

A new polytype of orthoboric acid, $\text{H}_3\text{BO}_3\text{-}3T^1$

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The crystal structure of $\text{H}_3\text{BO}_3\text{-}3T$, a new trigonal polytype of orthoboric acid, consists of sheets of hydrogen-bonded $\text{B}(\text{OH})_3$ molecules similar to those found in the triclinic structure of orthoboric acid, $\text{H}_3\text{BO}_3\text{-}2A$. In each case, van der Waals forces connect the sheets. However, the stacking sequences of the sheets differ between the two polymorphs. In $\text{H}_3\text{BO}_3\text{-}3T$ (space group $P3_2$), the sheets are stacked in the repeating sequence $ABC\dots$, whereas in $\text{H}_3\text{BO}_3\text{-}2A$ (space group $P1$), the sheets are stacked in the repeating sequence $AB\dots$.

Comment

Structures of boric acids known to date include triclinic orthoboric acid, $\text{H}_3\text{BO}_3\text{-}2A$ (Zachariasen, 1934), its deuterated analog, D_3BO_3 (Craven & Sabine, 1966), and three modifications of metaboric acid [first described by Kracek *et al.* (1934)], *viz.* orthorhombic $\alpha\text{-HBO}_2$ (Tazaki, 1940; Peters & Milberg, 1964), monoclinic $\beta\text{-HBO}_2$ (Zachariasen, 1952, 1963*b*) and cubic $\gamma\text{-HBO}_2$ (Zachariasen, 1963*a*). The crystal structures of the first three compounds contain sheets formed by $\text{B}(\text{OH}/\text{D}_3)$ groups in orthoboric acid and by $\text{B}_3\text{O}_3(\text{OH})_3$ groups in $\alpha\text{-HBO}_2$, with hydrogen bonding between these groups within a given sheet. In $\beta\text{-HBO}_2$, two-thirds of the B atoms have triangular coordination, and one-third are tetrahedrally coordinated and linked into infinite $^1[\text{B}_3\text{O}_4(\text{OH})(\text{H}_2\text{O})]$ chains, arranged in sheets. In $\gamma\text{-HBO}_2$, all B atoms have tetrahedral coordination and are linked into a

three-dimensional $^3[\text{BO}(\text{OH})]$ framework [see Lima-de-Faria *et al.* (1990) for formula nomenclature].

As mentioned by Craven & Sabine (1966), $\text{H}_3\text{BO}_3\text{-}2A$ was one of the first compounds with a hydrogen-bonded crystal structure to be examined by X-ray diffraction methods (Zachariasen, 1934), and it has been a 'textbook' example ever since. In the original work of Zachariasen (1934), an approximate crystal structure of $\text{H}_3\text{BO}_3\text{-}2A$ was reported. The $(\text{BO}_3)^{3-}$ groups, of nearly perfect C_{3h} symmetry, were found to form pseudo-hexagonal sheets in which each $(\text{BO}_3)^{3-}$ group has three adjacent groups. The H atoms were assumed to be positioned midway between the two nearest O atoms of adjacent $(\text{BO}_3)^{3-}$ groups, but arguments favoring $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds in this structure were subsequently forwarded by Bernal & Megaw (1935). Studying disorder in the stacking of the sheets in thin microcrystals of $\text{H}_3\text{BO}_3\text{-}2A$ using electron diffraction, Cowley (1953) found that the H atoms are systematically displaced from the nearly collinear arrangement suggested by Zachariasen (1934). This model has not been verified in further X-ray (Zachariasen, 1954; Gajhede *et al.*, 1986) or neutron (Craven & Sabine, 1966) diffraction experiments. Dorset (1992) performed electron diffraction studies of thin microcrystals of $\text{H}_3\text{BO}_3\text{-}2A$ at low temperature (128 K and below) and determined that, as a result of a stacking disorder as discussed by Cowley (1953), microcrystals of orthoboric acid diffract as if single sheets were independent of one another. Among the most recent studies of triclinic orthoboric acid are the *ab initio* calculations of Zapol *et al.* (2000). Their theoretical results are in good agreement with the experimental data, *e.g.* the binding energy of the molecules within a sheet is much higher than the interaction energy between the sheets, which could explain the good lubricating properties of orthoboric acid (Erdemir *et al.*, 1991).

