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Structures of the 12-Vertex Oxa- and Thia-*nido*-dodecaborates and $B_{13}H_{13}^{2-}$: A Theoretical DFT/GIAO/NMR Investigation

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Although several oxametallaboranes had been observed previously,[1] Frange et al.[2] synthesized the first simple oxaborane ($OB_{11}H_{12}^-$) by oxidation of $B_{11}H_{14}^-$ in aqueous sodium hydroxide. This anion is very stable and does not react with H_2O, EtOH, MeI, NaOMe, I_2, NaH, and HBF_4. Unfortunately, experimental efforts to obtain a crystal structure of $OB_{11}H_{12}^-$ failed.[2] Simple skeletal electron counting rules[3] suggest that the 12-vertex 28-electron $OB_{11}H_{12}^-$ cluster should have a *nido*-framework. The seven ^{11}B NMR signals with 2:1:1:2:2:2:1 intensity ratios imply a C_s symmetrical structure. The presence of one three-coordinate oxygen and one bridged hydrogen in the boron framework (**1**) was inferred,[2] since similar 12-vertex *nido* structures have been found in azaborane[4] and in oxametallaboranes.[1b,c] Semiempirical (AM1) calculations also have been used to justify the proposed structure.[2c]

This note presents the results of theoretical investigations on the structure of oxa-*nido*-dodecaborate (**1**) (as well as another possible C_s isomer, **2**) based on the DFT/GIAO/NMR method,[5] which has been employed very successfully by our group and others for determining accurate structures of relatively large boranes and heteroboranes.[6] To aid future experimental investigations, we also predict here the geometries and the ^{11}B NMR chemical shifts for the related thia-*nido*-dodecaborate $SB_{11}H_{12}^-$ (**3**), as well as $B_{13}H_{13}^{2-}$ (**4**).

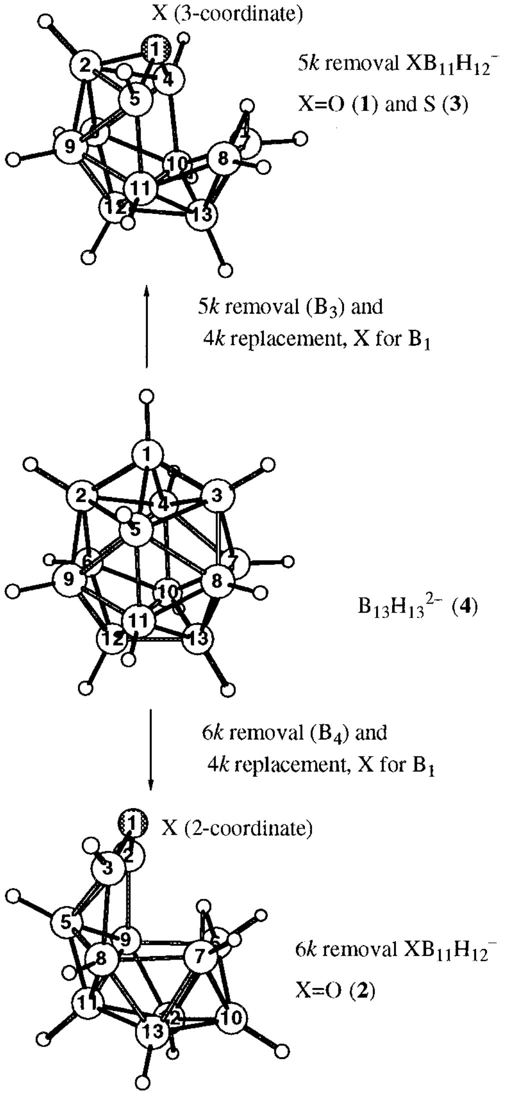

Figure 1. C_s symmetrical hetero-*nido*-dodecaborates $XB_{11}H_{12}^-$, X = O (**1**, **2**) and S (**3**), constructed from the hypothetical *closo*-$B_{13}H_{13}^{2-}$ by removal of $5k$ and $6k$ boron.

