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The Crystal Structures of Free Radical Salts and Complexes. III. (*N*,*N*′-Dibenzyl-4,4′-bipyridylium)$^{2+}$-(7,7,8,8-Tetracyanoquinodimethane)$_4^{2-}$

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The 4:1 complex formed between tetracyanoquinodimethane (TCNQ) and dibenzylbipyridylium (DBBP) crystallizes in the triclinic system with the space group $P\bar{1}$ and lattice constants $a=7{\cdot}15$, $b=16{\cdot}82$, $c=12{\cdot}10$ Å, $\alpha=99{\cdot}5°$, $\beta=83{\cdot}8°$, $\gamma=91{\cdot}8°$ and having $Z=1$. The structure was solved by Patterson methods and refined by block-diagonal least squares using 1936 reflexions measured on a linear diffractometer. The four TCNQs are packed plane-to-plane to form a column along the *b* axis. The characteristic overlap and short interplanar spacings indicate charge transfer interaction between the four TCNQ moieties stacked as tetramers.

Introduction

Molecular complexes containing TCNQ ions and molecules include some of the best electrically conducting organic compounds known. TCNQ is a powerful electron acceptor and forms TCNQ$^{\dot{-}}$ by accepting an additional electron. The TCNQ$^{\dot{-}}$ forms simple salts with cations of many types and complexes containing neutral TCNQ in addition to TCNQ$^{\dot{-}}$. These complexes of the type M$^+$TCNQ$^{\dot{-}}$ TCNQ have been found to exhibit higher electrical conductivity than most simple salts M$^+$TCNQ$^-$. In most crystal structure determinations of this type of complex the TCNQs have been found to be indistinguishable moieties with a formal charge $\frac{1}{2}-$. The 4:1 TCNQ DBBP complex salt is a member of the same series of complexes since it has equal numbers of TCNQ^0 and TCNQ$^{\dot{-}}$. Its structure determination was undertaken to see how it is related structurally to M$^+$ TCNQ$^{\dot{-}}$ TCNQ^0 complexes and in general to provide data for relating structures to conductivity.

Experimental

Crystal data

$(C_{24}H_{22}N_2)(C_{12}H_4N_4)_4$, M.W. 1155·2.
Triclinic,
$a=7{\cdot}15\pm0{\cdot}03$, $b=16{\cdot}82\pm0{\cdot}04$, $c=12{\cdot}10\pm0{\cdot}04$ Å,
$\alpha=99{\cdot}5\pm0{\cdot}1°$, $\beta=83{\cdot}8\pm0{\cdot}1°$, $\gamma=91{\cdot}8\pm0{\cdot}5°$;
$U=1422{\cdot}8$ Å^3;
$D_m=1{\cdot}341$ g.cm^{-3}, $Z=1$, $D_c=1{\cdot}348$ g.cm^{-3},
$F(000)=596$.
Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å), $\mu=0{\cdot}91$ cm^{-1}.
Space group $P\bar{1}$ (assumed).

Black plate-like crystals of the complex were deposited when equimolar solutions of Li$^+$TCNQ$^-$ and TCNQ were dissolved in a minimum qunatity of hot acetonitrile, and added to a concentrated solution of DBBP Cl_2 in water, the mixture being allowed to cool very slowly. The space group and the cell constants were obtained initially from oscillation and Weissenberg photographs taken with the crystals rotating about all the three crystallographic axes using Cu $K\alpha$ radiation and were subsequently refined on a Hilger and Watts linear diffractometer. Intensity data for the layers $0kl$ to $7kl$ were collected with the crystal rotating about the *a* axis on the diffractometer using a scintillation counter and molybdenum $K\alpha$ radiation with balanced filters. Out of the 4750 reflexions measured, significant counts were recorded for 1936. No absorption corrections were made because of the small size of the crystal, ($1\times0{\cdot}5\times0{\cdot}1$ mm). The intensities were corrected for Lorentz and polarization factors.

Structure determination

If the space group is $P\bar{1}$, the single DBBP ion in the cell must occupy a centre of symmetry, while the four TCNQ moieties may lie in general positions as two centrosymmetrically related pairs. A three-dimensional Patterson map was computed using F_o^2 as coefficients. Vectors typical of TCNQ were recognized round the origin and round peaks at (1) $x=0\cdot000$, $y=0\cdot230$, $z=0\cdot043$; (2) $x=0\cdot014$, $y=0\cdot296$, $z=-0\cdot120$ and (3) $x=-0\cdot014$, $y=0\cdot452$, $z=0\cdot085$. These peaks could all be interpreted in terms of a trial structure in which the TCNQs are stacked along the *b* axis, spaced roughly *b*/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 TCNQs (*A′* and *A*), while the peak at (2) was taken to represent the vectors between the other pair (*B* and *B′*) of centrosymmetrically related TCNQs. The relatively weaker peak at (3) was taken to represent the vectors between the TCNQs *A′* and *B*. The presence of strong vectors between the two crystallographically independent TCNQs (*A* and *B*) suggests that the TCNQs are packed parallel to each other and thus the common orientation of the TCNQs was deduced from the vector pattern around the origin.

Using the signs of the structure factors calculated on the basis of the trial structure for the TCNQs, a three-dimensional Fourier electron density map was computed. This confirmed the positions of TCNQs and showed six of the thirteen atoms of the DBBP ion. Three subsequent structure factor calculations followed by Fourier maps showed the remaining seven atoms of the DBBP ion. Four cycles of least-squares refinement of the positional and isotropic thermal parameters of all the 45 atoms gave an *R* value of

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

The figures in parentheses indicate the standard deviations.