This paper reports the crystal structure of a new polytype of orthoboric acid, which was isolated as an unexpected product during our attempts to synthesize new sodium uranyl borate compounds. As can be seen from Fig. 1, each of the two symmetrically independent $\text{B}(\text{OH})_3$ molecules has nearly perfect C_{3h} symmetry and is hydrogen bonded to three adjacent molecules, thus forming pseudo-hexagonal $^2[\text{B}(\text{OH})_3]$ sheets, which are parallel to the (001) plane; details are given in Tables 1 and 2. The average values of the B—O, O—H and $\text{O}\cdots\text{H}$ bond distances, and the O—B—O, B—O—H and $\text{O}-\text{H}\cdots\text{O}$ angles within a sheet are 1.36 (1), 0.91 (5) and 1.88 (5) Å, and 120.0 (9), 111 (5) and 152 (6)°, respectively. These values are similar to those of $\text{H}_3\text{BO}_3\text{-}2A$ (1.361, 0.88 and 1.85 Å, and 120.0, 112 and 171°; Zachariasen, 1954). The unit-cell parameters parallel to the (001) plane in both structures are also comparable (Table 3). Although the sheets in the crystal structure of $\text{H}_3\text{BO}_3\text{-}3T$ are of the same type as those in $\text{H}_3\text{BO}_3\text{-}2A$, the stacking sequences of the sheets are different in these two structures. The sheets are stacked in the sequence $ABC\dots$ in $\text{H}_3\text{BO}_3\text{-}3T$ (Fig. 2*a*), whereas in $\text{H}_3\text{BO}_3\text{-}2A$, the sheets are stacked in the sequence $AB\dots$ (Fig. 2*b*). The distances between the planes of two adjacent sheets, calculated as half of d_{001} in $\text{H}_3\text{BO}_3\text{-}2A$ and as one-third of d_{001} in $\text{H}_3\text{BO}_3\text{-}3T$, are 3.182 (2) and 3.1869 (2) Å, respectively,

¹The $\text{H}_3\text{BO}_3\text{-}3T$ and $\text{H}_3\text{BO}_3\text{-}2A$ symbolism used in this paper refers to two different polytypes of orthoboric acid and is in agreement with the recommendations of the International Union of Crystallography *Ad hoc* Committee on the Nomenclature of Disordered, Modulated and Polytype Structures [Guinier, Bokij, Boll-Dornberger, Cowley, Durovic, Jagodzinski, Krishna, de Wolff, Zvyagin, Cox, Goodman, Hahn, Kuchitsu & Abrahams (1984). *Acta Cryst.* **A40**, 399–404]. The capital letter denotes the crystal system (T = trigonal and A = triclinic) and the preceding number indicates the periodicity along the c axis of the compound relative to the smallest hypothetical subcell of the system.

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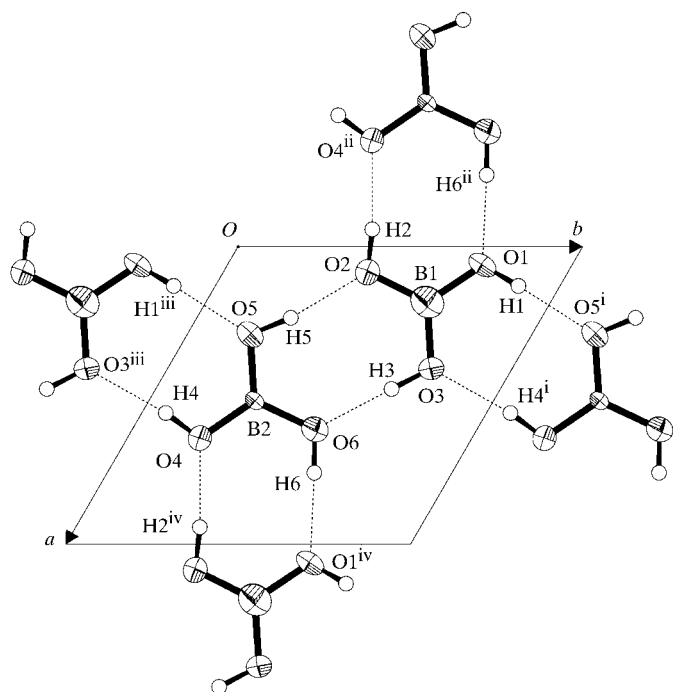


