Acta Cryst. (1968). B**24**, 542

The Crystal and Molecular Structure of *N,N,N',N'*-Tetramethyl-*p*-diaminobenzene Iodide (Wurster's Blue Iodide)

By J. L. de Boer and Aafje Vos
Laboratorium voor Structuurchemie, Rijksuniversiteit Groningen, Bloemsingel 10, *Groningen, The Netherlands*

and K. Huml
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 6, *Czechoslovakia*

(*Received* 21 *June* 1966 *and in revised form* 1 *September* 1967)

Crystals of Wurster's blue iodide have orthorhombic symmetry, with $a=5{\cdot}919$, $b=9{\cdot}855$, $c=9{\cdot}901$ Å, space group *Pnnm*, $Z=2$. Intensities were collected with an automatic Nonius diffractometer. Atomic coordinates were obtained from Fourier and difference Fourier maps. Anisotropic least-squares refinement gave $R=2{\cdot}27\%$ for 821 independent reflexions with reliable intensity. The *N,N,N',N'*-tetramethyl-*p*-diaminobenzene (TMPD) molecule lies at a special position with symmetry $2/m$. The nitrogen atom is at a distance of 0·095 Å from the plane through its surrounding carbon atoms. The benzene ring is planar. The *p*-diaminobenzene group has a quinoid character as may be seen from the bond lengths C(1')–C(1) 1·361, e.s.d. 0·008 Å; C(1)–C(2) 1·422, e.s.d. 0·005 Å; C(2)–N 1·344, e.s.d. 0·006 Å. The hydrogen atoms could be clearly identified in a difference Fourier synthesis. After least-squares refinement the average C–H distance was $0{\cdot}96^5$ Å (s.d. calculated by the least-squares program 0·04 Å for the individual values).

Introduction

Wurster's blue iodide has been investigated as part of a program to study compounds containing *N,N,N',N'*-tetramethyl-*p*-diaminobenzene (TMPD) molecules. Among these compounds there are diamagnetic and paramagnetic species and it seemed interesting to find out in which respect the structures of the two types of compound differ. Some compounds, *e.g.* Wurster's blue perchlorate, undergo a phase transition and are paramagnetic at high and diamagnetic at low temperatures. In Wurster's blue perchlorate the phase transition occurs at −87 °C. Wurster's blue iodide is paramagnetic from room temperature till liquid nitrogen temperature, and no phase transition has been observed in this temperature interval.

First Wurster's blue perchlorate was studied at room temperature by one of the authors (J.L.d.B.). Bond lengths and angles obtained for the TMPD group, however, possibly suffered from systematic errors as it appeared that the perchlorate ions are statistically distributed in the crystal. To avoid this difficulty, Wurster's blue iodide was chosen for further research. The iodide was preferred above the corresponding chloride and bromide, as the latter compounds are unstable. At the end of the investigation of the iodide we noticed that the systematic errors in the TMPD unit of the perchlorate had been kept small, as the TMPD units in the two compounds show good agreement.

Study of Wurster's blue perchlorate will be continued at liquid nitrogen temperature. This work is severely hampered, however, as the crystals are twinned below the transition point (Thomas, Keller & McConnell, 1963).

Experimental

Crystal data

Wurster's blue iodide, $C_{10}H_{16}N_2I$, F.W. 291·157. M.P. 150–153 °C. Orthorhombic, *Pnnm*, $a=5{\cdot}919(3)$, $b=9{\cdot}855(4)$, $c=9{\cdot}901(4)$ Å. $V=577{\cdot}5(5)$ Å^3, $Z=2$, $D_m=1{\cdot}68(4)$ g.cm^{-3} (flotation method), $D_c=1{\cdot}674$ g.cm^{-3}. Linear absorption coefficients: μ(Cu $K\alpha$) = 219·1 cm^{-1}, μ(Mo $K\alpha$) = 27·66 cm^{-1}. Crystals of ap-

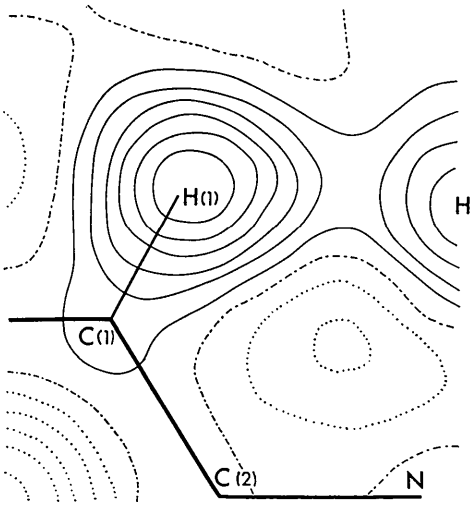

Fig. 1. Difference Fourier synthesis of low order reflexions in the plane of the benzene ring (approximated by the plane $-0{\cdot}55431\,X+0{\cdot}83231\,Y+0\,Z=0$ Å, with $X=xa$, $Y=yb$ and $Z=zc$). Contours at intervals 0·07 e.Å^{-3}. The zero line is chain-dotted. The numbering of the atoms refers to Fig. 4, their positions are those of Table 1.

proximate dimensions of 0·09 mm perpendicular to the rotation axis were used for the determination of the cell constants, which were obtained from zero layer Weissenberg photographs, superimposed with NaCl reflexion spots for calibration purposes. The standard deviations given above are twice the standard deviations as calculated by the least-squares program used for the adjustment of *a*, *b* and *c* to the $\sin^2 \theta/\lambda^2$ values of 182 reflexions ($\lambda(\text{Cu } K\alpha_2) = 1{\cdot}54434$, $\lambda(\text{Cu } K\alpha_1) = 1{\cdot}54050$ Å, $a(\text{NaCl}) = 5{\cdot}64006$ Å).

The systematic absences on the X-ray photographs were characteristic of both the space groups *Pnnm* and *Pnn*2. Space group *Pnnm*, having the general positions

$$\pm(x,y,z;\ -x,-y,z;\ \tfrac{1}{2}+x,\tfrac{1}{2}-y,\tfrac{1}{2}-z;\ \tfrac{1}{2}-x,\tfrac{1}{2}+y,\tfrac{1}{2}-z)$$

was adopted for the structure determination. In this space group, both the iodine atoms and the TMPD groups lie at special positions with symmetry 2/*m*. The results of the structure determination subsequently confirmed the choice of the centrosymmetric space group.

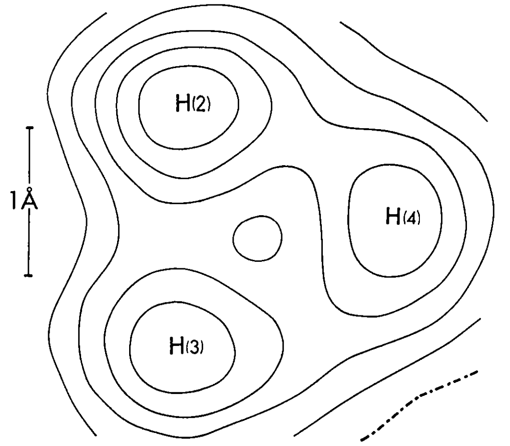

Fig 2. Difference Fourier synthesis of low order reflexions in the plane of the methyl hydrogen atoms (approximated by the plane $0{\cdot}38289\,X + 0{\cdot}45994\,Y + 0{\cdot}80115\,Z = 3{\cdot}421$ Å, with $X = xa$, $Y = yb$ and $Z = zc$). Contours at intervals 0·07 e.Å^{-3}. The zero line is chain-dotted. The numbering of the atoms refers to Fig. 4.

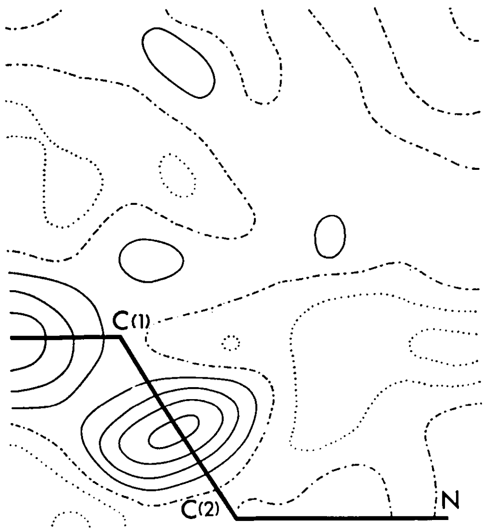

Fig. 3. Final difference Fourier synthesis (real part of ΔF only) in the plane of the benzene ring. Details are as in legend of Fig. 1.