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

	x/*a*	*y*/*b*	*z*/*c*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	−1054 (11)	1307 (5)	−635 (6)	187 (22)	25 (3)	39 (6)	−13 (13)	−59 (18)	2 (7)
C(2)	882 (11)	1525 (4)	−610 (6)	216 (21)	9 (3)	52 (6)	−1 (11)	−66 (19)	2 (7)
C(3)	1872 (11)	1318 (4)	260 (6)	167 (21)	21 (3)	55 (7)	29 (12)	−3 (18)	13 (7)
C(4)	987 (11)	928 (4)	1061 (6)	183 (21)	22 (3)	42 (6)	21 (12)	−22 (18)	6 (7)
C(5)	−955 (11)	695 (4)	1032 (6)	215 (21)	15 (3)	35 (6)	−5 (12)	−12 (17)	−8 (7)
C(6)	−1920 (12)	890 (5)	139 (7)	202 (22)	24 (3)	52 (7)	26 (13)	−54 (19)	14 (7)
C(7)	1763 (11)	1974 (5)	−1409 (7)	171 (21)	26 (3)	51 (7)	−7 (13)	−35 (19)	7 (8)
C(8)	3688 (13)	2220 (5)	−1380 (7)	283 (26)	29 (4)	48 (7)	−4 (15)	−27 (21)	28 (8)
C(9)	858 (12)	2228 (5)	−2260 (7)	195 (22)	25 (3)	54 (7)	−4 (13)	−46 (19)	−1 (8)
C(10)	−1865 (11)	282 (5)	1850 (7)	165 (21)	23 (3)	59 (7)	11 (12)	−36 (19)	−4 (8)
C(11)	−934 (13)	69 (5)	2732 (7)	228 (24)	27 (4)	67 (8)	−22 (14)	−30 (21)	9 (8)
C(12)	−3796 (13)	42 (5)	1877 (7)	256 (25)	26 (4)	63 (7)	17 (14)	−75 (21)	7 (8)
C(13)	−1181 (12)	3602 (5)	−185 (7)	226 (25)	20 (3)	88 (9)	−17 (14)	−65 (23)	1 (9)
C(14)	770 (12)	3831 (5)	−224 (7)	254 (24)	20 (3)	65 (8)	9 (14)	−36 (22)	14 (8)
C(15)	1842 (12)	3628 (5)	624 (7)	210 (23)	23 (3)	70 (8)	−9 (13)	−3 (21)	−10 (8)
C(16)	1024 (13)	3206 (5)	1410 (7)	244 (25)	25 (3)	71 (8)	14 (14)	−86 (22)	6 (8)
C(17)	−936 (11)	2957 (4)	1420 (6)	210 (23)	21 (3)	41 (6)	28 (13)	−23 (18)	2 (7)
C(18)	−2002 (12)	3185 (5)	605 (7)	190 (23)	25 (3)	75 (8)	−26 (13)	−52 (20)	26 (8)
C(19)	1623 (13)	4235 (5)	−1061 (8)	278 (26)	17 (3)	82 (8)	24 (14)	4 (23)	23 (8)
C(20)	3628 (14)	4432 (5)	−1143 (8)	297 (28)	36 (4)	78 (9)	11 (16)	−1 (24)	28 (10)
C(21)	595 (14)	4461 (5)	−1907 (8)	312 (28)	21 (4)	98 (9)	22 (15)	−30 (25)	38 (9)
C(22)	−1756 (11)	2540 (4)	2234 (6)	175 (21)	21 (3)	36 (6)	21 (12)	−3 (17)	4 (7)
C(23)	−824 (12)	2317 (5)	3108 (6)	251 (24)	30 (4)	40 (6)	−23 (14)	2 (19)	17 (8)
C(24)	−3722 (13)	2304 (5)	2247 (7)	275 (26)	31 (4)	49 (7)	34 (15)	−31 (21)	21 (8)
C(25)	−5010 (11)	450 (4)	5119 (6)	180 (20)	18 (3)	41 (6)	−7 (11)	−46 (17)	8 (7)
C(26)	−6383 (13)	925 (5)	4839 (8)	210 (25)	32 (4)	110 (10)	−7 (15)	−155 (24)	37 (10)
C(27)	−6351 (13)	1750 (5)	5097 (7)	268 (25)	18 (3)	70 (8)	−9 (13)	−93 (22)	−1 (8)
C(28)	−3569 (13)	1673 (5)	5883 (8)	255 (26)	28 (4)	82 (8)	−17 (15)	−74 (23)	38 (9)
C(29)	−3539 (13)	847 (5)	5633 (7)	256 (25)	17 (3)	84 (8)	19 (13)	−78 (22)	22 (8)
C(30)	−5062 (14)	3016 (5)	6049 (7)	373 (30)	21 (3)	53 (7)	4 (15)	−70 (23)	−16 (8)
C(31)	−5360 (12)	3486 (4)	5163 (7)	246 (24)	18 (3)	48 (7)	−20 (13)	31 (20)	4 (7)
C(32)	−7217 (14)	3674 (5)	4999 (8)	323 (29)	23 (4)	91 (9)	−6 (16)	−64 (26)	5 (9)
C(33)	−7589 (16)	4135 (6)	4198 (9)	418 (35)	31 (4)	116 (11)	−23 (19)	−131 (31)	36 (11)
C(34)	−6110 (18)	4411 (6)	3564 (9)	561 (42)	29 (4)	86 (10)	23 (21)	−102 (32)	21 (10)
C(35)	−4299 (16)	4245 (5)	3699 (8)	481 (38)	22 (4)	84 (9)	−60 (18)	65 (29)	10 (9)
C(36)	−3840 (15)	3794 (5)	4528 (8)	355 (31)	25 (4)	84 (9)	−1 (16)	26 (26)	−12 (9)
N(1)	5255 (11)	2417 (5)	−1400 (6)	243 (21)	42 (4)	90 (7)	−22 (13)	−70 (20)	29 (8)
N(2)	129 (11)	2454 (4)	−2949 (6)	271 (21)	40 (3)	64 (6)	−56 (13)	−131 (18)	29 (7)
N(3)	−5355 (11)	−150 (5)	1889 (7)	231 (21)	47 (4)	107 (8)	−26 (14)	−68 (20)	42 (9)
N(4)	−226 (11)	−88 (5)	3482 (6)	265 (22)	56 (4)	68 (7)	−6 (15)	−23 (19)	41 (8)
N(5)	5194 (13)	4571 (6)	−1277 (8)	334 (28)	75 (5)	132 (10)	−49 (19)	−20 (26)	93 (12)
N(6)	−137 (14)	4663 (6)	−2578 (8)	373 (28)	68 (5)	113 (9)	74 (19)	20 (25)	75 (11)
N(7)	−5271 (12)	2104 (5)	2284 (7)	273 (24)	56 (4)	105 (8)	−42 (15)	−68 (22)	9 (9)
N(8)	−93 (12)	2135 (5)	3830 (6)	344 (25)	47 (4)	74 (7)	−10 (15)	−56 (21)	44 (8)
N(9)	−4955 (10)	2112 (4)	5638 (5)	284 (20)	18 (3)	42 (5)	0 (11)	−40 (16)	4 (6)

