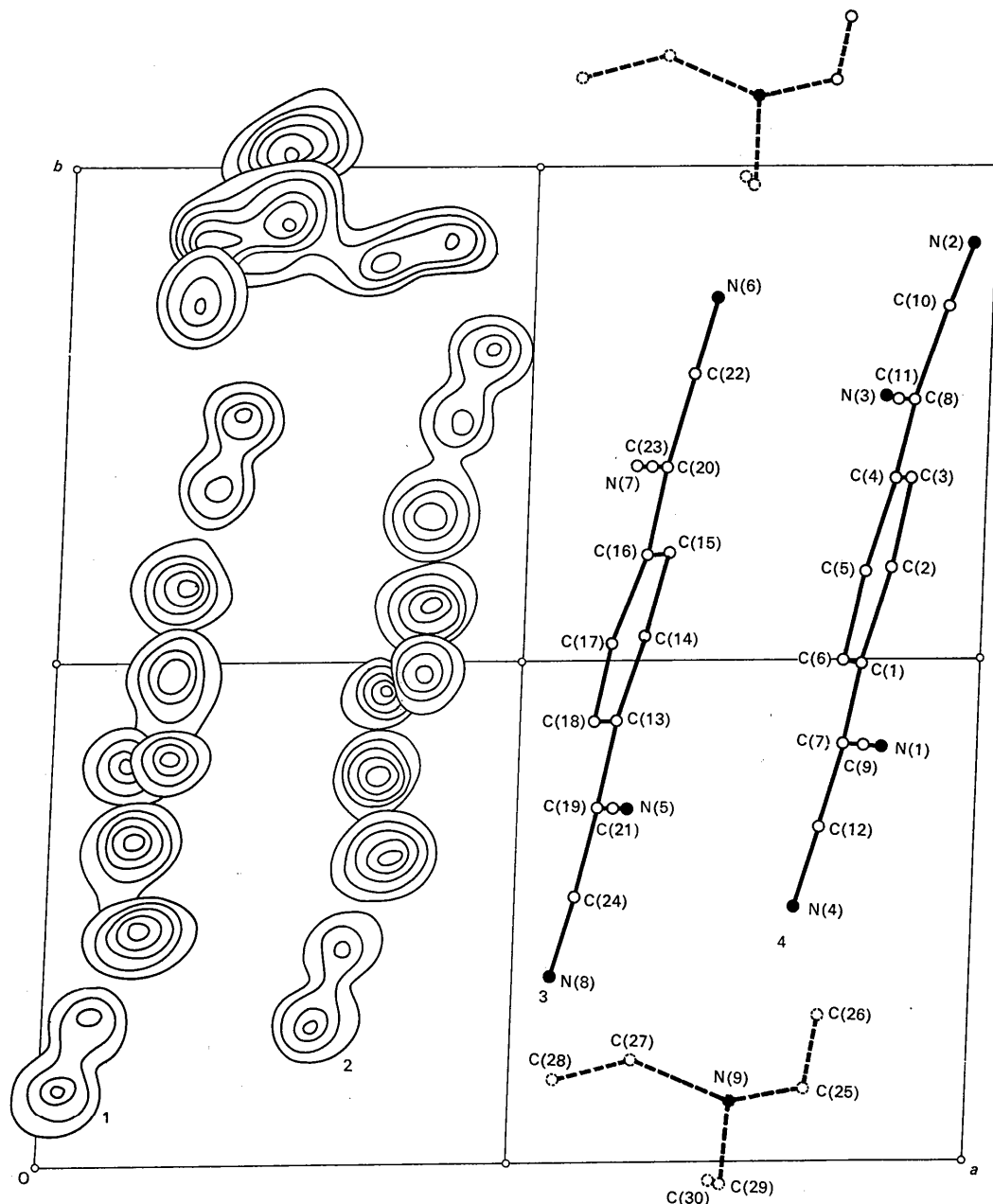
Fig. 1. The structure viewed along the c axis. Contours are at interval of 1·2 e.Å^{-3} around TCNQ and 0·6 e.Å^{-3} around TEA, the lowest contour being 2·5 e.Å^{-3}.

Table 1. *Final parameters and estimated standard deviations of non-hydrogen atoms*

