Acta Cryst. (1972). B28, 835

The Crystal Structure of the Room- and Low-Temperature Modifications of Wurster's Blue Perchlorate, TMPD.ClO$_4$.

I. The Room-Temperature Phase

BY J.L. DE BOER AND AAFJE VOS

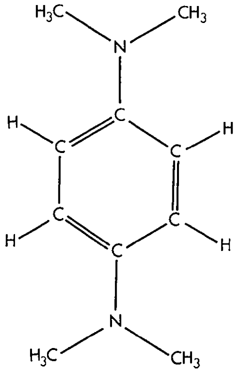
Laboratorium voor Structuurchemie, Rijksuniversiteit Groningen, Zernikelaan, Paddepoel, Groningen, The Netherlands

(*Received* 27 *May* 1971)

Crystals of *N,N,N',N'*-tetramethyl-*p*-diaminobenzene perchlorate (TMPD.ClO$_4$) have orthorhombic symmetry at room temperature. The space group of this (RT) modification is *Pnnm*, $a=5{\cdot}956$ (3), $b=10{\cdot}229$ (6), $c=10{\cdot}187$ (5) Å, $Z=2$. The TMPD as well as the ClO$_4$ groups lie at special positions with symmetry $2/m$. The intensities were collected on an automatic Nonius three-circle diffractometer. Anisotropic block-diagonal least-squares refinement gave an index R of 0·059 for 693 independent non-zero F values. The TMPD groups are stacked at equal distances in rows along the a axis, as is also the case in TMPD iodide. The bond lengths and valence angles of the TMPD groups in TMPD.ClO$_4$ (RT) indicate a strong similarity to the TMPD groups in TMPD iodide. PPP calculations show that in both compounds the TMPD groups are present as TMPD$^+$, as had, for instance, been anticipated from the almost completely paramagnetic behaviour of the compounds. By use of the bond lengths from the next paper it could be concluded that the TMPD groups in the low-temperature form of TMPD.ClO$_4$ also have to be classified as TMPD$^+$.

Introduction

As part of a program to study complexes containing *N,N,N',N'*-tetramethyl-*p*-diaminobenzene (TMPD) groups,



TMPD

the crystal structures of the room- and low-temperature modifications of TMPD.ClO$_4$ have been determined accurately. TMPD.ClO$_4$ has interesting magnetic properties. The paramagnetic susceptibility shows a sharp decrease below the transition point (Chu, Pake, Paul, Townsend & Weissman, 1953; for a χ–T curve see Pott, van Bruggen & Kommandeur, 1967). Thomas, Keller & McConnell (1963) have ascribed the sharp decrease in χ to a dimerization of TMPD groups induced by strong exchange interaction. The idea of exchange interaction between organic radicals was later worked out by Soos (1965) and by Soos & Hughes (1967). Other authors (Pott, 1966; Pott & Kommandeur, 1967) have proposed the theory of a 'mol-ionic' lattice, in which concept the decrease in χ below the transition point (186°K) is explained by assuming the disproportionality $2\text{TMPD}^+ \rightarrow \text{TMPD}^0 + \text{TMPD}^{2+}$. To obtain a better appreciation of the theoretical models, we have performed a complete structure determination of the low-temperature (LT) and room-temperature (RT) modifications of TMPD.ClO$_4$. Use could be made of the preliminary work by Turner & Albrecht and by Hughes & Kamb published by Thomas, Keller & McConnell (1963). In the present paper the structure of the RT form is described. The work on the LT form is presented in the next paper.

Determination of the structure of the RT form

The structure determination will be described rather concisely; details can be found in the thesis of one of the authors (de Boer, 1970). A summary of the experimental work is given in Table 1.

An approximate model of a projection of the structure along the twofold axis was available from the preliminary study of Turner & Albrecht (see Fig. 1 in Thomas, Keller & McConnell, 1963). This projection is strongly analogous to that found for TMPD iodide [see Fig. 4 in de Boer, Vos & Huml (1968)]. In the adopted space group *Pnnm** the ClO$_4$ groups, as well as the TMPD groups, lie at special positions with symmetry $2/m$, which means that the ClO$_4$ tetrahedra are disordered. The lower symmetric space group *Pnn*2 in which the special positions have symmetry 2,

---

* Compared with Thomas *et al.* (1963), we interchanged **b** and **c**, and transferred the origin over $\frac{1}{2}$**a**.