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

L	FO	FC
H=	0, K=	0
2	361	460
4	72	-72
-2	801	-647
-6	64	79
-8	134	144
-11	114	-122
H=	0, K=	1
2	68	-55
3	113	98
4	104	103
5	78	80
6	185	-165
10	54	47
-2	43	-47
-3	450	-467
-4	318	336
-5	101	116
-6	390	375
-7	96	-104
-8	271	-279
-10	94	86
-11	72	64
H=	0, K=	2
2	294	-298
3	377	387
4	206	-203
6	126	111
13	348	-336
-2	360	389
-3	380	-395
-4	132	127
-5	103	-95
-6	176	176
-7	182	-202
-10	166	163
-11	534	543
-12	217	216
H=	0, K=	3
0	124	130
2	424	414
3	467	-459
4	128	126
5	141	135
6	407	413
8	128	-120
9	109	-112
10	72	63
-1	52	-42
-2	178	-169
-3	245	250
-4	129	121
-5	125	-133
-6	170	147
-7	76	-66
-9	64	-70
-11	74	91
H=	0, K=	4
0	289	280
1	623	-607
2	2540	-2701
3	579	-575
4	287	-265
5	170	184
6	335	332
7	77	82
10	84	-66
12	71	-72
-1	297	287
-2	382	-335
-4	203	-196
-5	135	126
-6	303	-320
-8	78	79
-9	91	82
-10	98	86
H=	0, K=	5
0	782	753
1	336	-324
2	48	56
3	143	-144
5	109	109
6	204	-197
7	76	-65
-1	488	-477
-2	813	-789
-3	192	-137
-4	90	74
-5	325	344
-6	617	632
-7	82	-74
-8	122	-125
-12	68	-60
H=	0, K=	6
0	198	-223
1	127	-133
2	98	95
4	68	74
5	58	-58
12	91	61
-1	205	199
-2	102	99
-3	134	-135
-4	206	206
-5	182	181
-6	217	222
-7	340	-346
-8	219	-207
-9	474	-494
-10	224	-215
-12	73	80
H=	0, K=	7
0	188	-172
1	332	325
2	482	-448
3	284	269
4	477	-460
5	241	236
7	99	-100
8	181	-190
9	91	-124
11	92	117
-2	143	-138
-3	138	132
-4	206	-187
-7	82	-26
-9	157	-149
-13	170	-160
H=	0, K=	8
2	120	-107
3	259	265
4	662	659
5	93	83
6	188	193
7	90	-80
8	198	-209
-1	226	217
-2	68	-66
-3	111	109
-4	194	190
-6	69	-97
-9	78	92
-10	89	46
H=	0, K=	9
0	555	555
1	249	257
2	229	-234
4	115	131
-1	64	-42
-2	558	-534
-3	198	-186
-4	324	-333
-5	102	104
-12	70	-50
H=	0, K=	10
	132	-147
2	166	172
4	108	-120
6	146	-167
7	101	95
8	98	-87
-2	283	-271
-3	85	-76
-4	178	-198
-5	233	232
-6	141	137
-7	196	162
-8	157	151
H=	0, K=	11
0	82	87
1	63	-63
4	111	118
6	161	172
7	92	-64
-2	225	208
-3	88	-75
-4	75	86
-8	103	107
-11	178	169
H=	0, K=	12
2	78	-20
5	86	-98
8	125	-124
-1	72	-60
-2	194	-148
H=	0, K=	13
0	263	267
2	186	-190
-1	158	147
-2	70	77
-5	96	99
-7	99	96
H=	0, K=	14
0	191	189
1	56	48
3	84	69
-2	95	99
-5	67	50
-6	158	-148
-8	88	-76
-9	83	77
-10	67	-80
H=	0, K=	15
0	156	-171
1	65	51
5	60	75
-1	102	92
-4	73	34
-6	81	-63
-10	109	-104
H=	0, K=	16
-7	65	-77
H=	0, K=	17
0	64	-43
1	120	-105
2	72	-71
-8	94	42
H=	0, K=	18
0	70	-65
H=	1, K=	0
2	107	124
3	522	541
5	274	-252
6	134	-155
7	66	72
8	154	-163
-1	437	389
-2	805	-872
-3	1037	1080
-4	77	77
-6	51	-59
-7	62	48
-9	73	-50
H=	1, K=	1
2	101	-110
3	129	-133
4	151	-148
5	211	200
6	133	138
7	83	54
8	69	-70
9	61	70
-1	36	57
-2	216	-230
-3	1419	1487
-4	666	-690
-5	251	-246
-6	526	-526
-7	145	-154
-9	118	149
-11	112	110
-12	81	-73
H=	1, K=	-1
0	142	250
1	228	305
2	214	202
3	475	519
4	760	-788
5	900	-915
6	80	-88
7	105	-106
8	381	383
10	59	-42
-1	206	-232
-2	229	242
-3	167	-201
-4	244	-247
-5	64	-73
-6	184	198
-13	76	-65
H=	1, K=	2
0	199	208
1	359	-369
2	397	400
3	149	-134
4	68	68
5	89	24
6	261	-282
7	72	57
8	69	80
9	61	36
10	70	-108
13	78	-75
-1	109	108
-2	363	-348
-3	94	95
-4	193	-169
-5	234	235
-6	308	-320
-7	72	63
-9	158	148
-10	129	130
-11	108	99
-12	110	121
-13	92	-79
H=	1, K=	-2
0	290	-309
2	258	-258
3	134	120
4	185	190
5	66	-71
6	68	-64
8	170	166
