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The Crystal and Molecular Structure
of N,N,N',N' -Tetramethyl-p-diaminobenzene–Chloranil, TMPD-Chloranil

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Crystalline TMPD–chloranil has been shown to be predominantly a molecular complex, although the presence of a minority (up to some 20%) of doubly charged $TMPD^{2+}$ and $chloranil^{2-}$ ions, as indicated by absorption spectra, could not be excluded from X-ray work. Electron spin resonance measurements have shown that the crystals do not contain $TMPD^+$, and that $chloranil^-$ ions are present only to a small extent (0·8%). The methyl groups of TMPD do not show free rotation about the $N-CH_3$ bonds.

Introduction

N,N,N',N'-Tetramethyl-p-diaminobenzene–chloranil, TMPD–chloranil,
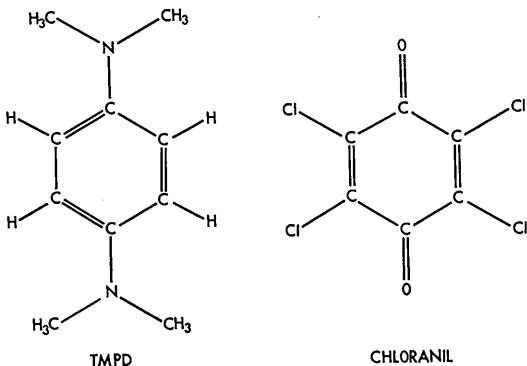
TMPD   CHLORANIL

has been studied as part of a program to obtain more information on compounds containing TMPD units (for another paper see de Boer, Vos & Huml, 1968). TMPD–chloranil is an interesting charge-transfer complex (Pott, 1966). At room temperature the compound is weakly paramagnetic. In accordance with electron spin resonance (e.s.r.) measurements, this paramagne-

tism has been ascribed to the presence of a small number of $chloranil^-$ ions (approximately 0·8%). A $TMPD^+$ signal is not observed. To check whether the absence of the signal is not due to somehow hampered recognition, Pott & Kommandeur (1967) also investigated some purposely made non-stoichiometric crystals (with a TMPD-excess of the order of 0·1%) and found that in these, as well as the $chloranil^-$, the $TMPD^+$ signal was readily observable. As the e.s.r. measurements thus give evidence for the absence of $TMPD^+$ ions in the pure crystals, the TMPD units are either neutral or doubly charged. Absorption spectra indicate the presence of $TMPD^{2+}$ and $chloranil^{2-}$ ions. However, the number of doubly charged ions is difficult to estimate from the spectra.

The compound undergoes a phase transition at lower temperatures, as may be noticed from a splitting of the $chloranil^-$ e.s.r. absorption signal below 250°K. The splitting increases with decreasing temperature. X-ray pictures show that the crystals of the low temperature phase are twinned, presumably owing to a change in symmetry from monoclinic to triclinic during the transition.

According to Pott (1966) there are two different types of TMPD–chloranil, which may be distinguished

by the asymmetry of their e.s.r. signals. Both at room and at low temperatures, however, the X-ray diffraction patterns of the two types appeared to be identical. Only the structure of the room temperature phase has been studied by X-ray diffraction. Two independent structure determinations have been carried out: by Daniels, Russell & Wallwork (1967) and that described in the present paper. The two structures obtained do not show significant differences. The discussion in the present paper is based on the latter structure determination as this may be considered as being the more accurate.

Experimental

The crystals are monoclinic with $a = 16.320$ (e.s.d. 0.015), $b = 6.568$ (e.s.d. 0.010), $c = 8.811$ (e.s.d. 0.010) Å; $\beta = 111.91°$ (e.s.d. 0.03°); $Z = 2$. From the possible space groups $C2$, Cm and $C2/m$, the space group $C2/m$ was adopted during the structure determination as the crystals are not piezoelectric. Confirmation of this choice was subsequently provided by successful refinement of the structure. The cell constants were determined from θ values measured with a single-crystal diffractometer ($\lambda(Mo\ K\alpha) = 0.7107$ Å). Owing to gradual decomposition of the crystals at room temperature, the cell constants obtained are not very accurate, the values of b and β being affected most by the aging of the crystals.

The intensities were collected with an automatic Nonius diffractometer, using Zr-filtered Mo radiation and the moving-counter moving-crystal method. All independent reflexions up to $\theta = 26°$ were considered. Because of the decomposition of the compound two crystals had to be used for the intensity measurements, the dimensions of these crystals being approximately $0.11 \times 0.14 \times 0.33$ mm^3 and $0.12 \times 0.20 \times 0.46$ mm^3. Corrections were made for (1) the gradual decrease in diffracted beam intensity by considering the intensities of reference reflexions which had been measured every two hours, (2) the Lorentz and polarization effect, and (3) absorption (Busing & Levy, 1957), taking $\mu(Mo) = 6.86$ cm^{-1}. The scaling of the two sets of reflexions was made possible by the two sets of measurements having 263 reflexions in common. The disagreement factor $\Sigma |\Delta F|/\Sigma |F|$ amounted to 8.8% for these reflexions. Reflexions with $|F| < 1.25\sigma(F)$, in which $\sigma(F)$ is the s.d. estimated for F due to counting statistics, were excluded from the further work, and the structure determination was carried out with 708 out of the 944 independent reflexions considered.

