Note

Crystal and Molecular Structure of 6,6′-Bis(*nido*-decaboranyl) Oxide,[†] $(B_{10}H_{13})_2O$

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The crystal and molecular structure of $(B_{10}H_{13})_2O$ has been determined by single-crystal *X*-ray diffractometry. The crystals are monoclinic with a = 24.838(6), b = 6.816(3), c = 10.132(3) Å, β = 98.43(2)°, U = 1 697(1) Å^3, Z = 4, D_c = 1.011 g cm^{-3}, $F(000)$ = 536. Space group $C2/c$. The molecular structure comprises two $B_{10}H_{13}$ groups joined at the 6,6′-positions to the O atom. The molecule has crystallographic symmetry C_2 with B–O distances of 1.358(2) Å and a large B–O–B angle of 139.1(2)°. The conformation may be specified by the B(2)–B(6)–O–B(6′) torsion angle of −71°. The intra-cluster B–B distances are similar to those in $B_{10}H_{14}$, though there is a slight increase in the five B–B distances in each cluster involving those boron atoms [B(2), B(5), and B(7)] directly linked to B(6). There is also an enhanced asymmetry of the B–H–B(6) bridge bonds, with the H–B(6) being 0.14 Å longer than H–B(5) and H–B(7).

THE compound $B_{20}H_{26}O$ is unique in borane chemistry. It is prepared as a single isomer of $(B_{10}H_{13})_2O$ by the reaction of concentrated sulphuric acid on the bis-ligand complex $B_{10}H_{12}(SR_2)_2$.[1] It is remarkably stable to reagents such as HF, $SOCl_2$, BCl_3, or PBr_3 but reacts rapidly at room temperature with ligands (L) such as NEt_3, SMe_2, or tetrahydrofuran to give several products including $B_{10}H_{14}$ and $B_9H_{13}L$. Unusual reactions with heavy-metal complexes such as $[PtCl_2(PR_3)_2]$ have also been reported.[2] A recent ^1H and ^{11}B n.m.r. study [3] has confirmed that the structure is 6,6′-$(B_{10}H_{13})_2O$, but more detailed information on interatomic distances and angles was desirable to help in the elucidation of its chemistry. Accordingly we now report the detailed crystal and molecular structure of the compound.

EXPERIMENTAL

The compound $(B_{10}H_{13})_2O$ was prepared by the method of Heřmánek and co-workers.[1] The yield (*ca.* 50%), m.p. (137—139 °C), and i.r. spectrum agreed with those reported. The stoicheiometry of $B_{20}H_{26}O$ was confirmed by its mass spectrum: parent molecular ions at m/z 262 and 261 were extremely weak but were shown by high-resolution measurements to correspond to $^{11}B_{20}H_{26}O$ and $^{10}B^{11}B_{19}H_{26}O$ (Found: 261.386, 260.394. Calc.: 261.388, 260.392). The dominant fragmentation was by loss of H_2 molecules, the most abundant ions in the parent envelope being due to $[B_{20}H_{24}O]^{\cdot +}$ species. Other abundant ion envelopes centred around m/z ratios 247, 217, 202, 144, 115, 103, and 93. Crystals suitable for *X*-ray analysis were obtained from hexane solution.

Crystal Data.—$B_{20}H_{26}O$, M = 258.4, Monoclinic, a = 24.838(6), b = 6.816(3), c = 10.132(3) Å, β = 98.43(2)°, U = 1 697(1) Å^3, Z = 4, D_c = 1.011 g cm^{-3}, $F(000)$ = 536. Space group $C2/c$. Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 0.40 cm^{-1}.

Cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles for 15 reflections with $35 < 2\theta < 40°$ and all independent reflections (1 134) with $4 < 2\theta < 45°$ were measured in the ω—2θ scan mode. The structure analysis used the 899 reflections having $I > 3\sigma(I)$ and the structure was solved using MULTAN.[4] Full-matrix least-squares refinement with anisotropic temperature factors for B and O atoms and isotropic parameters for hydrogen gave a final R of 0.045 and R' 0.060. Atomic scattering factors were calculated using the analytical approximation and coefficients given in ref. 5. Weights were derived from counting statistics; absorption corrections were not applied. The atomic co-ordinates are given in Table 1 and the vibration parameters

