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Diborane(4) (B_2H_4): The Boron Hydride Analogue of Ethylene

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Abstract: The geometrical structure and vibrational frequencies of the yet unobserved B_2H_4 species have been studied via ab initio molecular electronic structure theory. A standard double-zeta plus polarization basis set, designated B(9s5p1d/4s2p1d), H(4s1p/2s1p), was used in conjunction with self-consistent-field (SCF) and single plus double excitation configuration interaction (CISD) techniques. The equilibrium geometry predicted from explicitly correlated wave functions is r_e(B–B) = 1.669, r_e(B–H) = 1.195 Å; θ_e(HBH) = 116.6°. This structure fits perfectly into the series of experimentally determined geometries for B_2F_4, B_2Cl_4, and B_2Br_4, when the accepted order of electronegativities F > Cl > Br > H is employed. Comparison is also made with five previous theoretical studies of B_2H_4. It is hoped that the predicted vibrational frequencies of B_2H_4 will assist in the experimental identification of this hitherto unknown molecule, and these theoretical frequencies are compared with those observed for B_2H_6, C_2H_4, and C_2H_6. The barrier to rotation about the B–B single bond is predicted to be 10.9 kcal (SCF) and 11.9 kcal (CI).

By comparison with the hydrocarbons, boron hydrides represent a relatively recent chapter in the history of chemistry.[1] Although the first boron hydride was prepared in 1879, the pioneering early synthetic studies, reported between 1912 and 1936, were those of Alfred Stock and co-workers.[2] The detailed structural characterization of most of the boron hydrides, of course, awaited the much more recent crystallographic studies of Lipscomb.[3] These structures, with cages of boron atoms and bridging hydrogens, obviously did not fit into the classical two-center two-electron bond picture and led to the development of the notion of many-centered bonds.[4,5]

Probably the best known structure of any of the "electron-deficient" compds. is that of B_2H_6, the boron analogue of ethane.[6] Perhaps surprisingly the corresponding boron analogue of ethylene has not been observed experimentally,[7] though derivatives of B_2H_4 [designated diborane(4)] are known and their structures have been determined.[8,9] Diborane(4) has two electrons less than ethylene, which means that the π orbital, which dominates ethylene chemistry, is not occupied in B_2H_4. This can be expected to have far ranging effects on the chemistry of B_2H_4. From a structural point of view, the boron–boron bond could be bridged by hydrogens or it could be a simple single bond, about which fairly free rotation could take place. If it is a single bond, as is the case with the derivatives of B_2H_4, then an important question is whether the minimum on the rotational energy surface be ethylene-like (D_{2h} symmetry) or allene-like (D_{2d} symmetry)? Substituted B_2H_4 compounds show both as minimum. Thus B_2F_4 has a D_{2h} structure[9] while B_2Cl_4 has a D_{2d} structure.[8] In both these cases the rotation barrier around the B–B bond is very small. The exact shape of the rotational potential is also of interest. Are the rotational conformers both minima or is one a transition state for interconversion of equivalent forms of the other conformer?

There have been several previous theoretical studies of B_2H_4 using various levels of sophistication.[10–17] Lipscomb and co-workers have carried out systematic theoretical studies on a range of B_nH_m isomers.[10,14,15] In one of these[15] they used the partial retention of diatomic differential overlap (PRDDO) method to obtain geometries and then carried out further calculations with both minimal and split-valence basis sets on these structures. Dill, Schleyer, and Pople[12] performed geometry optimization on D_{2d} and D_{2h} B_2H_4 with the STO-3G basis set and then did single-point calculations with the 6-31G* basis set on these structures. That study was the only previous one to use polarization functions. Armstrong[13] has performed double-zeta SCF calculations on a variety of B_2H_4 isomers and determined that the D_{2d} and D_{2h} structures are of lowest energy. In a similar manner Bigot, Lequan, and Devaquet[17] have investigated a series of B_2H_4 isomers at the SCF level by using the STO-3G and 4-31G basis sets. There have also been two additional studies, one using semi-empirical methods[16] and one using floating spherical Gaussians.[11]