Preparation of the crystals

The substance was prepared by mixing, at room temperature, solutions of iodine (0·16 g.at.l^{-1}) and of TMPD (0·32 mol.l^{-1}) in acetonitrile in a 2:1 ratio. By slow evaporation of the acetonitrile in about 2 days, purple-black crystals, prismatic along **a**, could be obtained. A great number of the larger crystals appeared to contain mother liquor in channels parallel to the *a* axis. Several crystals were cut perpendicular to this axis to select a good specimen. For the intensity measurements, part of a crystal without channels in the section perpendicular to **a**, was used. The approximate dimensions of this crystal fragment are $0{\cdot}39 \times 0{\cdot}42 \times 0{\cdot}44$ mm^3.

Structure factors

The crystal was mounted on the tip of a glass fibre and aligned along **a**. The intensity data were collected with an automatic Nonius diffractometer, using the moving counter-moving crystal method and Zr-filtered Mo radiation. Deviations from linearity of the (scintillation) counting equipment were kept below 1% by the use of attenuation filters. Every 90 minutes a reference reflexion was measured accurately. Two equivalent sets of independent reflexions, *hkl* and $hk\bar{l}$, with $\sin\theta/\lambda < 0{\cdot}8171$ Å^{-1}, were subsequently measured. Corrections were made for intensity changes in the primary beam (by use of the reference intensities), for the Lorentz and polarization effects and for absorption. The latter corrections were calculated according to the Busing & Levy (1957) scheme; $6 \times 6 \times 6$ volume fragments and 11 accurately located bounding planes were taken into account. In the part of reciprocal space explored, 1381 independent reflexions were measured. From both sets of measurements were omitted (1) reflexions with a negative net intensity (background > integrated intensity) and (2) reflexions with a weight *w* smaller than a seventh of the average weight of the reflexions with positive net intensity. The weights were calculated from the relation $w = \sigma^{-2}(F)$, $\sigma(F)$ being the standard deviation in *F* due to counting statistics.

Set 1 (*hkl*) contained 917 reliable reflexions, set 2 ($hk\bar{l}$) 903. The two sets had 823 reliable reflexions in common; 174 reflexions were above the threshold weight in only one of the two sets. From a comparison of the 823 reliable reflexions common to both sets, the scaling factor *K* calculated according to $K = \Sigma|F(\text{set 1})|/\Sigma|F(\text{set 2})|$ amounted to 1·002 and the discrepancy $\Sigma|\Delta F|/\Sigma|F|$ to 2·4%.

The structure determination was carried out with the 823 common reflexions. As F_o (*hkl*), the average *F* value of *hkl* and $hk\bar{l}$ was taken.

Determination of the structure

Both the TMPD group and the iodine atom are situated at twofold positions with symmetry $2/m$. In order to facilitate comparison with Wurster's blue perchlorate (Thomas *et al.*, 1963), the iodine atoms were located at $(0,\frac{1}{2},0)$ and $(\frac{1}{2},0,\frac{1}{2})$. Apart from possible anisotropic vibrations, the iodine atoms contribute only to reflexions hkl with $h+k+l=$even. A Fourier synthesis based on this set of reflexions, with signs deduced from the iodine contributions alone, was calculated. The synthesis showed the TMPD molecule around $(0,0,0)$ and the related one at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. For each molecule two images were found as a result of the pseudo-symmetry introduced in the Fourier map owing to the fact that only reflexions hkl with $h+k+l=$even were considered. One image was arbitrarily regarded as the spurious one and the positions of the one independent nitrogen and the three independent carbon atoms could be determined from the map.

The parameters of I, C and N were refined with the least-squares method in which the scattering factors were taken from Moore (1963) and anisotropic thermal parameters were considered. The calculations were done on a TR4 computer with a program according to Cruickshank's (1961*b*) scheme. The weighting scheme adopted was $w=710/(710+F_o^2)$ and R decreased to 3·4%. To find the hydrogen atoms, a difference Fourier synthesis of the reflexions with $\sin\theta/\lambda<0{\cdot}4$ Å^{-1} (H not included in F_c) was calculated in the plane of the benzene ring and in the plane through the hydrogen atoms of the methyl group; the latter plane was calculated with the assumption that the C–H distances are 1·08 Å and that the angles at the methyl carbon atom are tetrahedral. Figs. 1 and 2 clearly show the four independent H atoms. The hydrogen atoms were included in the least-squares refinement, with isotropic parameters. For these atoms the scattering factor as given by Stewart, Davidson & Simpson (1965) was used. In the latter stage of the refinement the anomalous part of the iodine scattering factor, $\Delta f'=-0{\cdot}6$, $\Delta f''=2{\cdot}2$ (*International Tables for X-ray Crystallography*, 1962), was taken into account and the weighting scheme $w=525/(525+F_o^2)$ was adopted. The reflexions 002 and 121, which clearly suffered from extinction, were not considered during the refinement. In the last cycle the changes in the parameters of I, N and C atoms were smaller than 0·05 times the standard deviations as calculated by the least-squares program, those of the hydrogen atoms were smaller than 0·1 of

Table 1. *Final coordinates and isotropic temperature factors*

x,y,z are obtained from the least-squares refinement; x',y',z' are corrected for libration. For numbering of atoms see Fig. 4.

	x	y	z	B	x'	y'	z'
I	0	$\frac{1}{2}$	0				
C(1)	0·09484 (44)	0·03907 (23)	0·12225 (21)		0·09501	0·03910	0·12297
C(2)	0·19763 (51)	0·08290 (29)	0		0·19801	0·08298	0
C(3)	0·47241 (39)	0·22005 (30)	0·12391 (29)		0·47306	0·22028	0·12454
N	0·38209 (46)	0·16244 (27)	0		0·38276	0·16259	0
H(1)	0·15741 (432)	0·06443 (265)	0·20680 (261)	3·5 (5) Å^2			
H(2)	0·48628 (451)	0·15065 (468)	0·19696 (431)	6·5 (10)			
H(3)	0·62502 (616)	0·25274 (333)	0·10945 (341)	6·6 (8)			
H(4)	0·37493 (604)	0·28879 (332)	0·15338 (354)	6·4 (8)			

Table 2. *Thermal parameters of the temperature factor*

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

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
I	0·0540 (2)	0·0590 (2)	0·0515 (2)	0·0077 (3)	0	0
C(1)	0·0506 (11)	0·0449 (9)	0·0316 (8)	0·0015 (19)	−0·0017 (15)	−0·0054 (18)
C(2)	0·0399 (13)	0·0359 (12)	0·0350 (12)	0·0128 (22)	0	0
C(3)	0·0484 (14)	0·0626 (14)	0·0522 (12)	−0·0165 (21)	−0·0070 (23)	−0·0165 (20)
N	0·0393 (12)	0·0424 (12)	0·0421 (12)	0·0042 (21)	0	0

Table 3. T(Å^2) *and* ω(rad^2) *tensors and the corresponding 'calculated' thermal parameters*

p, q and r are the main axes for T; p', q' and r' those for ω. r and r' coincide with c; p and p' are obtained by rotating the x axis about c over angles of 40·03° and 40·37° respectively in the direction of y.

T_p	T_q	T_r	$\omega_p{}'$	$\omega_q{}'$	$\omega_r{}'$
0·0443	0·0276	0·0304	0·0121	0·0017	0·0015

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	0·0465	0·0463	0·0313	0·0008	−0·0002	−0·0035
C(2)	0·0384	0·0366	0·0341	0·0136	0	0
C(3)	0·0537	0·0581	0·0520	−0·0175	−0·0060	−0·0143
N	0·0413	0·0423	0·0441	0·0054	0	0

their standard deviations. The value of $\langle w(\Delta F)^2\rangle$ appeared to be approximately independent of $|F|$. The final R index is 2·27 % for the 821 reflexions.