10	185	-198
11	115	142
12	302	317
13	83	91
-2	207	206
-3	175	-172
-4	238	232
-5	63	58
-6	100	-86
-9	88	97
-10	72	-67
-11	78	-68
-12	269	-247
H=	1, K=	3
0	103	-199
1	435	435
2	502	-476
3	476	459
4	235	-226
6	233	238
7	441	423
8	189	201
9	146	146
10	198	-184
-1	76	-78
-2	457	448
-3	164	-176
-4	125	-119
-5	110	96
-6	62	-100
-7	166	173
-8	64	-66
-9	66	76
-11	105	106
H=	1, K=	-3
0	349	355
1	41	51
2	164	164
3	233	-223
4	189	-191
5	87	105
6	61	-84
12	77	87
-1	204	184
-2	194	-190
-3	304	301
-4	143	-185
-5	357	-352
-7	71	58
-8	164	161
-9	209	219
-11	109	-116
-12	67	-89
H=	1, K=	4
0	462	449
1	536	-522
2	237	-230
3	170	166
4	48	47
5	100	-108
7	91	94
8	132	134
10	116	92
-1	453	-426
-2	130	-124
-4	108	111
-5	168	-181
-6	49	65
-8	70	-60
-9	71	75
-13	67	43
H=	1, K=	-4
0	693	-702
1	198	-184
3	223	209
4	148	155
5	84	-69
6	240	237
7	77	-85
9	89	-76
10	72	43
-1	2033	-2107
-2	898	-885
-3	290	308
-4	182	201
-5	258	-253
-6	174	-170
H=	1, K=	5
1	161	140
2	187	-182
3	61	-30
4	77	79
6	86	93
7	78	-76
-1	566	-511
-2	267	248
-3	870	839
-4	406	374
-6	122	120
-7	110	-114
-8	127	120
-9	132	-140
-10	113	113
-11	79	-62
H=	1, K=	-5
0	439	-434
1	43	-28
2	868	895
3	948	927
4	406	-386
5	147	-142
6	383	-385
7	118	119
10	84	77
11	62	63
-1	833	-829
-2	463	-488
-3	136	136
-4	77	-86
-5	61	61
-6	182	181
-9	86	-57
H=	1, K=	6
1	79	-70
3	147	149
4	209	-241
5	107	110
7	98	82
8	58	55
9	89	90
10	111	-104
-1	141	141
-2	83	-77
-3	179	162
-5	144	130
-6	93	83
-10	191	-206
-11	91	104
H=	1, K=	-6
2	179	-179
3	156	144
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-1	270	-263
-2	66	-57
-3	92	-88
H=	3, K=	-13
0	220	234
2	304	318
3	185	-183
4	192	133
5	196	-142
H=	3, K=	14
0	100	-92
-1	190	-201
-2	107	-200
-3	198	-192
-6	122	133
H=	3, K=	-14
1	170	190
2	63	41
4	109	-109
6	78	60
7	165	-146
-5	76	63
H=	3, K=	15
0	77	11
3	84	79
-5	101	108
H=	3, K=	-15
0	111	-80
H=	3, K=	16
-1	99	-93
-4	73	56
H=	3, K=	-16
0	84	87
H=	3, K=	17
0	133	138
1	124	136
H=	3, K=	-17
0	96	-99
H=	3, K=	-17
-1	86	-76
-2	86	-118
H=	3, K=	18
0	188	212
1	187	222
H=	3, K=	18
-1	136	151
H=	3, K=	-18
2	121	92
3	76	-73
5	110	100
6	80	103
H=	3, K=	-20
1	72	66
H=	4, K=	0
-1	286	-304
-2	107	-97
-3	137	126
H=	4, K=	1
0	127	-133
1	59	62
2	85	-78
3	90	92
4	93	-93
6	96	-80
9	69	56
-1	179	-171
-2	92	104
-3	181	188
-4	114	-110
-6	216	226
H=	4, K=	-1
0	53	-56
2	79	-82
3	91	89
4	144	141
5	179	179
6	274	286
7	136	-143
9	97	99
10	67	-86
-1	92	90
-2	73	68
-3	49	41
-4	96	-92
H=	4, K=	2
0	63	42
1	24	-22
3	65	-59
4	77	79
5	56	39
6	76	71
12	117	111
-1	149	148
-2	101	-113
-5	96	74
-6	106	90
-9	72	30
-10	65	-76
-11	130	-106
H=	4, K=	-2
0	36	-44
1	100	101
2	64	-67
3	63	-59
5	68	-65
6	140	158
7	122	-119
8	96	96
10	92	-88
11	52	-163
-3	116	-120
-4	138	130
-5	47	-55
H=	4, K=	3
1	162	-144
2	121	123
3	66	-64
4	63	29
5	240	-237
6	116	-122
7	272	-280
8	90	-90
11	93	-78
12	80	81
-1	96	-86
-2	119	120
-6	62	-80
-7	94	-82
-8	87	-77
-11	59	-62
H=	4, K=	-3
0	98	91
2	96	111
6	98	92
7	154	-161
8	161	170
9	147	-163
10	167	162
11	114	-109
12	91	66
13	79	-79
-1	122	-119
-2	181	189
-3	38	-37
-4	79	-71
-5	49	-32
-6	143	166
-7	94	-88
-9	64	-26
H=	4, K=	4
0	253	215
1	227	203
2	262	228
3	164	157
4	117	-130
5	156	-180
6	182	-188
9	191	-190
11	79	97
12	105	-93
-1	310	-298
-2	106	108
-3	84	-81
-5	71	68
-6	101	96
-7	80	79

