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Letter

The solid-state structure of diboronic acid, $B_2(OH)_4$

R. Angharad Baber, Nicholas C. Norman,* A. Guy Orpen and Jean Rossi

University of Bristol, School of Chemistry, Bristol, UK BS8 1TS

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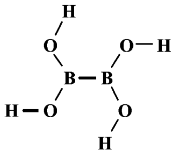
The crystal structure of diboronic acid contains molecules of $B_2(OH)_4$ hydrogen-bonded into two-dimensional sheets linked by B···O interactions.

Of the oxo-acids of boron, orthoboric acid, $B(OH)_3$, is by far the most studied although several modifications of metaboric acid, HBO_2, are also known.[1] The orthorhombic modification of HBO_2 comprises layers constructed from hydrogen-bonded $B_3O_3(OH)_3$ units which has much in common with the layer structure of $B(OH)_3$.[2] These species all contain B(III). Far less studied and hitherto structurally uncharacterised is the B–B bonded, formally boron(II) compound $B_2(OH)_4$ (**1**), usually referred to as diboronic acid or tetrahydroxydiboron. Herein we describe the solid state structure of **1**, the parent compound for a new class of boronic acids and B–B bonded borates.



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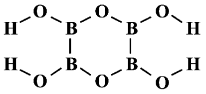

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Some of the earliest reports of a lower oxidation state, B–B bonded oxo-acid (or boron hydroxide) refer to $H_2B_2O_2$ and various adducts and salts thereof although these formulations should probably be considered with some caution.[3] The first reports of $B_2(OH)_4$ come from the same era in papers by Stock and Wiberg describing the hydrolysis of B_2Cl_4 and $B_2(OMe)_4$ respectively.[4] In the 1950s several further reports appeared on the preparation and properties of a white solid material formulated as $B_2(OH)_4$. Wartik and Apple described the hydrolysis of B_2Cl_4,[5] Nöth and Meister the hydrolysis of the amido species $B_2(NMe_2)_4$,[6] whilst the most detailed studies were reported by McCloskey and Brotherton on the hydrolysis of $B_2(NMe_2)_4$, $B_2(OEt)_4$ and $B_2(O^iPr)_4$;[7] quantitative yields of $B_2(OH)_4$ (characterised by elemental analysis) were obtained from hydrolysis of the alkoxydiborane(4) compounds in water. Many of these reports, particularly those of McCloskey and Brotherton, referred also to the dehydration of **1** and the formation of boron monoxide, BO. Much of this work was subsequently reviewed by Brotherton.[8] We note also a patent on the use of **1** in the palladium catalysed preparation of organic boronic acid derivatives.[9]

More recently, we reported the X-ray crystal structure of the tetrahydroxyborinane compound $B_4O_2(OH)_4$ (**2**) (obtained as a co-crystal with two equivalents of the ammonium salt $[NH_2Me_2]Cl$)[10] which is formally a condensation product of **1**. Compound **2** was initially obtained as a minor side product in the preparation of $B_2(1,2\text{-}O_2C_6Cl_4)_2$[10] although we have subsequently shown that it can be obtained in high yield from hydrolysis of $[B_2Cl_4(NHMe_2)_2]$[11] in aqueous acetone.[12] The fact that either **1** or **2** are available from very similar hydrolysis procedures was an indication that the solution behaviour of diboronic acid might be more complex than had hitherto been supposed prompting us to characterise **1** more definitively.

Samples of **1** were prepared either by hydrolysis of B_2Cl_4 according to the method of Wartik and Apple[5] or by hydrolysis of $[B_2Br_4(NHMe_2)_2]$.† In both cases, recrystallisation of white solid **1** from water afforded well formed colourless crystals of **1** the structure of which was determined by X-ray crystallography.§ Crystals of **1** contain two centrosymmetric, crystallographically independent half molecules in the asymmetric unit. The molecules are planar and of approximately C_{2h} symmetry. One molecule is shown in Fig. 1. The B–B distances [1.715(5) and 1.710(4) Å] are towards the long end of the range found for tetra-oxo diborane(4) compounds whilst the B–O distances [av. 1.368(2) Å] are slightly shorter than typical values.[11b] Both distances are similar to those found in **2**, however; B–B 1.732(3), B–OH 1.361(3), 1.350(3) Å.[10] Inter-bond angles are unexceptional [see caption to Fig. 1] although we note an asymmetry in the pairs of O–B–B angles [av. 119.45 *vs.* 124.65°]. This distortion serves to maximise the non-bonded eclipsed B···H four-bond distance (2.83 Å). The torsion angles about the B–B bonds, with respect to the BO_2 planes, are zero. The crystal structure shows that molecules of **1** are extensively hydrogen bonded into two-dimensional sheets [Fig. 2a]. These planes are linked by B···O contacts in