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

	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	B_{11} ($\times 10^4$)	B_{22} ($\times 10^4$)	B_{33} ($\times 10^4$)	B_{12} ($\times 10^4$)	B_{13} ($\times 10^4$)	B_{23} ($\times 10^4$)
			TCNQ (1)*						
C(1)	1255	4927	1279	56	57	198	11	66	71
	6	6	11	5	5	17	8	15	15
C(2)	944	4029	1450	67	60	212	13	79	85
	6	6	11	6	5	18	9	17	17
C(3)	793	3198	49	60	57	204	−3	55	85
	6	6	11	5	5	18	9	16	17
C(4)	965	3197	8319	62	62	210	15	69	58
	6	6	11	6	5	18	9	17	17
C(5)	1291	4102	8119	68	62	201	16	60	72
	6	6	11	6	5	18	9	17	17
C(6)	1423	4940	9539	57	46	182	−1	40	63
	6	5	10	5	4	16	8	15	15
C(7)	1390	5793	2720	68	56	222	5	79	72
	6	6	11	6	5	19	9	17	17
C(8)	807	2337	6862	80	59	218	4	64	71
	6	6	12	6	5	19	10	18	18
C(9)	1219	5832	4455	70	61	220	−3	73	73
	6	6	11	6	5	19	9	18	17
C(10)	476	1480	7050	107	69	223	3	106	27
	7	7	12	8	6	21	12	22	20
C(11)	937	2309	5101	113	77	258	5	83	72
	8	7	14	9	7	25	13	25	23
C(12)	1696	6704	2564	71	58	261	−1	86	73
	6	6	12	6	5	21	9	19	18
N(1)	1089	5842	5852	112	91	256	5	85	73
	6	6	11	7	6	19	11	19	19
N(2)	218	756	7222	151	87	362	−14	133	77
	7	7	12	9	7	25	13	25	22
N(3)	1045	2314	3674	155	96	294	22	130	71
	7	7	12	9	7	23	13	24	21
N(4)	1929	7428	2513	116	72	369	16	120	83
	7	6	12	7	6	24	11	22	20
			TCNQ (2)						
C(13)	3834	5626	4680	54	56	174	−4	37	65
	5	6	10	5	5	16	8	15	15
C(14)	3541	4739	4815	62	63	178	9	62	66
	6	6	10	5	5	17	9	16	16
C(15)	3394	3877	3397	60	65	221	10	57	71
	6	6	11	6	5	19	9	17	17
C(16)	3590	3931	1690	52	54	185	6	49	65
	5	6	10	5	5	17	8	15	15
C(17)	3904	4812	1508	55	56	186	0	65	37
	6	6	10	5	5	17	8	15	15
C(18)	4045	5657	2948	66	62	207	−1	55	62
	6	6	11	6	5	18	9	17	17
C(19)	3996	6479	6185	69	61	199	6	57	70
	6	6	11	6	5	18	9	17	17
C(20)	3439	3072	187	66	61	203	0	70	74
	6	6	11	6	5	18	9	17	17
C(21)	3811	6469	7870	83	66	218	11	77	38
	7	6	12	7	6	20	10	19	18
C(22)	3164	2164	265	83	65	215	6	96	61
	7	6	12	7	6	20	10	19	18
C(23)	3582	3062	8469	84	67	205	−3	55	39
	7	6	12	7	6	19	10	19	18
C(24)	4285	7401	6090	87	71	225	3	78	74
	7	7	12	7	6	20	11	20	19
N(5)	3698	6472	9244	125	93	269	16	98	58
	7	6	11	8	7	21	12	21	20
N(6)	2898	1402	326	138	79	349	−11	157	83
	7	6	12	8	6	⸗ 24	12	24	21
N(7)	3715	3074	7063	134	83	290	16	155	84
	7	6	11	8	6	21	11	22	19
N(8)	4535	8135	6021	140	81	359	−15	142	51
	7	6	12	9	6	25	12	25	22

Table 1 (cont.)

TEA⁺

C(25)	1761	9249	129	223	96	656	3	64	207
	15	11	26	24	13	69	28	66	51
C(26)	1673	8511	8570	261	153	542	−4	−111	−15
	17	14	27	29	18	66	37	70	59
C(27)	3602	8959	1711	190	224 ·	871	35	389	−36
	17	17	32	25	24	96	39	81	80
C(28)	4493	9182	1434	156	157	888	7	357	−136
	14	14	30	21	18	89	30	71	66
C(29)	2661	265	3507	365	143	473	272	562	255
	20	14	26	38	19	63	45	85	60
C(30)	2695	115	5023	271	149	466	115	230	44
	16	13	24	28	17	58	36	67	54
N(9)	2611	9424	1761	187	210	381	41	114	97
	12	12	18	17	16	40	27	43	42

* The numbering of the TCNQ molecule is illustrated in Fig. 1.

refinement gave some chemically unreasonable distances and angles, for example, C–C = 1·27–1·34 Å ∠ CNC = 112–124°. Thus the atomic coordinates of these carbon atoms may be regarded as the average values of various atomic coordinates related to some randomness in atomic positions.

The positions and temperature factors of all hydrogen atoms of TCNQ molecules found in the three-dimensional difference synthesis were fixed throughout the refinement. The weighting scheme adopted was:

$$w = 1 \text{ for } F_0 > 6\cdot 0 ,$$

$$w = 0\cdot 3 \text{ for } F_0 < 6\cdot 0 .$$

The final R value was 0·123. Clearly the uncertainty in atomic positions in the TEA⁺ ion is responsible for comparatively high value of R. The final positional and thermal parameters are listed in Table 1. Table 2 lists the observed and calculated structure factors.

Description of the structure and discussion

The structure of the salt viewed along the c axis is presented in Fig. 1, which shows the columnar structure of the TCNQ molecules. Least-squares planes through the two independent TCNQ molecules were calculated and are listed in Table 3. The modes of nearest-neighbour packing of the TCNQ molecules are very similar to those found for other TCNQ salts (Fritchie & Arthur, 1966; Fritchie, 1966; Hanson, 1968). The interplanar spacings of (1)–(2), (2)–(3) and (4)–(1) pairs in Fig. 1 are 3·24, 3·32 and 3·30 Å respectively. Nearest-neighbour overlapping within a TCNQ column is shown in Fig. 2. The mode of overlapping of a pair of TCNQ molecules (1)–(2), of which the formal charges are 0 and −1 respectively, as described below, differs from those of other pairs. As shown in Fig. 1, the TCNQ molecules form a tetrad of TCNQ units within the columns. Such columnar structures of triadic, diadic and monadic units have already been found in Cs₂(TCNQ)₃, TMPD(TCNQ)₂* and (N-methyl-

phenazinium) (TCNQ) respectively (Fritchie & Arthur, 1966; Fritchie, 1966; Hanson, 1968).

