Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# The monoclinic and cubic phases of metaboric acid (precise redeterminations)

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Received 21 October 1999
Accepted 8 December 1999

In monoclinic $\beta$-$HBO_2$, endless $[B_3O_3(OH)(H_2O)(O_{2/2})]$ zigzag chains are linked *via* an extensive system of hydrogen bonds with stronger major [H···O between 1.67 (1) and 1.77 (1) Å] and weaker minor components [H···O between 2.48 (1) and 2.63 (1) Å]. The unique three-dimensional tetrahedral $[BO_{2/2}O_{2/2}(H)]$ network structure of cubic $\gamma$-$HBO_2$ is stabilized by very short asymmetric hydrogen bonds [H···O2 1.48 (1) Å] with a donor–acceptor distance of 2.485 (1) Å and possesses small empty cages with a free diameter of *ca* 3.2 Å.

## Comment

Metaboric acid exists in three crystalline phases (Wells, 1984), which are prepared by dehydration of orthoboric acid and subsequent heat treatment. The monotropic phase transitions of $HBO_2$ are caused by polymerization and change from trigonal planar $BO_3$ to increasing numbers of tetrahedral $BO_4$ units. Structural information available for the monoclinic $\beta$- and cubic $\gamma$-phases stems from the room-temperature single-crystal X-ray studies of Zachariasen (1963*a*,*b*) which were based on low numbers of reflections only (for today's standard). Nevertheless, reasonable H-atom positions were obtained by inferring initial sites using geometrical criteria and subsequent refinements. In the course of our studies on borate clathrates, we have carried out new structure refinements of both $\beta$-$HBO_2$, (I), and $\gamma$-$HBO_2$, (II), based on low-temperature single-crystal X-ray diffraction data which allowed the localization of all H atoms on difference Fourier maps. Our results are in close agreement with those of Zachariasen but of considerably higher precision and we can supplement his structure discussions regarding the hydrogen-bonding schemes and the unique tetrahedral network structure of the $\gamma$ phase. These structural details may be of interest, for example, for studies on boron-oxide-containing glasses and high-silica zeolites.

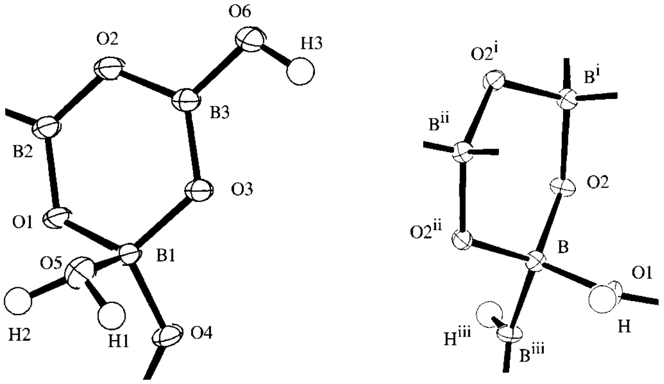

**Figure 1**
Six-membered $B_3O_3$ rings of $\beta$-$HBO_2$ (left) and of $\gamma$-$HBO_2$ (right). Displacement ellipsoids correspond to the 90% probability level. H atoms are represented as spheres of arbitrary radii (*ORTEP*-3; Farrugia, 1997). [Symmetry codes: (i) $y, z, x$; (ii) $z, x, y$; (iii) $-x + \frac{3}{2}, -z + \frac{3}{2}, y - \frac{3}{2}$.]

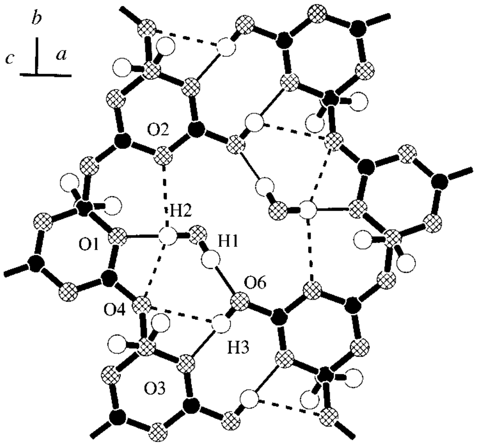

**Figure 2**
Two parallel polymeric chains of one layer in $\beta$-$HBO_2$ projected on (102). The two $H_2O$ molecules seen between the two chains belong to chains in adjacent layers above and below. B atoms are shown as black spheres, O atoms as hatched spheres and H atoms as white spheres of arbitrary radii. Major (minor) components of hydrogen bonds are represented as thin (dashed) lines (*DIAMOND*; Brandenburg & Berndt, 1999).