The final parameters with the standard deviations as calculated by the least-squares program are listed in Tables 1 and 2. The final difference map in the plane of the benzene ring is shown in Fig. 3. It may be seen that there are maxima between the bonded atoms of the benzene ring. These maxima are about 5 times the standard deviation, 0·06 e.Å^{-3}, obtained by Cruickshank's (1949) method and may be ascribed to bonding effects. Apart from these maxima, the difference map

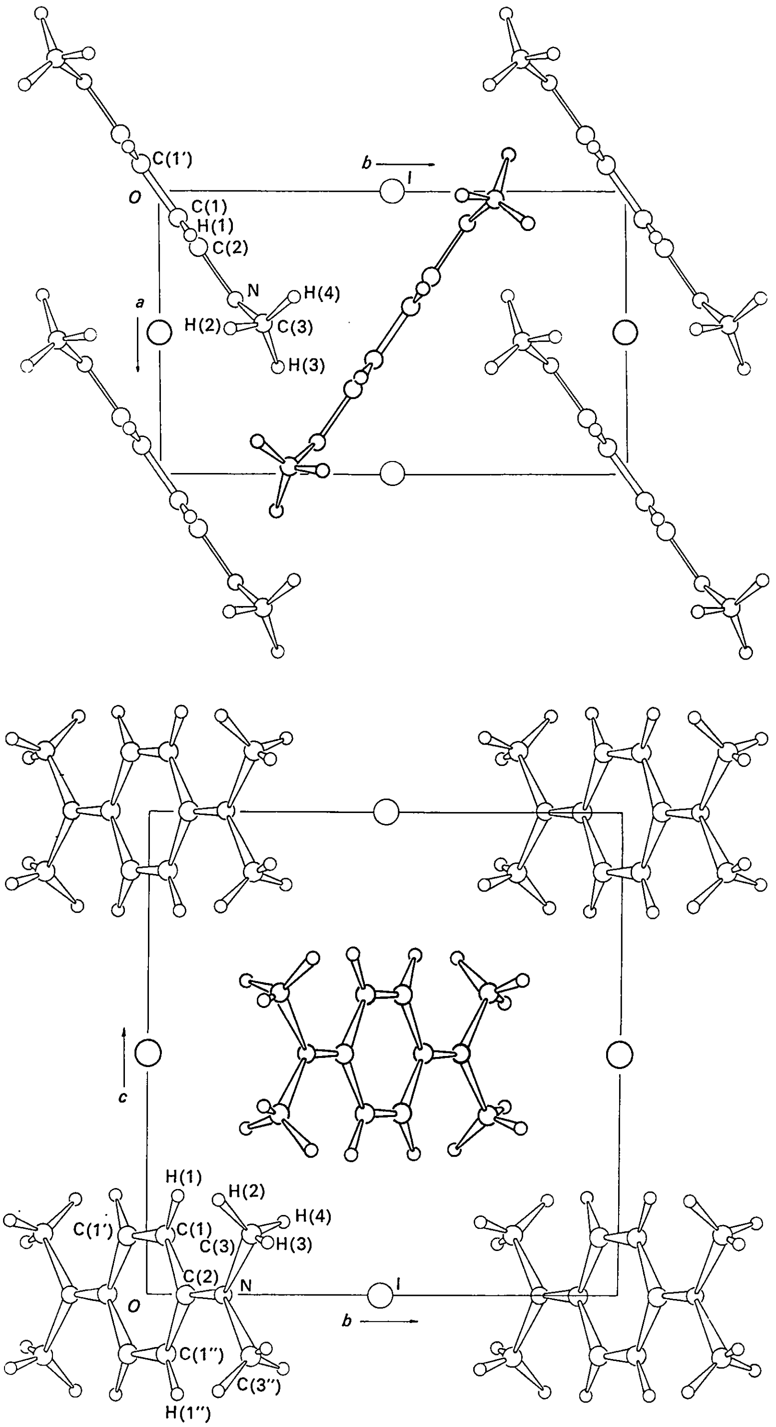

Fig. 4. Projections of the structure along [001] and [100].

shows some maxima (four times the e.s.d.) at distances of 0·8 Å from the iodine atom. The map shows negative values (up to 5 times the e.s.d.) in a region related to the position of the molecule by a translation $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. No significant features are further found in the difference map.

It is noteworthy that the final positions of the hydrogen atoms are approximately 0·96 Å from the car-