Structure determination and refinement

The structure was determined from a Patterson map and refined by anisotropic least-squares methods (Cruickshank, 1961b). Scattering factors according to Moore (1963) were used for the 'heavy' atoms and the f curve according to Stewart, Davidson & Simpson (1965) was taken into account for hydrogen. As may be seen from Fig. 1, the hydrogen atoms are readily

(a)

(b)   (c)
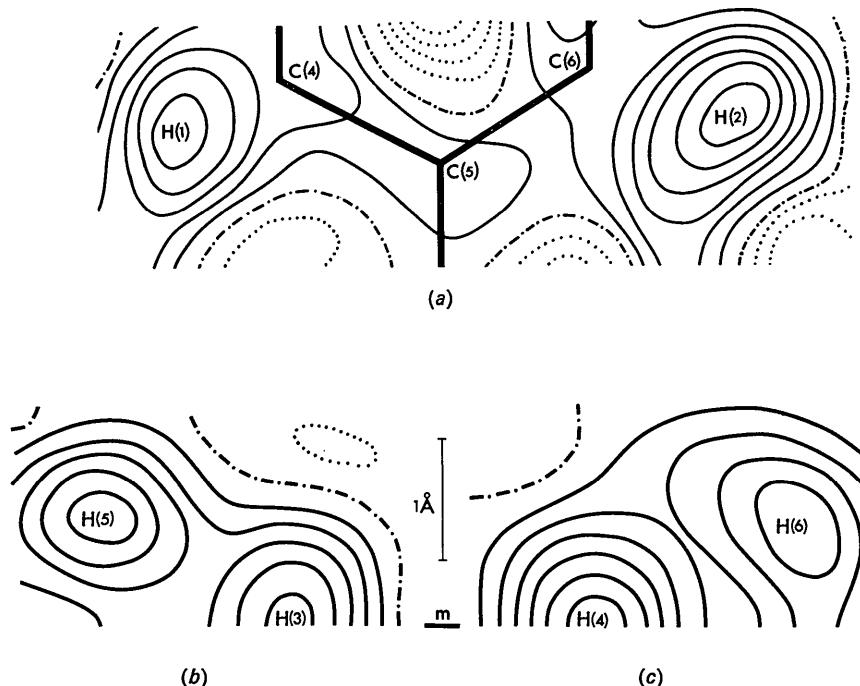
Fig. 1. Difference Fourier map showing the hydrogen atoms of the benzene ring (a) and of the methyl groups, (b) and (c). Only reflexions with $\sin \theta/\lambda < 0.4$ Å^{-1} are considered; hydrogen atoms are not included in F_c. Contours are at intervals of 0.046 e.Å^{-3}. The equations of the planes are $0X + Y + 0Z = 0$ Å (a); $-0.2156X + 0Y + 0.9765Z = -1.326$ Å (b) and $0.9675X + 0Y - 0.2530Z = 11.351$ Å (c), with $X = xa \sin \beta$, $Y = yb$ and $Z = zc + xa \cos \beta$.

recognizable in a difference map based on reflexions with $\sin \theta/\lambda < 0.4$ Å^{-1}. Their peak heights vary from 3·6 to 4·9 times the e.s.d. (0·06 e.Å^{-3}) of the electron density. The clear appearance of all six independent hydrogen atoms in the difference Fourier map lends strong support to the assumption that $C2/m$ is the correct space group. In the structure factor calculations of the last few cycles of least-squares refinement, the hydrogen atoms were included, with fixed parameters. They were located at 1·08 Å from the C atoms in directions based on geometrical considerations, for each of the hydrogen atoms the isotropic thermal parameter B was taken to be 2 Å^2 greater than the B value of the carbon atom to which it is attached. The weighting scheme used was $w = 475/(475 + (25 - F_o)^2)$; the reflexions 020 and 001, which showed extinction, were not considered during the refinement. The final disagreement index R is 7·60% for the 706 reflexions used. The final parameters are listed in Tables 1 and 2, with (in parentheses) their standard deviations as calculated by the least-squares program. In Table 3 the observed and calculated structure factors are compared. The weak reflexions, which were not considered during the structure determination, are not included in this Table; the calculated and observed values for these reflexions were shown to agree within experimental error.