The purpose of the present research was to investigate the B_2H_4 molecule at a consistently high level of theory. Thus the geometries of several structures of diborane(4) have been determined by using a double-zeta plus polarization (DZ + P) basis set. Particularly pertinent to the (future) spectroscopic observation of B_2H_4 is the prediction of vibrational frequencies, made for the first time here. In addition, the relative energies of several points on the B_2H_4 potential-energy hypersurface have been determined by using large, explicitly correlated wave functions.[18]

Theoretical Approach

The contracted Gaussian basis set used in this research was of double-zeta plus polarization (DZ + P) caliber. The sp basis sets come from the work of Huzinaga[19] and Dunning,[20] and the polarization function exponents were 1.0 (p on hydrogen) and 0.6 (d on boron). The technical designation[21] of this basis is B-

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Table I. Theoretical Structures for Diborane(4)

method	FSGO[11]	STO-3G[12]	double zeta[13]	PRDDO[15]	STO-3G[17]	DZ + P SCF[a]	DZ + P CI[a]
Twisted (D_{2d})							
r_e(B-B), Å	1.769	1.644	1.683	1.619	1.644	1.684	1.669
r_e(B-H), Å	1.257	1.162	1.202	1.170	1.162	1.196	1.195
θ_e(HBH), deg	117.0	117.2	116.2	117.0	117.2	116.8	116.6
energy, hartree		−51.01071		−51.6206	−51.01071		
	−43.60291	−51.63216[b]	−51.48703	−51.5577[c]	−51.55751[d]	−51.64111	−51.82601
Planar (D_{2h})							
r_e(B-B), Å	1.783	1.713	1.775	1.683	1.713	1.762	
r_e(B-H), Å	1.255	1.162	1.199	1.170	1.162	1.196	
θ_e(HBH), deg	117.1	116.7	116.2	117.0	116.7	116.5	
energy, hartree		−50.99053		−51.5996	−50.99053		
	−43.59981	−51.61545[b]	−51.46805	−51.5381[c]	−51.53850[d]	−51.62380	
$\Delta E(D_{2d} - D_{2h})$, kcal/mol	1.9	12.7 10.5[b]	11.9	13.2 12.3[c]	12.7 11.9[d]	10.9	

[a] This work. [b] Single 6-31G* calculation at optimum STO-3G geometry. [c] Single 4-31G calculation at optimum PRDDO geometry. [d] Single 4-31G calculation at optimum STO-3G geometry.

(9s5p1d/4s2p1d), H(4s1p/2s1p). This DZ + P basis would be capable of yielding quantitatively reliable predictions for most of the properties of B_2H_4.

Previous theoretical studies[10-17] have suggested that the twisted or D_{2d} conformer is the lowest lying isomer for the ground electronic state of B_2H_4. The electron configuration for this closed-shell singlet state is[22]

$$1a_1^2 1b_2^2 2a_1^2 2b_2^2 3a_1^2 1e^4$$

1

while that for the higher-lying planar (D_{2h}) structure is[23]

$$1a_g^2 1b_{1u}^2 2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 1b_{3g}^2$$

2

The latter configuration is identical with that for the ground state of ethylene, except that the $1b_{3u}$ or π orbital is unoccupied for B_2H_4. That is, the $1b_{3u}$ orbital is the HOMO for C_2H_4 but the LUMO for planar B_2H_4. Since B_2H_4 has only a B–B single or σ bond, rotation should not be costly energetically. For geometries intermediate between D_{2d} and D_{2h} the highest symmetry possible is D_2, and the ground-state electron configuration becomes

$$1a_1^2 1b_2^2 2a_1^2 2b_2^2 3a_1^2 1b_1^2 1b_3^2$$

3

Initially, the geometrical structures of the constrained D_{2d} (**1**), D_{2h} (**2**), and 45° dihedral angle D_2 (**3**) minima were determined at the restricted Hartree–Fock or self-consistent-field (SCF) level of theory. The D_{2d} structure as expected[10-17] was the lowest and accordingly was subjected to a harmonic vibrational analysis, which verified that it is a true minimum.

