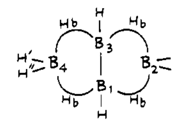
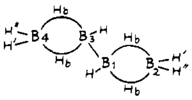
Table I. Optimized Distances (Å) for B_4H_{10} Structures

C_{2v}, Known Structure (I)



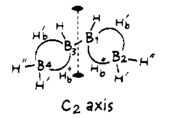
B_1B_3	1.7326 (1.718)[a]	B_2H'	1.1813
B_1B_2	1.9017 (1.854)	B_2H''	1.1841
B_2B_4	2.8510	B_1H_b	1.2477 (1.428)
B_1H	1.1770	B_2H_b	1.4296 (1.425)

C_{2h} Bis(diborane) Structure (II)



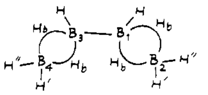
B_1B_3	1.7032	B_2H'	1.1831
B_1B_2	1.8020	B_2H''	1.1827
B_2B_3	3.0526	B_1H_b	1.3208
B_2B_4	4.7150	B_2H_b	1.2170
B_1H	1.1866		

C_2 Bis(diborane) Structure (III)



B_1B_3	1.6973	B_2H''	1.1827
B_1B_2	1.7975	B_1H_b'	1.3224
B_2B_3	3.0662	B_1H_b''	1.3245
B_2B_4	4.0371	B_2H_b'	1.3146
B_1H	1.1872	B_2H_b''	1.3114
B_2H'	1.1838	HB_1B_3H	67.3°

C_{2v} Bis(diborane) Structure (IV)



B_1B_3	1.7132	B_2H'	1.1826
B_1B_2	1.8023	B_2H''	1.1823
B_2B_3	3.1098	B_1H_b	1.3214
B_2B_4	3.7490	B_2H_b	1.3159
B_1H	1.1865		

[a] Experimental values in parentheses are from: Simmons, N. P. C.; Burg, A. B.; Beaudet, R. A. *Inorg. Chem.* 1981, *20*, 533.

polarization and configuration interaction corrections in order to obtain the last column. In a previous study of eight molecules[10] (H_2O, NH_3, N_2, F_2, B_2H_4, $BH_3\cdots H_2$, BH_5, and B_2H_6) we have shown that addition of these two corrections gives very nearly the same result as a full calculation in which both polarization and MP3 correlation corrections are included. The cost of doing both in B_4H_{10} is prohibitive at the present time.

Our results show that the observed structure is more stable than the *gauche*-bis(diborane) structure by only 2.7 kcal/mol (Table II, last column). It is likely that further corrections for electron correlation will increase the relative stability of the observed structure as predicted by theory. Further study is required to determine whether the bis(diborane) structures lie in local minima relative to the observed structure and whether they are involved in chemical properties of B_4H_{10}.

Table II. Energies of B_4H_{10} Structures Relative to the Observed Form[a]

	6-31G	6-31G*	MP3/6-31G	6-31G* + MP3/6-31G
obsd (C_{2v})	0	41.85	204.32	246.17
	(0)	(0)	(0)	(0)
gauche-bis(diborane)	0	43.14	193.42	236.56
(C_2)	(−6.92)	(−8.21)	(3.98)	(2.69)
trans-bis(diborane)	0	43.07	192.37	235.44
(C_{2h})	(−6.26)	(−7.48)	(5.69)	(4.47)
cis-bis(diborane)	0	43.08	192.26	235.34
(C_{2v})	(−4.64)	(−5.87)	(7.42)	(6.19)

[a] A negative number in parentheses means stability with respect to the observed structure of B_4H_{10}. All energies are in kcal/mol. Values not in parentheses are energy lowerings relative to the 6-31G basis as zero for each separate geometry. The last column is obtained by addition of corrections of the second and third columns. Values in parentheses are referred to the zeros of energy for the observed geometry at each level of approximation. The total energy of the observed (C_{2v}) structure for B_4H_{10} is 104.390 070 hartrees.

Correlation corrections account for about 40–45% of the dissociation energy of B_2H_6 to 2 BH_3 molecules. The Hartree–Fock limit is about 20 kcal/mol,[11,12] and the theoretical value[12] including correlation is 36.6 kcal/mol in agreement with the experimental value[13] of 35.5 kcal/mol. Correlation corrections favor more highly bridged structures of B_3H_7 and B_4H_8,[14] are required in the isomerization of hypothetical B_4H_4[15] and in distinguishing relative stabilities of classical and nonclassical isomers,[16] and may yet favor the C_1[17] vs. the C_s[18] structure of B_5H_{11}. Also correlation will be required for a theoretical understanding of the pyrolysis reaction, which yields higher hydrides from diborane.

Finally, we have yet to find the limitation to the additivity of polarization and configuration interaction corrections. We anticipate that difficulties will occur when heavier elements and metastable states are studied.

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Registry No. B_4H_{10}, 18283-93-7.

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Correct Assignment of Stretching Frequencies of Tetraoxometalates in Unusual Oxidation States

Sir:

Recently, an interesting paper was published on the CaO–Cr_2O_3–O_2 system[1] in which an incorrect assignment for the

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stretching frequencies of the CrO_4^{3-} ion has been given.

