Zhdanov sequence is even) as well as the cubic (∞) structure will be generated in this way. The 'parent polytype' could thus be formed from the $2H$ structure.

All the above considerations deal only with the geometrical framework of polytypism in ZnS crystals. Further experiments are in progress in order to ascertain the physical mechanism underlying the slip process.

Actually it seems that all polytypes in vapour-phase grown crystals are even*. In this Laboratory, altogether about 35 polytypes were found, with 21 different layer periodicities, all being even. The literature on polytypes in vapour-phase grown ZnS seems also to confirm this rule, except for a very early publication (Strock & Brophy, 1955) on a single extremely small specimen (0·1 × 0·01 mm) which was reported to include altogether nine structures.

Direct observations in this Laboratory (to be published) revealed that the hexagonal $2H$ structure can actually be transformed to polytypes, and that this transformation takes place by the periodic slip process. The overall route of polytype formation is therefore probably the following: hexagonal – parent polytype – polytype family.

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* Uneven polytypes $9R$, $15R$ and $21R$ were found in ZnS minerals. A $27L$ polytype reported by two of us (O.B. & I.T.S.) was later found to be a $26L$ (17 4 2 3) polytype.

References

Brafman, O., Alexander, E. & Steinberger, I. T. (1967). *Acta Cryst.* **22**, 347.

Brafman, O. & Steinberger, I. T. (1966). *Phys. Rev.* **143**, 501.

Farkas-Jahnke, M. (1965). *Acta Cryst.* **18**, 571.

Krishna, P. & Verma, A. R. (1965). *Z. Kristallogr.* **121**, 36.

Mardix, S., Brafman, O. & Steinberger, I. T. (1967). *Acta Cryst.* **22**, 000.

Mardix, S. & Steinberger, I. T. (1966). *Israel J. Chem.* **3**, 243.

Strock, W. & Brophy, V. A. (1955). *Amer. Min.* **40**, 94.

Verma, A. R. & Krishna, P. (1966). *Polymorphism and Polytypism in Crystals.* New York: John Wiley.

Acta Cryst. (1967). **22**, 812

Reinvestigation of the Crystal Structure of Ammonium Bromochloroiodate(I), NH_4BrICl, at 140° K

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(*Received* 5 *September* 1966)

Reinvestigation of the crystal structure of NH_4BrICl at 140°K shows that the $(BrICl)^-$ ions are statistically distributed in the crystal. Owing to this disorder no accurate values could be obtained for the bond lengths. The discussion of the observed average structure indicates, however, that for $(BrICl)^-$ ions with an orientation as reported earlier by Mooney, the I–Cl bond is much longer (*ca.* 0·5 Å) than the value which Mooney observed (2·38 Å). The I–Br distance is comparable to Mooney's value, 2·50 Å.

Description of the structure

As part of a programme to obtain accurate values for bond lengths and angles in polyhalide ions consisting of different halogen atoms ($KICl_4 . H_2O$, Elema, de Boer & Vos, 1963; $N(CH_3)_4ICl_2$, Visser & Vos, 1964), the structure of NH_4BrICl (Mooney, 1937) was reinvestigated at 140°K.

The structure as reported by Mooney is shown in Fig. 1. The present refinement shows that accurate values for the bond lengths and angles cannot be obtained because of disorder in the crystals. The discussion given in the present paper indicates, however, that for the $(Br–I–Cl)^-$ ion shown in Fig. 1, the I–Cl bond is much longer, approximately 0·5 Å, than the value observed by Mooney, 2·38 Å, and considerably longer than the sum of the covalent radii, 2·33 Å. The I–Br distance is comparable to Mooney's value, 2·50 Å.

As in the isomorphous compound CsI_2Br (Carpenter, 1966) there is one short intermolecular distance, I(3)···Br(1) ≃ 3·64 Å (van der Waals distance 4·10 Å). This distance is observed in a nearly linear I···Br–I–Cl chain (Fig. 1, Table 3), suggesting that the bonding may be described as 4-center, 6-electron bonding (Hach & Rundle, 1951; Pimentel, 1951).

Experimental

Crystals were prepared according to Mooney's method. The halogen composition of the sample found by chemical analysis (I = 46·9, Br = 31·1, Cl = 13·6%) showed reasonable agreement with the formula NH_4BrICl (I = 48·7, Br = 30·7, Cl = 13·6%).

