Why are B_2O_2 rings rare?

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Received (in Cambridge, UK) 15th August 2000, Accepted 6th October 2000
First published as an Advance Article on the web

The single-crystal X-ray structure of $\{[HPPh_3]^+\}_2[B_4F_{10}O_2]^{2-}$ 2 reveals trigonal planar oxygen atoms in a rare example of a B_2O_2 ring; extended Hückel and *ab initio* molecular orbital calculations provide insight into the bonding and the geometry about oxygen.

As part of a study of the solid-state structures and NMR spectra of $R_3P{\cdot}BX_3$ adducts, we found that addition of $BF_3{\cdot}OEt_2$ to a hexane solution of PPh_3 yielded $Ph_3P{\cdot}BF_3$ **1**† as a white precipitate. Adduct **1** was previously synthesised from BF_3 and PPh_3 in CH_2Cl_2.[1,2] Attempts to grow single crystals of **1** from CH_2Cl_2–toluene led to the formation of several cube-shaped crystals. X-Ray diffraction studies showed these to be $\{[Ph_3PH]^+\}_2[B_4O_2F_{10}]^{2-}$ **2**,‡ which contains an unusual B_2O_2 ring. This salt apparently resulted from hydrolysis of **1** due to traces of adventitious water.

The novel dianion in the crystal of **2** (Fig. 1) lies on a centre of inversion and thus the B_2O_2 ring is rigorously planar. The B–O bond distances in the ring are 1.498(2) and 1.505(2) Å. The ring is nearly square, with O–B–O and B–O–B internal angles of 88.8(1) and 91.2(1)°, respectively. A BF_3 group is coordinated to each oxygen atom, with the B–O bond distance of 1.512(2) Å, and two fluorine atoms are bonded to each ring boron atom. The B–F bond distances in the BF_2 and BF_3 groups are very similar, averaging 1.362(3) and 1.374(5) Å, respectively. Interestingly, the coordination about oxygen is trigonal planar with the sum of the angles being 359.9(2)°.

Although fluoroborates with rings containing five or more atoms are known,[3,4] the dianion in **2** represents the only structurally well characterised discrete ring consisting solely of boron, fluorine and oxygen atoms. Unlike the common six-membered rings containing alternating boron and oxygen,[5] and four-membered rings containing alternating aluminium and oxygen,[6] only four crystal structures containing four-membered B_2O_2 rings have been reported.[7–10] Three of the structurally characterised compounds contain trigonal planar oxygens at the B_2O_2 ring: the porphyrin complex,[7] $[B_2O_2(BCl_3)_2(TpClpp)]$ (TpClpp = dianion of 5,10,15,20-tetra-*p*-chlorophenylporphyrin), neutral $[Me_2B–O–BMe_2]_2$,[8] and the 4-oxa-3-borahomoadamantane dimer.[10] A further example of trigonal planar oxygen was recently described by Schröder's group[11] in a complex with alkoxide bridging between BF_3 and a copper atom. In $\{C_6F_4\text{-}1,2\text{-}[B(C_6F_5)_2]_2(\mu\text{-}OR)\}^-$ (R = Me, C_6F_5), it was suggested[12] that the planar geometry about the oxygen could be due either to the bulky groups about O, or to the bite angle of the bidentate moiety coordinated to it. Our dianion $B_4O_2F_{10}^{2-}$ in **2** is simple and elegant with only 16 atoms, making it ideal for theoretical studies.

