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The Crystal Structure of Monoclinic Metaboric Acid

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β–HBO_2 is monoclinic, space group $P2_1/a$, with twelve molecules in a unit cell of dimensions

$$a=7{\cdot}122\pm0{\cdot}002,\ b=8{\cdot}842\pm0{\cdot}002,\ c=6{\cdot}771\pm0{\cdot}002\ \text{Å},\ \beta=93{\cdot}26\pm0{\cdot}01^\circ\ .$$

All atoms are in general positions.

Least-square refinements based on 844 reflections gave $R=0{\cdot}06$. The position coordinates have been determined to a precision of 0·006 Å for boron, 0·003 Å for oxygen and 0·07 Å for hydrogen.

The structure consists of endless zigzag chains of composition $[B_3O_4(OH)(OH_2)]_\infty$ directed along the b-axis with hydrogen bonds between the chains. Two thirds of the boron atoms are in triangular and one third in tetrahedral configuration. The water oxygen is an unshared corner of a BO_4 tetrahedron, the hydroxyl oxygen an unshared corner of a BO_3 triangle, while each of the other oxygen atoms is bonded to two boron atoms.

Introduction

As shown by Kracek, Morey & Merwin (1938) metaboric acid can be prepared in three crystalline modifications. Approximate crystal structures have been reported for the orthorhombic α-form (Tazaki, 1940) and for the monoclinic β-HBO_2 (Zachariasen, 1952), and the precise structure of the cubic γ-modification has been found (Zachariasen, 1963). It is the purpose of the present paper to give the detailed results of the crystal structure examination of β-HBO_2.

The monoclinic unit cell has dimensions

$$a=7{\cdot}122\pm0{\cdot}002,\ b=8{\cdot}842\pm0{\cdot}002,$$
$$c=6{\cdot}771\pm0{\cdot}002\ \text{Å},\ \beta=93{\cdot}26\pm0{\cdot}01^\circ.$$

There are twelve molecules per unit cell, giving a calculated density of 2·051 g.cm^{-3} whereas the directly measured value is 2·044 g.cm^{-3} (Kracek *et al.*). The space group is $P2_1/a$. All atoms are in general positions with coordinates $\pm(x, y, z)(\frac{1}{2}+x, \frac{1}{2}-y, z)$.

Small single crystals of β-HBO_2 selected from the original material presented to the writer by Dr Kracek in 1936 were used in the investigation. The structure determination is based upon a complete set of intensities measured on a single-crystal counter spectrometer using Cu $K\alpha$-radiation. The intensity data were collected more than ten years ago.

Determination of the structure

A detailed account of the method used to find the approximate positions of the boron and oxygen atoms has been published (Zachariasen, 1952). Accordingly, only the subsequent steps in the structure determination will be described.

The 1952 parameters for boron and oxygen atoms were used as starting values for least-square refinements based on the Busing–Levi program. The McWeeny (1951) f-curves were assumed for boron and hydrogen, the f-curve of Berghuis *et al.* (1955) for oxygen. The results of ten years ago showed three short distances of 2·63–2·73 Å between oxygen atoms of different boron–oxygen polyhedra which could be explained only by the existence of hydrogen bonds. The midpoints of these short oxygen–oxygen connection lines were used as the initial sites for the hydrogen atoms. Anisotropy was assumed for the thermal motion of boron and oxygen atoms, while an isotropic thermal factor $B=2{\cdot}5$ Å^2 was postulated for the hydrogen atoms. In the last refinement stage a small correction for secondary extinction was applied according to the formula $I_{\text{corr.}}=I_{\text{obs.}}/(1-gI_{\text{obs.}})$. This correction was negligible for the vast majority of reflections, but amounted to 10% in the extreme case of the reflection (201).