The crystallographic data were obtained from Weissenberg photographs taken at 140°K. The crystals are orthorhombic; the systematic absences indicate as possible space groups *Pnma* and $Pn2_1a$. Inspection of the *hk*0 and 0*kl* reflexions showed that all reflexions with *k* even (or odd) and common *h* and *l*, have the same intensity, except for general variations with sin θ/λ. This strongly suggests a systematic location of the four NH_4BrICl groups on mirror planes at $y=\frac{1}{4}$ and $y=-\frac{1}{4}$, as required by the special position with symmetry *m* in *Pnma*. Space group *Pnma* was therefore adopted during the structure determination. Because of the *y* values being fixed, only the projection along *y* was refined. The difficulties encountered during the structure refinement (see below) could not be explained by a wrong choice of space group, as *Pnma* and $Pn2_1a$ have the same symmetry in [010] projection (plane group *pgg*).

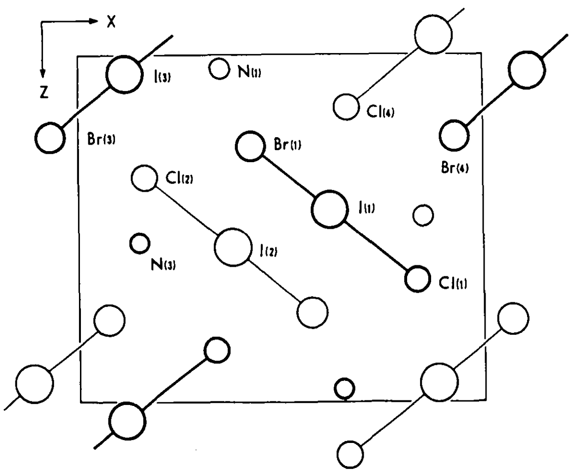
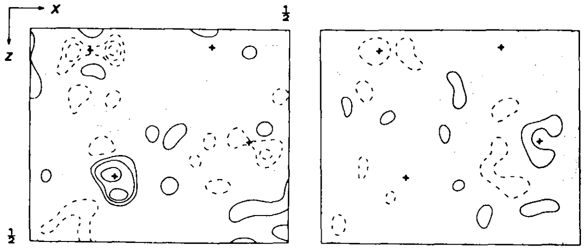


Fig. 1. Structure of NH_4BrICl as reported by Mooney. The heavily outlined atoms lie at $y=\frac{1}{4}$, the lightly outlined ones at $y=-\frac{1}{4}$. The majority of the $(BrICl)^-$ ions in our disordered crystals are oriented as shown in the Figure; a minority of these ions have the reverse orientation.



(*a*) (*b*)

Fig. 2. Difference maps for NH_4BrICl (*a*) after isotropic refinement without assuming disorder, (*b*) after anisotropic refinement with coinciding atoms, but with 25% of the $(BrICl)^-$ ions in the reverse orientation. The crosses indicate the mean atomic positions. Contours are drawn at intervals of 2 e.Å^{-2}, the zero line is dotted, and negative contours are given by broken lines.

The experimental data used during the refinement are summarized in Table 1. The absorption corrections were calculated with a program written according to the Busing & Levy (1957) scheme; the dimensions of the bounding planes of the crystal were measured as accurately as possible.

Table 1. *Observed data for* NH_4BrICl *at* 140°K

Observed data	Method used
Space group *Pnma* $Z=4$, at *m* $a=10{\cdot}280$ Å $b=6{\cdot}075$ $c=8{\cdot}648$ e.s.d. 0·03%	Weissenberg photographs Ni-filtered Cu radiation Calibration with NaCl reflexion spots $\lambda(\mathrm{Cu}\ K\alpha)=1{\cdot}5418$, $\lambda(\mathrm{Cu}\ K\alpha_1)=1{\cdot}54051$ $\lambda(\mathrm{Cu}\ K\alpha_2)=1{\cdot}54433$ Å Least-squares adjustment of 80 reflexions 0*kl* and *hk*0
163 reflexions *h*0*l*	Integrated and ordinary photographs, Zr-filtered Mo radiation. Corrections for Lp and absorption ($\mu d\simeq 3{\cdot}4$).

Refinement

The [010] projection was refined by least-squares methods. The calculations were done on a TR4 computer with a program written by Palm & Peterse according to Cruickshank's (1961) scheme; scattering curves were taken from Moore (1963).

