with T_{onset} sets in at *slightly lower* temperature with increasing deviation from ideal nonstoichiometry.

Nonstoichiometry also causes a rapid reduction in the magnitude of the CDW anomalies. The drop-off in $\chi_{Pauli-CDW}$ in the 0.5%-excess sample is nearly twice as great as in the 1%-excess sample. Thus, since the magnitude of the effect reflects the change in the density of states at the Fermi level, increased deviation from ideal stoichiometry leads to a decrease in the number of Fermi surface states destroyed. The cause of the effect is not well understood. It may be that donation of electrons to the conduction band by interlayer vanadium acts to remove inherent Jahn–Teller type distortion in VSe_2 layers. This appears to be the case on intercalation of lithium to form $LiVSe_2$, where the lattice expands by only 0.25 Å in spite of the Li introduced between the layers.[16] Alternatively, band filling may move the Fermi surface off a peak in the density of states and make CDW effects increasingly unfavorable with increased deviation from ideal stoichiometry.

Compared to other layer compounds, stoichiometric VSe_2 has an anomalously large c/a ratio.[9] As seen in Figure 1, the c parameter decreases and the a parameter increases with increasing deviation from stoichiometry. The former comes from the action of interlayer vanadium atoms to pin the layers together; the latter, from increased Coulombic repulsion due to electrons donated into the layer by excess vanadium atoms in the gap.

Registry No. VSe_2, 12299-51-3.

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(16) Beal, A. B.; Liang, W. Y. *J. Phys. C* **1973**, *6*, L482.

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Ground States of Molecules. 54.[1] MNDO Study of Carboranes

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MNDO calculations are reported for all the known carboranes up to and including $(B,C)_{12}$ which have not been treated in an earlier paper of this series. If appropriate symmetry constraints are applied, the calculated geometries are in good agreement with experiment. In some cases, however, the symmetrical structures are not local minima on the MNDO potential surface. Other calculated properties also agree well with the available data.

Introduction

The boron hydrides and carboranes represent an area of chemistry of unusual theoretical interest in view of the prevalence of multicenter bonds. While the basic principles governing bonding in such "electron deficient" molecules were established many years ago by Longuet-Higgins,[2] this is clearly a field where quantitative calculations of molecular structure and chemical reactivity would be of great interest and value. Numerous calculations have of course been reported, but virtually none so far has been of value in this connection, for the following reasons.

The first is purely technical. If we are concerned with interpreting or predicting the structures of molecules, we must calculate their geometries properly, by minimizing their energies with respect to all the relevant geometrical parameters and without making *any* assumptions. We must also make sure that the stationary points we find do in fact correspond to local minima and not to saddlepoints (i.e., transition states). This is particularly necessary in cases of molecules with potential symmetry because it is very easy to mistake for a minimum a symmetrical structure which in fact is the transition state for the interconversion of two unsymmetrical mirror-image isomers. This situation arises frequently in the boron hydrides and carboranes where symmetrical "nonclassical" structures are related in this way to pairs of "classical" isomers. It is important to establish whether the latter are stable species, interconverted via a "nonclassical" transition state, or unstable species, only the "nonclassical" structure representing a local minimum. At present the only reliable procedure for this purpose is one introduced by McIver and Komornicki,[3] i.e., calculating and diagonalizing the Hessian (force constant) matrix. At a minimum, the eigenvalues of the Hessian are all positive, apart from six zero values corresponding to translation and rotation), while at a transition state one, and only one, is negative. The presence of six vanishing eigenvalues also serves as a useful criterion of convergence to the stationary point. The need for these precautions has been demonstrated very clearly by our own calculations for the boron hydrides.[4]

Similar considerations apply even more forcefully to studies of chemical reactions where it is necessary to establish not only that a given stationary point is of the right type (i.e., a saddlepoint) but also that it is a transition state for the reaction under consideration and not for some different process. One must establish that there are downhill paths from it to both reactants and products. Here again our own experience has shown these precautions to be absolutely essential.[5]

No calculations which met these conditions have as yet been reported for any carborane.