0·161. The weighting scheme used was:

$$\sqrt{w}=1 \text{ if } |F_o| \le F^* \text{ or}$$

$$\sqrt{w}=\frac{F^*}{|F_o|} \text{ if } |F_o| > F^*$$

where F^* was given a value of 300 on the scale of Table 2.

The 19 hydrogen atom positions were calculated and peaks were found at these positions in a difference Fourier synthesis. A further six cycles of least-squares refinement of all the non-hydrogen atoms with anisotropic temperature factors gave the final residual $R=0·080$. Hydrogen atoms were given temperature factors 0·5 Å^2 greater than the atoms to which they are attached and were included in the final structure factor calculation. The scattering factor curves of Cromer & Waber (1965) were used throughout. The final positional and thermal atomic parameters for the non-hydrogen atoms together with their standard deviations are given in Table 1. Final observed and calculated structure factors are listed in Table 2. Least-squares planes calculated through each of the TCNQ moieties and through the bipyridylium and benzyl groups of the DBBP ion are shown 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 TCNQs are summarized in Table 4. Owing to rather large standard deviations of atomic coordinates it is difficult to decide from these dimensions whether the

Table 2 (*cont.*)

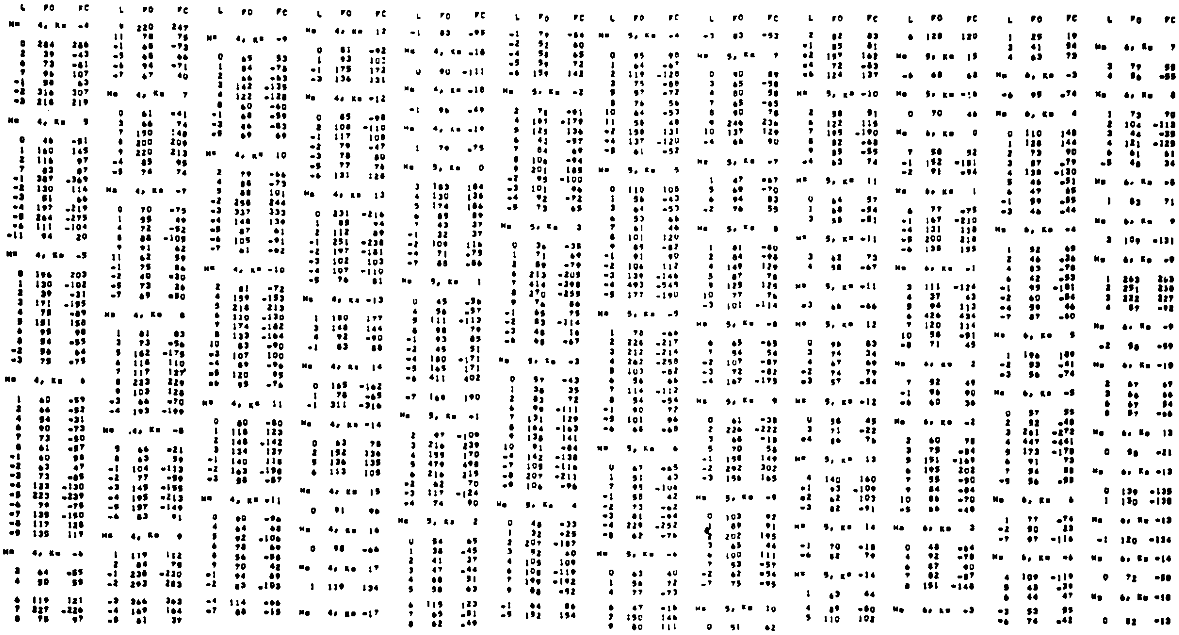


Table 3. *Details of molecular planes*

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

TCNQ

Molecule *A*		Molecule *B*	
Equation to the plane: $0·2256x-0·7795y-0·5843z+1·6189=0$		Equation to the plane: $0·1984x-0·7816y-0·5914z+4·7973=0$	
	Distance from the plane Å		Distance from the plane Å
C(1)	0·048 (8)	C(13)	−0·037 (8)
C(2)	0·059 (7)	C(14)	−0·043 (8)
C(3)	0·047 (7)	C(15)	−0·066 (8)
C(4)	0·010 (7)	C(16)	−0·035 (8)
C(5)	0·019 (7)	C(17)	0·012 (7)
C(6)	0·063 (8)	C(18)	−0·014 (8)
C(7)	0·018 (8)	C(19)	−0·018 (8)
C(8)	−0·011 (8)	C(20)	0·050 (9)
C(9)	−0·028 (8)	C(21)	−0·019 (9)
C(10)	−0·001 (8)	C(22)	0·021 (7)
C(11)	−0·021 (8)	C(23)	−0·010 (8)
C(12)	−0·009 (8)	C(24)	0·047 (8)
N(1)	−0·009 (8)	N(5)	0·158 (10)
N(2)	−0·092 (7)	N(6)	−0·039 (10)
N(3)	−0·013 (8)	N(7)	0·074 (9)
N(4)	−0·083 (8)	M(8)	−0·044 (8)