All calculations were carried out with the Gaussian 94 program.[7] Geometries were fully optimized (Figure 1) with density functional theory employing Becke's three-parameter exchange functional,[8] the nonlocal correlation potential of Lee, Yang, and Parr,[9] and the 6-31G* basis set (B3LYP/6-31G*). Frequency analyses (B3LYP/6-31G*) confirmed the optimized geometries to be minima.[10] Selected bond distances are listed

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Table 1. Selected Interatomic Distances (Å) for $B_{13}H_{13}^{2-}$ and $XB_{11}H_{12}^{-}$ with X = O (**1**, **2**) and S (**3**) at the RB3LYP/6-31G* Level,[a] with the Atom Numbering Shown in Figure 1

	$B_{13}H_{13}^{2-}$	**1**[b]	**2**	**3**
X_1-B_2	1.620	1.495 (1.494)	2.436 (X_1-B_5)	1.897
X_1-B_4	1.860	1.523 (1.524)	1.396 (X_1-B_2)	1.954
B_2-B_4	1.996	1.929 (1.931)	1.966 (B_2-B_5)	2.012
B_2-B_6	1.786	1.768 (1.769)	1.746 (B_5-B_9)	1.764
B_2-B_{12}	2.975	2.944 (2.945)	1.679 (B_5-B_{11})	2.958
B_4-B_5	2.721	2.585 (2.586)	2.221 (B_2-B_3)	2.837
B_4-B_6	1.928	1.848 (1.848)	1.789 (B_2-B_9)	1.813
B_4-B_7	1.928	2.106 (2.107)	2.503 (B_2-B_6)	2.247
B_4-B_{10}	1.833	1.783 (1.782)	3.396 (B_2-B_{12})	1.797
B_6-B_9	1.761	1.800 (1.798)	2.705 (B_8-B_9)	1.799
B_6-B_{10}	1.754	1.785 (1.785)	1.835 (B_9-B_{12})	1.785
B_6-B_{12}	1.750	1.762 (1.760)	1.821 (B_9-B_{11})	1.760
B_6-B_7	3.004	3.130 (3.130)	1.934 (B_6-B_9)	3.134
B_7-B_8	1.761	1.777 (1.775)	1.931 (B_6-B_7)	1.775
B_7-B_{10}	1.754	1.735 (1.734)	1.828 (B_6-B_{12})	1.738
B_7-B_{13}	1.750	1.743 (1.743)	1.734 (B_6-B_{10})	1.735
$B_{10}-B_{12}$	1.806	1.802 (1.802)	1.784 ($B_{12}-B_{11}$)	1.806
$B_{10}-B_{13}$	1.806	1.806 (1.805)	1.693 ($B_{12}-B_{10}$)	1.817
$B_{10}-B_{11}$	2.856	2.783 (2.782)	1.797 ($B_{12}-B_{13}$)	2.805
$B_{12}-B_{13}$	1.776	1.792 (1.791)	2.914 ($B_{11}-B_{10}$)	1.774
H_b-B_7		1.314 (1.312)	1.309	1.304

[a] The B3LYP/6-31G* total energies (in au) are −331.076 33 ($B_{13}H_{13}^{2-}$), −356.066 48 (**1**), −356.006 17 (**2**), and −679.005 45 (**3**). [b] The B3LYP/6-311+G** values are given in parentheses.