The number of molecules in the repeating unit in the TCNQ column does not appear to be determined only by the molecular ratio of the donor and acceptor molecules but may also be affected by the shape, the size and the charge of the cation molecules. Bond distances and angles are shown in Figs. 3 and 4. Recent investigations have shown a small but significant dependence of the molecular geometry of TCNQ on its formal charge. In Table 4 the bond lengths, averaged by assuming D_{2h} symmetry, of the two independent TCNQ molecules found in TEA⁺(TCNQ)₂⁻ are compared with those of
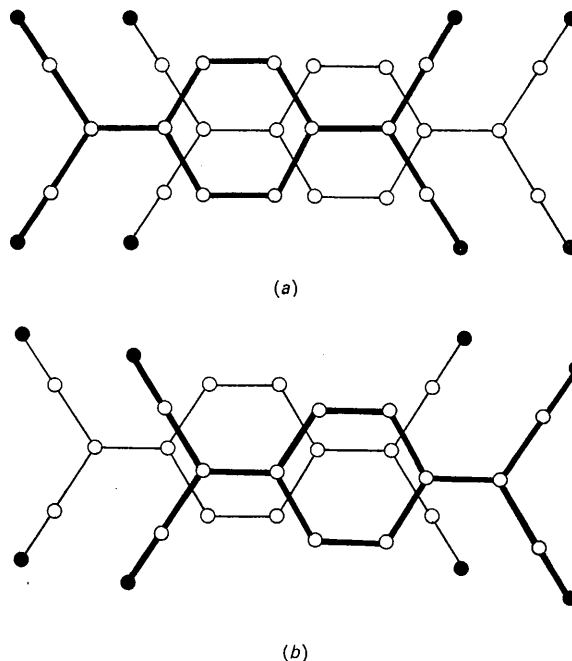

(a)

(b)

Fig. 2. Nearest neighbour packing. (a) TCNQ (1)–(2). (The numbering of the TCNQ molecule is illustrated in Fig. 1.) (b) TCNQ (1)–(4), (2)–(3). (The modes of overlapping of these two pairs are very similar, though they are not crystallographically equivalent.)

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* TMPD: N,N,N′,N′-tetramethyl-p-phenylenediamine.

$TCNQ^0$ and $TCNQ^-$ obtained from $Cs_2(TCNQ)_3$. It may easily be seen from Table 4 that $TCNQ^0$ and $TCNQ^-$ ions exist in crystals of $TEA^+(TCNQ)_2^-$. The negative charge in TCNQ columns seems to be localized predominantly in molecules 2 and 3. When the electrons move through the column, $TCNQ^-$ should change to $TCNQ^0$ and $TCNQ^0$ to $TCNQ^-$. Thus the movement of the electrons would be accompanied by distortion of the molecular geometries. The energy of this molecular deformation was calculated by use of the force constants listed in Table 5. The differences were about 0·06 eV for $TEA(TCNQ)_2$ and 0·08 eV for $Cs_2(TCNQ)_3$. In crystals of $TEA(TCNQ)_2$ and $Cs_2(TCNQ)_3$, $TCNQ^0$ and $TCNQ^-$ are arranged regularly, so that there exists a potential difference between the site occupied by $TCNQ^0$ and that occupied by $TCNQ^-$. The difference, ΔE, which increases the activation energy of electron hopping motion, will be at least 0·02 eV (kT at room temperatures), since the Boltzmann factor $\exp(-\Delta E/kT)$ has to be considerably diffe-

Table 2. *Observed and calculated structure factors*

The values listed are $10F_c$ and $10F_o$.