Table 1. *Final coordinates**

For numbering of atoms see Fig.2.

	x	z
Cl(1)	−0·06383 (15)	0·29210 (23)
Cl(2)	0·20180 (13)	0·07167 (26)
O	0·11838 (33)	0·31101 (53)
N	0·63087 (36)	0·31001 (66)
C(1)	−0·03090 (44)	0·12885 (70)
C(2)	0·06435 (45)	0·16949 (77)
C(3)	0·08994 (43)	0·02675 (80)
C(4)	0·47692 (41)	0·13648 (73)
C(5)	0·56667 (39)	0·15817 (69)
C(6)	0·58751 (41)	0·01780 (78)
C(7)	0·61013 (58)	0·45734 (79)
C(8)	0·72478 (45)	0·33261 (94)
H(1)	0·45872	0·24254
H(2)	0·65573	0·02909
H(3)	0·67066	0·56387
H(4)	0·76474	0·46187
H(5)	0·57215	0·45841
H(6)	0·73922	0·27651

* y[H(5)] = y[H(6)] = 0·13426, for the remaining atoms $y = 0$.

Analysis of the thermal parameters according to Cruickshank (1956) showed that the thermal parameters of the molecules do not show significant deviations from 'rigid-body' parameters. In view of the high values of the thermal parameters, it is not certain, however, whether the molecules really behave as rigid bodies (Busing & Levy, 1964). The calculated corrections for librations (Cruickshank, 1961a) will therefore not be considered in the discussion of the structure. The corrections correspond with increases in bond lengths from 0·004 to 0·010 Å.

Discussion of the structure

The molecules lie in mirror planes perpendicular to the b axis at special positions with symmetry $2/m$. With the exception of two of the hydrogen atoms of each of the methyl groups, the molecules are thus planar. The arrangement of the molecules at $y = 0$ is shown in Fig. 2. At $y = \frac{1}{2}$ there is an equivalent layer related to the one at $y = 0$ by the C centring. The TMPD and chloranil molecules of successive layers are arranged on top of each other. In [010] projection the benzene rings of the two molecules nearly coincide. The short distances between the successive benzene rings, $\frac{1}{2}b = 3\cdot284$ Å, indicate that a strong intermolecular interaction takes place along the b direction. Within each layer, on the other hand, intermolecular interaction is smaller. Only one of the independent intermolecular distances in a layer, O–H(4′) = 2·190 Å, is shorter than expected from the sum of the conventional van der Waals radii.

The intramolecular bond lengths and angles are given in Fig. 2. The standard deviations, as calculated from the standard deviations in the coordinates of Table 1, are 0·007 Å for the C–Cl bonds, and 0·010 Å for the remaining bonds. The standard deviations in the angles C–C–Cl were calculated to be 0·6°; those of the remaining angles are 0·7° on the average. It is evident from the figure that the chloranil unit has a strong quinonoid character, thus giving evidence that most of these molecules are uncharged. No valuable direct comparison can be made with chloranil itself, however, as the bond lengths reported for this substance (Chu, Jeffrey & Sakurai, 1962) are not very

Table 2. *Thermal parameters of the temperature factor*

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2ha^*kb^*U_{12} + 2kb^*lc^*U_{23} + 2ha^*lc^*U_{13})]$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	$2U_{13}$
Cl(1)	0·0944 (15)	0·1092 (18)	0·0535 (10)	0	0	0·0554 (20)
Cl(2)	0·0561 (11)	0·1142 (19)	0·0796 (13)	0	0	0·0177 (20)
O	0·0762 (32)	0·1029 (45)	0·0401 (24)	0	0	−0·0275 (46)
N	0·0592 (34)	0·0707 (43)	0·0503 (30)	0	0	−0·0104 (52)
C(1)	0·0683 (43)	0·0576 (46)	0·0389 (32)	0	0	0·0163 (60)
C(2)	0·0665 (41)	0·0595 (45)	0·0471 (35)	0	0	0·0019 (62)
C(3)	0·0566 (38)	0·0526 (43)	0·0554 (38)	0	0	0·0111 (61)
C(4)	0·0514 (38)	0·0859 (58)	0·0426 (34)	0	0	0·0172 (59)
C(5)	0·0463 (33)	0·0570 (42)	0·0410 (32)	0	0	−0·0022 (53)
C(6)	0·0471 (35)	0·0809 (54)	0·0493 (35)	0	0	0·0224 (57)
C(7)	0·1065 (63)	0·0934 (67)	0·0377 (36)	0	0	0·0008 (76)
C(8)	0·0489 (41)	0·1091 (72)	0·0681 (46)	0	0	−0·0316 (71)

accurate. The largely non-ionic character of TMPD–chloranil also appears from the structure of the TMPD units, as in these units the quinonoid character is less pronounced than estimated for $TMPD^{2+}$ from theoretical considerations as may be seen from the following data. For $TMPD^{2+}$ the central bond of the benzene ring is expected to be 0·092 Å shorter than the non-central bonds; for neutral TMPD this difference is only 0·014 Å (Monkhorst & Kommandeur, 1967; the bond lengths d were obtained from the relation $d = 1·51 - 0·18p$, p being the π bond order). The observed difference, 0·029 Å, between the central and non-central bonds for TMPD in TMPD–chloranil approaches the theoretical value for neutral TMPD. As has been mentioned in the introduction, e.s.r. measurements exclude the presence of $TMPD^+$. From the X-ray work (and the e.s.r.