The ultimate refinement, based on observed structure factors for 844 reflections, gave $R=0{\cdot}06$ and the parameter values shown in Tables 1 and 2. The agreement between observed and calculated structure

Table 1. *Position parameters*

Atom	x	y	z
B_I	0·2618	0·2891	0·4780
B_{II}	0·4015	0·3383	0·1714
B_{III}	0·2324	0·5422	0·3295
$\sigma(B)$	±0·0008	±0·0007	±0·0009
O_I	0·2121	0·1939	0·6208
O_{II}	0·2160	0·4390	0·4945
O_{III}	0·3538	0·2379	0·3159
O_{IV}	0·3557	0·4866	0·1824
O_V	0·4979	0·2838	0·0180
O_{VI}	0·0333	0·5467	0·2237
$\sigma(O)$	±0·0005	±0·0004	±0·0005
H_I	0·020	0·620	0·151
H_{II}	0·547	0·357	0·949
H_{III}	0·933	0·552	0·342
$\sigma(H)$	±0·011	±0·010	±0·012

factors is illustrated in Tables 3 and 4. The former of these tables lists all reflections up to $\sin^2\theta/\lambda^2=0{\cdot}075$, while Table 4 gives the reflections in the range $0{\cdot}3500<\sin^2\theta/\lambda^2<0{\cdot}4000$.

Table 2. *Thermal parameters*

($\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
B_{I}	71 ± 10	9 ± 8	51 ± 11	3 ± 7	22 ± 9	-2 ± 7
B_{II}	83 ± 10	17 ± 8	74 ± 11	3 ± 7	17 ± 9	-7 ± 7
B_{III}	79 ± 10	22 ± 8	47 ± 11	4 ± 7	15 ± 9	-1 ± 7
O_{I}	100 ± 7	16 ± 5	56 ± 7	9 ± 5	35 ± 6	7 ± 5
O_{II}	81 ± 7	13 ± 5	58 ± 7	6 ± 5	31 ± 6	5 ± 5
O_{III}	112 ± 7	16 ± 5	66 ± 7	11 ± 5	43 ± 6	5 ± 5
O_{IV}	96 ± 7	19 ± 5	62 ± 7	5 ± 5	43 ± 6	1 ± 5
O_{V}	116 ± 7	18 ± 5	77 ± 7	1 ± 5	55 ± 6	-8 ± 5
O_{VI}	68 ± 7	29 ± 5	66 ± 7	0 ± 5	16 ± 6	5 ± 5

Table 3. *Observed and calculated structure factors*

HKL	F_o	F_c	HKL	F_o	F_c
001	29.4	-31.0	230	10.9	-11.2
110	5.2	-5.4	003	6.5	-5.7
011	14.1	-12.7	032	6.9	-6.4
020	10.6	-8.9	040	63.4	65.4
$11\bar{1}$	33.9	-29.8	$31\bar{1}$	25.9	-24.8
111	59.2	64.7	$22\bar{2}$	66.2	-63.0
120	5.2	5.3	013	7.0	6.8
021	1.7	-1.5	$23\bar{1}$	1.9	2.0
200	28.2	-25.9	$13\bar{2}$	26.7	-26.0
002	8.6	-8.1	311	7.2	-5.2
$12\bar{1}$	19.1	19.4	231	27.3	27.8
210	27.5	26.5	$11\bar{3}$	nil	0.7
121	27.3	-27.4	140	27.8	24.6
$20\bar{1}$	41.2	38.8	041	1.1	-0.9
012	16.2	-15.6	132	10.4	8.9
201	133.0	133.7	222	nil	-1.4
$21\bar{1}$	12.4	11.7	320	nil	0.1
$11\bar{2}$	11.8	11.9	113	nil	0.1
211	1.0	0.5	$14\bar{1}$	2.4	-2.1
112	13.1	13.4	$32\bar{1}$	20.7	19.6
220	3.1	-2.7	023	58.7	-60.0
130	29.2	-30.2	141	44.5	-43.4
031	36.2	36.4	321	3.4	-4.0
022	34.8	-34.9	$12\bar{3}$	43.8	-44.1
$22\bar{1}$	6.8	-6.5	$20\bar{3}$	12.1	10.2
$12\bar{2}$	39.8	39.0	$31\bar{2}$	9.4	9.2
$13\bar{1}$	18.3	-18.2	$23\bar{2}$	16.2	-15.0
221	40.5	-40.5	$21\bar{3}$	23.3	21.6
$20\bar{2}$	15.6	-14.4	123	24.5	-23.7
131	nil	-0.5	240	5.9	-5.8
122	3.6	2.6	203	10.7	11.5
$21\bar{2}$	36.1	-33.7	232	3.1	3.2
202	22.0	-19.7	042	12.7	-11.9
212	14.0	-13.9	312	54.8	55.2
310	22.5	-21.2	330	18.0	-17.6

Description of the structure

The parameter values of Table 1 give the interatomic distances shown in Table 5, and the main structural features are illustrated in Fig. 1.