This renews a problem which has not been always clearly understood and has contributed to many controversies and misunderstandings. Although it is essentially a spectroscopic problem, it is of great interest to many inorganic chemists dealing with oxoanions of the transition elements and those in unusual oxidation states in particular.

The fact that the $\nu_1(A_1)/\nu_3(F_2)$ frequency ratio for MO_4^{n-} species apparently shows erratic variations (for example, in the cases of VO_4^{3-}, WO_4^{2-}, or ReO_4^-, ν_1 lies at higher frequency than ν_3, whereas for MnO_4^-, CrO_4^{2-}, or RuO_4, the opposite behavior is observed) was the principal reason for the numerous misassignments made some time ago.

More than ten years ago, during a systematic investigation of the vibrational behavior of tetraoxometalates, we found that the variations of the ν_1/ν_3 frequency ratio could be correlated with the mass and the oxidation number of the central atom,[2,3] and we were also able to justify our findings with the aid of a very simple theoretical model.

The fact that these results have been published in a journal of restricted circulation has probably limited their diffusion, although they were included later in a review on the vibrational spectra of chalcogenometalates of the transition elements published in ref 4.

So that these results can be diffused definitively, the basic rules should be newly reformulated, as follows.

(1) For ions with the central atom belonging to the same group of the periodic system and possessing the same charge, the ratio ν_1/ν_3 increases with the mass of the central atom (for example, the ratio for ReO_4^- is larger than that for MnO_4^-).

(2) For a given central atom, the ν_1/ν_3 ratio grows with increasing charge of the anion (for example, it must be larger for CrO_4^{3-} than for CrO_4^{2-}, which are the species discussed in the paper of ref 1).

(3) For isoelectronic ions where the central atom mass remains approximately constant, the ratio ν_1/ν_3 increases with the increasing charge of the anion (for example, it is larger for WO_4^{2-} than for ReO_4^-).

(4) The ν_1/ν_3 ratio remains practically constant for ions of the same period and charge (for example, ν_1/ν_3 values are practically identical for CrO_4^{2-}, MnO_4^{2-}, and FeO_4^{2-}).

These rules can be extended to thio and seleno anions of the transition elements[3-5] and are also applicable to oxo and thio anions of the main-group elements.[6]

The fact that the well-known and widely used book of Nakamoto quotes, even in his last edition,[7] some incorrect values and misassignments for species of the discussed type has probably contributed, to some extent, to the delay of recognition of the correct relations between the ν_1 and ν_3 vibrations.

Finally, it should be remembered that similar rules which facilitate the assignment in the deformation region (ν_2(E) and $\nu_4(F_2)$ species) of tetraoxometalates are also well established.[8,9]

We hope that these brief comments will help solve definitively the assignment problems for these species.

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Convenient Procedure for the Conversion of Sodium Borohydride into Lithium Borohydride in Simple Ether Solvents

Sir:

Treatment of suspended sodium borohydride with lithium bormide in ethyl ether or tetrahydrofuran provides solutions of lithium borohydride readily separated from the precipitated sodium bromide. The heterogeneous metathesis is facilitated either by magnetic stirring or by mechanical stirring with glass beads present. This development makes lithium borohydride readily available from economical, readily available reagents.

In contrast to sodium borohydride, lithium borohydride is easily soluble in simple ether solvents such as ethyl ether and tetrahydrofuran.[1] Such solutions possess valuable reducing properties.[2] Unfortunately, commercial lithium borohydride is relatively expensive.[3] Moreover, there are problems in handling the solid.[4] There would be advantages to a procedure which would provide solutions of lithium borohydride in ethyl ether or tetrahydrofuran without the need for isolating or handling the solid.

Sodium borohydride is significantly soluble in isopropylamine,[5] ethanol,[6] isopropyl alcohol,[1] and diglyme[1], and lithium borohydride has been prepared by metathesis with lithium chloride in all of these solvents[1,5,6] (eq 1). Unfortunately, it

$$NaBH_4 + LiCl \rightarrow LiBH_4 + NaCl\downarrow \qquad (1)$$

requires high temperatures to remove isopropylamine or diglyme from the lithium borohydride. More seriously, lithium borohydride undergoes fairly rapid hydrolysis in the alcohol solvents.[1] It appeared desirable to find a means of achieving the metathesis in EE or THF, solvents very commonly used for reductions.

No significant reaction was observed between sodium borohydride and lithium chloride vigorously stirred magnetically as suspensions in ethyl ether at 25 °C or reflux (35 °C). Both salts are essentially insoluble in this solvent, and this evidently provides a major hurdle for the metathesis reaction. On the other hand, lithium bromide and lithium iodide are soluble in ethyl ether.[7] Indeed, these reactions proved much more favorable, proceeding to essential completion in 48 h at 25 °C (eq 2). At reflux the reactions appeared to be essentially

$$NaBH_4 + LiBr \xrightarrow[48\ h]{25\ ^\circ C,\ EE} \underset{100\%}{LiBH_4} + NaBr\downarrow \qquad (2)$$

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