Table 1. *Experimental work*

Preparation of substance	According to Michaelis & Granick (1943); recrystallization from methanol
Unit-cell data	Space group *Pnnm*, $a=5\cdot956$ (3), $b=10\cdot229$ (6), $c=10\cdot187$ (5) Å, $Z=2$. Cell constants from zero-layer Weissenberg films calibrated with NaCl spots; least squares on $\sin^2\theta$ values, $\lambda(\text{Cu } K\alpha)=1\cdot5418$, $\lambda(\text{Cu } K\alpha_1)=1\cdot54050$, $\lambda(\text{Cu } K\alpha_2)=1\cdot54434$ Å.
Linear absorption coefficient	$\mu(\text{Mo } K\alpha)=3\cdot18$, $\mu(\text{Cu } K\alpha)=28\cdot1$ cm^{-1} at 20°C.
Intensity measurements	Mo radiation, Nonius three-circle diffractometer, θ–2θ scan; crystal mounted along [001], dimensions $0\cdot19\times0\cdot47\times0\cdot60$ mm.
Reflexions measured	hkl (all indices ≥ 0) with $0<\theta\leq33°$; $\bar{h}\bar{k}l$ $0<\theta\leq26°$.
Number of observed reflexions	666 hkl reflexions and 543 $\bar{h}\bar{k}l$ reflexions with $I(\text{net})>0$.
Absorption corrections	According to Busing & Levy (1957); crystal bounded by 11 planes.
Comparison of hkl and $\bar{h}\bar{k}l$	$K=\sum\lvert F(hkl)\rvert/\sum\lvert F(\bar{h}\bar{k}l)\rvert=1\cdot003$ (summation over the 514 common reflexions); $R=0\cdot023$.
Available F data	695 independent F values with $\sin\theta/\lambda\leq0\cdot766$ Å^{-1}.

was therefore considered. This space group was discarded as the distribution of the peaks in a $[F_o-F_c(\text{TMPD,Cl})]$-synthesis showed that, in this case too, disorder had to be assumed for the ClO_4 groups.

The least-squares refinement [minimization of $\sum(F_o-kF_c)^2$] was done in space group *Pnnm* with a least-squares program working in block-diagonal approximation (Cruickshank, 1961). The f values of hydrogen were taken from Stewart, Davidson & Simpson (1965), and those of the remaining atoms from Moore (1963). The oxygen atoms were first treated as being smeared out on a sphere with $r=1\cdot44$ Å around the Cl atom. A difference map then showed the approximate orientations of four oxygen tetrahedra related by the symmetry $2/m$. Fractional oxygen atoms ($\frac{1}{4}$O) were put on the observed positions. In the final stages of the refinement the N, C and $\frac{1}{4}$O atoms were given anisotropic temperature factors and the H atoms isotropic temperature factors. All reflexions were treated with equal weight, except for the reflexions 002 and 121 which were omitted because of extinction. The index R decreased to 0·059. When plotting $\langle(\Delta F)^2\rangle$ against $|F|$, two maxima in the curve were observed (at about $F=9$ and $F=18$), but, as there were no indications for the measuring errors to be larger at these places, no changes in the weighting scheme were considered. The final parameters are given in Table 2. The observed and calculated F-values are compared in Table 3. The results of a rigid-body analysis (Cruickshank, 1956) of the TMPD group are given in Table 4.

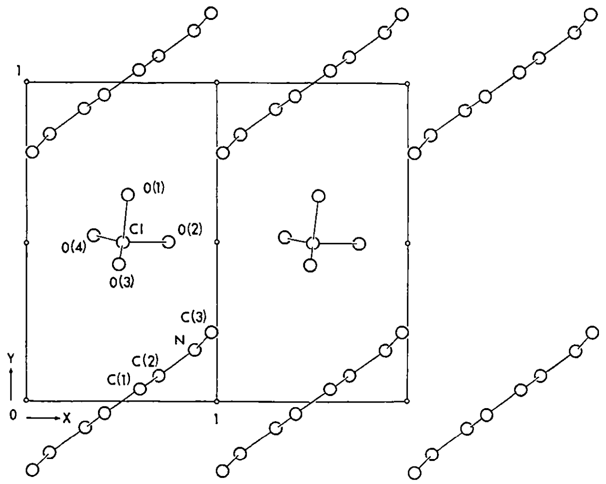


Fig. 1. Projection along [001] of the ions lying athwart the plane $z=0$ in the structure of TMPD.ClO_4(RT). The ions at $z=\frac{1}{2}$ can be obtained from those at $z=0$ by the operation of the screw axis $[\frac{1}{4},y,\frac{1}{4}]$. O(1) through O(4) are $\frac{1}{4}$O atoms (see text). Only the oxygen tetrahedron corresponding to the coordinates given in Table 2 is shown.

Description of the structure

The structure of TMPD.ClO_4(RT) in [001] projection is shown in Fig. 1. The TMPD groups are packed in rows along the a axis. All groups in a row are translationally equivalent and thus at equal distances from each other. Two neighbouring molecules of the row with some short distances and angles are shown in Fig. 2(a). From the legend of this Figure it is seen that the benzene ring is planar within experimental error, but that the molecule as a whole has a slight s shape.

Table 2. *Final parameters and standard deviations, as calculated by the least-squares program, in units of the last decimal place*

The errors in the $\frac{1}{4}$O parameters strongly exceed the calculated standard deviations because of correlation effects. For numbering of atoms see Fig. 1. H(1) is linked to C(1), and H(2) through H(4) to C(3).

