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DIBORANE AS A MODEL SYSTEM FOR CARBONIUM IONS[1]

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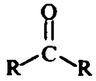
Abstract—The semi-empirical EHT method has been applied to diborane, B_2H_6. In agreement with structural data, the EHT method gives the lowest energy (most stable form) to the bridged form. Various computed molecular parameters of diborane as the B–H bond distances, various force constants, and the dissociation energy agree with the experimental values. Diborane is compared with ethyl cation and the dissimilarities noted. The relevance to the nonclassical carbonium ion problem is discussed.

Diborane is bridged because boron seems rather to pσ-bond to hydrogen than to form a pσ-bond with the B atom. The coefficients of the wave functions of diborane support this conclusion. Likewise the population of the B—B bond drops from 0·30 to 0·02 as the bridged ground state is transformed into the ethane-like form. Ethyl cation, $C_2H_5^+$, is more stable by EHT theory as an unbridged classical ion with a high barrier to isomerization via the bridged ion to form the rearranged $^+CH_2CH_3$ ion. The EHT method predicts an activation energy of 23 kcal/mole or greater, a value more than sufficient to prevent $CH_3CH_2^+$ from becoming $^+CH_2CH_3$. Ethyl cation is probably classical because the C—C pσ-bond is quite strong.

Thus the analogy that electron deficient systems of carbon should be bridged because the isoelectronic boron hydrides are bridged, is probably incorrect.

INTRODUCTION

In the three previous papers[1–3,*] in this series, the EHT quantum mechanical method was applied to questions relevant to the nonclassical carbonium ion problem. In particular, the conclusion was made as a result of calculations and by comparison with experimental data that a carbonyl compound 1 is too stiff to serve as an accurate energetic or vibrational model for 2. Likewise the monomeric borane 3 was observed to be too plastic to deform in an isosteric (an equal increase in energy for the same amount of deformation) manner with 2.



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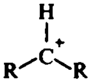

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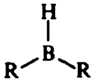

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In the present paper, the EHT method is applied to diborane. Several questions can be asked: can the EHT method really locate an electron-deficient system, that is bridged and, secondly, can an answer be provided for the "diborane argument" for nonclassical ions. For example, Linnett[4] has suggested that since B_2H_6 is bridged,

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[*] The reader is referred to the lengthy footnotes in Paper I[2] and in Paper III[1] on the nature of the approximations used in the EHT method. As with any theoretical method, the real test of the method is the agreement with experimental results. As noted in Paper III, we have observed that many of the errors of the approximation cancel against one another. Examination of the results of *ab initio* calculations using SCF methods on CH_3^+ shows that the EHT method does quite well on ionic species.

ions as $C_2H_6^{++}$ should also be bridged. Loss of H^- from that ion would produce $C_2H_5^+$, an ion for which bridge structures might have relatively low energies.

A reply[5] to the question[4] has been made, however, not by pointing out the quantum mechanical reasons but by stating that "the possibility of bridged structures for solvated carbonium ions... appears to be ruled out on the basis of available experimental evidence". We wish to answer the question from a theoretical point of view.

RESULTS

The electronic nature and energy of B_2H_6. The IR and raman spectra and electron diffraction data support the bridged structure of diborane. Most quantum mechanical studies[6–10] have been made on the bridged form; however, extensive variation of geometry of B_2H_6 was not undertaken in these earlier studies.

During the course of our investigation, a paper appeared on B_2H_6 and C_2H_6 using an extended basis set of Gaussian orbitals[11] using the Hartree–Fock method. Several deformations were considered. The bridged form was found to be more stable than the ethane-like form by 4·17 eV.

Some EHT calculations have been reported on the hydrides, halides, and alkyl compounds of boron and aluminum.[12] Yonezawa *et al.*[12] computed the molecular parameters of diborane using the ground state geometry. The authors discussed their results (which agree quite well with our computed data using the same geometry) concentrating on the values of the computed bond population data.