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† Cocondensation of B_2Cl_4 with four equivalents of H_2O afforded a white solid and a gas assumed to be HCl. Dissolution of the crude solid in degassed H_2O and slow evaporation at room temperature afforded colourless crystals of **1** (70%). $H_4B_2O_4$ requires H, 4.45; found H, 4.70%. In D_2O solution, the $^{11}B\text{-}\{^1H\}$ NMR spectrum of **1** shows a signal at 30.0 ppm although traces of $B(OH)_3$ ($\delta_B = 18.7$) are also present. Compound **2** exhibits a similar ^{11}B chemical shift at δ 31 although in both cases chemical shifts vary by up to 1 ppm depending on the solvent. Samples of $[B_2Br_4(NHMe_2)_2]$ were prepared by addition of excess BBr_3 in heptane to $[B_2Cl_4(NHMe_2)_2]$[11] in thf at room temperature.‡ Subsequent addition of hexane afforded $[B_2Br_4(NHMe_2)_2]$ as a white solid in 70–80% yields. $C_4H_{14}B_2Br_4N_2$ requires C, 11.15; H, 3.30; N, 6.50; found C, 11.45; H, 3.60; N, 6.15%. NMR (CD_2Cl_2): ^{11}B δ 4.3; ^1H δ 2.89 (d, 12H, Me, $^3J_{HH} = 5.7$ Hz), 5.12 (br s, 2H, NH); ^{13}C δ 41.0. Hydrolysis of $[B_2Br_4(NHMe_2)_2]$ was effected by adding aqueous thf (approx 25% H_2O by volume) to solutions of $[B_2Br_4(NHMe_2)_2]$ in thf which afforded a white solid after stirring for two days. Dissolution of the crude solid in degassed H_2O and slow evaporation at room temperature afforded colourless crystals of **1**. Solutions in D_2O showed mainly **1** and traces of $B(OH)_3$.

‡ The compound $[B_2Br_4(NHMe_2)_2]$ has previously been isolated from the reaction between $B_2(NMe_2)_4$ and HBr.[11c]

§ Crystal data for **1**: $H_4B_2O_4$, $M = 89.65$, monoclinic, space group $P2_1/c$ (no. 14), $a = 7.4090(15)$, $b = 7.6660(15)$, $c = 7.0421(14)$ Å, $\beta = 116.04(3)°$, $U = 359.39(12)$ Å^3, $Z = 4$, $D_c = 1.657$ Mg m^{-3}, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}_\alpha) = 0.162$ mm^{-1}, $F(000) = 184$, $T = 100(2)$ K, $R_1 = 0.056$.[13–16] CCDC reference number 202210. See http://www.rsc.org/suppdata/nj/b3/b302496m/ for crystallographic data in .cif or other electronic format.

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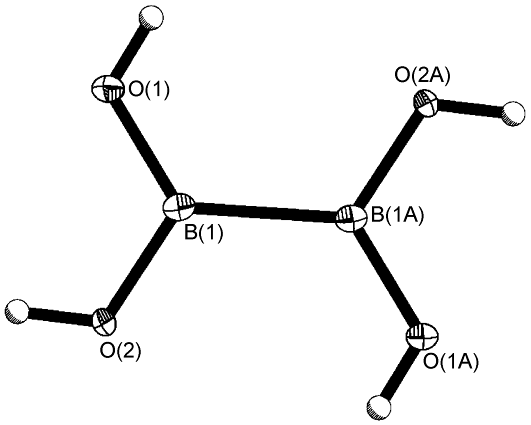

Fig. 1 A view of the molecular structure of one of the two independent molecules of **1**. Selected bond lengths (Å) and angles (°) with values for the second molecule in [ ]: B(1)–B(1a) 1.715(5) [1.710(4)], B(1)–O(1) 1.370(2) [1.370(3)], B(1)–O(2) 1.366(2) [1.366(2)], O(1)–B(1)–O(2) 115.77(18) [116.03(18)], O(1)–B(1)–B(1a) 124.8(2) [124.5(2)], O(2)–B(1)–B(1a) 119.4(2) [119.5(2)].