H	FO	FC
K,L=-15		0
3	13	-24
5	19	23
7	14	12
K,L=-14		0
1	33	39
7	61	68
9	26	-30
K,L=-13		0
1	45	60
2	24	-82
3	200	180
4	53	48
5	55	-61
6	35	42
7	172	-165
9	27	32
10	19	-30
K,L=-12		0
0	161	145
1	95	-82
2	117	118
3	403	-342
4	150	-142
5	51	49
6	78	-93
7	107	115
8	60	56
10	23	30
11	15	-23
K,L=-11		0
0	110	-206
1	16	35
2	108	-112
3	103	126
4	83	98
5	27	28
6	51	60
7	28	-39
K,L=-10		0
0	35	24
1	45	62
2	17	25
3	13	-20
4	15	-23
5	12	17
10	62	-67
K,L= -9		0
0	40	26
1	12	20
2	110	122
3	14	17
4	39	-40
5	27	37
6	159	-192
7	51	-41
8	19	19
9	21	-21
10	64	77
11	23	26
13	16	23
K,L= -8		0
0	28	-49
1	39	55
2	273	-279
3	67	-78
5	21	-25
6	88	80
7	21	35
9	41	38
10	40	-48
11	23	-29
K,L= -7		0
0	43	-48
1	128	136
2	155	-150
3	24	-35
4	15	21
5	82	-79
6	17	6
8	11	0
9	23	10
13	33	-44
K,L= -6		0
0	100	-112
1	384	-304
2	117	106
3	108	109
4	42	57
5	85	99
6	16	-33
7	17	-18
9	141	-164
K,L= -5		0
0	13	-30
1	92	102
2	37	-28
4	57	72
5	370	-350
6	56	-75
7	18	9
8	22	-5
K,L= -4		0
0	123	-90
1	33	18
2	122	-103
3	12	2
4	168	154
5	33	-47
6	90	-101
7	14	-24
8	89	-86
9	46	55
10	32	34
K,L= -3		0
0	301	216
1	711	-583
2	357	-304
3	138	-106
4	146	-154
5	269	242
6	11	22
7	22	15
8	21	47
10	43	45
11	44	58
12	35	111
13	21	-28
16	24	-34
K,L= -2		0
0	86	35
1	173	-128
2	191	-138
3	53	-57
4	50	-51
5	194	189
6	66	78
7	145	140
8	624	546
9	90	-84
10	16	-23
12	161	-151
15	16	15
K,L= -1		0
1	183	227
2	2	35
3	208	256
4	2211	2350
5	41	-37
6	19	-32
7	43	56
8	584	-513
9	34	-42
10	13	-21
11	16	-16
12	55	66
K,L= 0		0
2	177	-123
3	293	291
4	1346	-1415
5	107	-114
6	64	-87
7	79	-98
8	194	205
9	11	24
10	18	4
11	54	60
12	16	-20
K,L= 1		0
1	103	-124
2	445	-404
3	138	-160
4	164	187
6	13	16
7	109	120
8	29	-42
10	14	-8
11	55	70
14	15	-19
15	55	-61
K,L= 2		0
1	92	83
2	345	-347
3	53	-71
4	17	23
5	11	-9
6	29	28
7	312	299
8	31	-25
10	49	-53
11	175	-182
15	62	68
K,L= 3		0
1	206	204
2	52	-73
3	699	658
4	81	-61
5	12	-5
6	68	-79
7	443	-408
8	16	4
9	26	-27
10	16	-27
11	113	124
15	31	-36
K,L= 4		0
0	112	-90
1	173	159
2	56	-66
3	419	-395
4	39	43
6	53	-70
7	89	93
11	32	-37
K,L= 5		0
1	143	141
2	42	29
3	214	-242
4	62	-46
5	110	-119
6	122	-146
7	56	67
8	13	19
9	26	27
10	54	64
11	23	-29
K,L= 6		0
1	211	-190
2	315	-314
3	194	190
5	47	57
6	95	116
7	46	-66
8	18	15
10	56	-76
K,L= 7		0
1	44	-44
3	27	-42
5	58	-67
7	12	34
8	24	16
10	24	-21
12	21	-19
K,L= 8		0
2	29	115
3	33	45
4	24	38
5	89	-95
8	25	-37
9	15	-28
12	19	-22
14	12	11
K,L= 9		0
2	26	-96
3	44	31
4	31	-27
5	47	-43
6	22	34
8	52	-66
9	53	-62
10	33	45
12	58	50
13	37	42
K,L= 10		0
2	43	-50
3	10	-10
4	135	-150
5	213	-213
6	93	108
7	21	-24
8	125	110
9	144	[illegible]
10	13	-26
11	15	12
12	12	-17
K,L= 11		0
1	457	-391
2	132	148
3	57	-65
4	219	189
5	321	301
6	33	-44
7	43	46
8	23	-29
9	35	-54
K,L= 12		0
1	366	323
2	54	-53
3	62	71
5	50	-53
K,L= 14		0
7	29	32
8	44	50
K,L= 15		0
3	13	14
4	46	46
5	23	-19
6	15	19
7	24	-20
K,L= 16		0
1	17	-10
2	13	15
4	27	-29
K,L= 14		0
5	11	11
K,L=-17		1
-4	24	34
-3	21	-21
-2	15	15
-1	51	-59
0	49	-47
K,L=-16		1
-6	10	11
-5	31	-55
-4	55	-52
K,L=-15		1
-8	29	-34
4	21	-32
6	86	-102
7	31	-40
8	27	38
K,L=-14		1
2	116	-146
3	67	-80
4	28	47
5	31	-44
6	152	155
7	86	91
9	19	31
10	34	-58
K,L=-13		1
0	20	33
1	39	-55
2	130	157
3	108	116
5	44	30
K,L=-12		1
-6	16	-26
-5	25	-48
-3	51	-50
-2	63	96
-1	94	93
0	44	57
1	12	-27
K,L=-11		1
-7	26	-38
-6	19	35
-5	38	56
-4	21	18
-3	28	-44
-1	65	61
1	112	127
3	30	-30
K,L=-10		1
-9	20	22
-5	35	50
-4	23	23
-3	32	93
0	25	-32
1	39	121
2	24	36
3	22	-30
4	29	47
5	62	-76
K,L= -9		1
-7	40	49
-4	24	-27
-3	237	229
-2	84	100
0	74	100
1	190	-200
2	58	-67
4	77	-99
5	64	75
6	44	56
7	60	51
K,L= -8		1
-1	25	-39
2	35	71
3	28	64
4	21	15
8	26	28
K,L= -7		1
-12	24	35
-7	12	-31
-6	12	12
-5	22	-17
-4	147	171
-3	91	-112
-2	41	-55
0	123	-253
1	46	61
2	118	133
3	24	41
4	223	252
6	36	-42
8	115	-124
K,L= -6		1
-10	16	13
-8	162	155
-7	104	117
-6	87	-121
-5	11	-15
-4	373	-386
-3	61	41