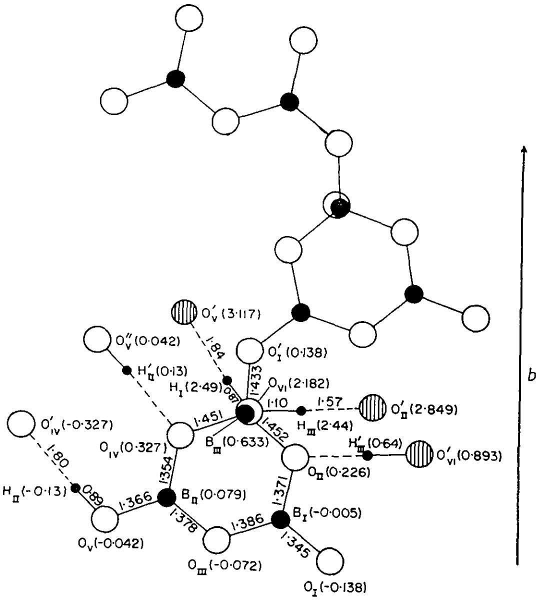

Fig. 1. Shows a part of the β-HBO_2 structure projected on the (201) plane. The numbers in parentheses give the heights (in Å) of the atoms above or below the plane $2x+z=1$. The lengths of various bonds are indicated in the figure except for the bond of length 1·553 Å between the superimposed atoms B_{III} and O_{VI}.

The large open circles represent oxygen atoms belonging to the endless chains which are associated with the plane $2x+z=1$, while the shaded large circles denote oxygen atoms belonging to chains of the adjacent plane $2x+z=0$.

Table 4. *Calculated and observed structure factors*

Range: $0{\cdot}3500 \leqq \sin^2\theta/\lambda^2 \leqq 0{\cdot}4000$

HKL	F_o	F_c	HKL	F_o	F_c	HKL	F_o	F_c	HKL	F_o	F_o
008	1.6	1.2	724	1.4	-1.3	$76\bar{2}$	2.7	2.7	$31\bar{8}$	1.8	2.0
812	nil	-0.2	$43\bar{7}$	10.7	-9.8	294	5.3	-4.9	$16\bar{7}$	nil	0.4
526	3.5	3.6	$25\bar{7}$	3.2	2.7	$72\bar{5}$	2.2	-2.0	$68\bar{1}$	1.4	-0.8
$80\bar{3}$	2.7	3.6	822	6.8	-7.1	3.10.1	nil	-0.2	$59\bar{1}$	5.9	6.0
$34\bar{7}$	2.0	2.3	$20\bar{8}$	9.6	-9.5	$1.10.\bar{3}$	2.3	-2.2	$80\bar{4}$	4.8	-4.0
752	nil	-1.2	635	6.0	5.8	128	nil	0.5	2.10.3	6.8	6.5
663	2.0	-2.1	$29\bar{4}$	1.3	-1.7	$22\bar{8}$	1.9	-1.5	762	2.5	-2.5
076	3.5	3.9	$71\bar{5}$	9.4	-8.7	$51\bar{7}$	9.1	10.2	$81\bar{4}$	nil	-0.5
194	3.2	3.6	176	2.3	2.5	734	11.5	-10.8	3.10.2	1.8	1.7
$60\bar{6}$	1.9	-1.5	028	4.6	-5.0	1.10.3	5.9	-5.9	591	5.8	-5.2
018	nil	-2.2	118	8.7	-8.4	832	nil	0.4	681	6.8	-7.0
$11\bar{8}$	2.9	-0.9	$12\bar{8}$	1.7	1.7	257	3.8	-3.7	1.11.0	8.2	8.0
337	7.0	-7.2	2.10.2	7.7	7.2	427	3.1	-2.4	0.11.1	4.8	5.9
$81\bar{3}$	10.6	11.1	407	4.7	-4.8	841	6.4	5.7	2.10.3	6.8	7.2
$45\bar{2}$	1.3	-1.5	3.10.0	2.1	-2.4	038	7.6	-6.2	167	4.2	-4.3
831	1.8	1.6	$82\bar{3}$	9.7	-9.3	$13\bar{8}$	3.5	-3.6	228	7.7	6.0
$17\bar{6}$	nil	-0.2	$21\bar{8}$	2.7	0.2	803	nil	0.7	673	3.6	3.5
$28\bar{5}$	6.9	-5.9	492	1.7	1.5	$84\bar{2}$	nil	0.2	095	9.8	10.4
582	10.4	11.0	$27\bar{6}$	nil	-0.1	208	2.6	3.2	850	11.1	11.9
$61\bar{6}$	1.6	-1.0	$62\bar{6}$	5.2	5.5	$83\bar{3}$	19.3	-18.1	606	3.4	-3.3
760	4.7	-5.5	761	1.1	1.0	276	2.3	1.9	$1.11.\bar{1}$	7.7	-8.4
$83\bar{2}$	8.7	8.9	285	7.8	-7.8	590	14.7	16.1	$85\bar{1}$	nil	0.3
157	3.9	3.9	536	0.7	-0.4	680	8.7	8.6	1.11.1	nil	-0.7
393	12.4	12.3	417	4.4	-4.3	$63\bar{6}$	9.7	-8.7	$82\bar{4}$	2.2	-2.2
743	3.8	3.8	840	9.2	8.7	813	4.0	3.8	$19\bar{5}$	3.5	3.3
$76\bar{1}$	4.7	4.9	$3.10.\bar{1}$	nil	0.3	218	17.1	-17.3	770	1.0	0.6
$75\bar{3}$	nil	0.4	$84\bar{1}$	7.0	-6.5	067	1.6	1.6	4.10.0	8.0	2.2
$2.10.\bar{2}$	6.3	6.2	0.10.3	1.3	2.2						