the third dimension approximately perpendicular to the molecular plane which fall in the range 3.12 to 3.27 Å. Within a plane each OH group acts once as a hydrogen bond donor and once as a hydrogen bond acceptor with each molecule of **1** participating in four R(2,2)9 and four R(4,4)8 hydrogen bond motifs resulting in a (4,4) net of molecules in each layer [Fig. 2a].[17] For comparison, the structure of $B(OH)_3$ has a (6,3) net of molecules in each layer linked by R(2,2)8 hydrogen bond motifs [Fig. 2b],[2a] while the structure of the orthorhombic modification of HBO_2 has a (3,6) net of molecules linked by R(2,2)12 and R(4,4)12 hydrogen bond motifs.[2b]

It is interesting to compare the experimentally determined structure of **1** with the results of several theoretical studies. In the first such study, Demachy and Volatron[18] predicted that planar $B_2(OH)_4$ is more stable by about 5.5–6.5 kcal mol^{-1} than a structure in which the two $B(OH)_2$ units are perpendicular. Calculated B–B and B–O distances are 1.733 and 1.358 Å respectively at the SCF level and 1.714 and 1.376 Å at the MP2 level, the latter in good agreement with the experimentally determined values reported here. Furthermore, these authors predicted that, with respect to the various conformers possible for four coplanar B–O–H groups, the C_{2h} structure is the most stable; this is the conformer found in crystals of **1** (Fig. 1). More recent density functional theory calculations at the B3LYP level by Cui, Musaev and Morokuma,[19] undertaken as part of a study of metal catalysed diboration reactions, predict the opposite order of stability with respect to planar and perpendicular conformers, the perpendicular being found to be more stable although only by 0.6 kcal mol^{-1}. Calculated B–B and B–O distances for the planar form are 1.722 and 1.375 Å respectively. In the most recent study of which we are aware, Politzer *et al.*,[20] as part of a study of the products of boron combustion, calculate that the planar, C_{2h} conformer of **1** is also the most stable (calculated B–B, 1.716, 1.717 and B–O 1.366, 1.373 Å from two different methods).

Further studies on the solution chemistry of **1** and its dehydration to BO are in progress.

Acknowledgements

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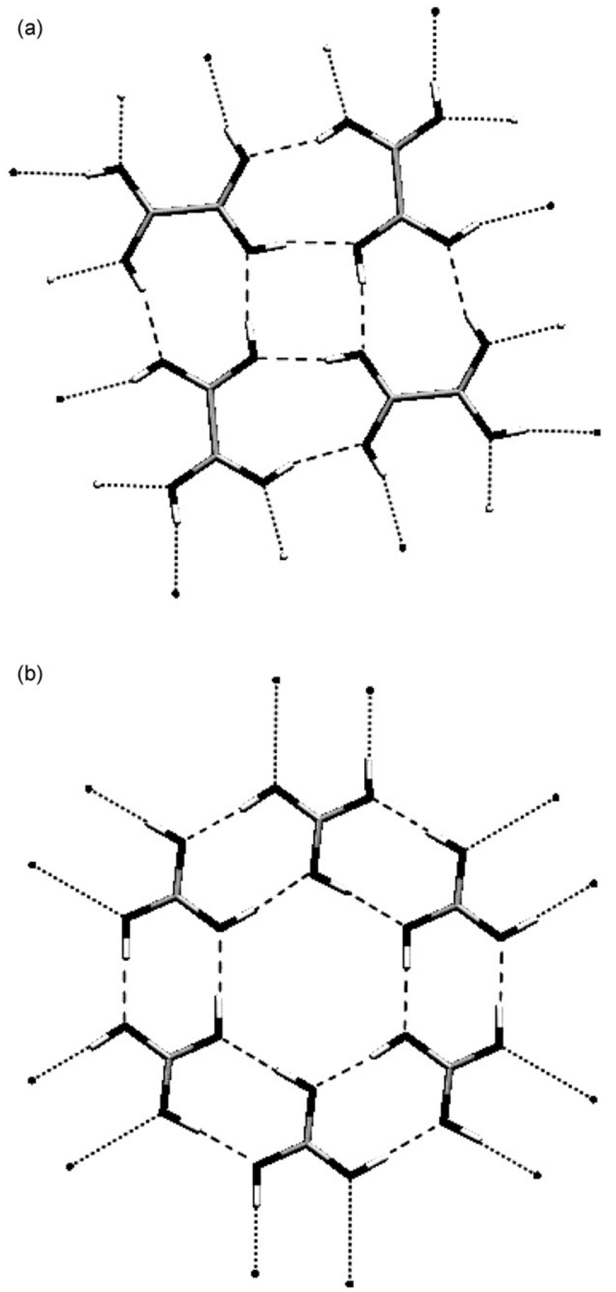

Fig. 2 (a) A view of part of the crystal structure of **1** showing hydrogen bonding in the two dimensional layers and (b) a related view of part of the crystal structure of $B(OH)_3$ for comparison.

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