Table 2. B3LYP-GIAO/6-311G*//RB3LYP/6-31G* Computed ^{11}B NMR Chemical Shifts[a] (in ppm) for $B_{13}H_{13}^{2-}$ and $XB_{11}H_{12}^{-}$ [X = O (**1**, **2**), S (**3**)] Compared with the Experimental Values with the Atom Numbering Shown in Figure 1

		$OB_{11}H_{12}^{-}$			
atoms	$B_{13}H_{13}^{2-}$	**1**[b]	exptl[c]	**2**	$SB_{11}H_{12}^{-}$ (**3**)
B_1	27.2				
B_2	−2.2	2.9 (3.8)	4.35	2.5 (B_5)	7.1
$B_{4,5}$	−19.6	−6.7 (−6.6)	−7.0	55.6 ($B_{2,3}$)	−4.0
$B_{7,8}$	−10.2	11.8 (11.6)	12.8	−35.2 ($B_{6,7}$)	22.2
$B_{6,9}$	−10.2	−17.1 (−17.1)	−16.4	−9.7 ($B_{9,8}$)	−18.4
$B_{10,11}$	−22.2	−14.7 (−14.8)	−14.2	−0.9 ($B_{12,13}$)	−16.8
B_{12}	−10.1	14.1 (14.0)	11.3	−31.3 (B_{11})	25.1
B_{13}	−10.1	−30.1 (−30.2)	−29.1	25.1 (B_{10})	−29.1

[a] B_2H_6 is the primary reference, and $\delta(B_2H_6) = 16.6$ ppm is used for conversion to the standard experimental $BF_3{\cdot}OEt_2$ scale. [b] The B3LYP-GIAO/6-311G*//B3LYP/6-311+G** values are given in parentheses. [c] Taken from ref 2a.

in Table 1. The B3LYP-GIAO/6-311G*//B3LYP/6-31G* computed ^{11}B chemical shifts are summarized in Table 2.

After we apply Williams' corollary for generating stable fragments from *closo*-deltahedra,[3] the most favorable isomer of $OB_{11}H_{12}^{-}$ can be predicted from the hypothetical *closo*-tridecaborate ($B_{13}H_{13}^{2-}$, **4**),[11] in which one of the two 5*k* (five-coordinate, without considering H−B connectivity) boron vertices connected to both 6*k* vertices is removed (or replaced by a bridged hydrogen) and the 4*k* coordinate and most negative boron is replaced by one oxygen atom (Figure 1). In contrast, when one 6*k* vertex is removed, the other 6*k* borons are not altered and a less stable geometry with unfavorably high connectivity should result (**2**, Figure 1). However, **1** has a highly distorted hypercoordinate oxygen, with two 79° BOB angles. In contrast, the BOB angle in **2** is 105°.

Nevertheless, Williams' reasoning is confirmed by our computations. At B3LYP/6-31G*, the C_{2v} symmetrical $B_{13}H_{13}^{2-}$ (**4**)[11] is an energy minimum (no imaginary frequencies) and the four-coordinate B_1 is the most negatively charged boron with a natural charge[12] of −0.258; the charges of the five-coordinate $B_{2,3}$ (−0.173) and six-coordinate $B_{4,5}$ (−0.037) are smaller. Both the 5*k*-removal structure **1** and the 6*k*-removal structure **2** have C_s symmetry (Figure 1), have bridged hydrogens, and are consistent with the observed ^{11}B NMR intensity ratio (2:1:1:2:2:2:1). While frequency analyses showed both **1** and **2** to be energy minima, **1** is 35.5 kcal/mol [B3LYP/6-31G*+ZPE-(B3LYP/6-31G*)] lower in energy than **2**. As suggested by Frange et al.,[2] **1** has a three-coordinate oxygen with normal O_1-B_2 (1.495 Å) and $O_1-B_{4,5}$ (1.523 Å) bond lengths and one bridged hydrogen between B_7 and B_8 ($B_{7,8}-H_b$ = 1.314 Å) (B3LYP/6-31G*). These structural parameters are nearly the same as those at the higher B3LYP/6-311+G** level. In contrast, the oxygen in **2** is only two-coordinate as revealed by the long O_1-B_5 distance (2.436 Å) and the normal $O_1-B_{2,3}$ bond lengths (1.396 Å) (Table 1).