As stated above, the initial hydrogen sites were the midpoints of short oxygen–oxygen connection lines. In the course of the refinement each hydrogen atom was displaced along the connection line so as to come much closer to one of the two oxygen atoms. Although the hydrogen positions are accurate to only ±0·1 Å it suffices to distinguish conclusively between the O–H and O · · · H components of the hydrogen bonds. The results are: $O_{VI}–H_{I} \cdots O_{V}$, $O_{V}–H_{II} \cdots O_{IV}$ and $O_{VI}–H_{III} \cdots O_{II}$. Thus the O_{VI} atom is established as the oxygen of a water molecule $O_{VI}H_{I}H_{III}$ and the O_{V} atom as the oxygen of a hydroxyl group $O_{V}H_{II}$.

Table 5. *Interatomic distances*

$B_{I}–O_{I}$	1·345±0·007 Å	$O_{I}–O_{II}$	2·335±0·005 Å
$B_{I}–O_{II}$	1·371±0·007	$O_{II}–O_{III}$	2·392±0·005
$B_{I}–O_{III}$	1·386±0·007	$O_{I}–O_{III}$	2·380±0·005
$B_{II}–O_{III}$	1·378±0·007 Å	$O_{III}–O_{IV}$	2·378±0·005 Å
$B_{II}–O_{IV}$	1·354±0·007	$O_{III}–O_{V}$	2·350±0·005
$B_{II}–O_{V}$	1·366±0·007	$O_{IV}–O_{V}$	2·368±0·005
$B_{III}–O_{I}'$	1·433±0·007 Å	$O_{I}'–O_{VI}$	2·423±0·005 Å
$B_{III}–O_{II}$	1·452±0·007	$O_{I}'–O_{II}$	2·449±0·005
$B_{III}–O_{IV}$	1·451±0·007	$O_{I}'–O_{IV}$	2·333±0·005
$B_{III}–O_{VI}$	1·553±0·007	$O_{II}–O_{IV}$	2·423±0·005
		$O_{II}–O_{VI}$	2·386±0·005
		$O_{IV}–O_{VI}$	2·325±0·005
$H_{I} – O_{VI}$	0·87±0·10 Å	$O_{VI}–H_{I} \cdots O_{V}$	2·676±0·005 Å
$H_{I} \cdots O_{V}$	1·84±0·10		
$H_{II} – O_{V}$	0·89±0·10 Å	$O_{V}–H_{II} \cdots O_{IV}$	2·685±0·005 Å
$H_{II} \cdots O_{IV}$	1·80±0·10		
$H_{III} – O_{VI}$	1·10±0·10 Å	$O_{VI}–H_{III} \cdots O_{II}$	2·683±0·005 Å
$H_{III} \cdots O_{II}$	1·57±0·10		

The configuration of oxygen atoms about boron is triangular for B_{I} and B_{II}, tetrahedral for B_{III}. The oxygen atoms O_{V} and O_{VI}, (*i.e.* the hydroxyl and water oxygens) are each bonded to one boron atom, while all the other oxygen atoms form bonds with two boron atoms. This is the first borate structure in which a bond between boron and a water oxygen has been observed.