The basic structural units of both $\beta$- and $\gamma$-$HBO_2$ are six-membered $B_3O_3$ rings which are displayed in Fig. 1. In the $\beta$ phase, the B2 and B3 atoms are both three-coordinated. An $H_2O$ molecule is bonded to the B1 atom resulting in a distorted tetrahedral coordination. The B1 atom is slightly displaced [0.228 (1) Å] from the otherwise nearly planar six-membered ring in the direction of the water O5 atom. As is shown in Fig. 2, six-membered rings are linked *via* the O4 atoms into polymeric $[B_3O_3(OH)(H_2O)(O_{2/2})]$ zigzag chains of $2_1$ symmetry (extended along [010]), which in turn are arranged in layers parallel to (102). Chains are linked *via* intra-layer hydrogen bonds between exocyclic O6—H3 hydroxyl groups and endocyclic O3 atoms [H3···O3 1.77 (1) Å], and *via* inter-layer hydrogen bonds donated by the water molecules to exocyclic hydroxyl O6 and endocyclic O1 atoms [H1···O6 1.70 (1) Å and H2···O1 1.67 (1) Å] . In addition to these nearly linear hydrogen-bonding systems of typical geometry, already discussed by Zachariasen (1963*a*), there are three further contacts [H2···O4 2.48 (1), H2···O2

2.63 (1) and H3···O4 2.62 (1) Å]. These contacts, according to recently reported considerations on hydrogen bonds (Steiner & Saenger, 1992), may be taken as weaker minor components of multi-centre hydrogen-bonding systems (thus H2···O1 and H3···O3 are the major components). This latter view finds some support by the bond-valence sum concept (Brown, 1992) when applying the graphical valence-distance correlation for H···O bonds of Brown & Altermatt (1985) to estimate O—H and H···O parameters. This method yields with (without) minor components the following valences for involved O atoms: 2.01 (1.96) for O2, 2.03 (1.92) for O4, 2.02 (2.13) for O5 and 2.00 (2.05) for O6 [valences for the remaining atoms: 2.03 for O1, 2.02 for O3, 3.07 for B1, 3.03 for B2, 3.02 for B3 and 1.0 for all H atoms].

In $\gamma$-HBO$_2$, the six-membered B$_3$O$_3$ ring of $3(C_3)$ symmetry possesses a flat chair conformation [torsion angles ±39.92 (6)°] and the B atom is tetrahedrally coordinated. Fig. 3 shows the unique three-dimensional tetrahedral [BO$_{2/2}$-O$_{2/2}$(H)] network structure. This is to our knowledge the only chemical representative which is topologically based on net 37 of O'Keeffe's (1992, 1995) compilation of uninodal four-connected three-dimensional nets (maximum symmetry $Pm3n$; short Schläfli symbol is $3.4.8^4$). Considering only the tetrahedral nodes, there occurs one type of three-ring, one type of four-ring, one type of puckered oval eight-ring and one type of puckered circular eight-ring. Formally, the eight-rings define two types of channel systems each running parallel to [100] directions (on $x$,0,0 and $x,\frac{1}{2}$,0, respectively), and on the intersection of the oval channels (on 0,0,0), there exists a small [$3^8 8^6$] cage of $23(T)$ symmetry formed by six oval eight-rings and eight three-rings, the latter being arranged with their centres on the corners of two interpenetrating tetrahedra of different sizes. Considering all atoms, the oval and circular channels are blocked by very strong, definitely asymmetric hydrogen bonds [H···O2 1.48 (1) Å], with a donor–acceptor distance of 2.485 (1) Å [geometrical parameters of short hydrogen bonds derived from neutron diffraction studies can be found by Joswig *et al.* (1982), and a review of very strong hydrogen bonds by Emsley (1980)]. Interestingly, according to the work of Schwarzmann & Christoph (1969), these strong hydrogen bonds exhibit an H/D isotope effect that results in a considerably larger cubic unit cell of the deuterated form (by 0.023 Å at room temperature) and renders the formation of $\gamma$-DBO$_2$ possible only after seeding and very long heating periods. The small empty cages of the $\gamma$-HBO$_2$ network have a free diameter of *ca* 3.2 Å (van der Waals radius for oxygen taken as 1.4 Å).

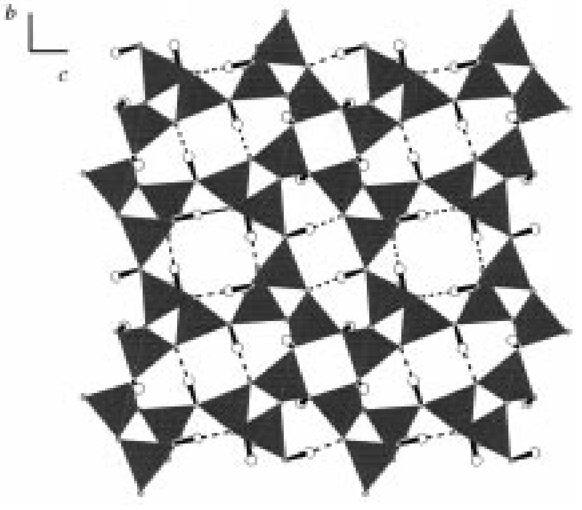

**Figure 3**
Structure of $\gamma$-HBO$_2$ as seen along [100] (*DIAMOND*; Brandenburg & Berndt, 1999).

## Experimental

Orthoboric acid was placed in an open crucible and dehydrated at 373 K for 24 h to yield orthorhombic $\alpha$-HBO$_2$, which was heated under closed conditions (Teflon-lined stainless steel autoclave) at 423 K for 24 h to yield crystalline $\beta$-HBO$_2$ (crystal size up to 3 mm). The $\beta$-phase was kept under closed conditions at 453 K for at least 7 d to give crystals of the $\gamma$ form (crystal size up to 0.5 mm). The conditions reported yield essentially pure-phase materials as checked by powder X-ray diffraction (Guinier diffractometer, Cu $K\alpha_1$ radiation).