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0	693	645
1	44	69
2	100	-67
3	184	181
4	586	-539
5	109	-115
6	41	31
7	35	-37
8	38	50
9	35	35
K,L= -5		1
-12	78	75
-10	50	-49
-8	221	-205
-7	15	-27
-6	87	87
-4	535	577
-3	132	121
-1	216	203
0	1006	-911
1	246	-216
2	23	49
3	80	133
5	23	-40
6	31	30
9	29	20
11	34	64
15	75	-91
K,L= -4		1
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-11	22	-29
-10	31	34
-9	18	-3
-8	233	221
-6	12	-11
-5	80	75
-4	352	-331
-3	134	-137
-2	110	127
-1	462	461
0	767	-585
1	350	-337
2	11	27
3	188	-187
4	172	194
5	54	63
6	60	63
7	218	288
8	100	-120
9	53	-70
10	15	-22
11	340	-330
15	116	124
K,L= -3		1
-16	26	-38
-15	22	-13
-12	71	81
-11	27	25
-9	29	44
-8	32	-69
-7	16	-18
-5	159	192
-4	397	-417
-3	359	-417
-2	8	33
-1	79	-106
0	35	-28
1	14	-31
2	128	150
3	901	851
5	179	-194
7	1020	-907
8	49	-36
9	31	32
11	345	325
15	53	-62
K,L= -2		1
-16	22	24
-13	25	26
-12	16	-19
-11	21	-36
-7	34	-51
-6	35	-29
-5	15	-34
-4	95	-102
-3	121	-155
-2	61	57
-1	1213	1128
0	185	-231
1	545	[illegible]
2	80	102
3	1572	-1753
4	148	-138
5	11	-6
6	22	-32
7	647	587
8	17	33
9	25	-17
10	45	44
11	56	-80
K,L= -1		1
-13	26	-38
-12	14	-23
-4	96	-122
-3	227	-238
-2	6	2
-1	724	-833
0	184	-213
1	405	-410
2	105	-138
3	497	520
5	10	-18
6	16	-40
7	60	83
9	16	9
10	55	56
14	18	-29
K,L= 0		1
-10	21	-30
-9	41	-63
-8	12	-31
-6	91	110
-5	210	-220
-4	222	-230
-3	300	-305
-2	392	-375
-1	505	447
0	189	183
1	320	-311
2	219	-292
3	322	388
4	34	43
5	66	91
6	231	249
7	29	-32
8	15	-12
9	12	-15
10	25	-34
11	18	16
14	31	42
K,L= 1		1
-11	25	20
-9	66	-83
-8	52	-87
-7	77	-100
-6	72	-100
-5	222	240
-3	148	-144
-2	537	-544
-1	428	408
0	379	322
1	42	-50
2	262	250
3	22	41
4	41	-58
5	27	33
6	227	248
11	22	9
14	15	-24
K,L= 2		1
-13	12	-17
-12	25	-35
-9	21	42
-8	12	20
-7	22	-47
-6	126	-148
-5	183	226
-4	17	[illegible]
-3	24	-24
-2	300	-372
-1	170	201
1	23	23
2	1024	1011
3	[illegible]	[illegible]
5	130	-17
6	16	-12
9	[illegible]	-27
K,L= 3		1
-10	27	-26
-9	32	32
-6	234	-233
-5	138	128
-2	1491	1223
-1	102	-91
0	131	136
1	62	69
2	243	-280
3	13	52
4	12	-46
5	62	-62
6	70	36
7	18	16
8	18	24
9	41	55
10	32	-43
K,L= 4		1
-11	21	17
-6	351	332
-5	47	66
-4	30	25
-3	51	-52
-2	345	298
-1	22	-48
0	91	88
1	150	166
2	134	-148
3	28	-32
4	23	-44
6	16	-24
7	14	15
8	15	24
9	35	59
K,L= 5		1
-10	62	61
-8	13	-13
-7	41	-74
-6	220	238
-5	50	56
-4	194	170
-3	316	291
-2	256	-235
-1	169	-180
0	233	-229
1	178	-211
2	71	92
4	86	80
5	308	324
6	39	-51
7	27	21
8	17	-18
9	75	-85
K,L= 6		1
-11	34	-47
-10	29	28
-8	53	81
-7	231	202
-6	130	-152
-5	71	-75
-4	133	-132
-3	374	-328
-2	[illegible]	123
-1	[illegible]	[illegible]
0	11	-12
1	620	627
2	24	-24
3	12	30
4	22	-27
5	123	-120
K,L= 7		1
-12	14	22
-11	[illegible]	[illegible]
-10	27	-47
-8	75	-56
-7	138	-142
-6	50	60
-5	65	-47
-3	231	[illegible]
-3	281	[illegible]
-1	24	12
0	32	-74
2	33	48
3	17	25
5	22	-27
6	36	-44
7	47	-28
8	25	-47
9	51	63
11	64	62
12	23	85
13	47	-50
K,L= 8		1
-11	62	-66
-7	29	59
-5	19	24
-3	50	30
-1	66	64
0	63	28
1	200	-201
3	120	-130
4	137	-168
5	127	145
7	110	119
8	221	223
9	102	-106
11	94	-81
12	152	-150
13	33	27
K,L= 9		1
-4	22	24
-2	29	-22
-1	22	-102
0	128	-243
1	112	144
2	118	131
4	205	223
5	135	-141
6	39	43
7	112	-112
8	268	-256
9	47	58
10	23	-31
11	15	18
K,L= 10		1
-5	35	-40
-4	90	-121
-3	52	73
-1	47	61
0	208	205
1	97	-104
2	69	70
3	48	-70
4	263	-273
5	35	54
6	32	-47
8	43	61
K,L= 11		1
-4	49	64
-2	53	70
-1	17	-14
0	162	-182
2	22	-40
K,L= 12		1
-8	24	30
-6	32	41
-4	79	-105
0	22	-23
2	39	-37
4	29	44
K,L= 13		1
-8	28	-39
2	29	-31
3	34	-52
K,L= 14		1
0	24	36
2	32	43
3	41	52
-2	24	-33
-1	50	-78
K,L= 15		1
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-4	14	19
-2	15	24
-1	40	46
K,L= 16		1
-1	25	23
K,L=-15		2
-3	30	44
-2	25	34
K,L=-14		2
-7	24	41
-6	25	42
-3	31	48
2	35	-44
K,L=-13		2
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-2	49	-54
[illegible]	45	-48
[illegible]	25	17