The D_{2d} geometry was also optimized by using explicitly correlated wave functions.[21] These were of the configuration interaction (CI) variety, including all single and double excitations. The core or 1s-like boron orbitals were removed from the CI procedure, thus eliminating two occupied and two virtual molecular orbitals. In this way the CI included a total of 3610 configurations (point group D_{2h}) or 5942 configurations (point group D_2). The single configuration studies were carried out by merging the Rys polynomial integral techniques[24] with Pitzer's SCF procedures.[25] The correlated wave functions were determined via the loop-driven unitary group approach.[18]

Self-Consistent-Field Geometries

Constrained equilibrium geometries predicted at the DZ + P SCF level of theory are given in Figure 1. The middle structure corresponds to a B–B rotation angle of 45° or exactly halfway between the D_{2d} (90°) and D_{2h} (0°) geometries. A comparison with previous theoretical predictions is made in Table I. The SCF energy for the optimum structure halfway between D_{2d} and D_{2h} is −51.63254 hartrees.

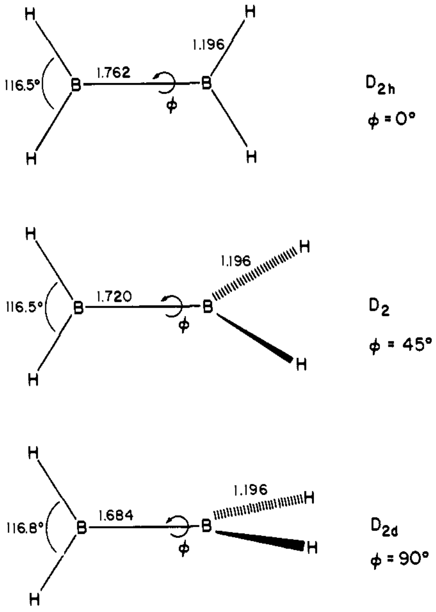

Figure 1. Theoretical equilibrium structures for planar (D_{2h} point group) B_2H_4, twisted (D_{2d} point group) B_2H_4, and a structure constrained to a dihedral angle ϕ of 45° (point group D_2). These geometries were obtained at the DZ + P SCF level of theory. For the D_{2d} structure only, an explicitly correlated structure was determined, with r_e(B–B) = 1.669, r_e(B–H) = 1.195 Å; θ_e(HBH) = 116.6°.

To our knowledge, there have been no previous ab initio inquiries into the D_2 portion of the B_2H_4 rotation barrier. Hence it has not been clear whether the D_{2h} structure is a transition state or a secondary minimum. The relative energies of the optimum D_{2d}, D_2, and D_{2h} structures in Figure 1 are 0.0, 5.4, and 10.9 kcal/mol, respectively. Although not completely definitive, the monotonic increase in energies suggests that the D_{2h} structure is a transition state, rather than a secondary minimum. A two degree torsional displacement from the D_{2h} structure results in an energy lowering, lending weight to the idea that the D_{2h} structure is a transition state. The progression of predicted B–B distances (1.684, 1.720, 1.762 Å) also suggests that the 45° D_2 geometry is structurally about halfway between the twisted and planar conformers.

It is probably justifiable to assume that the present SCF predictions come reasonably close to the limiting Hartree–Fock values, i.e., what would be obtained in the limit of a complete basis set of one-electron functions. Therefore one can evaluate the effectiveness of previous theoretical studies by comparison. The present theory predicts that the B–B distance increases by 0.078

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Table II. Harmonic Vibrational Frequencies for Diborane (4), the D_{2d} Equilibrium Geometry of B_2H_4[a]

frequency, cm^{-1}	symmetry	designation
2732 (2459)	E	BH_2 asymmetric stretch
2677 (2409)	A_1	BH_2 symmetric stretch
2649 (2384)	B_2	BH_2 symmetric stretch
1291 (1162)	A_1	BH_2 scissor
1230 (1107)	B_2	BH_2 scissor
1070 (963)	E	BH_2 wag
872 (785)	A_1	B–B stretch
494 (445)	E	BH_2 rock + some BH_2 wag
491 (442)	B_1	BH_2 twist

[a] These frequencies were obtained at the DZ + P level of theory, assuming ^{11}B and ^{1}H nuclear masses. Values in parentheses were empirically reduced to 90% of the ab initio predictions.