Second, one must naturally use a procedure which can reasonably be expected to give sufficiently accurate results. *No* theoretical treatment currently applicable to polyatomic molecules gives values for the total energies of molecules that are accurate enough for chemical purposes.[6] Nevertheless

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(1) Dewar, M. J. S.; Rzepa, H. S. *Inorg. Chem.* **1979**, *18*, 602.

(2) Longuet-Higgins, H. C. *J. Chim. Phys. Chim. Biol.* **1949**, *46*, 268.

(3) McIver, J. W., Jr.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625. Komornicki, A.; McIver, J. W., Jr. *Ibid.* **1973**, *95*, 4512.

(4) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1978**, *17*, 1569.

(5) See, e.g.: Dewar, M. J. S.; Ford, G. P.; Rzepa, H. S. *J. Chem. Soc., Chem. Commun.* **1977**, 728.

(6) The errors in molecular energies calculated by the Hartree–Fock procedure (i.e., those given in the limit by RH treatments if sufficiently large basis sets are used) are comparable with their heats of atomization, e.g., ca. 1000 kcal/mol for benzene. This error, due to neglect of electron correlation, can be reduced by CI to an extent depending on the size of the basis set. With the largest basis sets that have been used for polyatomic molecules (double ζ + polarization), ca. 80% of the correlation energy can be recovered. The higher percentages often quoted in the literature refer to *recoverable* correlation energy, not to total correlation energy. An error equal to 20% of the heat of atomization of a molecule is very large by chemical standards (e.g., 200 kcal/mol for benzene).

0020-1669/80/1319-2662$01.00/0

since heats of formation and heats of reaction depend on relative energies, not absolute energies, it is still possible for existing theoretical procedures to reproduce them, as a result of cancellation of errors in the absolute energies. There is, however, no way of telling a priori whether or not such a cancellation should occur. If it does occur, it can be shown to do so only by trial. All current treatments of chemical behavior are therefore empirical and they can be trusted only to the extent they have been tested by comparisons with experiment. This point needs to be emphasized because many chemists have been misled into accepting the label ab initio as a guarantee of accuracy and there has even been some tendency to extend the use of this term to procedures that should properly be classed as semiempirical.

It is now generally recognized that the Roothaan–Hall (RH; "ab initio SCF") MO method does not reproduce the energies of isomers in a satisfactory manner unless a large basis set is used. This is true in particular for comparison of isomeric "classical" and "nonclassical" species.[4,8,9] In the case of bond dissociation processes (e.g., $B_2H_6 \rightarrow 2BH_3$), or potential surfaces for reactions, it is certainly also essential to allow for electron correlation by either very extensive configuration interaction (CI) or some comparable procedure. Such "state of the art" calculations are limited at present to molecules containing no more than five or six atoms other than hydrogen while studies of reactions are even more restricted.

If therefore we wish to carry out chemically[10] useful calculations for carboranes, the only hope at the present time lies in some semiempirical approach. Most such procedures (e.g., CNDO, INDO, PRDDO, EH) have been parametrized to mimic minimum basis set RH calculations. Since the latter are themselves too inaccurate for chemical[10] purposes, the procedures designed to mimic them are also unsatisfactory. Two procedures have, however, been developed here (MINDO/3,[11] MNDO[12]) which were parametrized to reproduce experimental properties of molecules and do so with reasonable success. Comparative tests[13] have shown that MNDO is comparable in accuracy with RH procedures using large basis sets, in particular for boron compounds, and the computing time required is less by several orders of magnitude.