The present study. In the present study variations of the bond lengths and bond angles have been made to locate the minimum in energy and obtain theoretical estimates of the force constants. Calculations were begun using the known structural parameters of diborane.[13]

The $\mathbf{H}_{ij}$ matrix elements have been calculated using the approximation

$$\mathbf{H}_{ij} = k(\mathbf{H}_{ii} + \mathbf{H}_{jj})\mathbf{S}_{ij}/2 \tag{1}$$

rather than[7]

$$\mathbf{H}_{ij} = \mathbf{K} \cdot \mathbf{S}_{ij} \tag{2}$$

Previously it was found that Eq. (1) was superior to Eq. (2) in obtaining the correct B—H bond distance in borane and obtaining the B—H force constant. The use of Eq. (1) was superior to the use of Eq. (2) in these diborane calculations as well.

In Fig. 1, the total electronic energy in electron volts (eV) has been plotted versus the B—H (terminal) distance. The minimum was located at 1·201 Å. The literature value[13] is 1·196 ± 0·007 Å. The agreement of the EHT theory with the experimental value is quite satisfactory.

The second derivative of the energy curve, $\partial^2 U/\partial r^2$, near the minimum when corrected for the symmetry is equal to the harmonic valence force constant, **k**. The value computed from the data of Fig. 1 is 3·77 mdynes/Å. The literature value is 3·42 mdynes/Å[14a] or 3·54 mdynes/Å.[14b] The agreement is satisfactory.

The bridged structure (D_{2h} symmetry) is calculated to be more stable by 1·17 eV than the staggered ethane-like form (D_{3d}). This value is less than the value computed by Buenker[11] using a more exact procedure; earlier,[2] it was noted that EHT results tended to be low. The eclipsed ethane-like form (D_{3h}) is 3·64 kcal less stable than the

D_{3d} staggered ethane-like form.* It is rewarding to know that the EHT method predicts a bridged diborane structure and that reasonable molecular parameters as force constants can be obtained. This strengthens earlier conclusions[1-3] based on EHT theory. EHT theory can locate a bridged species.

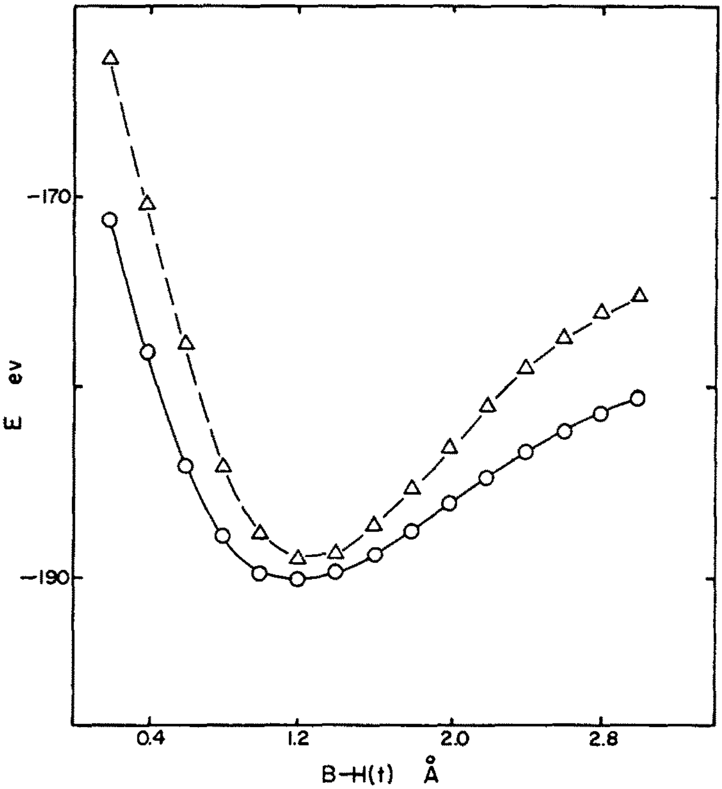

FIG. 1 Plot of energy in electron volts versus the B—H (terminal) bond distance for the bridged form of B_2H_6 and the most stable form of the ethane-like form of B_2H_6.