Table 4. *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	AC	BC
0	0	2	1222	1273	1272	42
0	0	4	475	472	470	37
0	0	6	668	662	662	30
0	0	8	598	609	609	23
0	0	10	279	283	282	16
0	0	12	75	77	76	10
0	0	14	75	75	75	6
0	0	16	73	73	73	3
0	1	1	306	284	-280	-43
0	1	3	858	860	-859	-40
0	1	5	579	577	-576	-34
0	1	7	246	242	-241	-26
0	1	9	121	119	-118	-19
0	1	11	146	146	-146	-12
0	1	13	89	91	-91	-8
0	2	0	823	814	813	42
0	2	2	818	825	824	40
0	2	4	699	697	696	36
0	2	6	453	453	452	29
0	2	8	316	319	318	22
0	2	10	194	195	195	15
0	2	12	90	89	88	9
0	2	14	55	52	52	5
0	2	16	46	40	40	3
0	3	1	905	927	-926	-39
0	3	3	855	862	-861	-36
0	3	5	671	652	-652	-30
0	3	7	390	390	-390	-24
0	3	9	232	235	-234	-17
0	3	11	164	164	-163	-11
0	3	13	103	101	-100	-7
0	3	15	35	39	-39	-4
0	4	0	857	867	866	36
0	4	2	525	531	530	35
0	4	4	188	200	197	31
0	4	6	293	299	298	25
0	4	8	302	302	301	19
0	4	10	129	132	132	13
0	4	12	32	31	30	8
0	5	1	482	482	-481	-32
0	5	3	623	617	-617	-30
0	5	5	502	501	-500	-25
0	5	7	240	237	-236	-20
0	5	9	149	149	-148	-14
0	5	11	137	137	-136	-9
0	5	13	83	82	-81	-6
0	6	0	437	431	430	29
0	6	2	452	456	455	27
0	6	4	404	410	409	24
0	6	6	283	285	285	20
0	6	8	173	173	172	15
0	6	10	108	109	108	10
0	6	12	68	67	67	6
0	7	1	454	447	-446	-24
0	7	3	281	279	-278	-22
0	7	5	217	219	-218	-19
0	7	7	221	224	-223	-15
0	7	9	153	156	-156	-11
0	7	11	67	65	-65	-7
0	8	0	214	220	219	20
0	8	2	241	245	244	20
0	8	4	221	220	219	17
0	8	6	150	150	149	14
0	8	8	89	88	87	11
0	8	10	60	61	61	7
0	8	12	45	44	44	5
0	9	1	260	259	-259	-16
0	9	3	232	235	-234	-15
0	9	5	191	193	-193	-13
0	9	7	130	135	-134	-10
0	9	9	95	96	-96	-7
0	9	11	63	58	-57	-5
0	10	0	129	126	125	13
0	10	2	150	151	150	13
0	10	4	152	154	154	11
0	10	6	105	105	104	9
0	10	8	52	52	51	7
0	10	10	43	40	40	5
0	10	12	40	39	39	3
0	11	1	135	136	-136	-10
0	11	3	48	45	-44	-9
0	11	7	73	71	-70	-6
0	11	9	53	54	-54	-4
0	12	0	83	82	82	8
0	12	2	120	120	119	7
0	12	4	142	143	143	7
0	12	6	79	86	85	5
0	12	8	40	36	36	4
0	12	10	35	41	41	3
0	13	1	44	45	-45	-6
0	14	0	39	38	38	4
0	14	2	45	44	44	4
0	14	4	36	49	49	4
0	15	1	36	46	-46	-3
0	15	3	32	24	-24	-3
1	0	1	734	713	711	42
1	0	3	787	779	778	39
1	0	5	534	528	527	33
1	0	7	353	352	351	26
1	0	9	239	240	240	18
1	0	11	126	128	127	12
1	0	13	59	60	60	7
1	0	15	43	42	42	4
1	1	0	723	721	-720	-42
1	1	1	306	302	-302	0
1	1	2	863	876	-875	-40
1	1	3	86	79	-79	0
1	1	4	841	825	-825	-36
1	1	5	105	92	-92	0
1	1	6	510	496	-495	-29
1	1	7	90	89	-89	0
1	1	8	252	252	-251	-22
1	1	9	53	54	-54	0
1	1	10	179	181	-180	-15
1	1	12	138	138	-138	-9
1	1	14	60	61	-61	-6
1	2	0	418	413	-413	0
1	2	1	1306	1390	1389	40
1	2	2	227	221	-221	0
1	2	3	460	458	457	37
1	2	4	133	117	-117	0
1	2	5	383	392	390	31
1	2	6	107	101	-101	0
1	2	7	501	503	502	24
1	2	8	91	94	-94	0
1	2	9	335	336	336	18
1	2	10	52	49	-49	0
1	2	11	99	106	105	12
1	2	13	41	45	45	7
1	2	15	58	58	57	4
1	3	0	288	282	-280	-38
1	3	1	211	203	-203	0
1	3	2	607	606	-605	-37
1	3	3	71	62	-62	0
1	3	4	665	661	-660	-32
1	3	5	47	46	-46	0
1	3	6	360	362	-361	-26
1	3	7	53	53	-53	0
1	3	8	163	154	-153	-20
1	3	9	56	56	-56	0
1	3	10	133	136	-135	-14
1	3	12	116	118	-118	-9
1	3	14	48	45	-45	-5
1	4	0	156	148	-148	0
1	4	1	657	641	640	35
1	4	3	620	619	618	32
1	4	4	44	39	39	0
1	4	5	483	485	484	27
1	4	7	313	307	306	21
1	4	8	41	41	-41	0
1	4	9	197	200	199	15
1	4	10	23	18	-18	0
1	4	11	115	118	117	10
1	4	13	59	62	62	6
1	5	0	687	676	-675	-32
1	5	1	49	40	-40	0
1	5	2	566	564	-563	-30
1	5	3	100	97	97	0
1	5	4	423	421	-420	-27
1	5	5	61	60	60	0
1	5	6	339	342	-341	-22
1	5	8	247	250	-250	-16
1	5	10	144	143	-143	-11
1	5	12	77	78	-78	-7
1	5	14	50	46	-46	-4
1	6	0	96	90	-90	0
1	6	1	397	402	401	27
1	6	3	292	292	291	25
1	6	4	68	66	66	0
1	6	5	215	212	211	21
1	6	7	200	199	199	17
1	6	8	34	38	-38	0
1	6	9	133	129	129	12
1	6	11	61	60	60	8
1	7	0	362	358	-358	-24
1	7	1	42	42	-42	0
1	7	2	383	375	-374	-23
1	7	3	26	34	34	0
1	7	4	377	378	-377	-20
1	7	5	32	31	31	0
1	7	6	244	246	-246	-16
1	7	8	141	140	-139	-12
1	7	10	105	107	-107	-8
1	7	12	76	72	-72	-5
1	7	14	35	35	-35	-3
1	8	0	35	35	-35	0
1	8	1	259	256	256	20
1	8	3	268	270	269	18
1	8	4	25	29	29	0
1	8	5	216	217	217	15
1	8	7	139	137	136	12
1	8	9	81	81	81	9
1	8	11	66	61	61	6
1	8	13	46	39	39	3
1	9	0	268	267	-266	-16
1	9	1	26	14	14	0
1	9	2	180	180	-179	-15
1	9	3	50	47	47	0
1	9	4	84	87	-86	-14
1	9	5	43	46	46	0
1	9	6	111	110	-109	-11
1	9	8	114	118	-117	-8
1	9	10	56	54	-54	-6
1	10	1	145	147	147	13
1	10	2	29	33	33	0
1	10	3	187	188	187	12
1	10	4	52	52	52	0
1	10	5	156	155	154	10
1	10	6	33	26	26	0
1	10	7	77	77	77	8
1	10	9	49	49	49	6
1	10	11	56	51	51	4
1	11	0	121	123	-122	-10
1	11	2	108	109	-109	-10
1	11	3	37	35	35	0
1	11	4	81	85	-85	-8
1	11	5	34	31	31	0
1	11	6	68	71	-71	-7
1	11	8	59	58	-58	-5
1	12	1	68	66	66	8
1	12	3	80	77	76	7
1	12	5	66	67	66	6
1	12	7	38	36	36	5
1	12	9	33	20	20	3
1	13	0	91	90	-90	-6
1	13	2	59	60	-59	-5
1	13	6	36	37	-37	-4
1	13	8	43	45	-45	-3
1	14	3	56	55	55	4
1	14	5	52	47	47	3
1	15	0	37	29	-29	-3
2	0	0	1068	1087	1087	39
2	0	2	659	626	625	37
2	0	4	274	288	286	33
2	0	6	379	371	370	27
2	0	8	352	341	341	20
2	0	10	161	154	153	14
2	0	12	39	44	43	9
2	0	14	33	38	37	5
2	1	0	133	134	134	0
2	1	1	708	730	-729	-38
2	1	2	85	86	86	0
2	1	3	787	790	-790	-35
2	1	4	68	57	57	0
2	1	5	597	589	-589	-30
2	1	6	72	68	68	0
2	1	7	335	335	-334	-23
2	1	9	207	211	-211	-17
2	1	11	158	156	-156	-11
2	1	13	94	91	-91	-7
2	1	15	36	36	-36	-4
2	2	0	509	502	501	37
2	2	1	10	3	-3	0
2	2	2	618	623	622	36
2	2	3	123	116	116	0
2	2	4	579	573	572	31
2	2	5	72	65	65	0
2	2	6	371	369	368	26
2	2	8	218	216	216	19
2	2	10	142	143	142	13
2	2	12	85	88	87	8
2	2	14	39	43	43	5
2	3	0	274	261	-261	1
2	3	1	679	685	-684	-35
2	3	2	17	13	-13	1
2	3	3	525	516	-515	-32
2	3	4	88	89	89	0
2	3	5	440	427	-427	-27
2	3	6	23	26	-26	0
2	3	7	304	307	-306	-21
2	3	8	73	78	-78	0
2	3	9	190	197	-196	-15
2	3	11	111	112	-112	-10
2	3	12	29	22	22	0
2	3	13	66	63	-63	-6
2	3	15	39	32	-31	-3
2	4	0	723	725	725	32
2	4	1	279	267	-267	-1
2	4	2	564	568	567	31
2	4	3	32	30	-30	-1
2	4	4	346	352	351	27
2	4	5	28	27	-27	-1
2	4	6	324	331	330	22
2	4	7	101	107	-107	0
2	4	8	282	279	279	17
2	4	9	83	89	-89	0
2	4	10	142	146	145	11
2	4	12	66	62	62	7
2	4	14	41	43	43	4
2	5	0	224	218	-218	1
2	5	1	333	332	-330	-29
2	5	2	94	87	-87	1
2	5	3	435	436	-435	-26
2	5	5	341	340	-339	-22
2	5	6	39	41	-41	1
2	5	7	166	168	-167	-17
2	5	8	80	79	-79	0
2	5	9	111	103	-102	-12
2	5	10	32	35	-35	0
2	5	11	91	89	-89	-8
2	5	13	49	50	-50	-5
2	6	0	433	428	427	25
2	6	1	89	89	-89	-1
2	6	2	412	413	412	24
2	6	3	31	30	30	-1
2	6	4	372	381	381	21
2	6	5	24	24	24	-1
2	6	6	270	273	272	17
2	6	7	40	37	-37	0
2	6	8	168	171	171	13
2	6	9	37	41	-41	0
2	6	10	114	115	115	9
2	6	12	72	74	74	6
2	6	14	45	41	41	3
2	7	0	28	22	-22	1
2	7	1	328	326	-326	-21
2	7	2	64	64	64	1
2	7	3	209	207	-206	-20
2	7	4	128	128	128	1
2	7	5	155	153	-152	-17
2	7	6	44	47	47	1
2	7	7	162	165	-164	-13
2	7	9	111	108	-107	-9
2	7	11	41	42	-42	-6
2	7	12	31	39	39	0
2	8	0	254	258	258	18
2	8	2	245	247	246	17
2	8	3	96	96	96	-1
2	8	4	220	218	218	15
2	8	5	86	86	86	-1
2	8	6	159	159	159	12
2	8	8	107	107	107	9
2	8	10	70	74	73	6
2	8	12	46	46	46	4
2	8	13	33	26	26	0
2	9	1	175	173	-172	-15
2	9	2	35	35	35	1
2	9	3	187	189	-189	-13
2	9	4	71	70	70	1
2	9	5	154	154	-153	-11
2	9	6	30	28	28	0
2	9	7	94	93	-93	-9
2	9	9	67	61	-61	-6
2	9	11	45	45	-45	-4
2	10	0	127	127	126	12
2	10	2	118	122	121	11
2	10	4	108	107	106	10
2	10	6	84	81	81	8
2	10	8	53	53	52	6
2	10	9	26	11	-11	0
2	11	0	28	17	-17	1
2	11	1	135	141	-140	-9
2	11	3	88	88	-88	-8
2	11	5	70	70	-70	-7
2	11	7	78	79	-78	-5
2	11	9	57	58	-58	-4
2	12	0	39	41	40	7
2	12	2	60	58	58	7
2	12	4	70	68	67	6
2	12	6	42	38	38	5
2	13	1	61	63	-62	-5
2	13	3	57	55	-55	-5
2	13	4	30	9	9	0
2	13	5	52	47	-46	-4
2	13	7	40	38	-38	-3
2	14	2	31	30	30	4
3	0	1	442	447	446	33
3	0	3	626	620	619	30
3	0	5	459	456	455	26
3	0	7	238	238	237	20
3	0	9	127	127	127	14
3	0	11	120	117	116	10
3	0	13	69	72	72	6
3	1	0	709	717	-717	-33
3	1	1	139	137	-137	0
3	1	2	553	546	-545	-32
3	1	3	43	43	43	0
3	1	4	434	429	-428	-28
3	1	5	17	15	15	0
3	1	6	344	346	-345	-23
3	1	7	53	58	-58	0
3	1	8	247	256	-256	-17
3	1	9	33	33	-33	0
3	1	10	148	154	-153	-12
3	1	12	75	75	-74	-7
3	1	14	41	44	-44	-4
3	2	0	155	148	-148	0
3	2	1	515	525	524	32
3	2	2	40	39	-39	0
3	2	3	377	383	382	29
3	2	4	36	38	38	0
3	2	5	285	287	286	25
3	2	7	260	258	257	19
3	2	8	48	51	-51	0
3	2	9	165	163	163	14
3	2	11	76	77	77	9
3	2	13	40	42	41	6
3	3	0	511	503	-502	-30
3	3	1	21	19	19	1
3	3	2	528	535	-534	-29