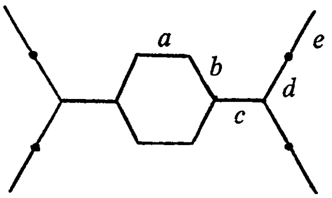
DBBP

Bipyridylium ring		Benzyl group	
Equation to the plane: $0·4209x+0·2301y-0·8774z+3·5626=0$		Equation to the plane: $-0·0766x-0·7333y-0·6756z+8·0041=0$	
	Distance from the plane (Å)		Distance from the plane (Å)
C(25)	−0·050 (7)	C(30)	−0·011 (8)
C(26)	−0·002 (10)	C(31)	0·021 (8)
C(27)	0·042 (8)	C(32)	0·001 (9)
C(28)	0·040 (9)	C(33)	−0·010 (10)
C(29)	0·006 (9)	C(34)	−0·005 (10)
C(30)	−0·089 (9)	C(35)	0·010 (9)
N(9)	0·037 (6)	C(36)	−0·016 (9)

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

Bond	Reference	*a*	*b*	*c*	*d*	*e*
TCNQ^0	1	1·344 (4)	1·443 (3)	1·373 (4)	1·436 (3)	1·138 (3)
TCNQ$^-$	2,3,4	1·362 (18)	1·424 (10)	1·405 (16)	1·416 (4)	1·156 (5)
TCNQ$^{1/2-}$	5,6,7,8	1·356 (4)	1·434 (6)	1·393 (9)	1·423 (6)	1·145 (5)
Molecule A		1·349 (8)	1·426 (6)	1·400 (8)	1·416 (6)	1·152 (6)
Molecule B		1·351 (8)	1·432 (6)	1·379 (8)	1·436 (6)	1·137 (6)

1. Long, Sparks & Trueblood (1965)
2. Hanson (1965)
3. Fritchie (1965)
4. Hoekstra, Spoelder & Vos (1972)
5. Hanson (1968)
6. Goldstein, Seff & Trueblood (1968)
7. Kobayashi, Marumo & Saito (1971)
8. Sundaresan & Wallwork (1972)