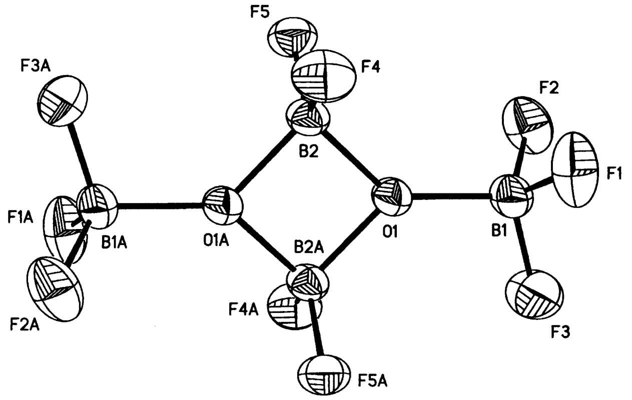

Fig. 1 Structure of the $B_4O_2F_{10}^{2-}$ dianion in **2** drawn with 50% probability ellipsoids showing the atom numbering. Selected bond distances (Å) and angles (°) for **3**: B(1)–O(1) 1.512(2), B(2)–O(1) 1.498(2), B(2)–O(1A) 1.505(2), B(1)–F(1) 1.380(3), B(1)–F(2) 1.372(2), B(1)–F(3) 1.369(3), B(2)–F(4) 1.362(2), B(2)–F(5) 1.362(2); O(1)–B(2)–O(1A) 88.83(12), B(2)–O(1)–B(2A) 91.17(12), B(1)–O(1)–B(2) 136.21(14), B(1)–O(1)–B(2A) 132.48(14).

We have carried out extended Hückel and *ab initio* MO calculations to gain insight into the bonding within the ring and the geometrical preference at oxygen in **2**. EHMO calculations[13,14] were performed on both the dianion $B_4O_2F_{10}^{2-}$ and the $B_2O_2F_4^{2-}$ fragment, and the resulting energy level diagram is shown in Fig. 2, along with plots of the frontier orbitals of the $B_2O_2F_4^{2-}$ fragment; lower lying orbitals include the B–F bonds, fluorine p electrons and the oxygen and boron s orbitals. The bonding in the $B_2O_2F_4^{2-}$ square can be seen to arise from the B–O σ bonds in HOMO-3 and HOMO-4. The in- and out-of-plane combinations of the other oxygen p orbitals produce the four remaining orbitals drawn at the left side of Fig. 2; from the HOMO downwards these are O–O σ*, π*, π, σ. The Lewis basicity of the $B_2O_2F_4^{2-}$ square arises from the in-plane HOMO and HOMO-5 which overlap with the out-of-phase and in-phase combinations of BF_3 acceptor orbitals in the $B_4O_2F_{10}^{2-}$ dianion. The O–O π* and π orbitals are not involved in bonding to the BF_3 groups. The fact that O–O σ* is the $B_2O_2F_4^{2-}$ HOMO is thus likely responsible for the observed trigonal planar coordination at oxygen.

Ab initio MO calculations (GAUSSIAN94)[15] on the $B_2O_2F_4^{2-}$ fragment at the MP2/6-31G* level of theory revealed the energies of the frontier orbitals to be in the same order as in Fig. 2 with the O–O σ* and σ orbitals (HOMO and HOMO-5) significantly lower in relative energies. On coordinating two BF_3 groups to $B_2O_2F_4^{2-}$ to generate **2**, the O–O σ and σ* orbitals provide the electrons used in O–BF_3 bonding and are significantly lowered in energy; as a result the unperturbed O–O π* and π orbitals become HOMO and HOMO-1 respectively.

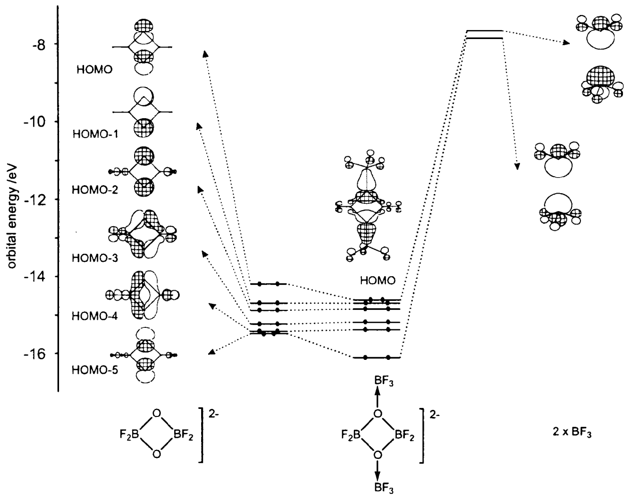

Fig. 2 Extended Hückel molecular orbital interaction diagram for the $B_4O_2F_{10}^{2-}$ anion in **2**.