One failing of MNDO, which it shares with most ab initio RH procedures, is a tendency to underestimate the energies of multicenter bonds relative to normal two-center ones. Thus MNDO underestimates the energies of "nonclassical" carbocations, relative to those of classical isomers, to about the same extent as RH calculations using the 4-31G basis set. The same tendency appeared in a preliminary study[14] of boron hydrides where B_5H_9, a compound with an unusually high proportion of three-center bonds, was predicted to have a less symmetrical structure of more "classical" type. However, since MNDO gives good estimates of the heats of formation of boron hydrides, it seems clear that the error cannot be large. Errors of this kind should therefore be expected only in similar cases of molecules of high symmetry, containing an unusual number of multicenter bonds. A very extensive study[4] of boron hydrides and borohydride anions supported this conclusion.

It should be emphasized that this defect of MNDO has become apparent only because it has been tested. *No* geometry optimizations by ab initio methods have been reported for any of the critical molecules and none, to our knowledge, for boron hydrides other than diborane. In view of the results for "nonclassical" carbocations referred to above, there is every reason to believe that ab initio RH methods will be found to suffer from the same defects as MNDO, if and when the appropriate calculations are carried out, unless a very large basis set is used. Similar remarks apply to the PRDDO procedure, which again has not been used to optimize geometries of boron hydrides in a rigorous manner. Subsequent to our report, Lipscomb et al.[15] found that PRDDO does indeed reproduce the (incorrect) MNDO geometries in some key molecules.

This work has nevertheless established MNDO as a useful procedure in boron hydride chemistry, giving good estimates of geometries and heats of formation in most cases. The exceptions have moreover been clearly delineated by our extensive tests. It should be noted that MNDO also reproduces a variety of other important properties of molecules with an accuracy again at least comparable with good ab initio methods. These include ionization energies,[10-14] vibration frequencies,[16] dipole moments,[10-14] electric polarizabilities,[17] nuclear quadrupole coupling constants,[18] and ESCA chemical shifts.[19]

We would nevertheless feel dubious about extending MNDO to carborane chemistry without appropriate additional tests because the multicenter bonds in carboranes often follow an even more complex pattern than they do in the boron hydrides, apart from involving carbon as well as boron. It is in our opinion scientifically improper to extend any current theoretical treatment into a new area without first testing it as thoroughly as possible. In some cases such tests may be hampered by lack of experimental data, but that is not the case here. Moreover the uncertainty concerning the ability of current procedures to reproduce multicenter bonds makes such tests mandatory.

We have therefore carried out detailed MNDO calculations for all the known carboranes containing up to 12 "heavy" atoms (i.e., other than hydrogen). Here we report our results. It will appear that MNDO seems likely to prove as useful in this area of chemistry as in the case of the boron hydrides.

Procedure

The calculations followed the procedures described previously,[12] using the parameters recommended there. Geometries were optimized by our standard[20] Davidon–Fletcher–Powell procedure, no assumptions being made other than that of symmetry in cases where species of specific symmetry were being studied. The nature of each calculated stationary point was then checked by calculating and diagonalizing the Hessian (force constant) matrix, as suggested by McIver and Komornicki.[23] In the case of a minimum, all eigenvalues of this

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(7) An ab initio procedure is one based on a rigorous solution of an approximation to the Schrödinger equation. The results are then subject to the variation theorem. The PRDDO method is not in this sense an ab initio procedure. Furthermore, it has always been used in a parametrized form because the original "ab initio" version proved very inaccurate.

(8) Lischka, H.; Köhler, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 5297.

(9) (a) Bischoff, P. K.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1975**, *97*, 2446. (b) Dewar, M. J. S.; Haddon, R. C.; Komornicki, A.; Rzepa, H. S. *Ibid.* **1977**, *99*, 377.

(10) Our comments refer specifically to chemical properties that depend on molecular energies. Simpler ab initio procedures can give useful results in other connections.

(11) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302, 1307.

(12) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(13) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5558.

(14) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1977**, *99*, 5231.

(15) Camp, R. N.; Marynick, D. S.; Graham, G. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6783.

(16) Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Thiel, W.; Yamaguchi, Y. *J. Mol. Struct.* **1978**, *43*, 135.

(17) Yamaguchi, Y.; Suck, S. H.; Dewar, M. J. S. *Chem. Phys. Lett.* **1978**, *59*, 541.