Å upon twisting the D_{2d} equilibrium structure into the planar conformation. This certainly appears to be a large change in bond distance to accompany rotation about a single bond. By comparison in ethane the C–C distance increases by ~0.01 Å in twisting from the staggered to the eclipsed conformation.[26] However the STO-3G studies of Pople[12] and Devaquet[17] also show a large B–B increase (0.069 Å) for the constrained planar structure. For the twisted–planar energy difference, all but the FSGO calculations give reasonable agreement with the DZ + P SCF prediction of 10.9 kcal. We will return to this point when discussing the explicitly correlated results.

The predicted DZ + P SCF bond distance, 1.684 Å, is 0.04 Å longer than the STO-3G result, 1.644 Å. The PRDDO result, 1.619 Å, is seen to be 0.065 Å shorter than the prediction approaching the Hartree–Fock limit. It should be pointed out that extension of the basis set beyond the present DZ + P level typically decreases equilibrium bond distances,[21] and the Hartree-Fock limit could conceivably be as short as 1.67 Å, although we think this unlikely. The STO-3G B–H distance (1.162 Å) is also significantly shorter than the DZ + P SCF result (1.196 Å), by 0.034 Å. It should be noted that for hydrocarbons, such a C–H bond distance difference between minimum basis and DZ + P SCF is essentially unheard of,[27] typical differences being less than 0.01 Å. All the theoretical methods do a good job of approximating the DZ + P HBH angle, the range of predicted values being 116.2–117.2°.

Vibrational Frequencies

From a strictly pragmatic perspective, the best hope for an experimental identification of a short-lived closed-shell molecule such as B_2H_4 is probably via matrix isolation infrared spectroscopy.[28] Since previous theoretical studies of diborane(4) have not attempted to predict the vibrational frequencies, this seemed a particularly significant goal for the present research. At the DZ + P SCF level of theory, all unique quadratic force constants in terms of Cartesian coordinates were obtained by using analytic gradients. The appropriate mass-weighted 18 × 18 matrix was diagonalized to yield the frequencies given in Table II.

In considering the predicted vibrational frequencies it is well to remember that for small molecules well characterized experimentally, DZ + P SCF frequencies are consistently too large. For example, for the four molecules HCN, H_2O, H_2CO, and CH_4, the average DZ + P harmonic vibrational frequency is 8.3% greater than the experimental harmonic frequency.[29] Furthermore, harmonic frequencies are typically a few percent larger than the observed (anharmonic) frequencies. Therefore a helpful rule of thumb is that DZ + P SCF harmonic vibrational frequencies are typically 10% greater than observed frequencies. For this reason we have also included in Table II a set of scaled frequencies, which are 90% of the ab initio values.

The torsional frequency, corresponding to internal rotation about the B–B bond, is predicted to be 491 (442) cm^{-1} in Table II. Although this is the smallest of the predicted vibrational frequencies, it is not so small as to completely discredit the use of the harmonic approximation. For the prototype internal rotation about a single bond, namely that in ethane (CH_3–CH_3), Herzberg[30] recommends 278 cm^{-1} for the torsional frequency. In contrast, for the prototype double bond, namely, ethylene (CH_2=CH_2), the CH_2 twist frequency is much larger, 1027 cm^{-1}. By this criterion, it is seen that the internal rotation in B_2H_4 is more characteristic of a single than a double bond.

The other low-frequency normal mode for B_2H_4 is the doubly degenerate BH_2 rocking (plus some BH_2 wag) frequency predicted at 494 (445) cm^{-1}. For $^{11}B_2H_6$ (ordinary diborane), the analogous BH_2 rocking frequencies[31-33] are observed at 950 and 915 cm^{-1}. These higher frequencies suggest (as do other considerations) that B_2H_4 is held together more loosely than is B_2H_6. For the isoatomic ethylene molecule the CH_2 rocking frequencies occur at 826 and 1236 cm^{-1}.