In Fig. 2, the energy has been calculated as a function of the boron-hydrogen (bridge) distance. The calculated minimum was located at 1·447 Å, in fair to poor agreement with the literature value[13] of 1·339 Å. Variation of the geometry from the bridged structure to staggered ethane-like structure was made. The energy increased smoothly and no other minima were located. (Figs 2 and 3). Thus diborane is not a resonating structure of two more stable but less symmetric forms.

The dissociation energy of B_2H_6. In Paper I, calculations[2] were performed on BH_3. In the present work the total electronic energy of B_2H_6 has been obtained.

$$B_2H_6 \rightarrow 2\,BH_3 \tag{3}$$

Dissociation energy computed	1·22 eV
experimental[16]	1·23 eV

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* Calculations by Hoffmann on ethane show a 4 kcal barrier to rotation. The experimental value is near 3 kcal.[15]

From these energies, the heat of dissociation has been computed to be 1·22 eV which compares with the experimental data[16,*] of 1·23 eV.

The wave functions. Examination of the computed wave functions shows that B—B bonding is due to good sσ bonding and very weak pσ in the lowest valence orbital, ϕ_1 (a_g). The coefficient is 0·32 on the boron$_a$ 2s + boron$_b$ 2s term and pσ term is 0·02 ($2p_{ya} - 2p_{yb}$). In the third molecular orbital of symmetry b_{1u}, a contribution of boron–boron pπ bonding is made with a term of 0·30 ($2p_{za} + 2p_{zb}$). In the highest filled orbital, an a_g, B—B pσ bonding is obtained with 0·37 ($2p_{ya} - 2p_{yb}$). In the other three filled orbitals nonbonding of the two B atoms is observed. The net Mulliken population density of the B—B bond† is 0·302. Using Eq. (2), Hoffmann and Lipscomb[7a] obtained a value of 0·38. Yamazaki[9] obtained 0·34 using a nonempirical LCAO-MO method. Burnelle and Kaufman[6] obtained 0·236 using a small basis set of Gaussian orbitals and naturally a much lower value of 0·064 using a large set of 54 Gaussian functions. Examination of the Burnelle–Kaufman paper shows that some individual orbitals have good overlap populations but these effects are completely wiped out by a few orbitals.

Likewise, the results of Buenker[11] using linear combination of Gaussian lobe functions show that the highest electron distribution is between the B and the terminal H atoms. The electron distribution between the two B nuclei is considerably less.

Our results indicate a B—H (terminal) overlap of 0·861 and 0·463 for the B—H (bridge) bond. The values of Hoffmann and Lipscomb[7] are 0·86 and 0·45 calculated using Eq. (2).

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[*] Hoffmann and Lipscomb[7a] using Eq. (2), computed the ΔH to be 1·53 eV. The results using Eq. (1) with $k = 1{\cdot}75$ are better both on BH_3 and B_2H_6. The same H_{ii} matrix elements have been used in both studies. Actually, a result of 1·53 eV is a quite satisfactory agreement.

The problem of using (2) can be seen if it is realized that K must be smaller than any diagonal matrix element, which are valence state ionization potentials. If all $H_{ii} = \gamma$ and $K = \gamma$, the secular equation reduces to $|(\gamma - E)S_{ij}| = 0$ which is satisfied by all $E = \gamma$. If $K > \gamma$, then inversion of energy levels results.

Using (1), the k value is chosen large enough so that the gross atomic populations are independent of the value of k. Likewise the wave function becomes independent of k. The only disadvantage is that the binding energy becomes proportional to $k - 1$ for large k values. Calibration of k with ethane works well in BH_3 and B_2H_6.

We have not used the Lohr technique of setting $H_{ij} = l(H_{ii}H_{jj})^{\frac{1}{2}}S_{ij}$ (with l an adjustable constant) nor the McGlynn method of using (1) by setting $k = (2 - |S_{ij}|)$. The McGlynn method works well on spectral transitions. Presently, the most severe test of a quantum calculation is the degree of agreement with spectral data.