(18) Unpublished work by L. Chantranupong and Y. Yamaguchi.

(19) Unpublished work by H. S. Rzepa.

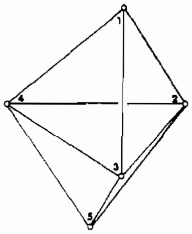
(20) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(21) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302, 1307.

(22) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163. Davidon, W. C. *Ibid.* **1968**, *10*, 406.

Table I. Calculated Properties of Carboranes

carborane	ΔH_f/ kcal·mol^{-1}	dipole moment/ D	HOMO/ eV	orbital sym	mol sym
1,5-$C_2B_3H_5$	26.8	0	11.49	e″	D_{3h}
1,2-$C_2B_3H_5$	69.6	1.35	10.95	a″	C_s
1,3-$C_2B_3H_5$	33.2	0.43	10.13	b	C_2
$C_3B_3H_7$	47.1	2.10	10.52	a″	C_s
$C_2B_4H_8$	33.6	1.14	10.57	a″	C_s
CB_5H_9	17.6	2.13	11.18	a′	C_s
2,4-$C_2B_5H_7$	33.7	1.24	11.61	b_1	C_{2v}
2,3-$C_2B_5H_7$	50.3	3.04	11.46	b_1	C_{2v}
1,7-$C_2B_5H_7$ (T.S.)	98.0	0	11.12	e_2'	D_{5h}
$C_2B_6H_8$	26.0	1.73	11.65	b	C_2
$C_2B_7H_9$ (T.S.)	31.2	2.41	11.07	b_2	C_{2v}
1,6-$C_2B_8H_{10}$ (T.S.)	26.9	2.20	11.35	a″	C_s
1,10-$C_2B_8H_{10}$	0.6	0	12.09	e_2	D_{4d}
$C_2B_8H_{12}$	20.6	2.53	10.98	a′	C_s
$C_2B_7H_{13}$	27.2	2.76	10.73	a′	C_s
$C_2B_9H_{11}$ (C_s)	5.2	2.21	11.56	a′	C_s
$C_2B_9H_{11}$ (C_{2v})	10.4	2.54	11.25	b_1	C_{2v}
$C_2B_9H_{13}$	34.9	3.40	11.25	a″	C_s
1,2-$C_2B_{10}H_{12}$	9.7	4.30	12.18	b_1	C_{2v}
1,7-$C_2B_{10}H_{12}$	−3.8	2.69	12.12	a_1	C_{2v}
1,12-$C_2B_{10}H_{12}$	−5.2	0	12.12	e_{2u}	D_{5d}
$CB_{11}H_{12}^-$	−123.6		7.36	e_2	C_{5v}
1,7-$C_2B_9H_{12}^-$	−81.8		5.96	a′	C_s
1,2-$C_2B_9H_{12}^-$	−62.0		5.65		C_1
1,2-$C_2B_9H_{11}^{2-}$	−28.0		0.29	a″	C_s
1,7-$C_2B_9H_{11}^{2-}$	−46.3		0.07	a′	C_s



1,5-$C_2B_3H_5$

C^1B^2	1.576	(1.556)
B^2B^3	1.928	(1.853)

1	-.18	.08
2	.02	.05

Figure 1. Electron gas diffraction structure by: McNeill, E. A.; Gallaher, K. L.; Scholer, F. R.; Bauer, S. H. *Inorg. Chem.* **1973**, *12*, 2108.

matrix must be positive. In cases where one or more of the eigenvalues were negative, the corresponding eigenvectors were studied to determine the type of distortion needed to lead to a true minimum.

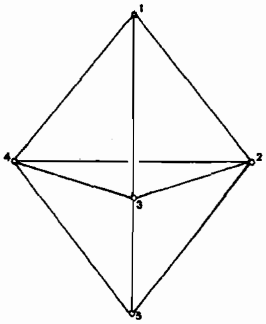
While this test is always advisable, it is essential in cases where geometry optimization has been carried out with enforced symmetry, since there is no other way in which one can tell reliably whether or not the symmetrical minimum is a true local minimum on the potential surface.