(a) Coordinates and parameters B for hydrogen

	z	y	z	B
Cl	$\frac{1}{2}$	$\frac{1}{2}$	0	
C(1)	0·5922 (5)	0·0394 (3)	0·1187 (3)	
C(2)	0·6908 (7)	0·0827 (4)	0	
C(3)	0·9667 (6)	0·2135 (3)	0·1210 (3)	
N	0·8732 (6)	0·1618 (3)	0	
O(1)	0·523 (2)	0·638 (1)	0·039 (1)	
O(2)	0·738 (2)	0·498 (1)	−0·048 (1)	
O(3)	0·485 (3)	0·431 (1)	0·109 (1)	
O(4)	0·356 (2)	0·525 (2)	−0·100 (1)	
H(1)	0·682 (5)	0·068 (2)	0·202 (3)	4·8 (7) Å^2
H(2)	1·015 (7)	0·152 (3)	0·183 (4)	8·6 (10)*
H(3)	1·090 (6)	0·259 (4)	0·106 (4)	9·8 (11)
H(4)	0·844 (7)	0·285 (4)	0·160 (4)	10·9 (12)

* The large B values of the hydrogen atoms linked to C(methyl) indicate a relatively strong libration around the N–C(methyl) bond.

Table 2 (*cont.*)

(*b*) Parameters U_{ij} (in 10^{-4} Å^2) of the temperature factor $\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots\ldots+2ha^*kb^*U_{12}+\ldots\ldots)]$

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Cl	674 (9)	559 (8)	422 (6)	90 (16)	0	0
C(1)	601 (17)	532 (15)	373 (12)	34 (26)	−42 (23)	−97 (25)
C(2)	465 (21)	426 (19)	438 (19)	181 (34)	0	0
C(3)	648 (21)	774 (21)	704 (20)	−204 (37)	−149 (37)	−284 (37)
N	484 (19)	515 (19)	565 (19)	75 (33)	0	0
O(1)	1138 (79)	728 (52)	1069 (129)	153 (116)	−509 (115)	36 (154)
O(2)	803 (61)	1289 (85)	1144 (109)	−105 (139)	−25 (172)	582 (124)
O(3)	1327 (98)	1590 (105)	581 (50)	102 (223)	991 (119)	505 (162)
O(4)	1058 (83)	2154 (153)	775 (64)	−101 (211)	1110 (192)	−530 (133)

Table 3. *Observed and calculated F values*

The columns are *l*, $|F_o|$, F_c. The values are on 10 times the absolute scale.