To establish the correct structure of this oxaborane, we computed the ^{11}B NMR chemical shifts for **1** and **2** and compared the results with the experimental values for $OB_{11}H_{12}^{-}$ (Table 2). The ^{11}B chemical shifts of **1** and **2** are quite different (Table 2). Only the results for the more stable isomer **1** agree well with the experimental data (the differences between calculated and experimental chemical shifts are between 0.3 and 2.8 ppm). Thus, we conclude that Frange et al.'s $OB_{11}H_{12}^{-}$ is indeed **1**.

To aid further experimental investigations, we have also calculated the thia-*nido*-dodecaborate $SB_{11}H_{12}^{-}$ (**3**), assuming a structure similar to the oxaborate **1**, as well as the hypothetical $B_{13}H_{13}^{2-}$ (**4**). Apart from the S−B distances, the B−B moiety of **3** hardly changes as compared with **1** (Table 1). The sulfur substitution also affects the ^{11}B chemical shifts (Table 2). Compared with **1**, $\delta(^{11}B_{7,8})$ and $\delta(^{11}B_{12})$ in **3** resonate at a lower field by more than 11 ppm. The other changes are relatively small (Table 2).

The three-dimensional *closo*-borane dianions $B_nH_n^{2-}$ ($6 \le n \le 12$) are known to have unusual chemical stability,[13] but higher $B_nH_n^{2-}$ ($n \ge 13$) members are still unknown. While $B_{12}H_{12}^{2-}$ was calculated to have the largest stabilization energy as compared with other lower *closo* species,[14] $B_{13}H_{13}^{2-}$ is only hypothetical.[11] The C_{2v} symmetrical $B_{13}H_{13}^{2-}$ results from the insertion of a neutral BH unit into one of the B−B bonds in the I_h $B_{12}H_{12}^{2-}$ cluster.[11] But, why is $B_{13}H_{13}^{2-}$ unknown?

As with other *closo*-borane dianions,[14] we have used eq 1 to evaluate the relative stability of $B_{13}H_{13}^{2-}$. The energy of the neutral BH increment in eq 1 is based on the difference between planar B_3H_5 (allyl cation like, C_{2v}) and planar B_2H_4 (ethylene-like, D_{2h}).[14] At the B3LYP/6-311+G** level, eq 1 is endothermic by only 13.9 kcal/mol.[15] Thus, the instability of

$$B_{12}H_{12}^{2-} + \text{BH (increment)} = B_{13}H_{13}^{2-} \qquad (1)$$

$$\Delta E = 13.9 \text{ kcal/mol}$$

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(15) The B3LYP/6-311+G** energies (in au) are as follows: −52.034 72 (B_2H_4), −77.446 76 (B_3H_5), −280.180 60 ($B_{11}H_{11}^{2-}$), −305.762 91 ($B_{12}H_{12}^{2-}$), −331.152 86 ($B_{13}H_{13}^{2-}$).

$B_{13}H_{13}^{2-}$, relative to other members of the *closo*-$B_nH_n^{2-}$ family, is quite modest.[14] For example, $B_{11}H_{11}^{2-}$ is destabilized by 106.9 kcal/mol[15] relative to $B_{12}H_{12}^{2-}$, based on the same treatment (eq 2).

$$B_{12}H_{12}^{2-} = \mathrm{BH\ (increment)} + B_{11}H_{11}^{2-} \qquad (2)$$

$$\Delta E = 106.9\ \mathrm{kcal/mol}$$

Despite the distorted heteroatom environment, the proposed structure of 12-vertex oxa-*nido*-dodecaborate (**1**, $OB_{11}H_{12}^{-}$), the first oxaborate species where oxygen is part of the boron−hydrogen cluster, is established by the agreement of computed (DFT/GIAO/NMR) ^{11}B NMR chemical shifts on the optimized geometry with the experimental values. The unknown 12-vertex thia-*nido*-dodecaborate (**3**, $SB_{11}H_{12}^{-}$), with a similar three-coordinate sulfur, and $B_{13}H_{13}^{2-}$ (**4**) appear to be good synthetic targets. The nonexistence of $B_{13}H_{13}^{2-}$ is not explicable on thermodynamic grounds.

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