The Refined Structure of Orthorhombic Metaboric Acid

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A three-dimensional X-ray diffraction study of the orthorhombic modification of metaboric acid, HBO_2, at a temperature of -130 °C has characterized the geometry of the $B_3O_3(OH)_3$ structural unit. Least-squares refinement of the structural parameters resulted in an agreement factor $R = \Sigma||kF_o| - |F_c||/\Sigma|kF_o|$ of 0·064. The structure may be described as hydrogen bonded sheets of trimeric HBO_2 molecules loosely stacked to form a mica-like, platey crystal in the orthorhombic system, space group $Pbnm$, $a = 8·019$, $b = 9·703$, $c = 6·13$ Å, with twelve molecules in the unit cell. The average B–O bond distance in the six-membered, boron–oxygen ring is 1·373 Å, while the average out-of-ring distance is 1·349 Å. The average O–H bond is 0·87 Å. Three distinct hydrogen bonds have O $\cdots$ O distances of 2·827, 2·748 and 2·680 Å. The anisotropic thermal behavior is such that the trimeric structural unit (considered as a rigid body) describes primarily a translational motion along three orthogonal axes with little angular contribution to this motion.

Introduction

Metaboric acid, HBO_2, crystallizes in the orthorhombic, monoclinic or cubic system, depending on the temperature and pressure (Kracek, Morey & Merwin, 1938). The structure of the orthorhombic monotrope was studied by Tazaki (1940a), who used single-crystal X-ray diffraction data. Tazaki's two-dimensional study located the heavy atoms in four trimeric $B_3O_3(OH)_3$ molecules in special position mirror planes of space group No. 62 $Pbnm$ (D_{2h}^{16}).

The planar B_3O_6 group is made up of three BO_3 triangles, each sharing two oxygen atoms, so as to form a six-membered B_3O_3 ring. The hydrogen bonding within the layers along with the layer separation of 3·12 Å accounts for the mica-like cleavage of the colorless rhombic plates characteristic of orthorhombic HBO_2. Tazaki was unable to detect significant differences among the B–O bond distances and the $O(H) \cdots O$ hydrogen bond separations, finding an average B–O distance of 1·37 Å and an average $O(H) \cdots O$ hydrogen bond of 2·74 Å.

This same ring configuration had been found earlier for the metaborate anion in potassium and sodium metaborate (Zachariasen, 1937; Fang, 1938). However, in $Ca(BO_2)_2$ the BO_3 units associate to form infinite polymeric chains (Zachariasen & Zeigler, 1932). A similar chain structure has recently been reported for $LiBO_2$ (Lehman & Tiess, 1959).

In the monoclinic and cubic forms of metaboric acid, it is known from nuclear magnetic resonance and X-ray investigations that both trigonal and tetrahedral coordination of the boron exist in the former and only tetrahedral in the latter (Parsons, Silver & Milberg, 1961; Zachariasen, 1952). Although precise X-ray studies of the structures for the monoclinic and cubic forms of HBO_2 have recently been completed by Zachariasen (1963), it is the planar $[B_3O_6]^{-3}$ unit

which is considered to be the parent structure from which all other polyborate anions originate (Edwards & Ross, 1960). In addition, recent structural studies of B_2O_3–H_2O glasses have indicated that they are most closely related to HBO_2 and, in the low H_2O region, the orthorhombic form thereof (Milberg & Meller, 1959; Meller & Milberg, 1960; Parsons & Milberg, 1960; Milberg, Belitz & Silver, 1960). The infrared vibrational spectra of this form of HBO_2 have been studied by Parsons (1960).

In view of the above, a precise, three-dimensional study of the structure of the orthorhombic HBO_2, with special emphasis on hydrogen atom locations, was considered worth while.

Experimental

Polycrystalline orthorhombic metaboric acid was prepared by dehydrating analytical reagent grade powdered orthoboric acid, H_3BO_3, at 95–100 °C for 24 hours (Tazaki, 1940b). Single crystals of the material were grown in a sealed tube from a melt, under reduced pressure, at a temperature of 165–170 °C (Kracek *et al.*, 1938). Single-crystal specimens of dimensions about $2·5 \times 2·5 \times 0·5$ mm were used to obtain the diffraction data. The hygroscopic crystals were coated with polymethyl methacrylate and cooled to -130 ± 10 °C with a nitrogen boiler. Precession photographs were taken of the hkL nets $L = 0 - 3$, and integrated Weissenberg photographs of the hKl nets, $K = 0 - 12$, utilizing filtered Mo $K\alpha$ radiation throughout. This asymmetric survey of reciprocal space resulted in a total of 416 unique reflections of measurable intensity. Within a sphere of radius defined by $\sin^2 \theta/\lambda^2 = 0·5$, 395 reflections of the 790 possible were observable while 40 were not sought.