The reader is referred to these papers and our own[1-3] for a discussion of the approximations used in the EHT method.

Palke and Lipscomb[7b] have reported results using an optimized minimum-basis-set SCF method on borane. In these calculations the hydrogens in BH_3 have a charge density of −0·034. While the most optimized set was not obtained for diborane, the charges on the terminal hydrogens were each −0·032. The bridge hydrogens had charges of −0·001 electrons. The B—B overlap population was computed to be 0·288. The authors noted that the SCF method required 3 hr on the IBM 7094 computer for one geometry.

However, the energy of dissociation of diborane was computed to be 0·32 eV. This value is below the experimental value.

Doubt has been expressed by Muetterties that the dissociation energy of diborane might be as large as 1·5 eV. Even a value like that is not that far off from the results of a semi-empirical calculation.

[†] Ogawa and Miyazawa (Ref. 13*b*) have obtained a B—B valence force constant of 2·721 mdynes/Å. They concluded that a weak bond, therefore, exists between the two B atoms.

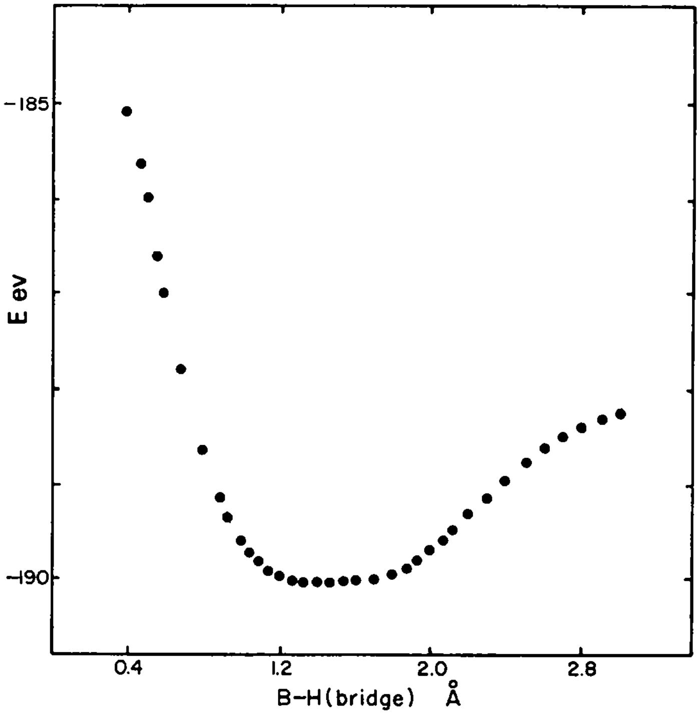


FIG. 1 Plot of energy in electron volts versus the B—H (bridge) bond distance.