### Monoclinic $\beta$-HBO$_2$

*Crystal data*

HBO$_2$
$M_r = 43.82$
Monoclinic, $P2_1/c$
$a = 6.758$ (1) Å
$b = 8.844$ (1) Å
$c = 7.075$ (2) Å
$\beta = 93.50$ (1)°
$V = 422.1$ (1) Å$^3$
$Z = 12$
$D_x = 2.069$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.95$–$23.67°$
$\mu = 0.205$ mm$^{-1}$
$T = 183$ K
Irregular polyhedron, colourless
0.45 × 0.30 × 0.30 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$–$2\theta$ scans
4617 measured reflections
4400 independent reflections
3549 reflections with $F > 4\sigma(F)$
$R_{\rm int} = 0.029$
$\theta_{\rm max} = 49.98°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 19$
$l = -15 \rightarrow 15$
3 standard reflections every 200 reflections intensity decay: 1.5%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.087$
$S = 1.076$
4400 reflections
94 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 0.006P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.50$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.57$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å) for (I).

| | | | |
|---|---|---|---|
| B1—O4 | 1.4284 (5) | B2—O1 | 1.3748 (4) |
| B1—O1 | 1.4512 (5) | B2—O2 | 1.3812 (5) |
| B1—O3 | 1.4512 (5) | B3—O3 | 1.3628 (5) |
| B1—O5 | 1.5612 (6) | B3—O6 | 1.3671 (5) |
| B2—O4$^{\rm i}$ | 1.3485 (5) | B3—O2 | 1.3738 (5) |

Symmetry code: (i) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

**Table 2**
Hydrogen-bonding geometry (Å, °) for (I).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O5—H1···O6$^{i}$ | 0.96 (1) | 1.70 (1) | 2.650 (1) | 170.2 (8) |
| O5—H2···O1$^{ii}$ | 1.01 (1) | 1.67 (1) | 2.675 (1) | 173.3 (8) |
| O5—H2···O4$^{iii}$ | 1.01 (1) | 2.48 (1) | 3.081 (1) | 117.1 (8) |
| O5—H2···O2$^{iv}$ | 1.01 (1) | 2.63 (1) | 2.902 (1) | 95.4 (8) |
| O6—H3···O3$^{v}$ | 0.94 (1) | 1.77 (1) | 2.678 (1) | 163.6 (8) |
| O6—H3···O4$^{v}$ | 0.94 (1) | 2.62 (1) | 3.155 (1) | 117.0 (8) |

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $2 - x, -y, -z$; (iii) $x, -\frac{1}{2} - y, z - \frac{1}{2}$; (iv) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $1 - x, -y, 1 - z$.

## Cubic γ-$HBO_2$

### *Crystal data*

$HBO_2$
$M_r = 43.82$
Cubic, $P\overline{4}3n$
$a = 8.8811$ (3) Å
$V = 700.49$ (4) Å$^3$
$Z = 24$
$D_x = 2.493$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 15.36$–$20.37°$
$\mu = 0.247$ mm$^{-1}$
$T = 183$ K
Rhombic dodecahedron, colourless
0.15 mm (radius)

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$–$2\theta$ scans
3758 measured reflections
686 independent reflections
628 reflections with $F > 4\sigma(F)$
$R_{\rm int} = 0.031$
$\theta_{\rm max} = 49.86°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 19$
3 standard reflections
every 200 reflections
intensity decay: 1.3%

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.045$
$S = 1.015$
686 reflections
33 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0197P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.29$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.26$ e Å$^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.393 (13)

**Table 3**
Selected geometric parameters (Å) for (II).

| | | | |
|---|---|---|---|
| B—O2$^{i}$ | 1.4428 (6) | B—O1$^{ii}$ | 1.4803 (6) |
| B—O2 | 1.4508 (6) | B—O1 | 1.5094 (6) |

Symmetry codes: (i) $z, x, y$; (ii) $\frac{3}{2} - x, \frac{3}{2} - z, y - \frac{1}{2}$.

**Table 4**
Hydrogen-bonding geometry (Å, °) for (II).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1···O2$^{i}$ | 1.01 (1) | 1.48 (1) | 2.485 (1) | 175.5 (8) |

Symmetry code: (i) $\frac{1}{2} + z, \frac{3}{2} - y, \frac{3}{2} - x$.

The coordinates of the non-H atoms were taken from the literature (Zachariasen, 1963*a*,*b*). All H atoms were located on difference Fourier maps, and in the case of γ-$HBO_2$, after refinement of an extinction parameter.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *SET*4 in *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1343). Services for accessing these data are described at the back of the journal.

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