Table 3. *Observed and calculated structure factors*

In order to obtain F on the absolute scale, the values in the Table must be divided by 10.

H	K	L	Fo	Fc
2	0	0	580	591
4	0	0	234	-216
6	0	0	631	-652
8	0	0	349	-355
10	0	0	140	146
12	0	0	160	-168
14	0	0	122	126
16	0	0	32	29
18	0	0	41	-44
1	1	0	471	471
3	1	0	54	-42
5	1	0	198	187
7	1	0	519	-505
9	1	0	141	-128
11	1	0	54	44
13	1	0	140	-128
15	1	0	140	123
17	1	0	46	-35
0	2	0	2190	2581
2	2	0	424	417
4	2	0	181	-187
6	2	0	438	-423
8	2	0	282	-274
10	2	0	119	118
12	2	0	135	-134
14	2	0	98	100
16	2	0	35	23
18	2	0	47	-37
1	3	0	281	288
3	3	0	27	-17
5	3	0	92	93
7	3	0	310	-312
9	3	0	81	-81
11	3	0	38	28
13	3	0	74	-77
15	3	0	65	72
17	3	0	52	-24
0	4	0	924	946
2	4	0	210	191
4	4	0	88	-87
6	4	0	159	-193
8	4	0	156	-144
10	4	0	63	56
12	4	0	77	-63
14	4	0	57	56
16	4	0	37	11
1	5	0	101	103
7	5	0	120	-122
9	5	0	47	-36
11	5	0	39	15
0	6	0	330	323
2	6	0	85	85
6	6	0	86	-82
8	6	0	51	-57
3	7	0	37	9
5	7	0	36	11
9	7	0	40	-11
0	8	0	66	96
2	8	0	46	35
-18	0	1	90	-85
-16	0	1	36	-21
-12	0	1	38	-28
-10	0	1	358	403
-8	0	1	767	-730
-6	0	1	313	-302
-4	0	1	281	-286
-2	0	1	661	658
0	0	1	676	727
2	0	1	415	-442
4	0	1	806	841
6	0	1	323	331
8	0	1	37	-34
10	0	1	80	84
14	0	1	99	113
16	0	1	53	-52
-19	1	1	32	-10
-17	1	1	40	-54
-15	1	1	44	61
-11	1	1	236	241
-9	1	1	137	138
-7	1	1	195	-198
-5	1	1	36	-40
-3	1	1	942	-958
1	1	1	361	372
3	1	1	142	-127
5	1	1	666	676
7	1	1	217	202
9	1	1	208	205
11	1	1	202	-208
13	1	1	169	-164
15	1	1	38	54
17	1	1	30	-51
-18	2	1	50	-68
-16	2	1	30	-17
-12	2	1	42	-17
-10	2	1	291	297
-8	2	1	559	-541
-6	2	1	266	-267
-4	2	1	183	-188
-2	2	1	432	430
0	2	1	535	542
2	2	1	285	-276
4	2	1	570	576
6	2	1	214	222
10	2	1	84	75
14	2	1	87	95
16	2	1	30	-44
-15	3	1	26	37
-13	3	1	41	36
-11	3	1	135	139
-9	3	1	87	89
-7	3	1	120	-108
-5	3	1	33	20
-3	3	1	480	-499
-1	3	1	37	8
1	3	1	110	108
3	3	1	31	-24
5	3	1	347	342
7	3	1	98	-89
9	3	1	133	131
11	3	1	133	-125
13	3	1	109	-111
15	3	1	38	30
-16	4	1	32	-12
-10	4	1	129	131
-8	4	1	267	-261
-6	4	1	138	-139
-4	4	1	64	-66
-2	4	1	185	178
0	4	1	250	241
2	4	1	106	-99
4	4	1	239	228
6	4	1	86	80
10	4	1	61	53
14	4	1	57	56
-11	5	1	39	54
-9	5	1	43	31
-7	5	1	45	-42
-5	5	1	29	-5
-3	5	1	177	-176
1	5	1	66	62
3	5	1	26	4
5	5	1	113	118
9	5	1	69	61
11	5	1	55	-49
13	5	1	45	-51
-10	6	1	46	34
-8	6	1	95	-98
-6	6	1	73	-56
-4	6	1	33	-12
-2	6	1	61	79
0	6	1	77	95
2	6	1	48	-25
4	6	1	65	59
8	6	1	33	-9
-9	7	1	45	6
-7	7	1	27	-13
-5	7	1	30	-8
-3	7	1	58	-48
-1	7	1	45	8
-2	8	1	42	36
-18	0	2	86	-91
-16	0	2	38	-15
-14	0	2	162	-181
-12	0	2	69	-71
-10	0	2	37	-34
-8	0	2	315	-311
-6	0	2	639	659
-4	0	2	33	-4
-2	0	2	311	-298
0	0	2	225	-248
2	0	2	513	-556
6	0	2	282	-284
8	0	2	160	155
10	0	2	601	607
12	0	2	103	101
14	0	2	48	70
16	0	2	129	-134
-15	1	2	59	56
-13	1	2	199	-183
-11	1	2	100	87
-7	1	2	198	187
-5	1	2	855	859
-3	1	2	421	-425
-1	1	2	176	180
1	1	2	993	-1028
3	1	2	133	-156
5	1	2	296	285
7	1	2	74	-75
9	1	2	270	265
11	1	2	100	-96
13	1	2	42	53
15	1	2	45	-13
-18	2	2	63	-73
-14	2	2	141	-150
-12	2	2	53	-62
-10	2	2	41	-35
-8	2	2	227	-216
-6	2	2	468	476
-4	2	2	61	70
-2	2	2	233	-245
0	2	2	182	-179
2	2	2	425	-453