Results and Discussion

Table I lists the calculated heats of formation, dipole moments, and molecular symmetries calculated for the various species.

Table II shows the calculated orbital energies of the occupied MO's which, according to Koopmans' theorem, should be equal to minus the corresponding ionization energies.

This use of MNDO has been shown to give very good estimates of ionization energies, reproducing them in the correct order and with reasonable accuracy even in cases where similar use of ab initio RH procedures fails.

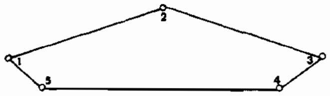


1,2-$C_2B_3H_5$

C^1C^2	1.593
C^1B^3	1.548
C^2B^3	1.871
C^2B^5	1.492
B^3B^4	1.942
B^3B^5	1.697

1	-.17	.10
2	.08	.09
3	.00	.07
5	-.32	.07

Figure 2.

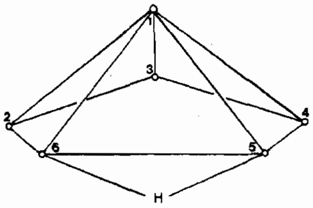


1,3-$C_2B_3H_5$

C^1B^2	1.485
C^1B^5	1.481
B^4B^5	1.631

1	.08	.07
2	-.25	.00
4	-.05	.03

Figure 3.



2,3,4-$C_3B_3H_7$

B^1C^2	1.783
B^1C^3	1.861
B^1B^5	1.778
C^2C^3	1.455
C^2B^6	1.530
B^5B^6	1.844
H_b	1.367

1	-.20	.07
2	-.05	.09
3	-.02	.09
5	-.10	.05
H_b	.09	

Figure 4.

The calculated geometries and distributions of formal charge are also given in Figures 1–17. Bond lengths are shown on the left of each diagram (experimental values in parentheses) and net (formal) atomic charges on the right. The first value refers to boron or carbon and the second to the hydrogen atom attached to it. A discussion of the results for individual molecules follows.

1,2-$C_2B_3H_5$. Three isomers of $C_2B_3H_5$ are possible, based on a trigonal bipyramid. Only the parent 1,5 isomer (**1**) is known while no 2,3 derivatives (**2**) have yet been prepared.

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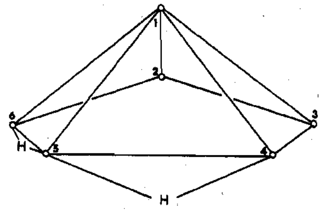
(23) McIver, J. W., Jr.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625. Komornicki, A.; McIver, J. S., Jr. *Ibid.*, **1973**, *95*, 4512.



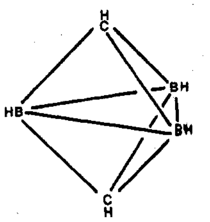
2,3-$C_2B_4H_8$

B^1C^2	1.791	**(1.762)**
B^1B^4	1.864	**(1.768)**
B^1B^5	1.677	**(1.705)**
C^2C^3	1.465	**(1.432)**
C^2B^6	1.509	**(1.520)**
B^4B^5	1.858	**(1.778)**
$B^4H_b^{45}$	1.301	**(1.284)**
$B^5H_b^{45}$	1.456	**(1.381)**

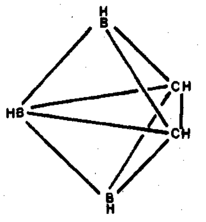
1	-.26	.07
2	.01	.08
4	-.14	.04
5	.03	.05
H_b	.05	

Figure 5. X-ray structure of 2,3-$(CH_3)_2$-$C_2B_4H_6$ (symmetrically averaged) by: Boer, F. P.; Streib, W. E.; Lipscomb, W. N. *Inorg. Chem.* **1964**, *3*, 1666.

MNDO calculations for **1** were reported previously[14] but are repeated here in more detail.