K,L=-12		2
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0	38	-29
2	24	26
4	36	-39
5	22	-28
6	43	45
K,L=-11		2
-6	47	-71
-5	39	40
-4	104	-120
-2	25	41
0	23	-10
1	23	-36
4	52	65
5	25	36
K,L=-10		2
-9	109	-155
-7	46	-63
-4	32	35
3	69	-95
4	40	37
5	42	37
7	82	36
9	36	-33
11	63	-59
K,L= -9		2
-12	79	-84
-4	39	39
-3	25	3
-1	173	-193
0	37	110
1	202	172
2	25	33
3	217	204
4	39	-38
5	98	-94
7	132	-164
9	32	42
11	75	77
K,L= -8		2
-11	19	-26
-9	17	-26
-8	22	17
-6	142	-125
-4	95	97
-3	129	174
-2	17	23
-1	240	203
0	33	9
1	82	-70
2	8	12
3	247	-252
4	52	-59
5	53	56
6	26	-18
7	139	158
8	53	44
10	20	-5
11	22	-25
K,L= -7		2
-9	37	-47
-8	13	21
-7	81	67
-5	131	140
-4	62	59
-1	230	-258
0	77	-82
1	45	78
3	178	196
4	40	37
8	21	27
K,L= -6		2
-11	30	33
-9	102	102
-8	39	43
-7	24	-27
-6	26	15
-5	167	-149
-4	33	-54
-3	93	100
-2	51	-9
-1	142	124
2	13	20
3	36	58
4	39	57
5	27	17
6	64	73
7	59	-63
10	94	-92
14	113	103
K,L= -5		2
-13	40	47
-9	75	-73
-6	99	-104
-5	156	163
-4	128	135
-3	104	112
-2	285	314
-1	136	-170
0	79	-117
1	23	42
3	17	26
7	19	4
8	23	41
9	22	17
10	179	183
-14	102	-105
K,L= -4		2
-10	46	-40
-9	64	64
-8	112	117
-7	15	34
-6	192	206
-5	151	-152
-4	167	-167
-3	41	42
-2	21	-43
-1	26	45
0	12	-43
2	337	351
3	47	40
5	159	[illegible]
6	30	-18
8	32	46
10	144	-151
14	16	24
K,L= -3		2
-12	17	21
-10	44	70
-9	35	-35
-8	11	-26
-6	18	-103
-4	17	-39
-2	279	294
-1	179	170
0	143	-153
1	55	67
2	31	-39
4	30	50
5	124	147
6	177	-192
7	48	-64
9	20	12
K,L= -2		2
-10	25	-19
-9	12	-22
-8	22	0
-6	251	287
-5	73	62
-4	105	-104
-3	78	-108
-2	132	126
-1	215	250
0	32	-47
1	439	422
2	522	-491
3	212	-230
5	43	41
7	23	-30
8	37	-33
9	15	[illegible]
K,L= -1		2
-11	20	-26
-10	50	36
-9	21	26
-6	101	119
-5	95	105
-4	31	-12
-3	264	252
-2	551	-504
-1	47	-47
0	104	-130
1	134	156
2	72	-105
3	142	-170
4	45	-50
6	21	32
8	18	-20
9	174	-182
13	42	46
K,L= 0		2
-11	19	13
-10	15	-17
-9	9	15
-8	18	-30
-7	18	22
-6	43	-48
-5	13	-8
-4	54	-47
-3	395	381
-2	480	-424
-1	64	-90
0	103	-115
1	197	-210
2	57	70
3	58	-96
4	20	-4
5	492	-474
7	11	16
8	22	-26
9	93	98
10	11	6
11	25	-6
K,L= 1		2
-14	17	-20
-11	59	-82
-9	22	46
-7	411	390
-6	159	-159
-5	113	-131
-4	116	-85
-3	554	-523
-2	228	-211
-1	20	11
0	93	111
1	548	-548
2	47	44
4	22	-16
7	23	-27
8	40	-60
9	54	59
10	23	28
11	26	28
12	35	36
13	16	-21
K,L= 2		2
-15	29	-62
-11	219	212
-10	55	-52
-5	65	-79
-4	52	51
-3	140	-117
-2	158	-172
-1	28	-23
0	208	137
1	452	-407
2	66	-50
3	32	-107
4	312	285
5	313	285
6	104	95
7	94	[illegible]
8	147	154
9	56	-83
12	73	-70
K,L= 3		2
-15	70	36
-11	25	-110
-10	21	-23
-8	52	27
-7	113	-107
-6	77	-82
-4	59	73
-3	161	-143
-2	143	-126
-1	196	-204
0	339	-329
1	378	357
2	107	109
3	131	179
4	350	327
5	135	-135
7	19	-17
8	180	-151
12	58	50
K,L= 4		2
-15	29	-43
-10	40	-46
-9	15	-12
-8	31	24
-7	13	-21
-6	25	-28
-5	67	-72
-4	307	-257
-3	281	257
-2	25	35
-1	51	53
0	355	423
1	80	-26
2	45	-52
4	143	-127
5	15	30
9	51	53
K,L= 5		2
-9	40	-37
-8	120	-122
-7	91	90
-5	71	54
-4	229	198
-2	15	-23
-1	50	-64
0	51	54
1	37	29
2	61	-53
3	17	18
4	47	51
8	54	66
11	40	50
12	51	-51
K,L= 6		2
-12	60	-73
-11	21	31
-8	131	119
-2	65	-73
-1	82	-106
0	217	213
1	81	67
4	69	66
6	19	15
7	88	96
8	79	-72
10	42	-38
11	110	-97
12	63	55
K,L= 7		2
-12	35	47
-8	41	-45
-6	90	-69
-5	95	-112
-4	259	264
-3	60	68
-2	56	51
4	31	-29
6	28	-31
7	91	-86
8	62	60
10	31	24
11	132	110
12	28	-26
K,L= 8		2
-9	38	-64
-8	77	102
-7	38	39
-6	19	25
-1	43	-52
4	28	31
7	134	121
11	44	-42
K,L= 9		2
-5	53	-64
-4	33	32
3	115	134
5	47	39
K,L= 10		2
-1	139	122
1	42	35
3	35	-35
3	35	-35
6	53	45
7	38	-26
9	30	-24
10	43	-27
K,L= 12		2
-2	50	36
-2	50	26
0	50	26
3	43	-33
6	71	-57
K,L= 13		2
-3	66	45
2	57	-46
K,L= 14		2
0	61	-45
4	47	-39
6	34	34
K,L= 15		2
-2	43	-41
0	53	-35
1	32	-27
2	32	36
K,L=-17		3
4	27	24
K,L=-16		3
1	27	26
K,L=-15		3
-3	44	38
K,L=-14		3
-7	35	41
7	26	-31
K,L=-13		3
-3	43	60
-1	117	157
K,L=-14		3
3	52	72
K,L=-13		3