As shown in Fig. 1 the BO_3 triangles and the BO_4 tetrahedra share corners so as to produce endless zigzag chains $[B_3O_4(OH)(OH_2)]_\infty$ along the *b*-axis. The two triangles and the base of the tetrahedron lie approximately in the lattice plane (201). Thus the chains are arranged in layers 3·075 Å apart with the tetrahedral apices extending alternately up or down from the (201) planes. Chains in the same layer are held together by the hydrogen bonds $O_{V}–H_{II} \cdots O_{IV}$, while the bonds $O_{VI}–H_{I} \cdots O_{V}$ and $O_{VI}–H_{III} \cdots O_{II}$ link together chains of adjacent layers.

As is to be anticipated from the structure, the cleavages of β-HBO_2 crystals reported by Kracek *et al.* (1938) are parallel to the chain direction. These writers observed strong negative birefringence ($\alpha = 1·434$, $\beta = 1·570$, $\gamma = 1·588$) with the acute bisectrix nearly normal to the (201) plane. Thus also the optical properties are in accord with the deduced structure.

Bond lengths

A number of borate structures have recently been determined in this laboratory giving an accuracy of ±0·007 Å for individual B–O bond lengths and ±0·005 Å for individual oxygen to oxygen distances. The results as to the average values for the B–O bonds are listed in Table 6, while Table 7 gives the experimental data for the O–H · · · O lengths. In the potassium borate structures the individual O–H · · · O distances vary so greatly that it is of little physical significance to give average values.

Although the average B–O bond length has a practically constant value of 1·365 Å for triangular and 1·475 Å for tetrahedral configuration, large deviations from the mean are observed for individual bond distances. Thus one finds values of 1·284 Å and 1·431 Å in the BO_3 triangles of $NaBO_2$, and, as seen in Table 5, the tetrahedral bond lengths range from 1·433 Å to 1·553 Å in β-HBO_2.

Table 6. *Mean* B–O *bond lengths*

	Configuration		
Structure	Triangle	Tetrahedron	Reference
H_3BO_3	1·361 Å		Zachariasen, 1954
β-HBO_2	1·367	1·472 Å	
γ-HBO_2		1·472	Zachariasen, 1963
$KB_5O_8 . 4H_2O$	1·359	1·477	Zachariasen & Plettinger, 1963
$K_2B_4O_7 . 4H_2O$	1·368	1·480	Marezio, Plettinger & Zachariasen, 1962
CaB_2O_4	1·372		Marezio, Plettinger & Zachariasen. 1963*a*
$NaBO_2$	1·382		Marezio, Plettinger & Zachariasen, 1963*b*

Table 7. O–H · · · O *dimensions*

Structure	Mean	Range
H_3BO_3	2·720 Å	2·707–2·734 Å
β-HBO_2	2·681	2·676–2·685
γ-HBO_2	2·486	
$KB_5O_8 . 4H_2O$		2·661–2·920
$K_2B_4O_7 . 4H_2O$		2·65 –3·14

It has long been known (and the data of Table 7 illustrate the fact) that the length of the group O–H · · · O varies very greatly from one structure to the next. In all instances where the hydrogen positions have been determined with accuracy it is found that the hydrogen atom is bonded much more closely to one of the two oxygen atoms (thus indicating that the midpoint between the oxygen atoms is invariably a potential maximum) and that the oxygen–oxygen decreases as the O–H component of the bond increases in length.

It is useful to interpret structural results for borates in terms of the principle of detailed neutralization of valence first set forth by Pauling (1929) in his discussion of the crystal chemistry of silicates. Let the index i denote a crystallographic species of atoms having a formal positive chemical valence v_i, while the index j

designates a crystallographic species of negative valence $-v_j$. If $v_{ij}(=v_{ji})$ represents the valence strength assigned to a chemical bond of length r_{ij} formed between atoms i and j, then the principle states that the conditions

$$\sum_j v_{ij} \approx v_i,\ \sum_i v_{ij} \approx v_j$$

shall hold for all crystallographic species i and j. Clearly, the principle is of practical value only if it is assumed that the observed bond length r_{ij} uniquely determines the bond strength v_{ij} independently of the particular structure under consideration.