Terminal B–H vibrational stretching frequencies generally fall in the range[32] 2300–2800 cm^{-1}, and those predicted for B_2H_4 fit into this general pattern. For ordinary diborane, B_2H_6, the four B–H terminal stretching frequencies are observed at 2520, 2530, 2597, and 2608 cm^{-1}, amounting to a range of only 88 cm^{-1}. The B_2H_4 stretching frequencies of the B–H type likewise fall in a narrow range—2649–2732 cm^{-1} for the ab initio frequencies and 2384–2459 cm^{-1} for those empirically reduced by 10%. Interestingly the ab initio and corrected frequencies for B_2H_4 bracket those observed experimentally for B_2H_6.

The BH_2 scissor frequencies of B_2H_4 and B_2H_6 are quite similar. Those predicted here for B_2H_4 are 1291 (1162) and 1230 (1107) cm^{-1}, while the observed scissor frequencies of B_2H_6 are 1180 and 1177 cm^{-1}. In the same manner the clearly identifiable BH_2 wag frequency 1070 (963) cm^{-1} of B_2H_4 is close to those 973, 850 cm^{-1}) observed for B_2H_6.[33] Note, however, that for B_2H_4 there is some BH_2 wag character in the much lower frequency predicted at 494 (445) cm^{-1}.

For the observed B_2H_6 it is apparently not possible to associate a single vibrational frequency with the B–B stretch.[31-33] For the more conventional (in the sense of lacking multicenter bonds) B_2H_4, the B–B stretching frequency is predicted at 872 (785) cm^{-1}. This is perhaps a somewhat low frequency, particularly by comparison with the double bonded but isoatomic ethylene, for which the C=C stretching frequency is 1623 cm^{-1}. For ethane, however, the prototype C–C single bond stretching frequency[30] is 945 cm^{-1}, not too much greater than that predicted here for B_2H_4. Therefore, *on this basis*, it is possible to conclude that the B–B single bond in B_2H_4 is perhaps 85% as strong as the C–C single bond in ethane.

Results from Correlated Wave Functions

In light of the strong dependence on basis set of the B_2H_4 equilibrium geometry, it was deemed advisable to carry out a structural prediction via the correlated wave functions described in the section entitled "Theoretical Approach". D_{2d} symmetry was assumed in the optimization process. This resulted in the DZ + P CI equilibrium geometry

$$r_e(\text{B–B}) = 1.669,\ r_e(\text{B–H}) = 1.195\ \text{Å} \qquad \theta_e(\text{HBH}) = 116.6° \tag{1}$$

which may be compared with the earlier theoretical structure in Table I. One sees immediately that electron correlation does not qualitatively alter the DZ + P SCF structure reported in the second from last column of Table I. The largest difference occurs

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for the B–B distance, which is shortened by 0.015 Å by CI. The other two geometrical parameters are hardly changed at all when correlation effects are explicitly incorporated in the wave functions. Although it would be premature to conclude that electron correlation will be qualitatively unimportant for other boron hydrides, this result is certainly encouraging in that regard. However, it is not clear that this applies to systems with extensive multicenter bonds.

The change in B–B bond distance is of special interest because it is of the opposite sign to that typically found upon inclusion of correlation effects.[21] That is, the bond distance decreases with CI rather than increasing, as is typically the case. However, this result does make sense in the light of a systematic series of studies by Chandler and McLean[34] of homopolar diatomic molecules. They find that CI increases bond distances when the primary configurations (after the Hartree–Fock configuration) involve the promotion of electrons from bonding orbitals to nonbonding or antibonding orbitals, thus reducing the "bond order" relative to the simple Hartree–Fock picture. Here, however, for B_2H_4 several important configurations involve excitation *into* a bonding orbital (the LUMO), which is analogous to the π orbital of ethylene. Thus the bond order is *increased* relative to the Hartree–Fock picture and correlation *decreases* the predicted B–B bond distance.