l	$\lvert F_o\rvert$	F_c
0, 0,L		
4	122	-117
6	189	193
8	346	358
10	174	175
14	32	28
1, 0,L		
1	387	-393
3	226	-241
5	33	-32
7	76	-79
9	106	-109
11	39	-43
2, 0,L		
0	527	554
2	169	133
4	196	-179
6	43	44
8	156	157
10	57	59
12	14	-9
3, 0,L		
1	47	-54
3	228	-237
5	177	-180
7	71	-69
9	19	-16
11	27	-29
13	26	-27
4, 0,L		
0	56	71
2	70	67
4	54	57
6	35	33
8	16	15
10	16	10
12	22	18
5, 0,L		
1	80	-80
3	167	-167
5	148	-153
7	44	-47
11	50	-39
13	42	-39
6, 0,L		
0	32	33
2	50	51
4	63	66
6	27	34
10	28	23
7, 0,L		
1	15	13
0, 1,L		
1	41	-33
3	319	-326
5	67	-69
7	43	49
9	31	32
11	43	-45
13	46	-43
1, 1,L		
0	377	381
1	306	323
2	360	369
3	74	71
4	255	253
5	91	79
6	130	122
7	80	81
8	58	54
9	50	52
10	55	57
11	16	16
12	61	62
14	35	29
2, 1,L		
0	148	147
1	185	-189
2	88	94
3	279	-282
4	59	52
5	223	-223
6	63	60
7	113	-109
8	24	27
9	71	-76
11	62	-68
13	42	-44
3, 1,L		
0	262	277
1	114	104
2	155	152
3	51	-43
4	103	106
5	26	-30
6	114	113
7	44	52
8	93	100
9	31	34
10	55	62
11	16	-8
12	30	25
4, 1,L		
0	94	91
1	201	-203
2	39	34
3	106	-114
4	12	-15
5	66	-66
6	17	17
7	75	-79
8	24	25
9	61	-66
11	22	-24
5, 1,L		
0	99	97
1	12	-7
2	35	31
3	60	-64
4	45	-47
5	47	-49
8	40	40
6, 1,L		
0	15	5
1	44	-43
2	27	-28
3	15	4
4	54	-57
5	15	10
6	22	-25
7	25	-26
9	27	-26
7, 1,L		
0	49	53
2	33	35
3	18	-13
4	18	16
6	27	23
8	35	30
0, 2,L		
0	489	504
2	357	361
4	115	118
6	65	63
8	129	129
10	89	90
12	19	19
1, 2,L		
0	406	418
2	246	234
3	88	76
4	129	117
5	85	76
6	103	100
7	205	-213
8	85	89
9	189	-192
10	45	45
11	32	-38
12	15	11
15	27	-29
2, 2,L		
0	52	-51
1	13	-11
2	59	70
3	92	98
4	119	122
5	62	53
6	100	100
7	14	18
8	73	73
9	18	-15
10	41	45
12	21	23
3, 2,L		
0	168	160
1	76	-84
2	59	60
3	18	-20
4	43	-49
5	16	-20
7	76	-72
8	38	43
9	50	-47
12	20	-13
4, 2,L		
0	34	32
1	23	19
2	115	120
3	29	26
4	182	189
5	43	46
6	97	101
7	20	26
9	16	9
10	20	16
12	43	38
5, 2,L		
1	46	-49
2	24	-25
3	74	-75
4	46	-50
5	58	-63
6	19	-24
7	19	-20
9	17	-14
11	28	-26
6, 2,L		
0	12	3
1	29	-35
2	31	32
3	53	-52
4	62	65
5	39	-43
6	35	39
7, 2,L		
3	27	-29
5	19	-21
0, 3,L		
1	458	-478
3	293	-306
5	220	-215
7	147	-148
9	89	-88
11	70	-69
13	53	-52
1, 3,L		
0	292	-288
1	213	215
2	79	39
3	79	76
4	199	206
5	39	40
6	70	68
7	44	42
8	12	-10
9	51	53
10	26	30
11	20	20
12	53	54
14	28	24
2, 3,L		
0	277	-279
1	86	-100
2	72	-35
3	21	-19
4	89	88
5	95	-92
6	18	-15
7	103	-107
8	69	-75
9	65	-71
10	25	-28
11	34	-39
3, 3,L		
0	79	66
1	11	-14
2	141	147
3	45	-43
4	186	189
5	48	-51
6	125	125
8	70	71
9	15	11
10	48	51
11	15	-17
12	32	34
4, 3,L		
0	19	-13
1	89	-95
2	47	49
3	16	16
4	106	112
5	17	16
6	33	31
7	41	-41
8	17	-19
9	40	-43
10	14	14
12	26	29
5, 3,L		
0	97	100
1	39	-43
2	76	78
4	43	45
6	46	47
7	14	-11
8	48	51
10	29	29
6, 3,L		
0	31	-32
1	49	-52
2	20	-15
3	18	-6
6	18	-17
7	29	-29
9	32	-32
7, 3,L		
3	28	25
8, 3,L		
1	26	-23
0, 4,L		
0	346	372
2	95	68
4	193	-181
6	14	5
8	122	122
10	47	46
12	17	-19
1, 4,L		
0	107	104
1	115	-141
2	77	-77
3	128	-135
4	37	-34
5	132	-130
7	119	-118
8	30	35
9	84	-82
10	20	21
11	36	-38
13	17	-19
2, 4,L		
0	172	184
1	260	-256
2	108	125
3	23	-20
4	32	36
5	19	-11
6	159	167
7	87	-99
8	131	128
9	76	-84
10	61	62
12	24	20
3, 4,L		
0	14	-19
1	18	-9
2	50	-52
3	91	-93
4	94	-93
5	124	-127
6	53	-54
7	63	-63
9	26	-26
11	32	-27
12	26	-22
13	23	-26
4, 4,L		
0	87	87
1	23	-25
2	102	102
3	86	86
4	95	99
5	80	84
6	63	67
7	13	-6
8	35	38
9	15	-11
10	26	29
11	24	20
12	27	25
5, 4,L		
0	13	-5
3	33	-34
4	22	21
5	36	-41
6	15	2
6, 4,L		
2	21	19
4	26	31
6	18	14
7, 4,L		
1	26	-24
2	21	19
3	28	-29
4	34	40
5	29	-29
7	23	-19
0, 5,L		
1	77	-88
3	264	-268
5	235	-239
7	71	-65
9	36	-33
11	58	-59
13	46	-45
1, 5,L		
0	253	267