3	3	3	56	58	58	1
3	3	4	466	471	-471	-25
3	3	5	64	59	59	1
3	3	6	311	319	-318	-21
3	3	8	200	205	-204	-15
3	3	10	135	138	-137	-11
3	3	11	24	17	17	0
3	3	12	82	83	-83	-7
3	3	14	41	42	-42	-4
3	4	1	379	382	381	27
3	4	2	63	64	64	-1
3	4	3	409	419	418	25
3	4	4	111	109	109	-1
3	4	5	342	349	348	21
3	4	6	44	49	49	-1
3	4	7	193	193	193	17
3	4	9	116	118	118	12
3	4	11	92	93	93	8
3	4	13	65	58	58	5
3	5	0	395	404	-403	-25
3	5	1	20	10	-10	1
3	5	2	308	310	-309	-24
3	5	3	147	147	147	1
3	5	4	195	193	-192	-21
3	5	5	120	122	122	1
3	5	6	185	189	-189	-17
3	5	8	160	160	-160	-13
3	5	10	78	81	-80	-9
3	5	11	42	41	41	0
3	5	13	37	33	33	0
3	6	0	127	126	-126	-1
3	6	1	398	403	403	22
3	6	3	329	333	333	20
3	6	4	84	85	85	-1
3	6	5	257	265	265	17
3	6	7	204	206	205	13
3	6	8	63	63	-63	-1
3	6	9	143	143	143	9
3	6	11	77	83	83	6
3	6	13	50	47	47	4
3	7	0	145	145	-144	-19
3	7	1	69	71	-71	1
3	7	2	191	196	-195	-18
3	7	4	204	208	-207	-16
3	7	6	125	126	-125	-13
3	7	7	39	40	-40	1
3	7	8	61	59	-58	-10
3	7	9	33	36	-36	0
3	7	10	52	47	-47	-7
3	8	0	88	92	-92	-1
3	8	1	213	217	217	15
3	8	2	56	59	-59	-1
3	8	3	181	183	182	14
3	8	5	152	152	152	12
3	8	6	32	34	-34	-1
3	8	7	116	115	115	9
3	8	8	49	49	-49	-1
3	8	9	72	78	78	7
3	8	11	49	46	46	4
3	8	13	38	27	27	3
3	9	0	190	194	-194	-13
3	9	1	39	39	-39	1
3	9	2	162	166	-165	-12
3	9	4	119	118	-117	-11
3	9	6	107	106	-106	-9
3	9	8	90	87	-87	-7
3	9	10	53	50	-50	-4
3	10	0	42	44	-44	-1
3	10	1	94	96	96	10
3	10	3	91	89	88	9
3	10	4	26	28	28	-1
3	10	5	70	71	71	8
3	10	7	49	49	48	6
3	10	9	32	35	35	4
3	11	0	78	77	-77	-8
3	11	2	93	93	-93	-8
3	11	3	32	27	27	1
3	11	4	102	99	-99	-7
3	11	6	69	67	-67	-5
3	12	1	71	67	66	6
3	12	3	40	42	42	5
3	12	5	36	33	32	5
3	12	6	27	0	0	0
3	12	7	44	36	36	4
3	13	0	49	51	-51	-4
3	13	2	46	47	-47	-4
3	13	4	43	41	-41	-4
3	13	6	30	33	-33	-3
3	13	8	37	24	-24	-2
4	0	0	346	350	349	27
4	0	2	347	346	345	26
4	0	4	293	296	295	23
4	0	6	218	218	217	19
4	0	8	143	142	141	14
4	0	10	94	90	90	10
4	0	12	61	61	60	6
4	1	0	106	106	106	0
4	1	1	484	483	-482	-26
4	1	2	39	35	35	0
4	1	3	358	354	-354	-24
4	1	5	273	273	-273	-21
4	1	6	33	33	33	0
4	1	7	234	236	-236	-16
4	1	8	31	38	38	0
4	1	9	160	166	-166	-12
4	1	11	71	75	-75	-8
4	1	13	40	34	-34	-5
4	2	0	302	303	302	26
4	2	1	47	44	44	-1
4	2	2	403	410	409	25
4	2	3	47	46	46	0
4	2	4	443	445	444	22
4	2	5	49	51	51	0
4	2	6	268	272	271	18
4	2	8	116	117	116	13
4	2	10	101	100	99	9
4	2	12	95	94	94	6
4	2	14	44	43	42	3
4	3	0	27	27	-27	1
4	3	1	371	372	-371	-24
4	3	2	57	55	55	1
4	3	3	207	203	-202	-22
4	3	4	133	132	132	1
4	3	5	168	165	-164	-19
4	3	6	35	40	40	1
4	3	7	184	182	-182	-15
4	3	9	127	129	-129	-10
4	3	11	48	45	-44	-7
4	3	12	39	36	36	0
4	4	0	346	349	349	22
4	4	1	40	36	-36	-1
4	4	2	332	337	336	21
4	4	3	68	67	67	-1
4	4	4	274	278	277	19
4	4	5	56	59	59	-1
4	4	6	205	208	207	15
4	4	8	144	144	144	12
4	4	10	90	92	92	8
4	4	12	52	57	56	5
4	4	14	40	30	30	3
4	5	1	281	285	-284	-20
4	5	3	289	296	-296	-18
4	5	4	45	42	41	1
4	5	5	241	234	-234	-15
4	5	7	155	152	-152	-12
4	5	9	102	100	-100	-9
4	5	11	68	69	-69	-6
4	6	0	177	175	174	18
4	6	1	24	23	-23	-1
4	6	2	167	170	169	17
4	6	4	161	162	162	15
4	6	6	115	115	115	12
4	6	8	62	67	67	9
4	6	10	49	45	44	6
4	7	0	42	45	-45	1
4	7	1	243	241	-241	-15
4	7	3	179	181	-180	-14
4	7	4	44	47	47	1
4	7	5	143	141	-140	-12
4	7	7	128	129	-128	-9
4	7	9	94	88	-88	-7
4	7	11	51	47	-46	-4
4	8	0	174	175	174	13
4	8	1	68	68	-68	-1
4	8	2	153	154	153	12
4	8	4	122	123	123	11
4	8	6	97	99	98	9
4	8	7	42	43	-43	-1
4	8	8	77	78	77	6
4	8	9	31	31	-31	0
4	8	10	46	50	50	4
4	9	0	39	32	-32	1
4	9	1	65	63	-63	-10
4	9	3	109	106	-105	-9
4	9	5	90	90	-89	-8
4	9	7	33	35	-35	-6
4	10	0	133	136	136	8
4	10	2	101	106	105	8
4	10	3	32	29	-29	-1
4	10	4	65	69	68	7
4	10	6	74	70	70	6
4	10	8	65	67	67	4
4	10	10	45	37	37	3
4	11	1	64	60	-60	-6
4	11	3	66	63	-62	-6
4	11	5	52	52	-52	-5
4	11	7	37	32	-32	-4
4	12	0	48	47	47	5
4	12	2	43	40	39	5
4	12	4	37	28	27	4
4	13	3	48	46	-45	-3
4	13	5	41	41	-41	-3
4	14	0	46	38	38	3
5	0	1	292	287	286	20
5	0	3	403	401	400	19
5	0	5	333	337	337	16
5	0	7	157	156	156	12
5	0	9	88	88	88	9
5	0	11	105	102	102	6
5	0	13	76	73	73	4
5	1	0	302	308	-307	-20
5	1	2	217	216	-215	-19
5	1	3	63	61	61	0
5	1	4	114	112	-111	-17
5	1	5	49	49	49	0
5	1	6	129	128	-127	-14
5	1	8	131	132	-132	-10
5	1	10	60	61	-60	-7
5	2	1	252	254	253	19
5	2	2	20	17	17	0
5	2	3	257	256	256	18
5	2	5	207	207	206	15
5	2	7	126	127	127	12
5	2	9	88	84	84	8
5	2	11	71	67	67	6
5	2	13	39	41	41	3
5	3	0	304	306	-306	-18
5	3	1	45	43	43	1
5	3	2	270	277	-276	-18
5	3	4	208	212	-212	-16
5	3	6	174	175	-175	-13
5	3	8	138	139	-138	-10
5	3	10	76	81	-81	-7
5	3	12	41	38	-38	-4
5	4	1	148	147	146	17
5	4	2	29	29	-29	-1
5	4	3	190	195	194	15
5	4	4	41	34	-34	-1
5	4	5	164	167	166	13
5	4	7	72	76	76	10
5	4	9	42	40	39	7
5	4	11	45	45	44	5
5	5	0	252	260	-259	-15
5	5	1	24	25	-25	1
5	5	2	199	202	-201	-15
5	5	4	130	132	-131	-13
5	5	6	132	128	-128	-11
5	5	8	115	118	-117	-8
5	5	10	67	66	-65	-5
5	6	0	39	46	-46	-1
5	6	1	161	162	162	13
5	6	3	141	145	145	12
5	6	5	112	112	112	10
5	6	7	82	83	82	8
5	6	9	56	57	57	6
5	6	11	38	35	35	4
5	7	0	115	116	-115	-11
5	7	1	25	29	29	1
5	7	2	134	134	-134	-11
5	7	3	25	20	20	1
5	7	4	143	142	-142	-10
5	7	6	92	96	-96	-8
5	7	8	55	51	-51	-6
5	7	10	41	40	-40	-4
5	8	1	103	102	101	9
5	8	3	68	71	70	9
5	8	5	58	56	55	7
5	8	7	57	55	55	6
5	8	9	41	38	38	4
5	9	0	96	99	-99	-8
5	9	2	97	97	-97	-8
5	9	4	93	87	-86	-7
5	9	6	65	65	-65	-5
5	9	8	39	44	-44	-4
5	9	10	41	32	-32	-3
5	10	1	69	72	71	6
5	10	3	49	52	51	6
5	10	5	40	40	40	5
5	10	7	38	41	40	4
5	11	4	55	47	-47	-4
5	12	1	68	70	70	4
5	12	3	34	38	38	3
5	12	5	38	30	30	3
6	0	0	174	174	174	15
6	0	2	177	177	176	14
6	0	4	171	170	169	12
6	0	6	113	114	113	10
6	0	8	69	68	68	8
6	0	10	58	57	56	5
6	0	12	48	42	42	3
6	1	1	195	198	-198	-14
6	1	2	40	38	-38	0
6	1	3	137	136	-135	-13
6	1	4	68	71	-71	0
6	1	5	108	103	-102	-11
6	1	6	33	26	-26	0
6	1	7	111	109	-108	-9
6	1	9	78	75	-75	-6
6	2	0	129	130	129	14
6	2	1	35	40	-40	0
6	2	2	170	171	170	13
6	2	3	67	67	-67	0
6	2	4	197	199	199	12
6	2	5	53	55	-55	0
6	2	6	121	124	123	10
6	2	8	53	51	50	7
6	2	10	51	47	47	5
6	2	12	48	49	49	3
6	3	0	41	40	-40	1
6	3	1	178	181	-180	-13
6	3	2	28	19	-19	1
6	3	3	108	108	-107	-12
6	3	5	81	82	-81	-10
6	3	7	95	96	-96	-8
6	3	8	28	21	-21	0
6	3	9	73	71	-71	-6
6	4	0	136	137	137	12
6	4	2	139	141	141	12
6	4	4	128	127	126	10
6	4	6	89	88	88	8
6	4	8	60	58	58	6
6	4	10	41	44	44	4
6	5	0	57	58	58	1
6	5	1	131	131	-131	-11
6	5	2	29	23	23	1
6	5	3	122	124	-124	-10
6	5	5	107	105	-105	-8
6	5	7	77	75	-75	-7
6	5	9	47	49	-49	-5
6	5	11	36	31	-31	-3
6	6	0	88	89	88	10
6	6	2	87	89	88	9
6	6	4	78	80	80	8
6	6	5	28	23	-23	-1
6	6	6	59	61	61	7
6	6	8	39	39	38	5
6	7	0	24	8	8	1
6	7	1	107	107	-107	-8
6	7	3	85	85	-85	-7
6	7	5	66	68	-68	-6
6	7	7	63	58	-58	-5
6	7	9	39	44	-44	-4
6	8	0	72	73	72	7
6	8	2	69	67	67	7
6	8	4	55	53	52	6
6	8	6	44	43	42	5
6	9	1	46	43	-43	-6
6	9	3	63	61	-61	-5
6	9	5	56	55	-55	-4
6	10	0	64	62	62	4
6	10	2	42	44	44	4
6	10	4	36	23	23	4
6	10	6	33	29	29	3
6	11	1	39	27	-27	-3
6	11	3	38	35	-35	-3
6	12	0	31	32	32	3
7	0	1	71	66	65	10
7	0	3	94	92	91	9
7	0	5	81	80	80	8
7	0	7	41	35	35	6
7	1	0	140	146	-146	-10
7	1	2	121	124	-123	-9
7	1	3	34	27	27	0
7	1	4	91	90	-89	-8
7	1	6	84	83	-83	-7
7	1	8	71	72	-72	-5
7	1	10	35	41	-41	-3
7	2	1	96	100	100	9
7	2	3	96	96	96	9
7	2	5	72	75	75	7
7	2	7	48	49	49	6
7	2	9	45	38	38	4
7	3	0	87	90	-90	-9
7	3	2	85	83	-82	-9
7	3	3	30	30	-30	0
7	3	4	66	69	-68	-8
7	3	5	33	29	-29	0
7	3	6	61	58	-58	-6
7	3	8	42	42	-42	-5
7	4	1	90	93	92	8
7	4	2	31	30	-30	-1
7	4	3	96	98	98	7
7	4	4	52	57	-57	-1
7	4	5	84	85	85	6
7	4	7	52	55	54	5
7	4	9	39	34	34	4
7	5	0	84	83	-83	-7
7	5	2	64	67	-67	-7
7	5	4	38	45	-45	-6
7	5	6	47	41	-41	-5
7	6	1	71	70	69	6
7	6	3	68	67	67	6
7	6	5	55	54	53	5
7	6	7	41	38	38	4
7	6	9	34	29	29	3
7	7	0	44	46	-46	-6
7	7	1	38	34	34	1
7	7	2	49	49	-49	-5
7	7	4	48	50	-50	-5
7	8	1	59	54	54	5
7	8	3	42	41	41	4
7	9	2	32	33	-33	-4
7	9	4	32	29	-29	-3
8	0	0	76	72	72	6
8	0	2	65	66	66	6
8	0	4	58	51	51	5
8	0	6	42	38	38	4
8	0	8	37	33	33	3
8	1	0	29	24	24	0
8	1	1	61	64	-64	-6
8	1	3	67	61	-61	-6
8	1	5	52	53	-52	-5
8	1	7	41	39	-38	-4
8	2	0	48	47	46	6
8	2	2	47	45	45	6
8	2	4	42	41	41	5
8	2	6	38	33	33	4
8	3	1	80	73	-72	-6
8	3	3	64	62	-62	-5
8	3	5	48	51	-51	-4
8	3	7	40	42	-42	-3
8	4	0	49	50	50	5
8	4	2	58	48	48	5
8	4	4	42	40	40	4
8	5	3	37	32	-31	-4
8	6	0	62	61	61	4
8	6	2	53	56	56	4
8	6	4	55	48	48	3
9	1	2	32	37	-37	-4
9	1	4	42	38	-38	-3
9	2	1	40	42	42	4
9	4	1	44	35	34	3
9	5	2	38	30	-30	-3