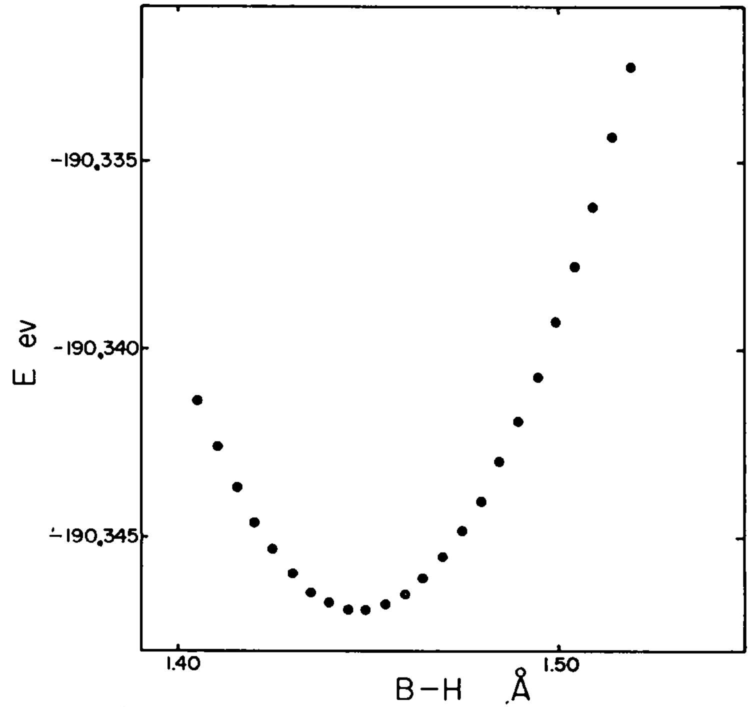


FIG. 2 Plot of the energy in eV versus the boron-bridge hydrogen distance in A° at a constant B—B bond distance (1·77 A°).

No other minimum was found. Thus the diborane molecule need not be viewed as an average resonance set or a nonresonating vibrating set of more asymmetric structures with an apparent structure of the more symmetric D_{2h} form.

DISCUSSION

It must be concluded that the semi-empirical EHT quantum mechanical method can yield good estimates of the properties of diborane with regards to equilibrium bond distances and valence force constants. It is also concluded that the EHT method can locate a real bridged structure involving hydrogen in an electron deficient system as B_2H_6. By analogy it was concluded[1] that C—C sigma bond bridging (nonclassical carbonium ion character) probably plays a minor role in the facile rearrangements of highly congested carbonium ion centers as the cyclobutyl cation system. The EHT method and the CNDO method do not support bridging in the cyclobutyl cation.[1]

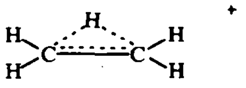
Of more immediate importance is the observation of Hoffmann using the EHT method that ethyl cation is more stable as the classical ion rather than as the nonclassical bridged structure.[17]

bridged

nonbridged
classical ion

most stable forms of
electron-deficient system

It was reported that the nonclassical structure of ethyl cation was of much higher energy:[*]



higher energy form of $C_2H_5^+$

possible nonclassical ion (see footnote *(c), this page

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[*] (a) In some future paper, we will report results of our studies on the $C_2H_5^+$ ion. The nonclassical structure in its ground state is 1·02 eV (23·5 kcal/mole) higher in energy than the most stable classical ion in its ground state.

The reader is directed to the "diborane-ethyl ion problem" as presented in the discussions following the talk by H. C. Brown, see H. C. Brown, *The Transition State* pp. 140–158 and 174–178. Spec. Publs. Chem. Soc. (1962);

(b) In Paper III (Ref. 1) detailed footnotes are presented on the use of the EHT method on cations. Perhaps the best justification of the EHT method is the comparison of the results on CH_3^+ using the semi-empirical EHT method and more detailed *ab initio* LCAO-MO-SCF methods. The charge distributions and the energy required to deform CH_3^+ are rather similar.

In Paper III EHT results on cyclopropyl carbinyl are compared with the CNDO results reported by Wiberg (article in Press). Both methods give a C^+ charge of 0·27; the energy to rotate the $\overset{+}{C}H_2$ group 90° is 8·0 kcal/mole for the CNDO or 8·7 kcal/mole for the EHT method.

(c) An ion would be defined by the present authors as being non-classical if it represents a local *minimum* in energy, being a metastable species. If it is only a transition state in between one $CH_3CH_2^+$ ion and the rearranged $\overset{+}{C}H_2CH_3$ ion, then it will not be called *nonclassical*.

Experimental evidence using isotopic tags shows that ethyl ion can be generated and transformed into products without equilibration of the carbon atoms as required by the bridged structure. It is rewarding to know that the EHT results are in agreement with these experimental facts.*

The dissimilarities of B_2H_6 *and* $C_2H_5^+$. The differences between B_2H_6 and $CH_3CH_2^+$ can be outlined.