Intensities were measured with a Leeds & Northrup

Table 1. *Observed and calculated structure factors for* HBO₂

h	l	Fo	Fc
(h=00)			
00	02	174.6	-185.2
00	04	92.1	90.3
00	06	40.6	-43.9
00	08	19.3	22.8
00	10	10.8	-11.5
02	00	14.7	-14.5
04	00	12.4	13.9
04	01	29.5	-29.7
04	02	11.9	-10.9
04	03	22.2	20.1
04		6.8	6.0
05		10.8	-10.7
06	01	1.9	2.7
03		3.7	-3.4
05		3.9	3.7
08	00	52.0	-51.0
01		60.8	-59.4
02		43.4	44.6
03		43.2	45.5
04		31.1	-30.8
05		29.6	-29.3
06		19.6	19.2
07		17.1	17.5
08		11.3	-11.0
10	00	7.2	8.1
02		8.3	-7.7
03		4.7	-5.5
12	01	7.9	6.1
02		4.9	5.3
(h=01)			
00	01	31.9	-32.2
03		19.5	16.8
05		8.3	-8.0
01	00	13.6	-12.0
01		33.5	-36.0
02		10.1	8.1
03		23.2	20.6
05		12.0	-11.6
02	00	24.4	24.6
01		33.9	35.4
02		19.2	-18.1
03		21.2	-19.9
04		9.9	10.2
05		10.0	10.0
06		6.6	-5.7
07		7.1	-5.4
03	00	27.1	-28.1
01		21.8	-23.2
02		23.0	20.6
03		16.6	14.4
04		12.7	-11.0
05		9.0	-8.2
06		7.2	5.8

h	l	Fo	Fc
04	00	47.3	45.4
01		22.2	20.9
02		39.2	-34.7
03		13.9	-12.5
04		16.2	17.5
06		7.9	-6.6
05	00	18.4	21.4
01		6.5	6.3
02		22.4	-17.3
04		11.6	11.2
06	00	16.5	17.8
01		3.2	-3.3
02		14.6	-15.2
04		9.7	10.4
06		5.2	-6.6
07	00	8.9	10.5
02		8.9	-9.1
04		5.7	6.7
07		1.7	1.8
08	00	12.1	-12.2
01		6.2	5.5
02		11.0	10.6
04		7.4	-7.2
09	00	11.5	-12.9
01		14.0	15.6
02		11.6	11.6
03		13.5	-12.3
04		8.9	-8.8
05		8.4	8.5
10	01	13.0	-13.1
02		3.8	-3.1
03		10.3	10.7
11	01	12.7	13.4
03		11.1	-11.0
12	01	10.4	-11.5
03		8.1	8.8
13	01	6.2	-6.1
03		5.2	5.0
(h=02)			
00	00	43.6	45.0
02		35.4	-32.9
04		19.1	18.3
06		10.3	-10.1
01	00	16.9	16.7
02		14.1	-13.6
04		9.3	9.0
02	00	7.7	9.1
01		5.9	-6.2
02		6.2	-6.3
03		5.1	4.3
04		3.4	3.6
03	00	40.3	-40.3
01		43.5	42.0
02		33.3	31.1

h	l	Fo	Fc
03	03	29.7	-26.6
04		17.5	-16.8
05		14.8	13.6
06		7.7	7.9
04	00	15.1	14.7
01		26.8	-26.1
02		12.4	-11.0
03		15.9	15.0
05	00	10.7	10.6
01		51.5	-51.4
02		10.7	-8.7
03		36.6	35.0
04		6.1	5.4
05		19.0	-18.8
06	01	5.1	-5.3
03		4.7	4.7
05		3.6	-3.9
07	00	3.3	2.9
01		2.1	1.9
02		2.7	-3.0
08	00	9.9	-11.1
01		8.5	-8.8
02		10.7	10.0
03		7.5	7.4
04		7.9	-7.5
09	00	7.5	-7.4
02		7.8	6.6
10	02	3.8	3.6
11	00	12.3	13.1
02		12.8	-11.8
12	02	4.0	4.2
13	00	17.1	-18.9
01		9.0	9.2
02		16.3	17.1
03		7.5	-7.5
(h=03)			
00	01	54.6	55.2
03		36.9	-35.5
05		19.5	19.7
07		10.2	-10.9
01	01	22.4	21.8
03		11.7	-11.8
02	00	19.4	18.4
01		25.3	24.9
02		13.1	-14.2
03		14.3	-14.7
05		5.8	7.2
05		6.0	5.5
03	00	7.0	6.3
01		10.4	5.4
04	00	37.5	35.7
01		15.4	15.0
02		29.4	-29.5
03		11.3	-10.7