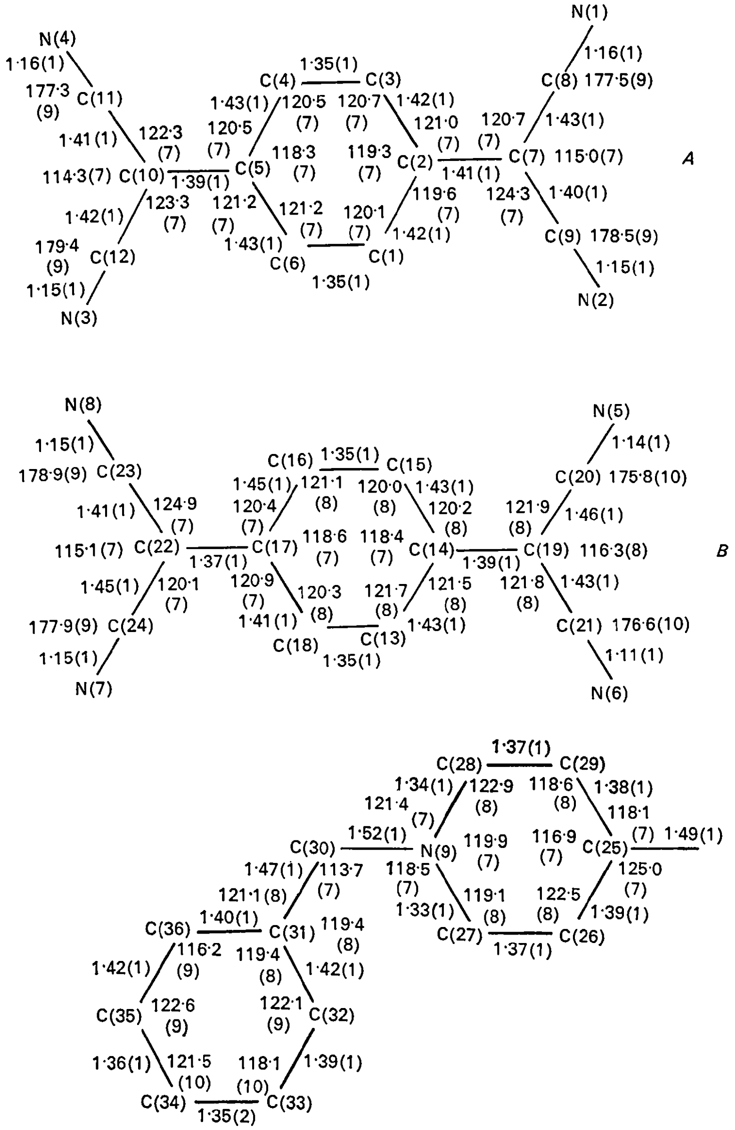

N(4)
1·16(1)
177·3 (9)
C(11)
1·41(1)
122·3 (7)
114·3(7) C(10)
1·39(1)
C(5)
123·3 (7)
1·42(1)
179·4 (9)
C(12)
1·15(1)
N(3)
1·35(1)
C(4)
C(3)
1·43(1)
120·5
120·7
1·42(1)
120·5 (7)
(7)
(7)
121·0 (7)
118·3 (7)
119·3 (7)
C(2)
121·2 (7)
121·2 (7)
120·1 (7)
119·6 (7)
1·43(1)
C(6)
C(1)
1·35(1)
1·42(1)
1·41(1)
N(1)
1·16(1)
C(8) 177·5(9)
120·7 (7)
1·43(1)
C(7) 115·0(7)
124·3 (7)
1·40(1)
C(9) 178·5(9)
1·15(1)
N(2)
A
N(8)
1·15(1)
178·9(9) C(23)
1·41(1)
124·9 (7)
115·1(7) C(22)
1·37(1)
C(17)
1·45(1)
120·1 (7)
177·9(9) C(24)
1·15(1)
N(7)
C(16)
1·35(1)
C(15)
1·45(1)
121·1
120·0
1·43(1)
120·4 (7)
(8)
(8)
120·2 (8)
118·6 (7)
118·4 (7)
C(14)
1·39(1)
120·9 (7)
120·3 (8)
121·7 (8)
121·5 (8)
1·41(1)
C(18)
C(13)
1·43(1)
1·35(1)
N(5)
1·14(1)
C(20) 175·8(10)
121·9 (8)
1·46(1)
C(19) 116·3(8)
121·8 (8)
1·43(1)
C(21) 176·6(10)
1·11(1)
N(6)
B
1·37(1)
C(28)
C(29)
1·34(1)
122·9 (8)
118·6 (8)
1·38(1)
121·4 (7)
118·1 (7)
1·52(1)
C(30)
N(9)
119·9 (7)
116·9 (7)
C(25)
1·49(1)
1·47(1)
113·7 (7)
118·5 (7)
125·0 (7)
121·1(8)
119·1 (8)
122·5 (8)
1·33(1)
1·39(1)
C(27)
1·37(1)
C(26)
1·40(1)
C(36)
C(31)
119·4 (8)
116·2 (9)
119·4 (8)
1·42(1)
1·42(1)
C(35)
122·6 (9)
122·1 (9)
C(32)
1·36(1)
121·5 (10)
118·1 (10)
1·39(1)
C(34)
1·35(2)
C(33)

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

TCNQs occur as TCNQ^0 and TCNQ$^-$ or whether they are really indistinguishable as TCNQ$^{1/2-}$. The bond lengths mostly tend towards the interpretation of molecule *A* as TCNQ and molecule *B* as TCNQ^0 but a multivariate significance test (Cruickshank & Robertson, 1953) of the differences in dimensions between the the two TCNQ moieties gave a value of $T^2=0{\cdot}31$ which is not significant for five degrees of freedom. There is also evidence from the ultraviolet, visible and infrared spectra of the complex that the TCNQs are indistinguishable.

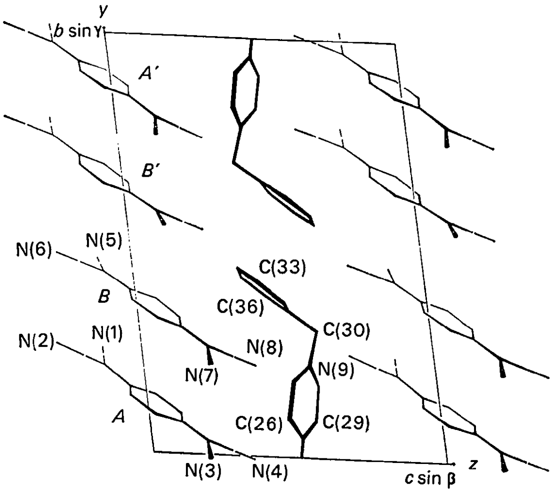


Fig. 2. The molecular arrangement, viewed along the *a* axis.

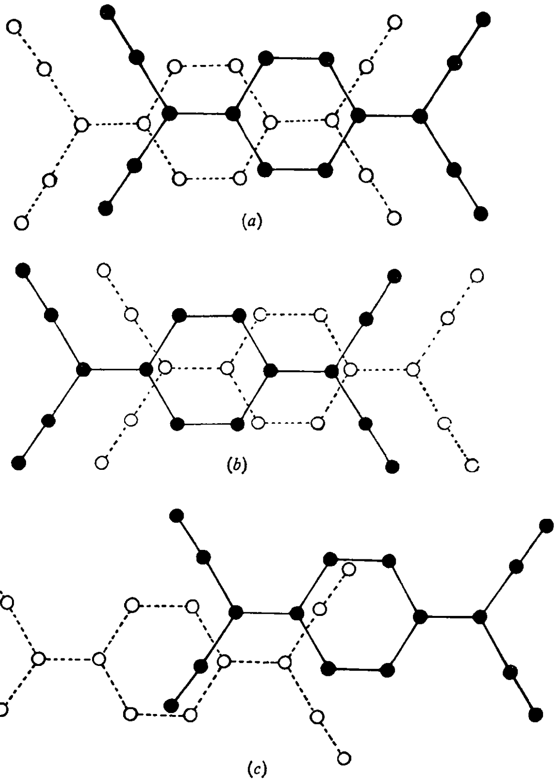


Fig. 3. Nearest neighbour overlap. (*a*) molecules *A*(−) and *B*(···) (*b*) molecules *A*(−) and *A'*(···) (*c*) molecules *B*(−) and *B'*(···).

The least-squares planes through the TCNQs indicate that they are not quite planar, the C–(CN)$_2$ groups being twisted out of the planes so as to increase the short contacts N(1)···C(30) = 3·43, N(5)···C(34) = 3·48 and N(8)···C(32) = 3·46 Å with the benzyl group of the DBBP ion. The contact N(5)···C(34) probably contributes also to the non-linearity of the C–(CN)$_2$ group C(19)–C(20)–N(5) and C(19)–C(21)–N(6), the bends being mainly in the plane of the molecule in such a direction as to reduce the distance between the nitrogen atoms of the C–(CN)$_2$ group.