6	2	2	222	-222
8	2	2	156	146
10	2	2	489	492
12	2	2	104	91
14	2	2	49	54
16	2	2	110	-111
-15	3	2	26	37
-13	3	2	104	-114
-11	3	2	71	65
-7	3	2	110	100
-5	3	2	341	375
-3	3	2	208	-206
-1	3	2	95	96
1	3	2	466	-463
3	3	2	84	-87
5	3	2	166	158
7	3	2	58	-38
9	3	2	158	163
11	3	2	37	-60
13	3	2	34	35
-14	4	2	64	-83
-10	4	2	26	-23
-8	4	2	102	-105
-6	4	2	201	200
-4	4	2	62	49
-2	4	2	86	-93
0	4	2	80	-74
2	4	2	204	-209
4	4	2	35	-14
6	4	2	107	-113
8	4	2	104	94
10	4	2	280	277
12	4	2	71	65
14	4	2	39	25
-13	5	2	39	-45
-7	5	2	40	32
-5	5	2	122	117
-3	5	2	68	-74
-1	5	2	51	42
1	5	2	151	-160
3	5	2	63	-45
5	5	2	68	61
9	5	2	71	70
-12	6	2	38	-15
-10	6	2	39	-14
-8	6	2	50	55
-6	6	2	50	-43
4	6	2	99	44
10	6	2	98	118
-3	7	2	41	-21
1	7	2	46	-38
5	7	2	47	17
7	7	2	36	6
-20	0	3	36	28
-18	0	3	50	-42
-16	0	3	99	81
-14	0	3	81	-54
-10	0	3	158	-135
-8	0	3	332	-325
-6	0	3	114	123
-4	0	3	374	-370
-2	0	3	160	177
0	0	3	495	516
2	0	3	633	-645
4	0	3	283	-275
6	0	3	470	-474
8	0	3	303	305
10	0	3	216	213
12	0	3	62	-31
14	0	3	86	97
-17	1	3	58	68
-15	1	3	83	84
-13	1	3	172	-166
-11	1	3	103	107
-9	1	3	328	-324
-7	1	3	49	52
-1	1	3	141	160
3	1	3	259	-254
7	1	3	137	128
9	1	3	32	40
13	1	3	48	14
15	1	3	39	-35
-16	2	3	55	60
-14	2	3	93	-89
-10	2	3	258	-260
-8	2	3	81	86
-6	2	3	74	76
-4	2	3	317	-312
-2	2	3	131	139
0	2	3	361	367
2	2	3	450	-437
4	2	3	220	-207
6	2	3	365	-360
8	2	3	249	245
10	2	3	186	176
12	2	3	39	-22
14	2	3	74	76
-17	3	3	36	45
-13	3	3	108	-102
-11	3	3	62	67
-9	3	3	181	-197
-1	3	3	394	386
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7	3	3	165	-159
9	3	3	95	86
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-10	4	3	56	-38
-8	4	3	120	-126
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-4	4	3	150	-149
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0	4	3	150	143
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4	4	3	110	-108
6	4	3	171	-169
8	4	3	139	142
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-9	5	3	71	-78
-5	5	3	42	-7
-3	5	3	42	5
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3	5	3	36	23
5	5	3	66	-62
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9	5	3	35	35
11	5	3	43	15
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-8	6	3	47	-39
-2	6	3	32	7
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8	6	3	45	-49
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-16	0	4	57	-55
-12	0	4	317	322
-10	0	4	302	309
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-4	0	4	421	-405
-2	0	4	1056	-1067
0	0	4	178	180
2	0	4	45	24
4	0	4	149	-141
6	0	4	252	257
8	0	4	109	-102
10	0	4	127	126
14	0	4	30	12
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-13	1	4	86	90
-11	1	4	158	-135
-9	1	4	231	-220
-7	1	4	155	-147
-5	1	4	321	-318
-3	1	4	139	-138
-1	1	4	219	220
1	1	4	70	-65
3	1	4	262	254
5	1	4	144	146
9	1	4	68	85
11	1	4	178	-180
13	1	4	36	35
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-12	2	4	249	257
-10	2	4	238	243
-4	2	4	158	-158
0	2	4	306	-288
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6	2	4	127	143
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3	3	4	115	-108
5	3	4	186	182
8	3	4	76	-74
13	3	4	108	101