h	l	Fo	Fc
04	04	19.1	18.9
06		11.1	-11.1
05	00	8.4	-8.6
02		7.3	6.2
06	00	16.6	17.5
01		5.4	-5.7
02		13.3	-13.9
03		4.3	4.1
04		6.0	7.3
06		2.7	-2.7
07	00	4.7	-5.1
01		4.8	4.9
02		3.9	3.7
08	00	17.1	18.1
01		15.3	-15.8
02		17.1	-16.0
03		13.0	12.5
04		12.0	11.6
05		9.1	-8.6
06		7.3	-7.8
09	00	5.6	6.7
01		4.2	-3.2
02		5.7	-5.3
10	01	4.4	-8.8
03		6.6	6.5
12	01	13.5	-12.4
02		3.8	3.9
03		10.8	10.6
(h=04)			
00	00	25.1	-24.0
02		18.8	18.1
01	00	52.5	52.7
01		15.5	-15.0
02		39.1	-41.8
03		10.6	9.9
04		22.1	23.9
02	00	6.6	-6.9
01		5.4	5.5
02		5.2	6.0
03	00	7.0	-5.9
02		3.9	4.8
04	00	7.4	-6.1
01		20.5	20.8
02		6.1	5.5
03		16.2	-15.7
05		10.7	10.4
05	01	7.2	-6.1
06	01	5.6	5.6
03		4.8	-4.7
07	00	6.5	7.2
01		20.1	20.9
02		6.9	-6.3
03		15.5	-15.5

h	l	Fo	Fc
07	04	4.2	4.3
05		7.5	9.4
08	00	8.1	7.2
01		5.2	4.6
02		6.0	-5.8
09	00	21.6	-22.4
01		12.9	-14.2
02		20.7	19.6
03		11.6	11.2
04		13.3	-14.1
10	02	5.1	-4.6
12	00	7.7	7.8
01		5.0	-4.9
02		7.8	-7.3
03		4.1	4.3
(h=05)			
00	01	24.7	24.5
03		16.5	-15.3
05		5.7	6.6
01	01	13.8	-13.8
02		7.5	7.1
02	00	14.0	13.8
01		18.0	18.9
02		11.1	-11.6
03		13.4	-14.0
04		6.7	7.5
05		9.0	8.9
03	00	14.8	-16.2
01		10.9	-11.7
03		9.3	8.9
04		9.4	-10.4
05		16.4	-16.1
01		7.8	-8.5
02		14.1	13.7
03		7.0	6.4
(h=07)			
00	01	21.1	-23.2
03		14.8	16.6
05		10.2	-9.2
01		12.0	11.6

h	l	Fo	Fc
09	01	8.3	7.2
02		3.7	3.1
03		6.6	-6.0
07	00	11.3	-9.4
01		8.0	-7.8
03		6.9	6.2
08	00	6.3	-5.3
01		7.6	6.1
11	01	7.6	6.1
03		6.3	-5.3
12	01	8.9	8.6
03		7.8	-7.1
(h=06)			
00	00	14.7	-14.7
02		12.3	12.5
04		8.2	-8.7
06		6.3	5.5
01	01	5.2	-4.6
02	02	5.3	-5.1
03	00	8.7	-8.4
02		6.8	7.3
04	00	30.0	-30.4
01		58.8	64.1
02		26.2	26.6
03		46.1	-49.5
04		18.8	-18.7
05		32.1	32.5
06		12.2	11.8
07		18.9	-19.5
05	02	5.2	4.6
06	01	8.8	-8.6
03		8.5	7.6
05		5.1	-6.2
07	00	3.3	-3.0
08	00	7.9	7.4
01		6.4	-6.9
03		4.8	-3.3
01	01	3.8	3.8

h	l	Fo	Fc
06	02	8.1	7.6
04		4.9	-5.9
07	00	11.3	11.2
01		8.0	-7.8
02		10.7	-10.3
03		6.9	6.2
08	00	12.2	-10.9
01		10.8	10.0
02		11.2	9.7
03		8.8	-0.0
09	00	6.5	-7.1
01		6.7	6.1
02		8.0	6.5
03		7.0	-5.3
10	01	3.7	4.0
03		3.7	-3.5
(h=08)			
00	00	11.7	-10.6
02		6.2	8.3
01	00	18.4	-21.9
02		15.9	19.3
04		12.2	-13.9
02	02	3.3	3.3
03	01	4.6	-5.4
04		4.6	5.1
04	01	8.8	8.6
02		3.6	3.4
03		8.6	-7.4
05	01	6.4	5.6
03		5.9	-5.2
06	01	3.6	3.5
03		3.5	-2.9
07	00	6.2	-7.1
01		10.6	-11.9
03		11.1	9.9
08	01	5.8	4.8
02		3.7	-3.4
05		12.1	-8.3
01	02	4.3	-4.4
02		4.9	-5.1
02		3.4	3.3
03		3.7	3.7
03		5.2	-4.2
05	00	9.9	10.5
02		10.5	-9.5
06	00	7.2	-8.4

h	l	Fo	Fc
04	02	13.4	13.9
03		6.0	5.6
04		13.7	-10.9
06		7.8	7.5
05	01	5.7	-6.0
02		4.1	3.7
03		4.9	4.6
06	00	3.6	-4.8
02		5.4	4.2
03		5.2	-2.8
07	01	4.4	-4.3
03		3.8	3.9
08	00	8.4	-7.4
01		7.7	6.4
02		7.1	6.8
03		6.3	-5.6
(h=10)			
00	00	9.0	9.0
02		6.8	-8.5
04		8.4	7.0
03	00	9.0	10.1
01		8.7	-8.4
02		8.7	-9.1
03		7.3	6.3
05	01	14.2	15.4
03		12.2	-12.5
08	00	8.8	-6.1
02		6.4	5.8
(h=11)			
00	01	10.6	8.9
03		7.8	-7.5
01	01	11.0	-12.8
03		9.8	11.0
02	01	9.1	-9.6
03		8.0	8.0
03	01	5.0	-4.9
08	00	6.9	5.6
09	00	9.6	-8.8
01		8.7	8.2
(h=12)			
00	00	29.9	30.0
02		27.5	-27.6
04		21.6	21.5
06		15.9	-14.0
08		8.7	7.8
08	00	15.9	-15.3
01		17.5	-18.0
02		14.6	14.2
03		14.1	14.6
04		8.2	-10.7
05		9.5	-10.6