Figure 1
The arrangement of hydrogen-bonded $B(OH)_3$ molecules within a single pseudo-hexagonal sheet parallel to the (001) plane in $H_3BO_3 \cdot 3T$. Displacement ellipsoids are shown at the 50% probability level, and H atoms are shown as open circles of arbitrary size (symmetry codes are given in Table 2).

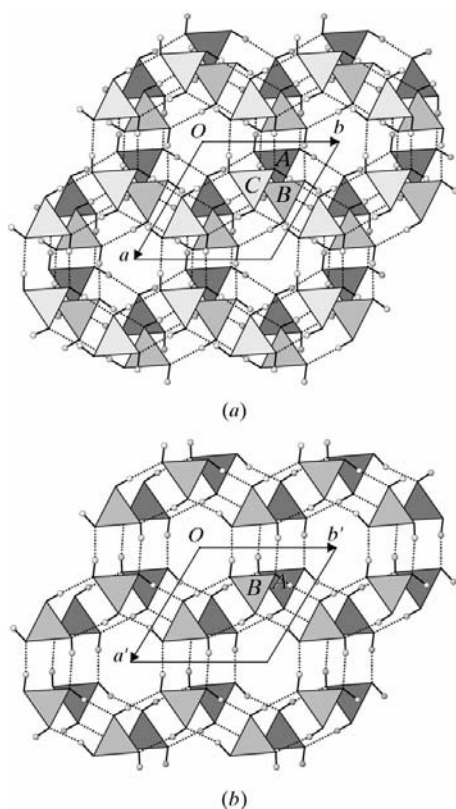


Figure 2
Stacking sequences of the sheets in (a) $H_3BO_3 \cdot 3T$ and (b) $H_3BO_3 \cdot 2A$ (Zachariasen, 1954), projected along the [001] axis. BO_3 groups, shown as triangles, are connected via H atoms, which are shown as gray spheres.

whereas the shortest interatomic distances between B and O atoms from neighboring sheets are 3.157 and 3.195 Å in $H_3BO_3 \cdot 2A$, and 3.172 (6) and 3.187 (8) Å in $H_3BO_3 \cdot 3T$. It appears that small tilts of the $B(OH)_3$ molecules relative to the (001) plane in the crystal structure of $H_3BO_3 \cdot 3T$, almost of the same magnitude as those in $H_3BO_3 \cdot 2A$, are mainly due to weak interactions between B and O atoms, as mentioned by Zachariasen (1954) for $H_3BO_3 \cdot 2A$.

Experimental

Crystals of the title compound were prepared by mild hydrothermal techniques. The initial solution was prepared from $NaBO_2(H_2O)_2$ (41 mg) and UO_3 (29 mg) (molar ratio 4:1) dissolved in ultrapure water (3 ml). The pH was adjusted to 0.5 using concentrated nitric acid (15.4 mol l^{-1}). The resulting solution was placed in a 23 ml Teflon-lined Parr bomb, heated at 453 K for 48 h and then cooled to ambient temperature. No crystals had formed after heating, so the solution was placed in a fume hood to evaporate. After 2 d, well shaped pseudo-hexagonal crystals of $H_3BO_3 \cdot 2A$ and small colorless crystals of $H_3BO_3 \cdot 3T$ were recovered.