Table 2 (cont.)

Table 3. *Least-squares planes*

	Direction cosines with respect to			Mean deviation	Maximum deviation
	a	b	c		
TCNQ (1)*	0·9057	−0·2746	0·1422	0·022 Å	0·045 Å
TCNQ (2)	0·9074	−0·2680	0·1415	0·014	0·030

* The numbering of the TCNQ molecule is illustrated in Fig. 1.

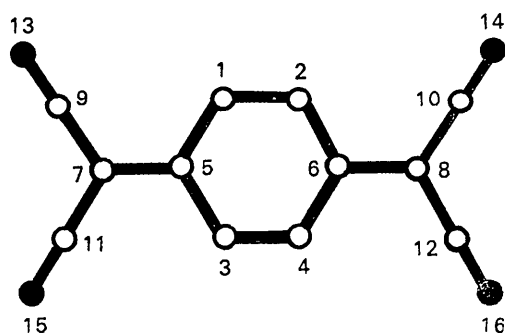Table 4. *Comparison of mean bond lengths*

The numbering system of atoms is as illustrated below.

	(1)–(2)	(1)–(5)	(5)–(7)	(7)–(9)	(9)–(13)
TCNQ (1)*	1·345	1·444	1·387	1·422	1·152
TCNQ (2)*	1·377	1·433	1·409	1·408	1·159
Δr	0·032	−0·011	0·022	−0·014	0·007
TCNQ⁰†	1·341	1·444	1·371	1·428	1·140
TCNQ⁻†	1·355	1·427	1·410	1·419	1·152
Δr†	0·014	−0·017	0·039	−0·009	0·012
Δr(MO)‡	0·014	−0·016	0·024	−0·011	0·008

* See Fig. 1.
† Fritchie & Arthur (1966).
‡ Goldstein, Seff & Trueblood (1968).

rent from unity at room temperature. Consequently, the activation energies of electron conduction in $Cs_2(TCNQ)_3$ and $TEA(TCNQ)_2$ would be greater than 0·1 eV and 0·08 eV respectively. From electron spin resonance studies, Ward & Weissman (1957) calculated the activation energy for the hopping motion of electrons in the lithium and potassium salts of naphthalene in tetrahydrofuran to be 0·1 eV. Thus the above values appear to be plausible.

Table 5. *Assumed force constants of* TCNQ*

		md.Å⁻¹
Quinomethane double bond	C=C	10·0
Benzene ring	C=C	5·5
Single bond	C–C	4·0
Cyano group	C≡N	20·0

* The differences between TCNQ⁰ and TCNQ⁻ are neglected.