densitometer. The peak intensities read from the precession transmission photographs were assumed to be proportional to the integrated values (Donnay & Donnay, 1954). Lorentz-polarization corrections were applied in the usual fashion. Since μ for Mo $K\alpha$ in HBO₂ is 2·2 cm⁻¹, no absorption corrections were employed. Relative intensity readings from all nets were placed on a common scale by a least-squares procedure described by Nordman (1960). The magnitudes for the observed structure factors may be found in Table 1.

Crystal data

Crystal system: orthorhombic. *Systematic absences*: $h0l$ when $h+l=2n+1$, $0kl$ when $k=2n+1$. *Space group*: No. 62 $Pbnm$ (D_{2h}^{16}). *Cell parameters*: (25 °C) $a = 8·046 \pm 0·004$, $b = 9·688 \pm 0·004$, $c = 6·261 \pm 0·005$ Å; (−130 °C) $a = 8·019 \pm 0·004$, $b = 9·703 \pm 0·004$, $c = 6·13 \pm 0·02$ Å. *Obs. density* (25 °C): 1·78 g.cm⁻³; calc. density (25 °C): 1·79 g.cm⁻³; $Z = 12$.

The alternative space group, No. 33, $Pbn2_1$ (C_{2v}^9) was ruled out by Tazaki on the basis of the holohedry exhibited by crystals of HBO₂. Since a satisfactory refinement was obtained in $Pbnm$, no further consideration was given $Pbn2_1$ in this work. Unit cell parameters were measured from calibrated back reflection

photographs of axial single-crystal reflections and revealed a small negative linear coefficient of expansion in the b axis direction.

Refinement of the structure

The boron and oxygen coordinates found by Tazaki were used to begin the least-squares refinement of the structure. First, only the boron and oxygen parameters were adjusted by a least-squares procedure which minimized the function

$$r = \Sigma w(hkl)(kF_o - F_c)^2 / \Sigma w(hkl)(kF_o)^2 .$$

Individual anisotropic thermal parameters were applied at the outset of the refinement. The complete matrix of coefficients resulting from minimizing r by least squares was approximated so that a 2×2 block was retained to allow for the interaction of the scale factor and an over-all temperature factor, a 3×3 block for the interaction of the β_{ii} for each atom, and the diagonal terms only for the positional and β_{ij} ($i \neq j$) parameters. A step function was utilized in the weighting scheme so that if $|F_o| > 3|F_{min}|$, $w = 3|F_{min}|/|F_o|$, and otherwise, $w = 1$.

Structure factors were calculated by use of the atomic form factor curves of McWeeny for the O and

Table 2. *Atomic coordinates in fractions of cell lengths and thermal parameters* for orthorhombic* HBO_2

Temperature factor of form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12})]$

$z=0.2500$ for all atoms. $\beta_{23} \equiv 0 \equiv \beta_{13}$

Atom	x	$\sigma(x)$	y	$\sigma(y)$	$\beta_{11}\times10^4$	$\beta_{22}\times10^4$	$\beta_{33}\times10^4$	$\beta_{12}\times10^4$
O(1)	−0·0909	0·0005	0·0531	0·0005	38 (4)	11 (4)	151 (8)	6 (4)
O(2)	−0·0885	0·0004	0·2943	0·0006	30 (4)	20 (2)	131 (10)	−6 (3)
O(3)	−0·0751	0·0004	0·5425	0·0005	32 (7)	21 (2)	219 (20)	−8 (6)
O(4)	0·1688	0·0012	0·1710	0·0005	30 (6)	12 (4)	272 (14)	3 (1)
O(5)	0·1704	0·0004	0·4150	0·0009	38 (6)	20 (5)	208 (16)	−1 (6)
O(6)	0·4239	0·0004	0·2966	0·0009	34 (2)	18 (4)	168 (15)	−3 (4)
B(1)	−0·0029	0·0016	0·1719	0·0002	41 (6)	23 (8)	89 (25)	−8 (6)
B(2)	0·0017	0·0006	0·4167	0·0004	42 (5)	23 (5)	130 (24)	2 (7)
B(3)	0·2560	0·0007	0·2926	0·0006	39 (9)	24 (10)	83 (30)	3 (6)
H(1)†	−0·029		−0·021					
H(2)†	−0·163		0·522					
H(3)†	0·471		0·231					

Isotropic $B = 0.5$ Å^2 arbitrarily assumed. *(for H(1), H(2), H(3))*

* Estimated standard deviations in parentheses.