Given what is likely to be a reliable molecular structure prediction (± 0.01 Å in bond distances, ± 0.5° in bond angles), it is reasonble to compare the theoretical structure with those experimentally characterized compounds. Perhaps the most obvious is B_2H_6 or diborane, for which Kuchitsu[6] recommends

$$r(\text{B–B}) = 1.770 \pm 0.005,\ r(\text{B–H}_{\text{terminal}}) = 1.192 \pm 0.01\ \text{Å} \\ \theta(\text{H}_t\text{–B–H}_t) = 121.8 \pm 3° \qquad (2)$$

The shortening of the B–B bond distance (to 1.669 Å) in the nonbridged B_2H_4 is expected, and the magnitude (0.101 Å) of the decrease appears reasonable. Further, the B–H_{terminal} distance in B_2H_6 is indistinguishable to within experimental error from that predicted here for B_2H_4. Finally, the HBH angle in B_2H_6 is seen to be 2.2–8.2° larger than that in B_2H_4. So one can conclude that the B_2H_4 structure is not too dissimilar from what might be anticipated from the experimental B_2H_6 structure plus a bit of chemical intuition.

Perhaps the only experimentally known B–B single bond distances are those for B_2F_4 (1.720 Å),[9] B_2Cl_4 (1.702 Å),[8] and B_2Br_4 (1.689 Å).[35] The good qualitative agreement between these three distances and the predicted 1.669 Å for B_2H_4 is encouraging. Possibly unexpected is the perfect fit of B_2H_4 in the series demonstrating monotonically increasing B–B distance with the electronegativity of ligand X in B_2X_4. This series is of course consistent with the view that the B–B bond is electron deficient and therefore weakened somewhat by electron-withdrawing ligands.

It was also considered worthwhile to assess the effect of electron correlation on the predicted rotational barrier for B_2H_4. Therefore, single DZ + P configuration interaction treatments of the SCF optimized structures of D_{2d} and D_{2h} B_2H_4 were carried out. The total energies were −51.82592 (D_{2d}) and −51.80693 (D_{2h}) hartrees, suggesting a rotation barrier of 11.9 kcal, to be compared with the DZ + P SCF value, 10.9 kcal. The CI energy at the SCF optimum geometry (middle structure of the Figure) for the D_2 structure with B–B rotation angle of 45° is −51.81657 hartrees or 5.9 kcal above the D_{2d} equilibrium energy. The analogous prediction at the SCF level of theory is 5.4 kcal; so it is seen that the two theoretical treatments of the torsional potential yield qualitatively similar results.

Concluding Remarks

In his recent review concerning the "boron sub-halides", Massey[7] noted that although B_2H_4 has never been identified experimentally, Schlesinger and co-workers actually had B_2H_4 as their goal in their important 1954 study[36] of B_2Cl_4. As the second (after BH_3) "saturated" (in the sense that each boron atom is trivalent) boron hydride, B_2H_4 stands in a critical position in this branch of chemistry. A primary conclusion of this study is that, based on the properties of B_2H_4 *itself*, there appears to be no reason to conclude that diborane (4) is an unmakable molecule.

For example, we have found no isomers (molecular entities with two boron atoms and four hydrogen atoms) such as $HB\cdots BH_3$ with lower or even comparable total energies. Furthermore, B_2H_4 is certainly stable with respect to B–B bond breakage. Even without correction for size consistency,[37] the DZ + P CI energy of B_2H_4 lies 100.1 kcal below twice the comparable energy[38] of the BH_2 radical. This suggests that the B–B bond energy in B_2H_4 is in fact significantly stronger than the prototype C–C single bond in ethane. Thus it would appear that diborane(**4**), the top structure in Figure 1, respresents the absolute minimum on its six-atom potential-energy hypersurface.

The only plausible reasons this molecule continues to evade laboratory identification would appear to be (a) its reactivity, which is expected to be quite high and/or (b) lack of a suitable synthetic approach to its preparation. We hope that the present theoretical results will encourage further experimental pursuit of this prototypical boron hydride.

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