A pair of the tetraethylammonium ions related by a centre of symmetry at $(\frac{1}{2}, 0, \frac{1}{2})$ are located in a space formed between the TCNQ columns. The positional parameters of the carbon atoms obtained by the least-squares refinement gave some chemically unreasonable bond distances and angles; moreover, their thermal parameters are unusually large. Consequently the atomic coordinates of these atoms may be regarded as the average values of various atomic coordinates related to some randomness in atomic positions. The projection of the structure along the b axis is illustrated in Fig. 5. The close contacts between the nitrogen atom [N(9)] of the TEA ion and the atoms of the TCNQ column occur between N(9) and N(4) (3·33 Å) and between N(9) and N(6) (3·44 Å). The region in which the carbon atoms are distributed is about 3·5 Å away from any atoms of the TCNQ columns. Recently Boer, Flynn & Turley (1968) have reported that large temperature factors, such as those of the atoms of the trimethylammonium ion, in crystals of tetramethylammonium bis-(o-phenylenedioxy)phenylsiliconate originate largely from thermal motion. Fritchie (1966) has found positional disorder of N-methylphenazinium ions in crystals of

N-methylphenazinium(TCNQ). Since the TEA ion possesses more freedom of internal rotation than the tetramethylammonium ion, such a disordered arrangement might be possible. This is somewhat analogous to the packing of the solvent molecules in some solvated crystals (*e.g.* McPhail & Sim, 1968).
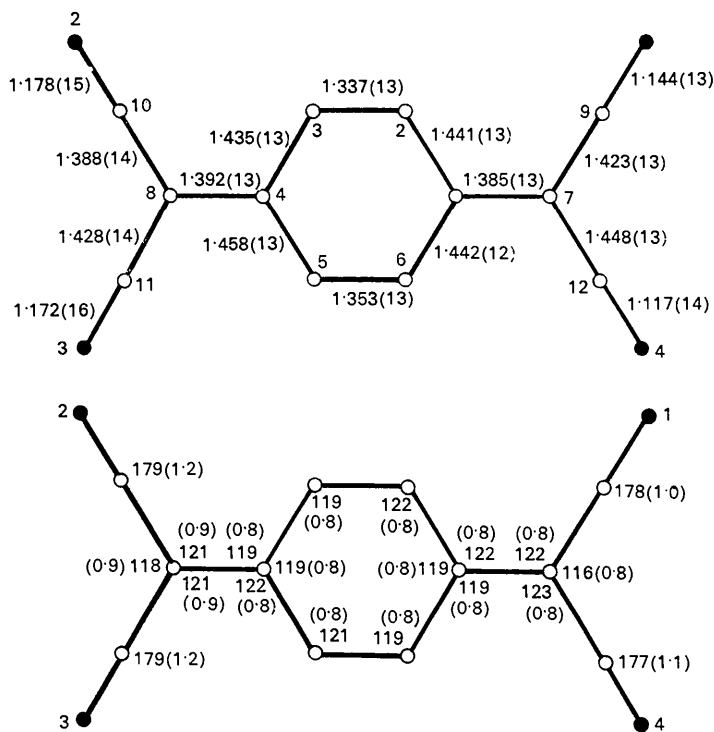
Fig. 3. Bond lengths (Å) and bond angles (°), with their standard deviations (in parentheses), in TCNQ (1) (see Fig. 1). The numbering of atoms refers to Fig. 1.
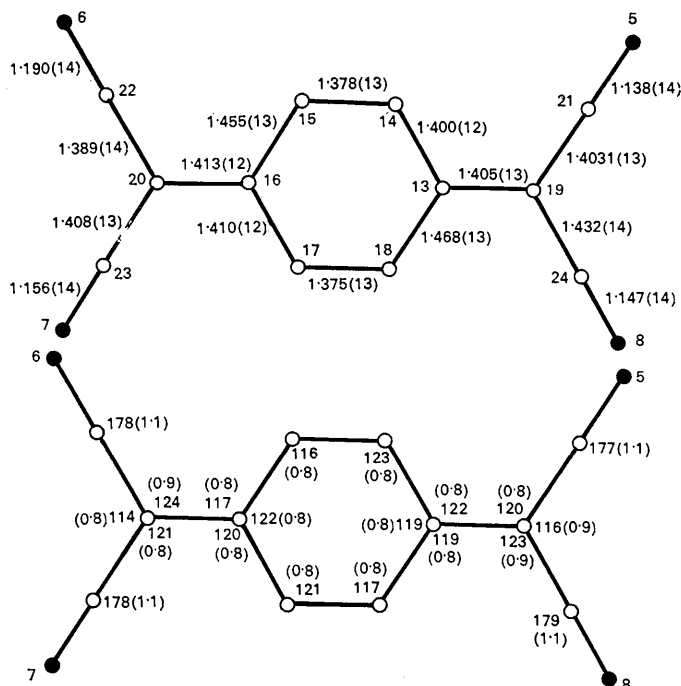
Fig. 4. Bond lengths (Å) and bond angles (°), with their standard deviations, in TCNQ (2). The numbering of atoms refers to Fig. 1.

Fig. 5. Projection of the structure along the *b* axis.

Calculations were carried out on the HITAC 5020E computer at the Computer Centre of this University.

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