The conditions

$$\sum_j v_{ij} = v_i,\ \sum_i v_{ij} = v_j$$

tend to minimize the potential energy, and hence to assure the stability of the structural configuration except that next nearest neighbor interaction also needs to be considered.

Table 8. *Strength and length of* B–O *bonds*

Strength	Length	Strength	Length
1·4	1·274 Å	0·9	1·409 Å
1·3	1·287	0·8	1·453
1·2	1·304	0·7	1·497
1·1	1·330	0·6	1·541
1·0	1·365	0·5	1·585

Table 9. *Strength and length of hydrogen bonds*

Strength				
H–O	H · · · O	O–H · · · O	O–H	O · · · H
0·9	0·1	3·09 Å	0·99 Å	2·10 Å
0·8	0·2	2·81	1·01	1·80
0·7	0·3	2·61	1·03	1·58
0·6	0·4	2·49	1·06	1·43

Tables 8 and 9 show the correlations used in this laboratory between length and strength of boron–oxygen and hydrogen–oxygen bonds. When applied to the borate structures which have been investigated it is found that the conditions

$$\sum_j v_{ij} = v_i\ ,\ \sum_i v_{ij} = v_j$$

are valid to ±0·1 valence unit. Since the hydrogen positions rarely are known with required accuracy, the strengths of H–O and H · · · O bonds will usually have to be inferred from the more precisely known lengths O–H · · · O. The valence balance for the various crystallographic species of the β-HBO_2 structure is shown in Table 10.

These bond strength considerations do explain many abnormally short and abnormally long bond distances which have been observed. (However, it should be remembered that also next nearest neighbor interactions affect the bond lengths, and hence one cannot expect to account for all observed bond length anomalies.) Were one to assign bond strengths of 1·00 to a triangular, 0·75 to a tetrahedral B–O bond (as would be true for regular polyhedra), and 1·00 to the H–O bond (corresponding to no bond component H · · · O), then in the β-HBO_2 structure the O_{VI} atom would be heavily 'overbonded' ($\sum_i v_{ij} = 2·75$) and the atoms O_I, O_{II}, O_{IV} correspondingly 'underbonded' ($\sum_i v_{ij} = 1·75$). It is seen from Tables 5 and 10 that these imbalances are in large measure removed in the actual structure by the shortening of some B–O bonds and by the lengthening of others, and by the diversion of some bond strength from the H–O to the H · · · O bonds.

Table 10. *Valence balance in* β-HBO_2

	B_I	B_{II}	B_{III}	H_I	H_{II}	H_{III}	$\sum_i v_{ij}$
O_I	1·06	—	0·85	—	—	—	1·91
O_{II}	0·99	—	0·80	—	—	0·26	2·05
O_{III}	0·95	0·97	—	—	—	—	1·92
O_{IV}	—	1·04	0·80	—	0·26	—	2·10
O_V	—	1·00	—	0·26	0·74	—	2·00
O_{VI}	—	—	0·57	0·74	—	0·74	2·05
$\sum_j v_{ij}$	3·00	3·01	3·02	1·00	1·00	1·00	12·03

In analogous manner the bond strength considerations do account for the unusual situation observed in the γ-HBO_2 structure in which a hydroxyl oxygen is bonded to two boron atoms.

Only a crude structure has been reported for crystalline B_2O_3 (Berger, 1952), with all boron atoms in tetrahedral configuration. Such a structure is possible from point of view of valence balance provided B–O ≈ 1·37 Å for an oxygen bonded to two boron atoms and B–O ≈ 1·51 Å for oxygens bonded to three boron atoms.

For bond strengths greater than unity the B–O bond length decreases more slowly with increasing strength than expected for a linear dependence. In the CaB_2O_4 and $NaBO_2$ structures (particularly in the latter) there is one very short bond distance in each BO_3-triangle. As a consequence one finds in these compounds (see Table 6) an abnormally large value for the mean triangular B–O bond length.