After the isotropic refinement ($R=0{\cdot}089$), disorder in the crystals was indicated by a remarkably high electron density at the chlorine position. This is illustrated by the difference map in Fig. 2(*a*), which shows a maximum for chlorine in spite of the low thermal parameter, $B=0{\cdot}1$ Å^2, taken into account for this atom. The effect was considered significant as similar results had been obtained earlier in a refinement with data collected at room temperature for a crystal from a different sample. The high electron density near chlorine was tentatively ascribed to a minority of $(BrICl)^-$ ions (ions *B*) having an orientation the reverse of that of the trihalide ions (ions *A*) shown in Fig. 1. *A* and *B* were assumed to be statistically distributed in the crystal. Owing to this statistical distribution an average structure is obtained consisting of three sets of two almost coinciding halogen atoms; for each of the sets only weighted mean positions can be found. The percentage of *B* in the average structure was estimated by trial and error, making use of anisotropic least-

Table 2. *Mean atomic parameters after anisotropic refinement* (*see text*)

The labelling of the atoms corresponds to Fig. 1. The standard deviations as calculated by the least-squares program are given in brackets.

	x	*y*	*z*	*B*	U_{11}	U_{33}	$2U_{13}$
Br(1)	0·4242 (4)	0·2500	0·2642 (4)		0·0126 (13)	0·0136 (13)	−0·0078 (24)
I(1)	0·6180 (2)	0·2500	0·4478 (2)		0·0115 (5)	0·0159 (6)	0·0002 (13)
Cl(1)	0·8371 (5)	0·2500	0·6473 (7)		0·0100 (17)	0·0126 (19)	0·0045 (32)
N(1)	0·3466 (36)	0·7500	0·0401 (41)	2·07			

squares refinements; the percentage assumed for *B* was represented by the scattering factors used for the composite terminal atoms in the trihalide ion. For approximately 25% of *B* the best result was obtained, *viz.* a low disagreement index *R* (0·061), and comparable values for the thermal parameters of the 'chlorine' and 'bromine' ends of the ion. The thermal parameters and weighted mean positions of the composite atoms are listed in Table 2; the corresponding interatomic distances are given in Table 3. The difference map based on the results of the above refinement is shown in Fig. 2(*b*); the highest maxima (minima) are approximately 3·5 times the e.s.d. The structure factors in Table 4 are based on the parameters listed in Table 2.

Table 3. *Interatomic distances* (*smaller than* 4 Å) *and angles for the ions shown in Fig.* 1

The values are based on the parameters in Table 2.

I(1)——Br(1)	2·55 Å	N(1)···Cl(4)	3·38 Å
I(1)——Cl(1)	2·84	N(1)···Br(1)	3·69
Cl(1)···Br(4)	3·67	N(1)···Cl(2)	3·29
Br(1)···I(3)	3·64	N(1)···I(3)	3·84
I(1) ···I(2)	3·99	N(3)···Cl(2)	3·45
Br(1)···I(2)	3·95	N(3)···Br(1)	3·67
		N(3)···Br(3)	3·54
Cl(1)-I(1)—Br(1)	179°		
I(1)—Br(1)-I(3)	172		

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	L	FC	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
4	0	-2314	-2460	4	3	-872	-843	5	6	931	968	10	9	-171	-156
6	0	-575	-494	6	3	842	793	6	6	825	795	11	9	258	258
8	0	450	459	7	3	621	644	7	6	446	457	13	9	633	601
10	0	139	143	8	3	547	553	9	6	-521	-537	17	9	-318	-309
16	0	263	267	9	3	239	236	10	6	-291	-261	0	10	-1180	-1221
18	0	291	278	13	3	-312	-292	11	6	-552	-528	1	10	195	229
20	0	-230	-307	14	3	263	231	15	6	443	453	3	10	300	353
22	0	-195	-296	15	3	-225	-153	16	6	-270	-253	4	10	822	847
3	1	-337	-426	17	3	274	272	19	6	-192	-281	5	10	135	113
4	1	1225	1132	18	3	-276	-322	1	7	-1001	-990	8	10	-279	-268
5	1	-1383	-1405	21	3	-201	-184	2	7	-1126	-1141	9	10	-217	-194
6	1	671	674	0	4	830	793	3	7	739	712	1	11	-479	-534
7	1	229	239	1	4	-1422	-1484	4	7	-549	-528	2	11	233	264
8	1	-622	-538	2	4	698	664	5	7	633	611	4	11	-210	-249
9	1	1162	1139	3	4	-1414	-1400	6	7	499	494	5	11	575	664
10	1	-638	-574	4	4	-425	-365	7	7	-180	-173	6	11	-299	-325
11	1	-217	-244	5	4	768	789	8	7	320	368	9	11	-455	-427
12	1	-316	-278	6	4	-967	-956	14	7	305	201	10	11	212	212
13	1	-747	-738	7	4	814	802	0	8	-220	-271	13	11	238	201
16	1	417	411	9	4	-230	-237	1	8	-209	-243	0	12	-201	-219
17	1	399	389	10	4	297	252	2	8	107	99	4	12	280	301
0	2	399	447	11	4	-416	-417	3	8	-639	-652	7	12	-326	-335
1	2	-199	-172	14	4	[illegible]	208	4	8	599	559	8	12	-353	-354
2	2	-520	-432	15	4	372	335	5	8	-207	-186	9	12	234	235
3	2	-621	-638	16	4	255	235	7	8	555	570	11	12	424	455
4	2	-943	-957	19	4	-297	-313	8	8	-833	-845	12	12	234	225
6	2	468	353	25	4	180	224	9	8	183	133	15	12	-272	-272
7	2	905	911	1	5	228	214	10	8	-308	-277	2	13	513	519
8	2	1334	1309	5	5	-160	-126	11	8	-272	-270	3	13	287	255
9	2	-310	-270	6	5	1071	1090	12	8	668	595	6	13	-317	-274
10	2	329	311	7	5	-253	-259	14	8	317	323	7	13	-326	-313
11	2	-792	-798	8	5	442	406	16	8	-229	-192	1	14	375	375
12	2	-868	-884	10	5	-1263	-1285	1	9	-170	-198	3	14	483	463
13	2	284	256	12	5	-495	-586	2	9	-129	-104	7	14	-263	-271
14	2	-463	-530	14	5	660	701	3	9	297	329	2	15	212	149
15	2	445	421	16	5	341	349	4	9	443	445	6	15	-267	-256
16	2	267	259	0	6	-764	-702	5	9	371	407	10	15	257	271
18	2	230	284	1	6	-879	-886	6	9	229	237	1	16	188	152
1	3	659	717	2	6	-527	-508	7	9	-428	-435	5	16	-221	-257
2	3	-2028	-2173	3	6	-533	-532	8	9	-242	-251	1	17	225	256
3	3	-951	-973	4	6	421	386	9	9	-664	-676				