Dissimilarities

B_2H_6	$CH_3CH_2^+$ (See footnote *)
long $B—H_t$ bonds	short CH bonds in CH_3
very long B—H bridge bonds	short $\overset{+}{C}H$ bonds in the CH_2^+ group
very weak B—B bond	very strong C—C bond
boron valence state ionization potentials:	carbon ionization potentials:
$H_{ii}(2s)_B = -15{\cdot}36$ eV	$H_{ii}(2s)_C = -21{\cdot}4$ eV
$H_{ii}(2p)_B = -8{\cdot}63$ eV	$H_{ii}(2p)_C = -11{\cdot}4$ eV

Buenker[11] suggested that diborane is bridged and ethane has the staggered configuration because the carbon p electrons are much more effective than those of boron in strengthening the $p\sigma$ bond between the heavy nuclei required for an ethane-like structure. In ethane the strong $p\sigma$–$p\sigma$ interaction forms a good C—C bond. In the bridged form of diborane effective BH bonding is obtained at the expense of BB bonding. The increased B—B nuclei repulsion then forces the system to an equilibrium position with a long boron–boron distance of 1·77 Å. These conclusions are identical with our own found independently.

Consider the diagram of the energies in eV of the various atomic orbitals on hydrogen, carbon, and boron. The important point to be noted about the atomic orbital diagram is that *the* 2p *orbitals of boron are so much further removed from the energies of the other orbitals under discussion.* The hydrogen 1s atomic orbital is close in energy to the energy of the carbon 2p electron. This means that diborane is bridged. (Fig. 3).

Thus if the B atom has a choice, it would rather form $p\sigma$-bonds with hydrogen than form a number of weaker B—B $p\sigma$-bonds to other B atoms. It also follows that boron would rather form more numerous but weaker bonds in a polyboron compound. Carbon would rather form a few highly directional strong bonds.

In Table 1 the overlap populations are presented for the bridged ground state and for the ethane-like form of diborane. It is obvious that in the ethane-like form, the B—H bonds have good strength with populations of 0·82 each. Yet the B—B bond is only 0·02 which represents about 0·02/0·80 of single bond since 0·80 in population represents an average single bond.

Therefore, it is concluded that diborane is not a good model system for the ethyl cation. The analogy, that electron deficient systems of carbon should be bridged (or nonclassical) because the isoelectronic boron hydrides are bridged, is probably incorrect.

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* The EHT method predicts a *minimum* activation energy of 23·5 kcal/mole for the isomerization of one ethyl ion to the other in the gas phase. Thus far our calculations indicate that the bridged ion is a transition state rather than a local minimum.

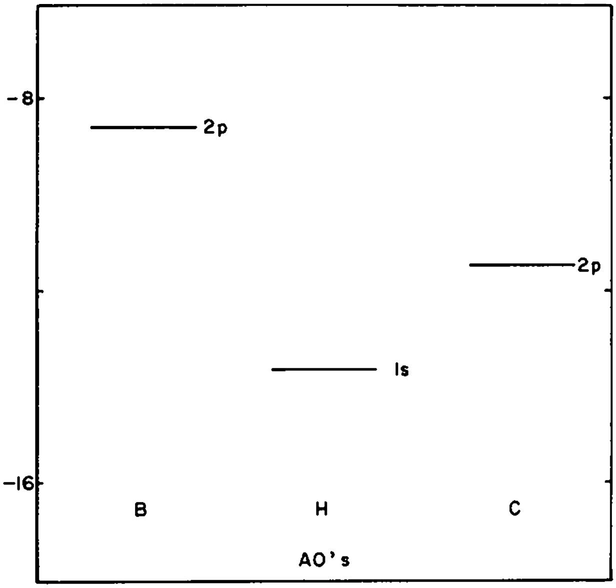

FIG. 3 Atomic orbital energies of the 2p Boron, Is Hydrogen and the 2p Carbon orbitals.

TABLE 1. OVERLAP POPULATIONS IN B_2H_6

	Ground state	Ethane-like form
B—B	0·302	0·023
B—H_t[a]	0·861	—
B—H_b[b]	0·46	—
B—H[c]	—	0·824

[a] Terminal.
[b] Bridge.
[c] For all six equivalent bonds.

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