Crystal data

H_3BO_3	Mo $K\alpha$ radiation
$M_r = 61.83$	Cell parameters from 1623 reflections
Trigonal, $P3_1$	$\theta = 3.3\text{--}33.8^\circ$
$a = 7.0453$ (4) Å	$\mu = 0.16 \text{ mm}^{-1}$
$c = 9.5608$ (7) Å	$T = 297$ (2) K
$V = 410.98$ (4) Å ³	Triangular plate, colorless
$Z = 6$	$0.14 \times 0.08 \times 0.02 \text{ mm}$
$D_x = 1.499 \text{ Mg m}^{-3}$	

Data collection

Bruker APEX CCD area-detector diffractometer	1143 independent reflections
ω scans	765 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (<i>XPREP</i> ; Bruker, 1997)	$R_{\text{int}} = 0.035$
$T_{\text{min}} = 0.851$, $T_{\text{max}} = 0.918$	$\theta_{\text{max}} = 34.4^\circ$
4615 measured reflections	$h = -11 \rightarrow 11$
	$k = -11 \rightarrow 11$
	$l = -14 \rightarrow 11$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
$wR(F^2) = 0.088$	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$
$S = 1.00$	Extinction correction: <i>SHELXTL</i>
1143 reflections	(Bruker, 1998)
99 parameters	Extinction coefficient: 0.051 (6)
All H-atom parameters refined	
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters (Å, °).

B1—O1	1.349 (5)	B2—O4	1.361 (4)
B1—O2	1.350 (6)	B2—O5	1.364 (4)
B1—O3	1.377 (6)	B2—O6	1.363 (5)
O1—B1—O2	120.4 (5)	O4—B2—O5	120.7 (3)
O1—B1—O3	119.9 (5)	O4—B2—O6	120.2 (3)
O2—B1—O3	119.6 (4)	O5—B2—O6	119.0 (2)
B1—O1—H1	113 (2)	B2—O4—H4	107 (2)
B1—O2—H2	108 (2)	B2—O5—H5	107 (2)
B1—O3—H3	117 (2)	B2—O6—H6	114 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1 \cdots O5 ⁱ	0.91 (2)	1.88 (2)	2.715 (7)	153 (2)
O2—H2 \cdots O4 ⁱⁱ	0.93 (2)	1.83 (2)	2.705 (6)	155 (2)
O3—H3 \cdots O6	0.91 (2)	1.82 (2)	2.688 (7)	159 (3)
O4—H4 \cdots O3 ⁱⁱⁱ	0.91 (2)	1.95 (2)	2.719 (5)	141 (3)
O5—H5 \cdots O2	0.91 (2)	1.89 (2)	2.723 (6)	151 (2)
O6—H6 \cdots O1 ^{iv}	0.91 (2)	1.91 (2)	2.740 (6)	151 (3)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $x - 1, y, z$; (iii) $x, y - 1, z$; (iv) $1 + x, y, z$.**Table 3**Comparison of the unit-cell parameters (Å, °) in the crystal structures of H₃BO₃-2A and H₃BO₃-3T.

Compound	a	b	c	α	β	γ
H ₃ BO ₃ -2A [†]	7.039 (2)	7.053 (2)	6.578 (2)	92.58 (2)	101.17 (2)	119.83 (2)
H ₃ BO ₃ -3T [‡]	7.0453 (4)	7.0453 (4)	9.5608 (7)	90	90	120

[†] Zachariasen (1954). [‡] This work.

The positions of most O and B atoms were determined by direct methods. The remaining non-H atoms, and approximate H-atom positions, were located from subsequent difference Fourier syntheses. O—H bond distances were restrained to 0.96 Å, with standard uncertainties of 0.02 Å. There are no atoms heavier than O atoms in this structure, so that the absolute configuration cannot be determined reliably. Both absolute structures were tested and gave the same results. The 764 Friedel opposites were merged before the final refinement, because the absolute structure parameter (Flack, 1983) was unreliable [4 (3)]. The twin law [010/100/00 $\bar{1}$] was introduced in the final cycles of structure refinement, thus reducing the $R(F)$ index from 0.089 to 0.044. The twin-component scale factor refined to 0.278 (2). The low standard uncertainties of the cell constants indicate the internal consistency of the measurements themselves, *i.e.* the precision of the measurements, not their accuracy.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ATOMS* (Dowty, 2000);

software used to prepare material for publication: *SHELXTL* and *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1014). Services for accessing these data are described at the back of the journal.

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