The thermal motion

The anisotropic thermal factors β_{ij}, for boron and oxygen atoms resulting from the least-square refinement were listed in Table 2. The corresponding root mean square thermal displacements along principal axes are shown in Table 11 together with the orientations of the principal axes expressed in terms of their direction cosines α_1, α_2, α_3 referred to a cartesian system chosen as follows (see Fig. 1): the Z-axis is the normal of the plane defined by atoms O_I, O_{II}, O_{III} and the X-axis is parallel to the O_I–O_{III} connection line. Thus the Z-axis is nearly normal to the (201) plane, and the Y-axis nearly parallel to the crystallographic b-axis, *i.e.* the chain direction.

Table 11. *Principal r.m.s. displacements,* Δ_i

Atom	i	Δ_i (Å)	α_1	α_2	α_3
B_I	1.	0·30	0·98	−0·13	−0·03
	2.	0·19	0·15	0·97	0·20
	3.	0·45	−0·01	−0·14	0·98
B_{II}	1.	0·39	0·99	−0·03	−0·12
	2.	0·25	0·03	0·98	0·22
	3.	0·46	0·11	−0·19	0·98
B_{III}	1.	0·32	0·95	−0·25	0·16
	2.	0·29	0·22	0·96	0·19
	3.	0·46	−0·23	−0·12	0·97
O_I	1.	0·30	0·94	0·33	0·07
	2.	0·24	−0·33	0·94	0·03
	3.	0·54	−0·07	−0·05	1·00
O_{II}	1.	0·30	0·97	0·26	0·02
	2.	0·23	−0·26	0·97	0·08
	3.	0·50	0·01	−0·06	1·00
O_{III}	1.	0·32	0·99	0·08	0·01
	2.	0·24	−0·08	0·99	0·07
	3.	0·58	−0·02	−0·06	1·00
O_{IV}	1.	0·29	0·94	−0·34	−0·08
	2.	0·27	0·36	0·93	0·11
	3.	0·54	0·04	−0·12	0·99
O_V	1.	0·32	0·99	−0·11	−0·12
	2.	0·25	0·14	0·98	0·18
	3.	0·60	0·09	−0·20	0·98
O_{VI}	1.	0·37	0·73	0·68	−0·05
	2.	0·33	−0·67	0·73	0·13
	3.	0·44	0·14	−0·05	0·99

It is seen from Table 11 that the direction of maximum thermal displacement for all atoms is nearly normal to the BO_3 triangles, while the direction of minimum displacement for all atoms except the water oxygen is nearly parallel to the chain axis. These results are entirely reasonable on physical grounds.

The boric acid structures

Orthoboric acid and the three modifications of metaboric acid complete the list of boric acids known to exist in crystalline form.

H_3BO_3 and α-HBO_2 have structural similarities. In both structures all boron atoms are in triangular configuration, and the BO_3 groups are arranged in pseudohexagonal layers (3·181 Å apart in H_3BO_3, 3·128 Å in α-HBO_2) with van der Waals binding between layers. The structural units of which a layer is composed are $B(OH)_3$ groups in orthoboric acid and $[B_3O_3(OH)_3]$ groups in α-HBO_2; but in both structures the groups of a layer are linked through hydrogen bonds. Being typical layer structures there is perfect cleavage parallel to the layers, the density is very low, the volatility relatively high, and there is strong negative birefringence with the acute bisectrix normal to the layers.

As explained earlier in this paper two thirds of the boron atoms are in triangular and one third in tetrahedral configuration in β-HBO_2. Endless chains $[B_3O_4(OH)(OH_2)]_\infty$ are present, and these are arranged in layers 3·075 Å apart with the water molecules, forming the tetrahedral apices, located 2·182 Å above and below the layers. Hydrogen bonds form links between chains of different layers as well as between chains of the same layer. As a consequence of the chain structure the crystals of β-HBO_2 are fibrous. Because the BO_3 groups are nearly parallel, the birefringence of β-HBO_2 is strong and negative with the acute bisectrix normal to the triangles.

All boron atoms are in tetrahedral configuration in γ-HBO_2. Every oxygen atom is shared between two tetrahedra so that an infinite three-dimensional network $[BO(OH)]_{3\infty}$ is formed. In addition there are unusually short hydrogen bonds between the tetrahedra. The $O-H\cdots O$ distance is 2·49 Å as compared with values of 2·68–2·75 Å in the other boric acid structures. Because of the much tighter binding crystals of γ-HBO_2 are much harder and much denser than the other forms of metaboric acid. The density of γ-HBO_2 is 2·487 $g.cm^{-3}$, while it is 2·044 for β-HBO_2 and 1·784 for α-HBO_2.

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