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-16	4	4	56	68
0	4	4	42	-17
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4	4	4	77	81
6	4	4	38	-32
8	4	4	51	55
10	4	4	70	-70
-15	5	4	28	10
-11	5	4	41	66
-9	5	4	49	-57
-7	5	4	49	-42
-5	5	4	78	-75
-3	5	4	36	-43
-1	5	4	51	47
5	5	4	24	22
-12	6	4	57	60
-10	6	4	62	59
-6	6	4	44	-63
-4	6	4	104	-132
0	6	4	37	-11
-5	7	4	46	-22
-18	0	5	65	-61
-12	0	5	366	370
-10	0	5	144	145
-6	0	5	77	110
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6	0	5	41	-70
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-13	1	5	73	-48
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9	1	5	82	98
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4	2	5	93	98
8	2	5	69	-61
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-1	3	5	78	-77
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5	3	5	68	55
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-12	4	5	165	176
-10	4	5	78	75
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0	4	5	179	-183
4	4	5	35	-40
6	4	5	35	-13
10	4	5	27	-27
-7	5	5	59	91
1	5	5	86	-89
3	5	5	42	26
7	5	5	37	23
-12	6	5	59	75
-10	6	5	42	36
-6	6	5	47	-8
0	6	5	27	-56
-7	7	5	49	24
-3	7	5	38	-12
-7	1	6	184	178
-5	1	6	47	52
-3	1	6	345	320
-1	1	6	126	132
1	1	6	203	-207
3	1	6	77	-61
5	1	6	245	-241
7	1	6	57	-57
11	1	6	36	34
-18	2	6	35	6
-16	2	6	41	38
-10	2	6	162	-165
-8	2	6	41	49
-6	2	6	158	157
-4	2	6	73	94
-2	2	6	272	266
0	2	6	172	167
2	2	6	90	83
4	2	6	202	-199
6	2	6	307	-306
-17	3	6	47	38
-15	3	6	56	-48
-13	3	6	72	-66
-11	3	6	54	-51
-9	3	6	101	-98
-7	3	6	109	112
-5	3	6	44	28
-3	3	6	216	210
-1	3	6	85	81
1	3	6	135	-134
3	3	6	50	-48
5	3	6	141	-152
7	3	6	34	34
9	3	6	40	6
-14	4	6	29	21
-12	4	6	40	29
-10	4	6	75	-83
-8	4	6	45	15
-6	4	6	62	74
-2	4	6	164	151
0	4	6	110	104
2	4	6	68	47
4	4	6	104	-115
6	4	6	158	-175
8	4	6	27	5
-13	5	6	35	-28
-7	5	6	39	42
-5	5	6	90	90
-1	5	6	29	40
1	5	6	29	-64
5	5	6	56	-65
-4	6	6	37	23
-2	6	6	59	64
0	6	6	60	53
-12	0	7	91	93
-10	0	7	96	-96
-8	0	7	137	-122
-6	0	7	233	-234
-4	0	7	42	22
-2	0	7	549	550
0	0	7	261	251
2	0	7	76	64
6	0	7	40	-47
9	0	7	149	-150
-5	5	7	30	-26
1	5	7	33	26
3	5	7	38	23
-8	6	7	47	-26
-2	6	7	86	109
-16	0	8	35	-62
-14	0	8	32	-12
-12	0	8	94	76
-8	0	8	59	47
-6	0	8	44	-28
-4	0	8	71	77
0	0	8	174	-158
2	0	8	86	88
4	0	8	35	54
6	0	8	80	83
-15	1	8	31	-39
-13	1	8	65	66
-11	1	8	48	56
-9	1	8	99	102
-5	1	8	103	-106
-1	1	8	112	-116
1	1	8	38	-44
3	1	8	32	54
-16	2	8	36	-51
-8	2	8	61	60
-6	2	8	36	33
-4	2	8	86	70
0	2	8	127	-124
2	2	8	57	68
6	2	8	68	-66
-15	3	8	49	40
-13	3	8	49	-26
-11	3	8	56	35
-9	3	8	51	68
-7	3	8	34	36
-5	3	8	68	-67
-3	3	8	32	-40
-1	3	8	72	-70
1	3	8	37	-28
5	3	8	38	22
-10	4	8	32	-17
-6	4	8	38	-31
-4	4	8	44	51
0	4	8	59	-61
-5	5	8	27	-28
-16	0	9	51	-56
-14	0	9	61	-46
-12	0	9	66	-70
-10	0	9	77	-80
-8	0	9	71	66
-6	0	9	46	53
-4	0	9	91	93
-2	0	9	44	-17
0	0	9	32	-28
-15	1	9	40	-36
-13	1	9	29	-29
-11	1	9	50	-59
-9	1	9	47	41
1	1	9	106	111
-5	1	9	70	67
-1	1	9	69	61
-1	1	9	100	-98
-12	2	9	50	-38
-8	2	9	53	-57
-2	2	9	59	47
0	2	9	44	-17
2	2	9	32	-28
-7	3	9	80	-84
-10	2	10	53	-61
-6	2	10	74	-78
-9	3	10	30	-27
-7	3	10	50	-47