Discussion of the average structure

From the average structure a great number of models for the ions *A* and *B* may be deduced depending on the amount of splitting assumed for the three composite atoms. If all pairs of fractional atoms are supposed to coincide with their weighted mean position, the bond lengths in *A* and *B* are as follows:

$$A\ \mathrm{Br}\ {}_{2.55}\ \mathrm{I}\ {}_{2.84}\ \mathrm{Cl}$$

$$B\ \mathrm{Cl}\ {}_{2.55}\ \mathrm{I}\ {}_{2.84}\ \mathrm{Br}$$

The differences between the lengths of corresponding bonds for the two orientations of the ion may be ascribed to the crystal field. The value of the difference, 0·29 Å, is, however, rather high in comparison with that observed for the I_3^- ion in the isomorphous compound CsI_3, 0·20 Å (Tasman & Boswijk, 1955). A model for which the bond length differences between *A* and *B* are 0·20 Å can be obtained by assuming small separations of the fractional atomic parts, for instance 0·10 Å in the bond direction for all three composite atoms. The atomic positions of this model are schematically shown in Fig. 3(*a*); the vibration ellipsoids of the split atoms are given in Fig. 3(*b*) and in Table 5. The assumed structure model seems reasonable in view of (1) the vibration ellipsoids (the values for chlorine are inaccurate; for errors see Table 2) and (2) the fact that the van der Waals radius of bromine is larger than

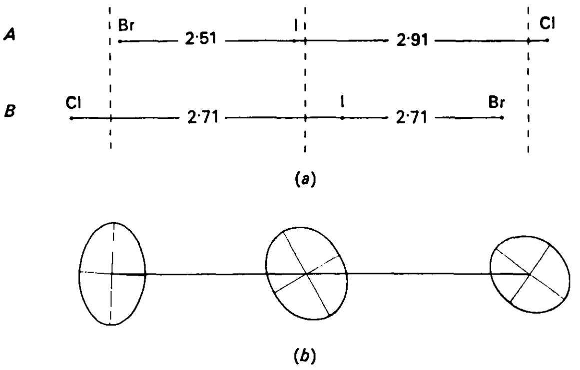


Fig. 3. Possible model for ions *A* and *B*. (*a*) Positions of the fractional atoms. Dashed lines indicate weighted mean atomic positions, for clarity of the figure the splitting of the fractional atoms is on an enlarged scale. (*b*) r.m.s. displacements due to thermal motion of the fractional atoms.