† Hydrogen atom coordinates obtained from difference synthesis and held constant in least squares refinement.

H atoms and that of Ibers for the B atoms (McWeeny, 1951; Ibers, 1957).

The heavy atom refinement was terminated at a value of $R=0.080$, where the agreement factor $R=\Sigma||kF_o|-|F_c||/\Sigma|kF_o|$. Then the difference Fourier section at $z=\frac{1}{4}$ (Fig. 1) was calculated in order to
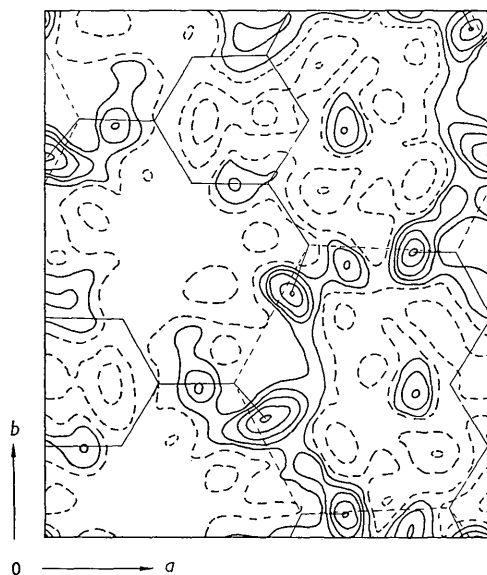
Fig. 1. ΔF synthesis showing hydrogen positions. Section at $z=\frac{1}{4}$. 00l and terms with $\sin^2\theta/\lambda^2 > 0.3$ omitted. Solid contours drawn at intervals of 0·1 e.Å^{-3}. Dashed contours drawn at intervals of −0·2 e.Å^{-3} beginning at 0·0 e.Å^{-3}. $\sigma(\Delta F)=0.3$ e.Å^{-3}.

determine the sensitivity of the data to the hydrogen atom locations. Three peaks of height 0·5 e.Å^{-3} are observed at reasonable positions for the hydrogen atoms. The smaller peaks of height 0·2–0·3 e.Å^{-3} must be considered insignificant since the expected error in the map is estimated to be 0·3 e.Å^{-3} (Cruickshank, 1949). As an additional test for the sensitivity of the data to the hydrogen atoms, their initial coordinates for least-squares refinement were assumed to be at the

Table 3. *Interatomic distances* (Å) *for orthorhombic* HBO_2

(a) Intramolecular

Bond distances

In-Ring		Out-of-Ring	
B(1)–O(2)	1·373 ± 0·008	B(1)–O(1)	1·351 ± 0·010
B(1)–O(4)	1·377 ± 0·011	B(2)–O(3)	1·367 ± 0·008
B(2)–O(2)	1·391 ± 0·006	B(3)–O(6)	1·347 ± 0·009
B(2)–O(5)	1·353 ± 0·008		
B(3)–O(4)	1·372 ± 0·007	Average	1·355 ± 0·009
B(3)–O(5)	1·372 ± 0·004		
Average	1·373 ± 0·007		

O(1)–H(1)	0·90 ± 0·10
O(3)–H(3)	0·80 ± 0·10
O(6)–H(6)	0·92 ± 0·10
Average	0·87 ± 0·10

Non-bonded distances

O(1) ··· O(4)	2·376	O(3) ··· O(2)	2·410
O(1) ··· O(2)	2·340	O(3) ··· O(5)	2·325
O(2) ··· O(4)	2·385	O(2) ··· O(5)	2·384
	O(6) ··· O(4)	2·381	
	O(6) ··· O(5)	2·335	
	O(4) ··· O(5)	2·367	
B(1) ··· O(5)	2·739	B(1) ··· B(3)	2·384
B(2) ··· O(4)	2·734	B(2) ··· B(3)	2·368
B(3) ··· O(2)	2·763	B(1) ··· B(2)	2·376
	O(2) ··· H(3)	2·50	
	O(4) ··· H(1)	2·65	
	O(4) ··· H(6)	2·69	

(b) Intermolecular

In-layer distances

O(3)[H(3)] ··· O(1)	2·680	O(4) ··· O(5)	2·799
O(6)[H(6)] ··· O(3)	2·748	O(2) ··· O(6)	3·910
O(1)[H(1)] ··· O(6)	2·827		
	O(1) ··· H(3)	1·88	
	O(3) ··· H(6)	1·88	
	O(6) ··· H(1)	1·91	

Layer-to-layer distances

B(1) ··· O(6)	3·136	O(2) ··· O(6)	3·191
B(2) ··· O(3)	3·146	O(3) ··· O(5)	3·177
		O(1) ··· O(1)	3·548
	O(2) ··· H(6)	3·15	
	O(5) ··· H(3)	3·09	
	O(1) ··· H(1)	3·27	

midpoints of the intermolecular O $\cdots$ O separations. After several cycles of least squares, the hydrogen coordinates had refined into the proper high density regions indicated in the difference map. However, the isotropic thermal parameters for two of the three hydrogens became negative, and the O–H bonds averaged a short 0·7 Å. These anomalies may possibly be attributed to the use of a neutral oxygen form factor. In view of this, the hydrogen coordinates determined from the difference synthesis and an arbitrary value for their isotropic thermal parameter, B, of 0·5 Å^2 were held constant in the final cycles of refinement. Refinement of the structure then proceeded to the point where none of the parameters changed by significant amounts within several successive cycles. At this point, the final value of R was 0·064 and of r, 0·008.