The dimensions of the DBBP ion [Fig. 1(*b*)] are in agreement with values reported in the structure of DBBP diiodide (Russell & Wallwork, 1971). The dihedral angle between the planes through the benzyl group and the pyridylium ring of the ion is 66·9°.

The structure viewed along the *a* axis is illustrated in Fig. 2. It consists of columns of TCNQs packed almost parallel to each other (dihedral angle between molecules *A* and *B* is 1·6°) along the *b* axis which is 16·82 Å long. The average interplanar spacings between *A*···*B* and *A*···*A'* are 3·16 and 3·24 Å respectively, indicating charge-transfer interaction between the pairs, but the separation *B*···*B'* is 3·62 Å suggesting that here there is no appreciable molecular interaction.

Fig. 3 shows the three types of overlap, *B* on *A*, *A'* on *A* and *B'* on *B*. The first two overlaps are virtually

Table 5. *Short intermolecular contacts*

(*a*) Molecule *A* to molecule *B*

C(1^{i})–C(18^{i})	3·32 Å
C(2^{i})–C(17^{i})	3·32
C(3^{i})–C(16^{i})	3·29
C(4^{i})–C(23^{i})	3·29
C(5^{i})–C(22^{i})	3·24
C(5^{i})–C(23^{i})	3·39
C(6^{i})–C(24^{i})	3·36
C(7^{i})–C(14^{i})	3·28
C(8^{i})–C(15^{i})	3·29
C(9^{i})–C(13^{i})	3·36
C(9^{i})–C(14^{i})	3·33

(*b*) Molecule *A* to molecule *A'*

C(1^{i})–C(11^{ii})	3·36 Å
C(2^{i})–C(10^{ii})	3·22
C(2^{i})–C(11^{ii})	3·39
C(3^{i}–)C(10^{ii})	3·39
C(3^{i})–C(12^{ii})	3·36
C(4^{i})–C(6^{ii})	3·21
C(5^{i})–C(5^{ii})	3·33

(*c*) Other intermolecular contacts

C(6^{i})—N(3^{iii})	3·35
C(18^{i})–N(1^{iv})	3·35
C(20^{i})–N(5^{v})	3·31
C(27^{i})–N(8^{i})	3·35
C(27^{i})–N(2^{vi})	3·36
C(28^{i})–N(1^{vi})	3·34
C(28^{i})–N(2^{vii})	3·27
C(29^{i})–N(4^{viii})	3·36
N(5^{i})—N(5^{v})	3·18

Superscripts indicate equivalent positions as follows:

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

identical and similar to that found in most of the TCNQ complexes. But the overlap *B′* on *B* is a new type of overlap involving a diagonal shift of centres. Thus the different modes of overlap combined with different interplanar spacings suggest that the TCNQs are packed as tetramers with a gap between *B′* and *B*. This situation has been observed in crystal structures of *N*-(n-propyl)-quinolinium 2TCNQ (Sundaresan & Wallwork, 1972), triethylammonium 2TCNQ (Kobayashi, Ohashi, Marumo & Saito, 1970) and 1,3,3-trimethyl-2-(*p*-*N*-methyl-*N*-*β*-chloroethylstyryl)indoleninium 2TCNQ (Shibaeva, Atovmyan & Rozenberg, 1971). In the last complex quoted, however, the 4TCNQs tend to form two dimers. The short intermolecular contacts are listed in Table 5.

We wish to thank the Science Research Council for the provision of the linear diffractometer, Dr F. R. Ahmed for the computer programs used, the Director of the Cripps Computing Centre of the University of Nottingham for computing facilities and Mr G. J. Ashwell for preparing the crystals.

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Structure Cristalline du Bis(bromo-4 phénylsulfonyl) Méthane

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The crystal structure of bis-(4-bromophenylsulphonyl)methane has been determined from diffractometer intensity measurements (779 reflexions) by means of the heavy-atom technique and refined by the full-matrix least-squares method, with anisotropic thermal parameters, to an R of 0·06. Crystals are orthorhombic with $a=30{\cdot}05$, $b=5{\cdot}015$, $c=11{\cdot}455$ Å, $\beta=118°$, space group $C2/c$ (No. 15), $Z=4$. The binary axis of the molecule coincides with the twofold axis of the space group. The molecules form layers approximately parallel to planes $\{001\}$. The slightly different surroundings of the two oxygen atoms of the SO$_2$ groups may explain some features of the infrared spectrum of the substance.

La détermination de la stéréochimie préférentielle du carbanion α-sulfonyle $RSO_2C^-R_1R_2$ a donné lieu à de nombreux travaux, depuis la mise en évidence de l'aptitude du groupement SO_2 à retenir la configuration, sur un carbone adjacent saturé, dans les réactions de substitution électrophile (Cram, 1965; Wolfe, Rank & Csizmadia, 1969). Le cas du carbanion bis(sulfonyle)-méthanique $(RSO_2)_2C^-H$, a été discuté dans le cadre de ces études (Cram, 1965; Corey, König & Lowry, 1962). Cependant, la structure moléculaire des β-disulfones n'a jamais été examinée avec précision.

Au cours d'une étude dans l'infrarouge moyen des composés $(X\text{–}C_6H_4\text{–}SO_2)_2CH_2$ (Jéminet, 1969), nous avons observé une structure complexe des bandes de vibration de valence du groupement SO_2, dans la région 1100–1350 cm^{-1}, en solution ou à l'état solide. La recherche d'une explication sur l'origine théorique de ce phénomène nous a conduits à préciser les con-