1	68	69
2	166	172
3	92	-87
4	102	104
5	66	-67
6	123	128
8	105	108
9	23	25
10	56	55
12	30	32
2, 5,L		
0	235	-241
1	75	80
2	126	-122
3	110	-117
4	11	-8
5	128	-125
6	31	-31
7	33	-32
8	70	-72
9	15	-7
10	35	-38
11	25	-28
3, 5,L		
0	73	72
1	32	38
2	35	28
3	107	-106
4	11	-8
5	97	-102
6	33	34
7	10	8
8	44	46
9	22	23
10	17	17
11	26	-23
13	27	-26
4, 5,L		
0	10	4
1	78	-71
2	17	17
3	105	-102
4	38	42
5	87	-89
6	20	18
7	45	-48
9	29	-26
11	25	-22
5, 5,L		
0	95	95
1	31	32
2	64	61
4	21	25
6	32	33
7	18	16
8	45	45
10	33	28
6, 5,L		
0	32	35
1	31	-33
2	14	17
3	26	-28
5	31	-30
7	31	-28
7, 5,L		
2	18	12
5	18	17
0, 6,L		
0	154	164
2	164	172
4	137	144
6	101	106
8	60	58
10	25	26
12	21	19
1, 6,L		
0	69	71
1	57	-71
2	24	-17
3	40	-47
4	69	-72
5	31	-28
6	10	-8
7	49	-45
8	31	36
9	33	-30
2, 6,L		
0	125	124
1	66	-57
2	122	116
3	24	22
4	136	141
5	26	24
6	117	118
7	28	-27
8	68	68
9	37	-39
10	39	40
12	30	30
3, 6,L		
0	114	116
1	164	-160
2	29	4
3	156	-154
4	91	-94
5	126	-130
6	15	-6
7	87	-89
8	51	57
9	58	-60
11	37	-40
12	24	-23
13	28	-27
4, 6,L		
0	36	24
2	29	23
4	29	29
5	14	15
6	20	22
7	13	-2
5, 6,L		
0	34	39
1	31	-29
3	33	-37
4	27	-35
5	23	-26
8	21	20
6, 6,L		
1	25	23
2	15	11
3	16	12
4	17	10
5, 6,L		
0	29	26
2	28	23
0, 7,L		
1	224	-223
3	80	-85
5	49	-51
7	84	-86
9	68	-67
11	26	-24
1, 7,L		
0	117	119
1	54	53
2	150	153
3	26	-25
4	184	186
5	33	-34
6	106	106
8	43	42
9	16	18
10	40	39
12	32	34
2, 7,L		
0	30	-29
1	99	-100
2	47	47
3	32	-33
4	111	114
5	20	-17
6	46	53
7	49	-52
8	15	-14
9	35	-36
12	28	26
3, 7,L		
0	28	-36
1	71	77
2	26	20
3	13	-10
4	62	61
5	14	-19
6	23	25
7	37	34
8	14	-10
9	33	35
4, 7,L		
0	44	-48
1	97	-94
2	17	-13
3	69	-66
4	21	25
5	42	-46
7	40	-41
8	29	-25
9	33	-30
5, 7,L		
0	23	29
1	14	-13
2	36	40
3	16	-20
4	49	54
5	15	-13
6	31	37
6, 7,L		
0	14	6
1	30	-30
3	25	-27
5	23	-20
7, 7,L		
1	19	-19
0, 8,L		
0	13	16
2	65	69
4	89	87
6	40	35
1, 8,L		
0	23	25
1	81	-79
2	16	3
3	87	-89
4	21	-22
5	71	-76
7	39	-43
8	16	12
9	21	-17
11	20	-19
2, 8,L		
0	58	60
1	12	2
2	76	78
3	93	94
4	92	95
5	83	84
6	56	56
8	25	25
10	25	26
11	22	24
3, 8,L		
0	70	69
1	87	-83
2	48	46
3	55	-56
4	19	14
5	47	-49
6	21	25
7	40	-43
8	33	35
9	27	-31
4, 8,L		
0	58	60
1	60	-66
2	53	57
4	43	46
6	27	31
7	37	-35
8	20	24
9	25	-30
5, 8,L		
0	17	-18
1	24	-29
7, 8,L		
0	27	-26
0, 9,L		
1	114	-113
3	93	-93
5	73	-74
7	54	-54
9	44	-44
11	19	-26
1, 9,L		
0	107	104
2	47	44
3	37	-37
4	22	-18
5	38	-41
6	20	15
8	47	47
10	23	24
2, 9,L		
0	16	-6
1	36	-37
2	30	32
3	54	-58
4	65	67
5	49	-51
6	28	28
7	27	-29
9	18	-19
3, 9,L		
0	70	71
1	30	31
2	59	61
4	39	45
6	32	36
7	20	15
8	34	32
9	27	22
4, 9,L		
0	40	-44
1	18	9
2	18	-17
3	23	-22
5	24	-26
6	20	-15
8	26	-25
5, 9,L		
0	20	24
1	17	-3
2	25	31
4	32	35
0, 10,L		
0	20	17
2	37	35
4	49	51
6	33	36
1, 10,L		
0	18	-17
1	21	-22
2	33	-37
3	83	-85
4	46	-48
5	75	-78
6	28	-26
7	20	-29
11	33	-26
2, 10,L		
0	28	27
2	23	24
4	20	22
6	21	22
3, 10,L		
0	29	34
2	15	2
3	12	-16
4	25	-27
5	16	-14
4, 10,L		
0	64	66
1	22	-22
2	39	43
3	16	-17
6	20	23
8	32	33
5, 10,L		
0	15	27
6, 10,L		
0	15	22
0, 11,L		
1	44	-44
5	21	22
7	20	-21
9	26	-28
1, 11,L		
0	42	43
1	28	-19
2	27	28
3	30	-31
4	14	11
5	27	-27
8	31	29
2, 11,L		
0	16	-15
1	91	-94
2	17	-10
3	22	-27
5	21	-21
7	35	-34
9	32	-31
3, 11,L		
0	24	24
2	30	32
3	23	-21
4	42	40
6	27	31
4, 11,L		
3	22	-23
0, 12,L		
0	19	21
2	56	58
4	89	90
6	91	51
10	21	19
1, 12,L		
1	17	-14
2	18	-4
3	23	-27
5	26	-28
2, 12,L		
0	15	-12
1	14	-9
4	32	27
3, 12,L		
1	23	-22
5, 12,L		
1	35	-39
1, 13,L		
0	41	42
2	30	24
8	30	22
2, 13,L		
1	30	-32
3	22	-21
5	23	-18
7	22	-21
3, 13,L		
2	20	10
4, 13,L		
3	22	-20
0, 14,L		
2	24	21
4	25	28
1, 14,L		
3	27	-29