TABLE 1

Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
O	0	0.083 9(3)	$\frac{1}{4}$
B(1)	0.121 79(9)	0.189 6(3)	0.021 2(2)
B(2)	0.059 53(9)	0.269 2(3)	0.066 6(2)
B(3)	0.118 06(9)	0.419 0(3)	0.099 5(2)
B(4)	0.180 62(9)	0.289 9(3)	0.117 9(2)
B(5)	0.083 19(9)	0.023 5(3)	0.097 4(2)
B(6)	0.045 87(8)	0.153 6(3)	0.208 2(2)
B(7)	0.076 54(10)	0.392 6(4)	0.222 7(2)
B(8)	0.157 54(10)	0.405 5(4)	0.255 5(3)
B(9)	0.193 40(10)	0.179 3(5)	0.269 8(3)
B(10)	0.163 47(10)	0.038 4(4)	0.130 5(3)
H(1)	0.122 5(8)	0.158(3)	−0.088(2)
H(2)	0.025 3(9)	0.309(3)	−0.011(2)
H(3)	0.115 9(8)	0.568(3)	0.052(2)
H(4)	0.213 4(9)	0.346(3)	0.067(2)
H(5)	0.066 4(8)	−0.109(3)	0.051(2)
H(7)	0.053 3(9)	0.510(3)	0.256(2)
H(8)	0.173 5(10)	0.534(3)	0.306(2)
H(9)	0.231 0(11)	0.159(3)	0.329(2)
H(10)	0.183 7(9)	−0.096(3)	0.094(2)
H(56)	0.081 9(8)	0.002(3)	0.216(2)
H(67)	0.077 8(8)	0.259(3)	0.300(2)
H(89)	0.160 5(8)	0.274(3)	0.336(2)
H(910)	0.167 9(9)	0.023(3)	0.256(2)

[†] 6,6′-Oxybis(*nido*-decaborane).

and observed and calculated structure factors are in Supplementary Publication No. SUP 22746 (8 pp.).*

RESULTS AND DISCUSSION

The molecular structure and atom numbering are shown in the Figure, with selected interatomic distances in Table 2. The molecule has crystallographic symmetry C_2 with B–O bond lengths of 1.358(2) Å and a large B–O–B angle of 139.1(2)°. The conformation may be specified by the B(2)–B(6)–O–B(6′) and B(6)–O–B(6′)–B(2′) torsion angles of −71°.

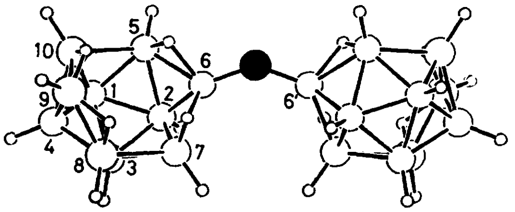
TABLE 2

Interatomic distances for 6,6′-bis(*nido*-decaboranyl) oxide

O(1)–B(6)	1.358(2)	B(8)–B(9)	1.776(4)
B(1)–B(2)	1.762(3)	B(9)–B(10)	1.777(4)
B(1)–B(3)	1.762(3)	B(1)–H(1)	1.13(2)
B(1)–B(4)	1.772(3)	B(2)–H(2)	1.11(2)
B(1)–B(5)	1.736(3)	B(3)–H(3)	1.12(2)
B(1)–B(10)	1.739(3)	B(4)–H(4)	1.10(2)
B(2)–B(3)	1.768(3)	B(5)–H(5)	1.07(2)
B(2)–B(5)	1.787(3)	B(7)–H(7)	1.07(2)
B(2)–B(6)	1.714(3)	B(8)–H(8)	1.06(2)
B(2)–B(7)	1.786(3)	B(9)–H(9)	1.04(3)
B(3)–B(4)	1.772(3)	B(10)–H(10)	1.13(2)
B(3)–B(7)	1.741(4)	B(5)–H(56)	1.22(2)
B(3)–B(8)	1.736(3)	B(6)–H(56)	1.36(2)
B(4)–B(8)	1.769(4)	B(6)–H(67)	1.34(2)
B(4)–B(9)	1.701(4)	B(7)–H(67)	1.20(2)
B(4)–B(10)	1.775(3)	B(8)–H(89)	1.20(2)
B(5)–B(6)	1.792(3)	B(9)–H(89)	1.30(2)
B(5)–B(10)	1.976(3)	B(9)–H(910)	1.24(2)
B(6)–B(7)	1.795(3)	B(10)–H(910)	1.26(2)
B(7)–B(8)	1.992(3)		

The B–O distance is similar to that in $B(OMe)_3$ 1.38(2), $H_3B_3O_3$ 1.376, $Me_3B_3O_3$ 1.39(2), $[B_3O_6]^{3-}$ 1.36, and $B(OH)_3$ 1.355—1.365 Å.[6] The large B–O–B angle can be compared with a value of 132(5)° in OBOBO (gas);[7] large bond angles at oxygen are also known for some silicates and for $O(SiH_3)_2$ 144(1)°.

The B–B and B–H distances are similar to those in $B_{10}H_{14}$,[8] although there appears to be a significant lengthening (by 0.012—0.019 Å) of the five B–B distances in each cluster involving boron atoms in the two triangular faces incorporating B(6) when compared with those incorporating B(9), *i.e.* B(5)–B(6), B(6)–B(7), B(2)–B(5), B(2)–B(6), and B(2)–B(7). The difference of 0.016 Å between B(7)–B(8) and B(5)–B(10) also appears to be real. The B–H distances call for little comment except to note the enhanced asymmetry of the B(5)–H–B(6) and B(6)–H–B(7) bridge bonds, the distances of H to B(6) being 0.14 Å longer (seven standard deviations) than to B(5) or B(7).



ORTEP drawing of the molecular structure of $(B_{10}H_{13})_2O$. The crystallographic two-fold axis passes vertically through the oxygen atom (shaded). Numbered atoms are boron; hydrogen atoms are numbered according to the boron atom(s) to which they are attached

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.