The final structural parameters for orthorhombic metaboric acid are listed in Table 2 along with the estimated standard deviations. Nordman & Reimann's (1959) procedure for estimating standard deviations was used, wherein the complete set of $F_o(hkl)$, arranged in order of sin^2 θ/λ^2, is randomly sorted into n subsets, each subset representing an independent set of data for a structure refinement. In this study, five such subsets of $F_o(hkl)$ were refined and the standard deviation, σ, of any structural feature, x, was then calculated from its arithmetic mean;

$$\bar{x} = \sum_{i=1}^{n} x_i/n, \qquad \sigma = \left\{ \sum_{i=1}^{n} |x_i - \bar{x}_i|^2/n(n-1) \right\}^{\frac{1}{2}}.$$

If the errors in the data are random, this procedure is adequate for assessing the expected errors in the structural parameters in Tables 2, 3 and 4.

Table 4. *Structural angles for orthorhombic* HBO$_2$

(a) Intramolecular

O(1)–B(1)–O(2)	118·5 ± 0·9°	O(3)–B(2)–O(5)	117·5 ± 0·6°
O(1)–B(1)–O(4)	121·2 ± 0·9	O(2)–B(2)–O(5)	120·7 ± 0·5
O(2)–B(1)–O(4)	120·3 ± 0·9	O(3)–B(2)–O(2)	121·8 ± 0·9

O(6)–B(3)–O(5)	118·4 ± 0·7°
O(6)–B(3)–O(4)	122·3 ± 1·0
O(4)–B(3)–O(5)	119·3 ± 0·6
B(1)–O(2)–B(2)	118·6 ± 0·7°
B(1)–O(4)–B(3)	120·3 ± 0·7
B(2)–O(5)–B(3)	120·7 ± 0·8
B(3)–O(6)–H(6)	129 ± 5
B(1)–O(1)–H(1)	127 ± 5
B(2)–O(3)–H(3)	116 ± 5

(b) Intermolecular

B(1)–O(1)[H(1)] $\cdots$ O(6)	120·2°
B(2)–O(3)[H(3)] $\cdots$ O(1)	119·0
B(3)–O(6)[H(6)] $\cdots$ O(3)	114·6
B(1)–O(1) $\cdots$ [H(3)]O(3)	123·7°
B(2)–O(3) $\cdots$ [H(6)]O(6)	127·0
B(3)–O(6) $\cdots$ [H(1)]O(1)	119·9
O(1) $\cdots$ O(6) $\cdots$ O(3)	125·5°
O(1) $\cdots$ O(3) $\cdots$ O(6)	114·0
O(3) $\cdots$ O(1) $\cdots$ O(6)	116·1

Description of the structure

The B$_3$O$_3$(OH)$_3$ molecule

The geometry of the trimeric HBO$_2$ structural unit is illustrated in Fig. 2. Some pertinent intramolecular distances are listed in Table 3. The average B–O bond distances are 1·373 ± 0·007 Å in the ring, and 1·355 ± 0·009 Å out of the ring. An average of the two distances, 1·364 Å, compares favorably with the average B–O distance found in earlier analyses of structures containing trigonally coordinated boron: 1·36 Å in Ca(BO$_2$)$_2$ (Zachariasen & Zeigler, 1932), H$_3$BO$_3$ (Zachariasen, 1934, 1954), KBO$_2$ (Zachariasen, 1937) and NaBO$_2$ (Fang, 1938) and 1·37 Å in the original study of orthorhombic HBO$_2$ (Tazaki, 1940a). Several studies of the structures of complex borates indicate an average B–O bond distance of 1·375 Å for trigonal boron (Christ & Clark, 1956; Clark & Christ, 1957; Christ, Clark & Evans, 1958 and Clark, 1959). The O–H bond distances average 0·87 Å. In H$_3$BO$_3$, Zachariasen (1954) found an average O–H distance of 0·88 Å. The average B–O–H angle is 124°.
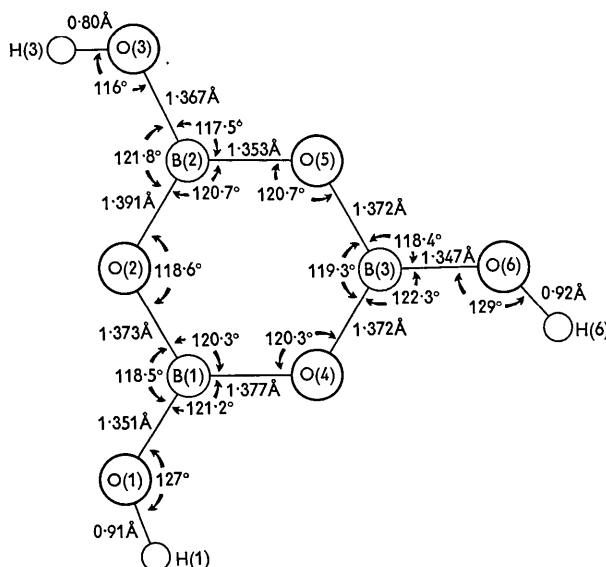
Fig. 2. Geometry of the B$_3$O$_3$(OH)$_3$ molecule.