Table 4. *Principal axes of T* (10^{-4} Å^2) *and* ω (10^{-4} rad^2) *with the corresponding* U_{ij} (10^{-4} Å^2) *values*

Principal axes *T* tensor: *p*, *q*, and *r* with $\mathbf{r}=\mathbf{c}$. Principal axes ω tensor: *p′*, *q′*, and *r′* with $\mathbf{r}'=\mathbf{c}$. **p** and **p′** lie in between **a** and **b** and make angles with **a** of 39·95 and 41·42° respectively.

$T(p)$	$T(q)$	$T(r)$	$\omega(p')$	$\omega(q')$	$\omega(r')$
542	297	358	159	28	23

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	570	554	371	42	−13	−50
C(2)	457	428	416	198	0	0
C(3)	681	731	717	−236	−104	−237
N	504	512	582	72	0	0

This is also the case for the TMPD group in TMPD iodide as is shown by Fig. 2(*b*). From Fig. 2(*a*) and 2(*b*) it is easily seen that the packing of the TMPD groups in TMPD.ClO$_4$(RT) and in TMPD iodide is strongly analogous, but that in TMPD iodide the intermolecular distances are shorter.

Comparison of the directions of the main axes of translation and libration given in Table 4, with the orientation of the molecule given in Fig. 2(*a*), shows that both sets of axes approximately coincide with the axes of inertia of the TMPD molecule. It may be noticed that both the translation and libration are largest for the molecular axis having the smallest moment of inertia.

The bond lengths and angles in the TMPD group of TMPD.ClO$_4$(RT) are listed in Fig. 3; the values in this Figure are not corrected for libration. By applying libration corrections, we obtained the bond lengths listed in Fig. 4(*a*).

Discussion of the bond lengths

In Fig. 4 the bond lengths obtained for the TMPD groups in TMPD.ClO$_4$(RT) and in TMPD iodide are compared. A great similarity is found. This is not too surprising as in both compounds the TMPD groups are present as TMPD$^+$, as follows from their approximately fully paramagnetic character (Monkhorst, Pott & Kommandeur, 1967) and from the fact that the respective unit cells contain one independent TMPD group and one independent negative ion.

It is interesting to check whether the experimental bond lengths for $TMPD^+$ show good agreement with theoretically predicted values for $TMPD^+$ and to see by how much these lengths are expected to differ from those in $TMPD^0$ and $TMPD^{2+}$. To this end PPP calculations were kindly carried out by Dr D. Kracht. The parameters used in these calculations are summarized in Table 5. The calculated values for the π-bond orders P and the charges Q are given in Table 6. The bond lengths listed in the Table were obtained by use of the relations

$R(\text{C–C}) = 1{\cdot}506 - 0{\cdot}17\,P$ and $R(\text{C–N}) = 1{\cdot}448 - 0{\cdot}17\,P$

(for motivation, see de Boer, 1970, pages 89–90).

Table 5. *Parameters for the PPP calculations**

All energies are in eV.

$\alpha_C = -11{\cdot}16$	$\alpha_N = -26{\cdot}04$	$\beta = -2517{\cdot}5 \exp(-5{\cdot}007\,R)$
$\gamma_{CC} = 11{\cdot}13$	$\gamma_{NN} = 14{\cdot}08$	$\gamma_{\mu\nu}$ according to the uniformly charged spheres approximation with $\xi_C = 3{\cdot}25$ and $\xi_{N^+} = 4{\cdot}25$.
$Z_C = 1$	$Z_N = 2$	

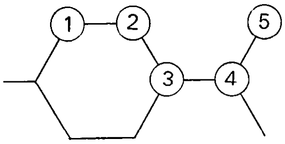
* Pariser & Parr (1953), Pople (1953).

Table 6. *Calculated bond orders, charges and bond lengths for $TMPD^0$, $TMPD^+$ and $TMPD^{2+}$*

For numbering, see insert.