measurements) one would thus conclude that TMPD–chloranil is a molecular complex, although in view of the rather large thermal parameters the presence of a small number of doubly charged $TMPD^{2+}$ and $chloranil^{2-}$ ions, as indicated by the absorption spectra, cannot be excluded. The fraction of charged molecules, roughly estimated at some 20%, is certainly smaller, however, than the number of 80% originally estimated from the absorption spectra by Pott & Kommandeur (1965).

In Fig. 3 the bond lengths and angles in the TMPD unit of TMPD–chloranil are compared with the values obtained for $TMPD^+$ in TMPD iodide (de Boer, Vos & Huml, 1968). As expected, TMPD in TMPD–chloranil (which is mainly neutral) has a smaller quinonoid character than $TMPD^+$.

Finally it is worth while mentioning that the Fourier maps of Fig. 1(b) and (c) give evidence that the methyl groups do not show free rotation about their N–CH_3 axes. For the hydrogen atoms of the methyl groups Pott (1966) observed, however, a narrow n.m.r. line (width about 4 Gauss). We can therefore reasonably assume that the methyl groups do not oscillate only about fixed positions but also undergo hindered rotation about the N–CH_3 bonds.
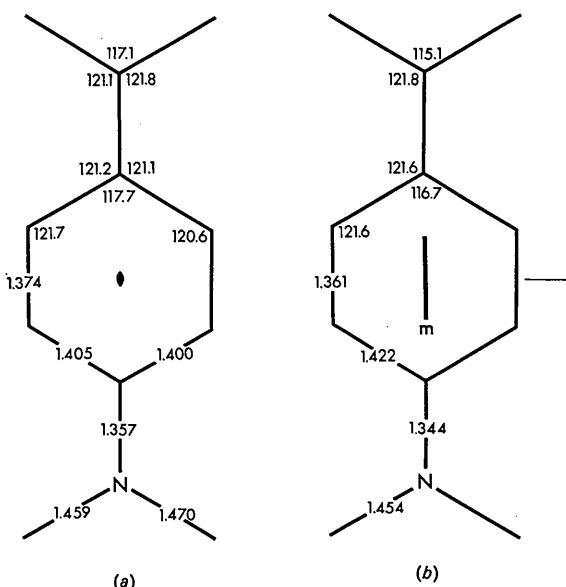
Fig. 3. Comparison of TMPD in TMPD–chloranil (a) with TMPD in TMPD iodide (b).
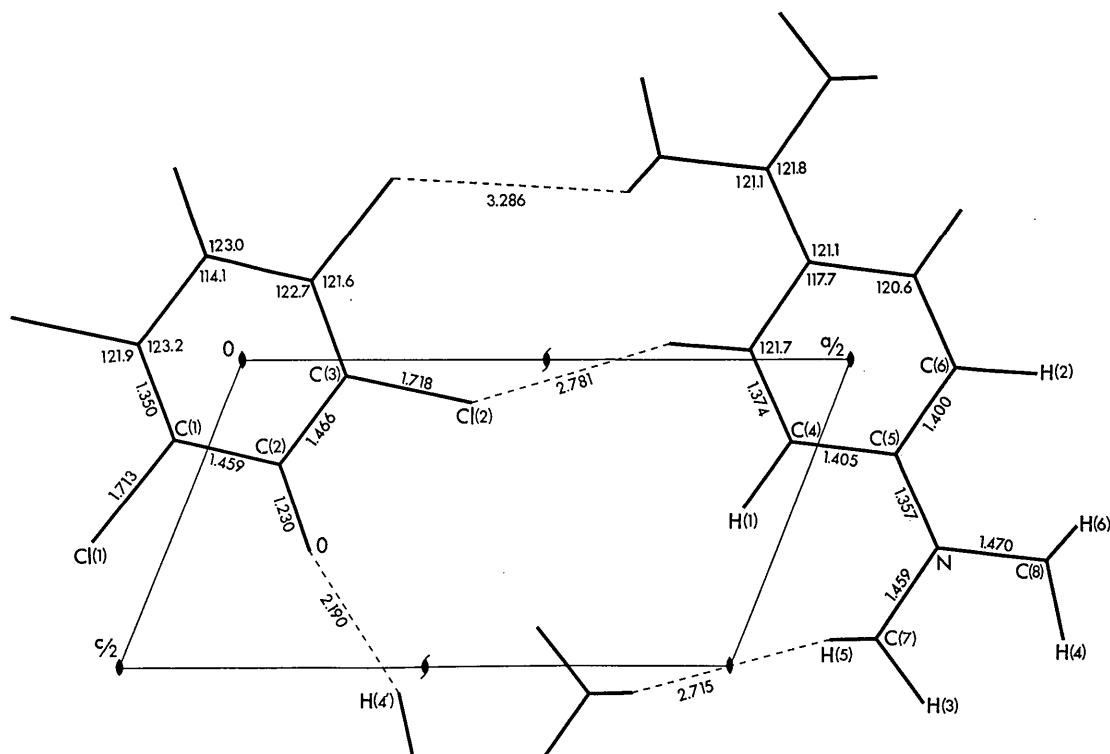
Fig. 2. The structure of TMPD–chloranil at $y=0$. The hydrogen atoms H(5) and H(6) are not in the mirror plane at $y=0$.