Table 5. *Thermal parameters of ion A*

	Before splitting			After splitting*		
	U_{11}	U_{33}	$2U_{13}$	U_{11}	U_{33}	$2U_{13}$
Br	0·0126 (13)	0·0136 (13)	−0·0078 (24)	0·0119	0·0131	−0·0090
I	0·0115 (5)	0·0159 (6)	0·0002 (13)	0·0104	0·0151	−0·0016
Cl	0·0100 (17)	0·0126 (19)	0·0045 (32)	0·0085	0·0117	0·0021

* See Fig. 3(*a*). The reduction of the thermal parameters in the bond direction was calculated with the formula

$$\Delta U = \frac{w_1}{w_1+w_2}\left(\frac{w_2\Delta l}{w_1+w_2}\right)^2 + \frac{w_2}{w_1+w_2}\left(\frac{w_1\Delta l}{w_1+w_2}\right)^2,$$

where Δl is the splitting in Å, and w_1 and w_2 are the weights of the fractional atoms.

Table 6. *Comparison of trihalide ions*

Compound	Ion	Bond lengths (Å)		Elongation* (Å)		Sum (Å)
See footnote†	I–I–I	2·92	2·92	0·26	0·26	0·52
CsI_3	I–I–I	2·83	3·03	0·17	0·37	0·54
CsI_2Br	I–I–Br	2·78	2·91	0·12	0·43	0·55
NH_4BrICl	Br–I–Cl	2·51	2·91	0·03	0·59	0·62‡

* Relative to the bond lengths of gaseous molecules I_2, IBr and ICl.

† Average values from $As(C_6H_5)_4I_3$, $N(C_2H_5)_4I_7$ and $N(C_2H_5)_4I_3$ (Rundle, 1961; Migchelsen & Vos, 1967).

‡ Values are approximate because of disorder.

that of chlorine. The bond lengths listed for ion *A* in Fig. 3(*a*) are compared with those of other trihalide ions in Table 6. The $(BrICl)^-$ ion in NH_4BrICl fits well in the series. The present results suggest that the I–Cl bond in NH_4BrICl (*A*) has a smaller bond order than the I–Br bond in the isomorphous compound CsI_2Br (Carpenter, 1966).

We are grateful to Professor E. H. Wiebenga for many valuable discussions and to Mr F. van Bolhuis and Mr J. Y. Talstra for their assistance during the experimental work. Calculations were done at the Groningen University Computing Centre. The work was supported by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

References

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

Carpenter, G. B. (1966). *Acta Cryst.* **20**, 330.

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

Elema, R. J., de Boer, J. L. & Vos, A. (1963). *Acta Cryst.* **16**, 243.

Hach, R. J. & Rundle, R. E. (1951). *J. Amer. Chem. Soc.* **73**, 4321.

Migchelsen, T. & Vos, A. (1967). To be published.

Mooney, R. C. L. (1937). *Z. Kristallogr.* **98**, 324.

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

Pimentel, G. C. (1951). *J. Chem. Phys.* **19**, 446.

Rundle, R. E. (1961). *Acta Cryst.* **14**, 585.

Tasman, H. A. & Boswijk, K. H. (1955). *Acta Cryst.* **8**, 59.

Visser, G. J. & Vos, A. (1964). *Acta Cryst.* **17**, 1336.

Acta Cryst. (1967). **22**, 815

The Crystal Structure of Sodium Tetraborate

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(*Received* 6 *September* 1966)

Single crystals of the high-temperature form of sodium tetraborate, $Na_2O.4B_2O_3$, have been synthesized and studied. The structure has been determined by the method of symbolic addition. The space group is $P2_1/a$ with unit-cell dimensions $a = 6·507 \pm 0·001$,† $b = 17·796 \pm 0·002$, $c = 8·377 \pm 0·001$ Å; $\beta = 96°34' \pm 2'$; $Z = 4$. The structure consists of two infinite, independent, and interlinking boron-oxygen networks, each containing alternating single and double rings. The sodium atoms serve to hold the networks together through coordination with oxygen atoms.

Introduction

This study has been made as part of a program designed for a better understanding of the structural principles underlying borate chemistry. There is additional interest in anhydrous borates with greater than 50 mole % B_2O_3 since these compounds readily form glasses. Several laboratories have been investigating these structures. Krogh-Moe (1959, 1960, 1962, 1965) has reported structures of anhydrous borates of K and Rb, Cs, Li, and Ag. The structures of strontium 1:2 borate (Krogh-Moe, 1964; Perloff & Block, 1966), lead 1:2 borate (Perloff & Block, 1966), barium 1:2 borate (Block & Perloff, 1965) and cadmium 1:2 borate (Ihara & Krogh-Moe, 1966) have also been determined. The structure of $Na_2O.4B_2O_3$ and its relation to several other borates are discussed here.

$Na_2O.4B_2O_3$ has been reported (Morey & Merwin, 1936) to exist in two forms. The present work refers to the high-temperature stable form which is usually obtained by crystallization from a melt.

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† Estimated uncertainty.