DOI: 10.1039/b006685k

Geometry optimization of the dianion $B_4O_2F_{10}^{2-}$ in **2** at MP2/6-31G* revealed a minimum virtually identical to that found experimentally with O–B–O and B–O–B internal angles of 89.1 and 90.9° respectively. However, geometry optimization of the discrete fragment $B_2O_2F_4^{2-}$, resulted in a minimum with O–B–O and B–O–B internal angles of 97.5 and 82.5° respectively, and the O–O π^* orbital as the HOMO. Thus, coordination of the two BF_3 Lewis acids to the in-plane oxygen orbitals stabilises the antibonding O–O σ^* level without the need for significant lengthening of the O–O separation *via* distortion of the B_2O_2 square.

Alternative structures involving pyramidalisation at each oxygen atom can be accounted for by a mixing of the oxygen in- and out-of-plane orbitals (HOMO/HOMO-1 and HOMO-2/HOMO-5) to generate donor orbitals in either *cisoid* or *transoid* arrangements. These have been examined through qualitative Walsh diagrams (Fig. 3) with the observed structure at the energy minimum.

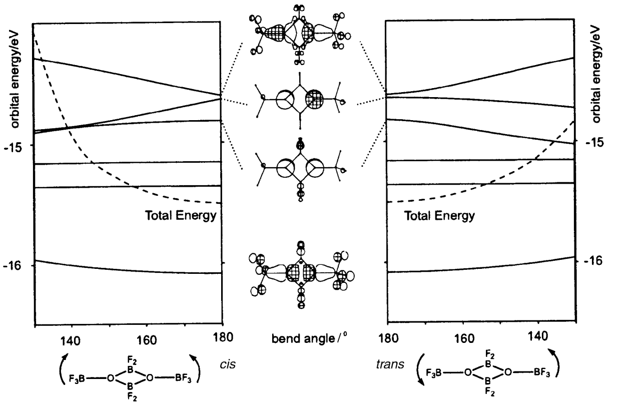

Fig. 3 Walsh diagrams for pyramidalisation at oxygen in the $B_4O_2F_{10}^{2-}$ dianion, calculated at the extended Hückel level. Total energies (in eV): planar, −2229.245; 130° *trans*, −2228.578; 130° *cis*, −2227.807.

Clearly, B_2O_2 rings are inherently destabilised by four-electron interactions of both σ- and π-symmetry between the oxygen atoms. Stable systems can be formed by complexation of Lewis acids such as BX_3, or, in the case of Al_2O_2 systems, by increasing the separation between the oxygen centres.

We thank EPSRC for a studentship (J. M. B.), for a research grant GR/M2308 (T. B. M.) and an Advanced Research Fellowship (M. A. F.). We also thank Dr D. Apperley for obtaining the solid-state ^{31}P NMR spectrum of **1**.

Notes and references

† Yield 84%. $C_{18}H_{15}BF_3P$ requires: C, 65.50; H, 4.58; Found: C, 65.03; H, 4.52%. Solid-state $^{31}P\{^1H\}$ NMR: δ −8.8. Partial characterisation of **1** has been reported.[2]

‡ *Crystal data* for **2**: $C_{18}H_{16}B_2F_5OP$, M = 395.90, monoclinic, a = 11.638(3), b = 12.174(3), c = 13.542(3) Å, β = 93.688(3)°, U = 1914.6(8) Å^3, T = 150 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 0.194 mm^{-1}, 22662 reflections measured on a Bruker SMART-CCD diffractometer, 5437 unique (R_{int} = 0.039) which were used in all calculations. Final $wR(F^2)$ = 0.1287 (all data) and $R(F)$ = 0.0482 [for 3923 data with $I > 2\sigma(I)$]. CCDC 182/1806. See http://www.rsc.org/suppdata/cc/b0/b006685k/ for crystallographic files in .cif format.

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