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The Crystal Structure of Tetracyanothiophene

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Tetracyanothiophene crystallizes in space group Pa with $a=13\cdot42$, $b=6\cdot56$, $c=7\cdot07$ Å, $\beta=137\cdot0°$, and two molecules in the unit cell. The structure has been determined from three-dimensional film data and refined with anisotropic thermal parameters using the method of least squares. The molecule has approximate C_{2v} symmetry with average distances: S–C, $1\cdot71$ Å; C=C, $1\cdot37$ Å; C–C, $1\cdot40$ Å; C–C$_N$, $1\cdot41$ Å; C≡N, $1\cdot17$ Å. Intermolecular distances as short as N---C, $2\cdot98$ Å, and N---S, $3\cdot22$ Å, suggest weak donor–acceptor bonding between molecules.

Introduction and experimental

As a part of a general study of intermolecular interactions between cyanide nitrogen atoms and heavy non-metal atoms, we have determined the crystal structure of tetracyanothiophene. This work was prompted by the discovery by Hazell (1963) of strong intermolecular nitrogen–selenium interactions in $Se(CN)_2$ and by the

Table 1. *Final atomic parameters and standard deviations for tetracyanothiophene from full-matrix anisotropic least-squares refinement*

	$x(10^4\sigma_x)$	$y(10^4\sigma_y)$	$z(10^4\sigma_z)$	Equivalent B
S	0	0·6990 (6)	$\frac{1}{2}$	3·56 Å²
C(2)	0·1058 (16)	0·9089 (20)	0·6211 (31)	3·14
C(3)	0·1849 (15)	0·9124 (22)	0·5622 (28)	3·24
C(4)	0·1530 (17)	0·7415 (20)	0·4077 (34)	2·97
C(5)	0·0583 (16)	0·6161 (21)	0·3629 (30)	3·55
C(22)	0·1133 (21)	1·0643 (35)	0·7657 (44)	6·55
C(33)	0·2783 (22)	1·0611 (29)	0·6384 (40)	5·01
C(44)	0·2152 (20)	0·7089 (28)	0·3088 (32)	4·24
C(55)	0·0032 (16)	0·4216 (23)	0·2128 (31)	3·52
N(2)	0·1195 (27)	1·1951 (34)	0·8856 (52)	8·83
N(3)	0·3559 (20)	1·2063 (36)	0·7120 (37)	6·81
N(4)	0·2743 (22)	0·6697 (35)	0·2541 (37)	8·20
N(5)	−0·0385 (17)	0·2640 (21)	0·0970 (33)	5·87

Thermal coefficients* (× 10⁴)

	$\beta_{11}(\sigma_{\beta 11})$	$\beta_{22}(\sigma_{\beta 22})$	$\beta_{33}(\sigma_{\beta 33})$	$\beta_{12}(\sigma_{\beta 12})$	$\beta_{13}(\sigma_{\beta 13})$	$\beta_{23}(\sigma_{\beta 23})$
S	114 (6)	184 (9)	497 (22)	−74 (8)	192 (10)	−149 (16)
C(2)	85 (19)	139 (35)	459 (79)	−44 (21)	149 (36)	−76 (45)
C(3)	73 (19)	201 (40)	230 (65)	9 (25)	65 (30)	−22 (45)
C(4)	113 (21)	132 (41)	354 (71)	40 (22)	155 (35)	18 (41)
C(5)	105 (21)	151 (37)	430 (88)	45 (24)	146 (39)	143 (43)
C(22)	164 (31)	475 (78)	681 (120)	6 (38)	252 (55)	−239 (81)
C(33)	173 (28)	287 (54)	395 (87)	−110 (37)	185 (44)	−106 (57)
C(44)	97 (23)	185 (37)	304 (73)	21 (31)	64 (36)	17 (56)
C(55)	103 (20)	178 (40)	352 (73)	−30 (24)	126 (34)	−104 (47)
N(2)	318 (40)	444 (62)	1190 (139)	−35 (47)	502 (68)	−201 (97)
N(3)	185 (30)	400 (62)	531 (94)	22 (40)	187 (46)	52 (72)
N(4)	200 (30)	720 (89)	577 (100)	65 (44)	248 (51)	−33 (78)
N(5)	187 (27)	186 (47)	671 (89)	−7 (25)	225 (44)	−3 (50)

* Anisotropic temperature factors are of the form $T=\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$.