	Bond order P			Bond length R (Å)		
	1-2	2-3	3-4	1-2	2-3	3-4
$TMPD^0$	0·692	0·612	0·348	1·388	1·402	1·389
$TMPD^+$	0·819	0·441	0·580	1·367	1·431	1·349
$TMPD^{2+}$	0·905	0·295	0·815	1·352	1·456	1·309

	Charge Q		
	2	3	4
$TMPD^0$	−0·059	−0·005	0·123
$TMPD^+$	0·014	0·145	0·326
$TMPD^{2+}$	0·069	0·309	0·552



From Table 6 and Fig. 4(*a*) and (*b*), we see that the experimental bond lengths in TMPD.ClO_4(RT) and in TMPD iodide lie surprisingly close to the calculated values for $TMPD^+$, and that the geometry observed for the TMPD groups is significantly different from that calculated for $TMPD^0$ and $TMPD^{2+}$. It is noteworthy that the same holds for the bond lengths observed for TMPD.ClO_4(LT) (de Boer & Vos, 1972), given in Fig. 4(*c*). This makes clear that in the low temperature form of TMPD.ClO_4 too the TMPD groups are present as $TMPD^+$. The implication of the presence of these ions with respect to the small paramagnetic susceptibility of TMPD.ClO_4(LT) will be dealt with in the next paper (de Boer & Vos, 1972).

The authors are grateful to Mr G. Kemper for his contribution to the structure determination and to Dr D. Kracht for performing the PPP calculations. We are pleased to acknowlege the cordial cooperation with the staff of the Computing Centre of the University of Groningen.

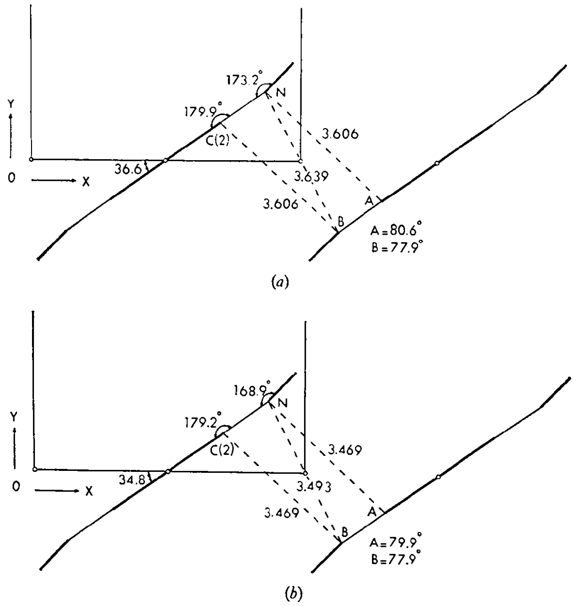


Fig. 2. The packing of the TMPD groups in TMPD.ClO_4(RT) and TMPD iodide. The planes through the benzene rings and through the C(methyl)-N-C(methyl) groups are represented by bold lines, the C(2)-N bonds are given by thin lines. (*a*) TMPD ClO_4(RT). The equation of the best plane through the benzene ring is $-0{\cdot}5960X+0{\cdot}8030Y+0Z=-1{\cdot}775$ Å; successive planes lie 3·550 Å apart. The distances of the atoms from the benzene planes are C(1) −0·004, C(2) +0·002, N +0·004, C(3) +0·097 Å. The N atom is distant 0·059 Å from the plane through its three surrounding C atoms. (*b*) TMPD. iodide The equation of the best plane through the benzene ring is $-0{\cdot}5713X+0{\cdot}8207Y+0Z=-1{\cdot}691$ Å; successive planes lie 3·382 Å apart. The distances of the atoms from the benzene plane are: C(1) −0·005, C(2) +0·002, N +0·022, C(3) +0·182 Å. The N atom lies at a distance of 0·095 Å from the plane through its three surrounding C atoms.

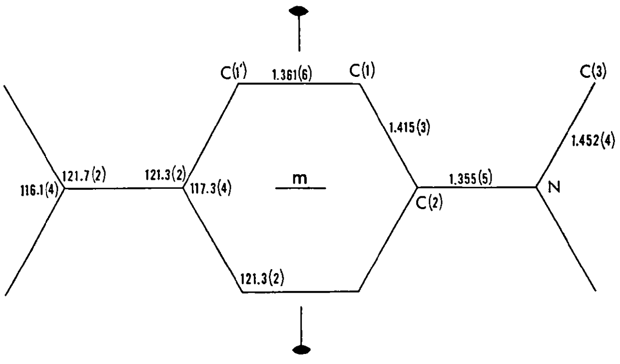


Fig. 3. Bond lengths and angles in the TMPD group of TMPD ClO_4(RT), not corrected for libration. The distances C(1)-H(1), C(3)-H(2), C(3)-H(3) and C(3)-H(4) are 1·04, 0·93, 0·88 and 1·11 Å respectively. The angles C(1')-C(1)-H(1), N-C(3)-H(2), N-C(3)-H(3) and N-C(3)-H(4) are 125·2, 116·4, 111·7 and 106·9° respectively.