Three of the O $\cdots$ O distances within the trimer are significantly shorter than the remaining six, averaging 2·333 Å compared with 2·384 Å. This short distance in each triangle is always an out-of-ring O $\cdots$ O distance and appears to result from the electrostatic attraction of a hydroxyl group toward the hydrogen atom of the neighboring hydroxyl group involved in a hydrogen bond. This distortion is also evident on examination of the bond angles, listed in Table 4, within each BO$_3$ group.

The hydrogen-bonded layer

The HBO$_2$ trimers are fixed in a perfectly planar network, illustrated in Fig. 3, by three distinct hydro-

gen bonds, O–H $\cdots$ O, of length 2·680, 2·748 and 2·827 Å. The b-glide related trimers are linked in an endless zigzag chain by the two longer hydrogen bonds. The neighboring chains, related by an a translation, are cross-linked at intervals of $b/2$ by the shortest hydrogen bond. Some intermolecular distances and angles are summarized in Tables 3 and 4. The longer, in-chain, hydrogen bonds of average length 2·788 Å are a consequence of the van der Waals repulsion limiting the non-hydrogen bonded intermolecular separation of atoms O(4) and O(5) to 2·799 Å. The shorter cross-chain hydrogen bond of 2·680 Å suffers no such restriction from the 3·910 Å intermolecular approach of O(6) $\cdots$ O(2). Apparently, the systematic angular distortion in each BO_3 triangle mentioned earlier is a result of an adjustment involving all the hydrogen bonds in response to this van der Waals limit on the approach of atoms O(4) and O(5) of neighboring trimers.
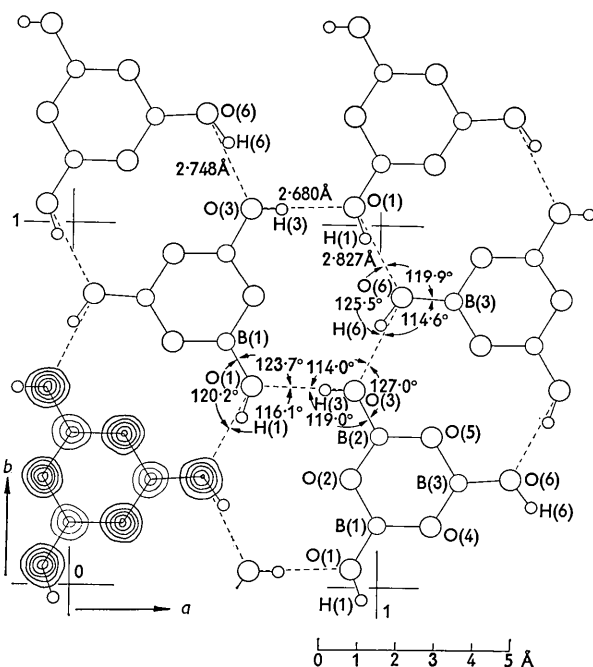
Fig. 3. Structure of a layer of orthorhombic HBO_2. Fourier contours drawn at 2·0 e.Å^{-3} intervals, initial contour: 2·0 e.Å^{-3}.

The crystal

Center-related sheets of the hydrogen-bonded $B_3O_3(OH)_3$ molecules are loosely stacked with a separation of 3·07 Å. The relative arrangement of neighboring layers is shown in Fig. 4. Two of the three hydroxyl groups, (–O(3)H(3)) and (–O(6)H(6)), are almost directly above and below the BO_3 groups of the boron atoms B(1) and B(2). Therefore, certain B $\cdots$ O and O $\cdots$ H layer-to-layer distances, listed in Table 3, are minimized as a result of an electrostatic influence on the arrangement of the layers. The
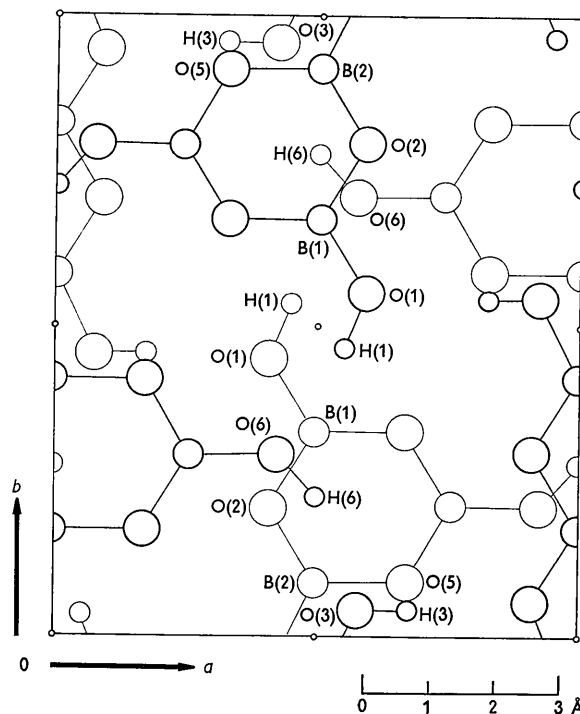
Fig. 4. [001] projection of unit cell content showing the arrangement of successive layers in the crystal.

remaining (–O(1)H(1)) group interacts to a lesser degree with its center related counterpart.