bon atoms to which they are attached, whereas visual inspection of the difference map of the low angle reflexions (see contour lines of H(1) in Fig. 1) suggests that the hydrogen atom H(1) lies close to its expected position at 1·08 Å from C(1). The shifts of the hydrogen atoms towards the carbon atoms during the least-squares refinement were assumed to be due to bonding effects being more pronounced when high order reflexions are taken into account. Attempts to determine the positions of the hydrogen atoms from the difference map of the low order reflexions failed, however, as their maxima are very flat. Least-squares refinement of the reflexions with $\sin \theta/\lambda < 0·4$ Å^{-1} with fixed parameters for I, N and C, again gave C–H distances of about 0·96 Å. The final parameters of the least-squares refinement with the 821 reflexions were therefore taken as the best parameters for the hydrogen atoms.

To check whether the TMPD molecule may be regarded as a rigid body, the thermal parameters of the C and N atoms were analysed according to Cruickshank's (1956) method. The values of T and ω are given in Table 3. Comparison of the 'experimental' and 'calculated' thermal parameters (Tables 2 and 3 respectively) shows that the rigid body assumption is not strictly true for our molecule. Therefore only approximate corrections for libration effects (Cruickshank, 1961*a*) could be obtained. The corrected coordinates are listed in Table 1. The further discussion is based on the uncorrected values. Use of the corrected values would have increased the bond lengths by 0·002 to 0·007 Å.