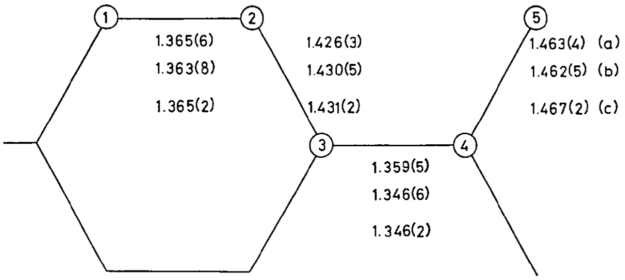


Fig. 4. Bond lengths observed in (*a*) TMPD.ClO_4(RT), (*b*) TMPD iodide and (*c*) TMPD.ClO_4(LT). The values are corrected for libration.

References

Boer, J. L. de, Vos, A. & Huml, K. (1968). *Acta Cryst.* B**24**, 542.

Boer, J. L. de (1970). Thesis, Groningen.

Boer, J. L. de & Vos, A. (1972). *Acta Cryst.* **B28**, 839.

Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180.

Chu, T. L., Pake, G. E., Paul, D. E., Townsend, J. & Weissman, S. I. (1953). *J. Phys. Chem.* **57**, 504.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754.

Cruickshank, D. W. J. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* London: Pergamon Press.

Michaelis, L. & Granick, S. (1943). *J. Amer. Chem. Soc.* **65**, 1747.

Monkhorst, H. J., Pott, G. T. & Kommandeur, J. (1967). *J. Chem. Phys.* **47**, 401.

Moore, F. H. (1963). *Acta Cryst.* **16**, 1169.

Pariser, R. & Parr, R. G. (1953). *J. Chem. Phys.* **21**, 466, 767.

Pople, J. A. (1953). *Trans. Faraday Soc.* **49**, 1375.

Pott, G. T. (1966). Thesis, Groningen.

Pott, G. T., van Bruggen, C. F. & Kommandeur, J. (1967). *J. Chem. Phys.* **47**, 408.

Pott, G. T. & Kommandeur, J. (1967). *J. Chem. Phys.* **47**, 395.

Soos, Z. G. (1965). *J. Chem. Phys.* **43**, 1121.

Soos, Z. G. & Hughes, R. C. (1967). *J. Chem. Phys.* **46**, 253.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Thomas, D. D., Keller, H. & McConnell, H. M. (1963). *J. Chem. Phys.* **39**, 2321.

Acta Cryst. (1972). B**28**, 839

The Crystal Structure of the Room- and Low-Temperature Modifications of Wurster's Blue Perchlorate, TMPD. ClO_4.

II. The Low-Temperature Phase

By J. L. de Boer and Aafje Vos

Laboratorium voor Structuurchemie, Rijksuniversiteit Groningen, Zernikelaan, Paddepoel, Groningen, The Netherlands

(*Received* 27 *May* 1971)

Crystals of the low-temperature modification of *N,N,N',N'*-tetramethyl-*p*-diaminobenzene perchlorate (TMPD.ClO_4) have monoclinic symmetry. The crystal structure is described in space group $B2_1/d$. The unit-cell data (in $B2_1/d$) are at 110°K: $a=11\cdot655$ (7), $b=10\cdot147$ (8), $c=20\cdot130$ (10) Å, $\beta=92\cdot57$ (2)°, $Z=8$. The a and c axes are almost doubled in length compared with those of the orthorhombic modification, space group *Pnnm*, existing above the transition point of 186°K. The mirror plane and twofold axis which vanish when going from *Pnnm* to $B2_1/d$ are preserved as twinning elements. Because of the twinning, difficulties were encountered during the intensity measurements. For two different crystals it appeared to be possible, however, to obtain reliable intensities for 3014 and 2737 independent reflexions respectively. The corresponding indices R are 0·093 and 0·103. The TMPD groups are arranged in rows, the distances between the benzene planes are alternately 3·10 and 3·62 Å. The bond lengths show that the TMPD groups are present as $TMPD^+$. This rules out the 'mol-ionic' lattice theory of Pott & Kommandeur. The magnetic behaviour of TMPD.ClO_4(LT) can be explained by the theory of Soos based on exchange interaction.

Introduction

In the previous paper (de Boer & Vos, 1972; to be referred to as dBV), the room-temperature (RT) modification of TMPD.ClO_4 is described. The crystals of the RT form are orthorhombic, space group *Pnnm*. When cooling the crystals of TMPD.ClO_4 below the transition point of 186°K, the symmetry is lowered from orthorhombic to monoclinic (Thomas, Keller & McConnell, 1963), and twinning of the crystals is observed. The present paper deals with the low-temperature study of TMPD.ClO_4, the comparison with the RT form, and the discussion of the magnetic properties.