While the BO_3 group for atom B(2) exhibits B–O bond distance distortion in comparison with the groups for atoms B(1) and B(3), all the groups appear equivalent when only non-bonded, intramolecular and layer–layer, intermolecular distances are considered. This fact substantiates the B–O bond distortions in the BO_3 group of atom B(2) and also implies the distortion is the consequence of the crystal packing. In H_3BO_3, Zachariasen (1954) attributed the small departure of the structure from trigonal symmetry to weak interactions between layers of 3·18 Å spacing. If the boron atoms in the BO_3 groups are truly influenced by such interactions between layers, we should expect the BO_3 group for the B(3) atom to exhibit bond distances most representative of the isolated trimer. Referring again to Fig. 2, both in-ring distances, B(3)–O(4) and B(3)–O(5), are observed to be identical, 1·372 ± 0·006 Å, with a significantly shorter out-of-ring distance, B(3)–O(6), of 1·347 0·009 Å. In $K_3(BO_2)_3$, where the metaborate group has demanded threefold symmetry, the in-ring B–O distance is 1·38 Å, and the out-of-ring 1·33 Å (Zachariasen, 1937).

Thermal anisotropy

The apparent thermal anisotropy of the (B_3O_6) unit is reflected in the tensor components for the individual atoms, β_{ij}, listed in Table 2. In the main, the observed

thermal ellipsoids appear to result from rigid-body translational vibrations of the mass center for the trimer. Pronounced angular oscillations about axes passing through the mass center would result in systematically larger β_{ii} values, for a given i, for the out-of-ring atoms compared with those in the ring. The observed β_{ii} in this study do not reveal any such systematic difference between the two kinds of atoms. Within experimental error, the principal directions of the translational vibrations for the mass center parallel those of the unit cell axes. Averaging together the β_{ii} for the B and O atoms and using the relations $\beta_{11} = 2\pi^2 \overline{\mu_{11}^2}(a^*)^2$, etc., we calculate the average mean-square displacements of the trimer's center of mass to be 0.012 ± 0.001 Å^2, 0.009 ± 0.001 Å^2 and 0.031 ± 0.004 Å^2 parallel to the unit cell axes a, b and c, respectively (Cruickshank, 1956). As is typical of layer structures, the largest displacement occurs perpendicular to the hydrogen bonded array.

This description of the rigid body vibrations may be rationalized on consideration of the layer structure shown in Fig. 3. The trimer is triangulated by three pairs of relatively stiff hydrogen bonds which restrict the angular oscillations about the center of mass for the trimer, especially about an axis perpendicular to the plane of the trimer.

The boron atoms appear to undergo larger displacements within the layer than do the oxygen atoms, while the converse is true for the displacements perpendicular to the layer. This fact suggests the thermal data are sensitive to the bond density around each of the atomic sites.

Conclusion

This study of the structure of orthorhombic metaboric acid, using three-dimensional X-ray data, substantiates the gross features of that proposed earlier by Tazaki. However, the present study reveals structural detail not found in the earlier work.

The average B–O bond distance for the planar $B_3O_3(OH)_3$ structural unit of orthorhombic metaboric acid is 1.364 Å and the average O–H distance is 0.87 Å. The longer in-ring B–O distance, 1.373 ± 0.007 Å, compared with the out-of-ring distance, 1.355 ± 0.009 Å, may be attributed to the repulsions between borons or to a smaller bond order for the in-ring bonds than for the out-of-ring bonds (Zachariasen, 1937). In the monoclinic form of HBO$_2$, tetrahedrally coordinated boron has an observed B–O distance of 1.47 ± 0.01 Å (Zachariasen, 1952).

The structure exhibits three distinct O–H $\cdots$ O hydrogen bonds of 2.680, 2.478 and 2.827 Å with

angles of the kind B–O(H) $\cdots$ O of $120.2°$, $119.0°$, $114.6°$ and of the kind B–O $\cdots$ (H)O of $123.7°$, $127.0°$ and $119.9°$.

Finally, the observed anisotropic atomic displacements are due primarily to rigid-body translations of the center of mass of the trimer. This thermal behavior is compatible with the concept of a network of hydrogen bonds triangulating the trimer in a stiff, planar array so that the oscillational vibrations about orthogonal axes, origin at the center of mass, are severely restricted, especially about the axis perpendicular to the plane of the trimer.

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