At the end of the structure refinement, the 174 reflexions which were above the threshold weight in only one of the two sets of measurements, were considered. As F_o, the average F value of hkl and $hk\bar{l}$ was taken, negative net intensities being considered as zero. The atomic shifts caused by inclusion of the 174 reflexions in the least-squares refinement were largest for C(1) and such that the length of the central bond of the benzene ring increases with 0·007 Å. For the remaining atoms the shifts are very small. From the standard deviations calculated by the least-squares program it appeared that the parameters of this refinement are less accurate than the final parameters in Tables 1 and 2, they were therefore not considered further.

The observed and calculated structure factors, as based on the parameters of Tables 1 (x,y,z) and 2, are listed in Table 4.

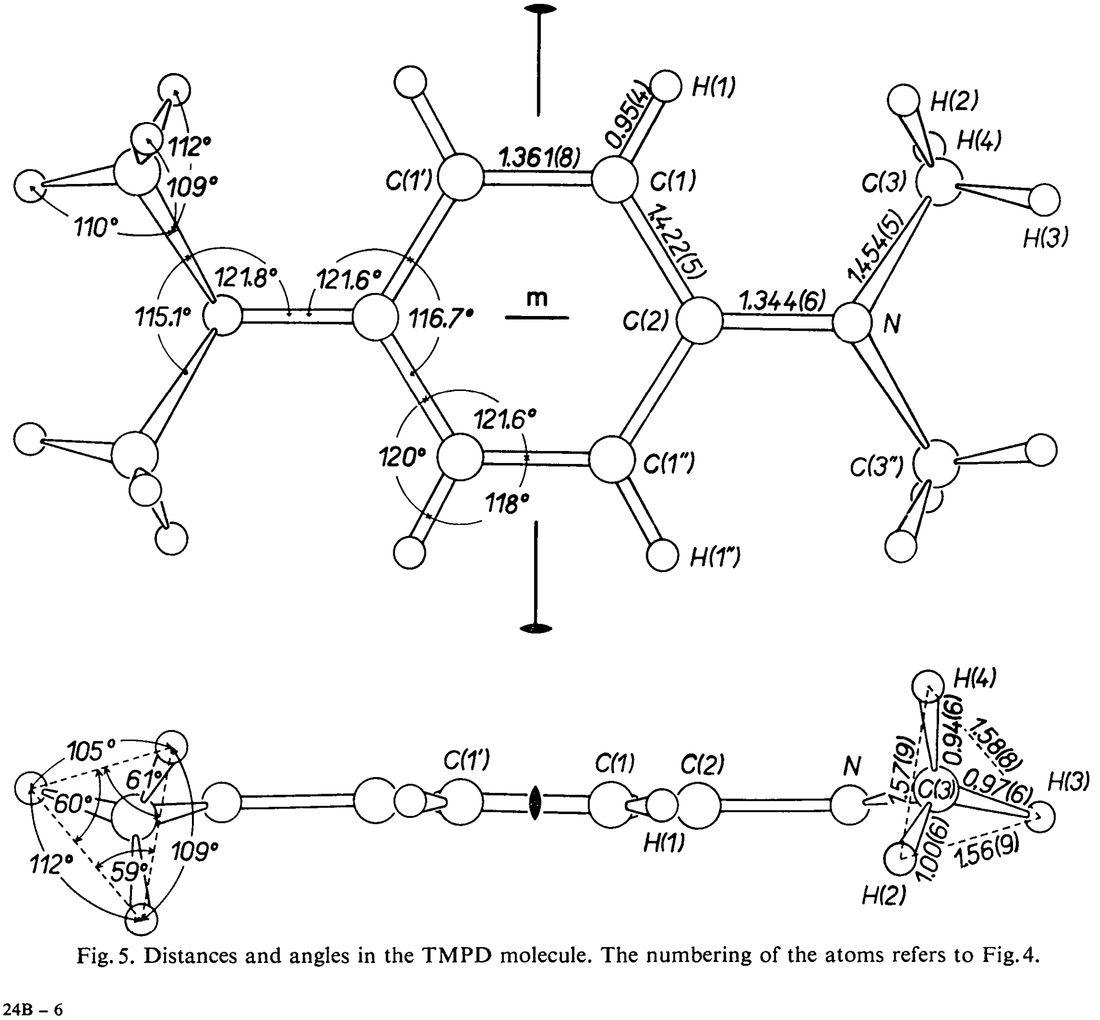

Fig. 5. Distances and angles in the TMPD molecule. The numbering of the atoms refers to Fig. 4.

Discussion of the structure

Projections of the structure along the [001] and [100] axes are shown in Fig. 4. The shortest intermolecular distances are given in Table 5. It appears that none of the intermolecular contacts is shorter than expected from the van der Waals radii (2·15, 1·7, 1·5 and 1·0 Å for I, C, N and H respectively (Nyburg, 1961)).

Table 5. *Intermolecular distances*

Only distances exceeding the sum of the van der Waals radii by less than 0·5 Å are given. For numbering of atoms see Fig. 4; C(3), *r* means C(3) at $1-x, -y, z$; C(1″), *n* means C(1″) at $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; *etc.*

I($0\frac{1}{2}0$)···C(2)	4·274 Å	C(1)···C(3), *r*	3·617 Å
I($0\frac{1}{2}0$)···N	4·023	C(1)···H(2), *r*	3·192
I($0\frac{1}{2}0$)···C(3)	4·115	C(2)···C(3), *r*	3·773
I($0\frac{1}{2}0$)···H(4)	3·400	C(2)···N, *r*	3·469
I($\frac{1}{2}0\frac{1}{2}$)···H(1)	3·598	N·····N, *r*	3·493
I($\frac{1}{2}0\frac{1}{2}$)···C(3)	4·312	C(3)···C(1″), *n*	3·532
I($\frac{1}{2}0\frac{1}{2}$)···H(2)	3·349	C(3)···H(1″), *n*	2·919

The TMPD molecule with bond lengths and angles is shown in Fig. 5; the standard deviations in the bond lengths are given in parentheses. The standard deviations in angles involving H atoms range from 2·6° to 5·0°, those of the remaining angles are 0·4° on the average. In calculating the standard deviations in the bond lengths and angles, the s.d. in the coordinates (Table 1), which are lower estimates, were multiplied by 1·6. The benzene ring is planar within experimental error, the atoms C(1) and C(2) lie only at distances of 0·005 and 0·002 Å respectively from the best plane through the ring. The C(2)–N bond and the N–C(3)–C(3″) plane are bent away from the benzene plane by 0·83° and 11·88° respectively.

Although, strictly speaking, the molecule is not a rigid body, a good impression of its thermal movement could be obtained. From the following data it appears that the translation and rotation are largest along axes which almost coincide with the direction in which the molecule is elongated most. The plane of the benzene ring makes an angle of 34·8° with the *a* axis, whereas the angle between the plane N–C(3)–C(3″) and the *a* axis is 46·7°. The main axes *p* and *p′* for which the components of **T** and **ω** are largest make angles of 40·0° and 40·4° respectively with the *a* axis. T_p is about 1·5 times the remaining *T* components, which are nearly equal, $\omega_{p'}$ exceeds the average values of the remaining ω components by as much as a factor 7·5.

The C–C bond lengths in the TMPD unit in Wurster's blue iodide, C(1′)–C(1) 1·361, C(1)–C(2) 1·422 Å, may be compared with the lengths obtained by theoretical calculations for the neutral TMPD molecule and the positive TMPD⁺ ion, 1·388 and 1·402 Å respectively for TMPD⁰ and 1·370 and 1·420 Å respectively for TMPD⁺. The π-bond orders *p* were calculated by the PPP method (Monkhorst & Kommandeur, 1967); to obtain the bond lengths *d* the equation $d = 1{\cdot}51 - 0{\cdot}18p$ was used. There appears to be good agreement between the experimental values and those calculated for the TMPD⁺ ion. As expected, TMPD iodide is thus TMPD⁺I⁻.

In Fig. 6 the TMPD⁺ ion is compared with the TMPD unit in TMPD chloranil, as recently determined by some of the authors (de Boer & Vos, 1968). The X-ray work on the latter compound indicates that the majority of the molecules is neutral although the presence of some 20% of doubly charged units, as required by spectral measurements (Pott, 1966), could not be excluded. The figure clearly shows that the TMPD⁺ ion in TMPD iodide has a more pronounced quinoid character than the 'neutral' TMPD unit in TMPD chloranil. In both TMPD units the bonds N–CH_3 are considerably longer than the bonds N–C_6H_4 which have a partial double bond character. The difference in length between the N–C_6H_4 bonds of the two molecules is in qualitative agreement with the calculated π bond orders, 0·417 for TMPD⁰ and 0·589 for TMPD⁺. The 'single' N–CH_3 bonds are, on the average, somewhat shorter than the value 1·47 Å quoted in *International Tables for X-ray Crystallography* (1962) for a single N–C(sp^3) bond.

Consideration of the bond angles in the TMPD units shows that the angles have a tendency to increase with increasing double bond character of the adjacent bonds. A similar behaviour has been observed in other compounds (Gillespie & Nyholm, 1957).

The authors thank Dr J. Honzl for preparation of the authentic material, Mr H. Zoer for growing the crystals and for the careful description of the crystal bounding planes, Mr J. Ludwig for the determination

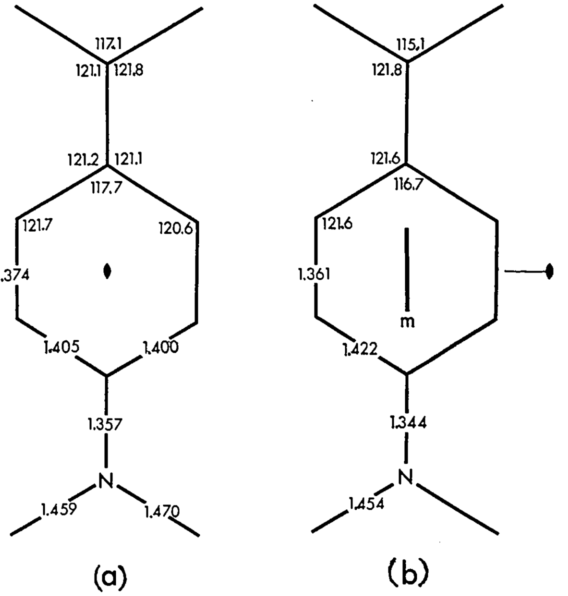

Fig. 6. Comparison of TMPD in TMPD chloranil (*a*) with TMPD⁺ in TMPD iodide (*b*). TMPD in TMPD chloranil is planar because of its special position in the unit cell.

of the cell constants and Drs R. Olthof-Hazekamp for writing and modifying many of the programs used. We are indebted to Dr K. Toman, Dr B. Sedlaček and Prof. E. H. Wiebenga for their interest in this work. We thank the staff of the Computing Centre of the University, Groningen, for their cordial cooperation.

References

BOER, J. L. DE & VOS, A. (1968). *Acta Cryst.* To be published.

BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.

CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.

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

CRUICKSHANK, D. W. J. (1961*a*). *Acta Cryst.* **14**, 896.

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

GILLESPIE, R. J. & NYHOLM, R. S. (1957). *Quart. Rev. Chem. Soc. Lond.* **11**, 339.

International Tables for X-Ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

MONKHORST, H. J. & KOMMANDEUR, J. (1967). *J. Chem. Phys.* **47**, 391.

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

NYBURG, J. C. (1961). In *X-Ray Analysis of Organic Structures.* New York, London; Academic Press.

POTT, G. J. (1966). Thesis, Groningen.

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. (1968). B **24**, 549

Hydrogen Bond Studies. XVII.* The Crystal Structure of Dimethylammonium Chloride

BY JAN LINDGREN AND IVAR OLOVSSON

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

(*Received* 11 *May* 1967)

The crystal structure of dimethylammonium chloride, $(CH_3)_2NH_2Cl$, has been determined from three-dimensional single-crystal X-ray data obtained at room temperature. The crystals are orthorhombic, space group *Ibam*, with eight formula units in the cell of dimensions $a = 7{\cdot}301$, $b = 14{\cdot}515$, $c = 9{\cdot}926$ Å. The structure contains infinite planar chains of chlorine and nitrogen atoms linked together by hydrogen bonds of lengths 3·12 and 3·09 Å. The dimethylammonium and chloride ions form a distorted NaCl-type structure.

Introduction

In conjunction with the study of simple hydrogen-bonded structures in progress at this Institute an investigation of the changes in the N–H···Cl bond lengths accompanying replacement of hydrogen in ammonium by methyl groups is of considerable interest. The crystal structure of monomethylammonium chloride was studied by X-ray diffraction technique by Hughes & Lipscomb (1946).

In the present investigation the crystal structure of dimethylammonium chloride has been determined from single-crystal X-ray diffraction data obtained at 20°C.

Experimental

The sample used was commercial dimethylammonium chloride. The salt was recrystallized three times from chloroform, and dried in a vacuum desiccator as described by Whitlow & Felsing (1944). The crystals had to be handled in a dry-box as they were highly hygroscopic. In the first attempts powder samples were sealed in glass capillaries and single crystals were grown by a zone-melting technique, the growth of the crystals being followed with a polarizing microscope. The melting point was found to agree with that earlier published, 167°C (Hunter & Byrkit, 1932). Most of the crystals thus obtained had their crystallographic axes orientated at an angle of 45° to the capillary axis. It proved very difficult to obtain a crystal with suitable orientation. Weissenberg photographs demonstrated that the crystals were probably twinned; furthermore the X-ray reflexions became unusually diffuse on passing from lower to higher layers. Owing to these difficulties crystals grown from solution were tried instead. Plate-like crystals were obtained with chloroform alone as a solvent, but from a solution with equal amounts of chloroform and ethyl alcohol needle-like crystals with a nearly circular cross-section were obtained. One of these with a diameter of 0·15 mm and a length of approximately 2 mm was chosen and sealed in a thin-walled glass capillary. An appropriate crystallographic axis was thus obtained parallel to the capillary axis. With this, the *a* axis, as rotation axis, equi-inclination Weissenberg photographs, layers $0 \le h \le 6$, were recorded with Ni-filtered Cu $K\alpha$ radiation. It was now clear that the previous crystal, grown by the zone-melting procedure, was indeed a twin

---

* Part XVI: *Acta Cryst.* (1967), **23**, 971.