1



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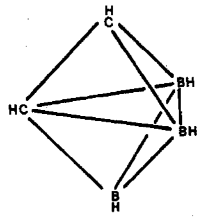

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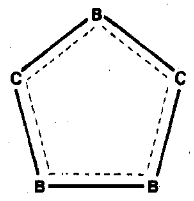
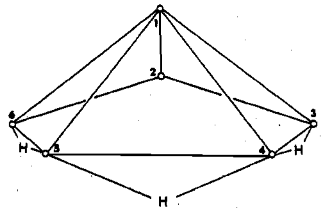


4

MNDO predicts both **1** and the 1,2 isomer (**3**) to have the expected geometries (Figures 1–3) but the heat of formation calculated for **3** is higher by 43 kcal/mol than that for **1** (Table I). According to MNDO, **2** is not a minimum on the potential surface, rearranging without activation to a planar species **4**, only 5 kcal/mol less stable than **1**. While the stability of **4** relative to **1** or **3** is probably overestimated, due to the tendency[4,14] of MNDO to disfavor three-center bonds, it seems likely that rearrangement of **3** to **1** via such an intermediate should be facile. No such rearrangement has been observed,[24] but this may well be due[25] to steric crowding of the substituents in the corresponding transition state. Only disubstituted derivatives of **3** are known possibly because the parent and monosubstituted derivatives of **3** are subject to this rearrangement.

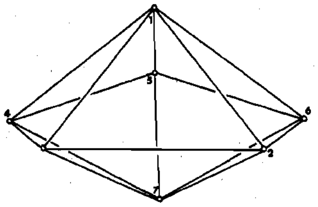


2-CB_5H_9

B^1C^2	1.777	
B^1B^3	1.883	(1.782)
B^1B^4	1.736	(1.781)
C^2B^3	1.505	
B^3B^4	1.811	(1.759)
B^4B^5	1.897	(1.830)
$B^3H_b^{34}$	1.363	
$B^4H_b^{34}$	1.378	
$B^4H_B^{45}$	1.374	

1	-.25	.06
2	.00	.08
3	-.05	.03
4	-.02	.04
H_b^{34}	.05	
H_b^{45}	.00	

Figure 6. Microwave structure by: Cheung, C. C. S.; Beaudet, R. A. *Inorg. Chem.* **1971**, *10*, 1144.



2,4-$C_2B_5H_7$

B^1B^3	1.908	(1.818)
B^1C^2	1.781	(1.708)
B^1B^5	1.812	(1.815)
C^2B^3	1.557	(1.546)
C^2B^6	1.607	(1.563)
B^5B^6	1.672	(1.651)

1	-.04	.08
2	-.06	.10
3	-.14	.07
5	-.12	.08

2,3-$C_2B_5H_7$

B^1C^2	1.889
B^1B^4	1.836
B^1B^5	1.754
C^2C^3	1.492
C^2B^6	1.540
B^5B^6	1.721

1	.00	.07
2	-.05	.10
4	-.18	.07
5	-.09	.08

1,7-$C_2B_5H_7$

C^1B^2	1.778
B^2B^3	1.641

1	.13	.10
2	-.18	.09

Figure 7. 2,4-$C_2B_5H_7$ microwave structure by: Beaudet, R. A.; Poynter, R. L. *J. Chem. Phys.* **1965**, *43*, 2166.

Similar conclusions have been reached by Camp et al.[26] in a recent ab initio RH study of this system, using the 4-31G basis set. Since they used geometries calculated by PRDDO (with assumed CH and BH bond lengths), their 4-31G energies are subject to errors of uncertain magnitude.

Armstrong[27] has reported a minimum basis set RH (Roothaan–Hall, "*ab initio* SCF") calculation for **1**. The order of orbital energies found by him agrees with that from MNDO (Table II), except for the inversion of the 1e′ and 2a′ MO's.

In **1** and **3**, there are quite large calculated negative charges on the boron atoms (Figures 1 and 2).

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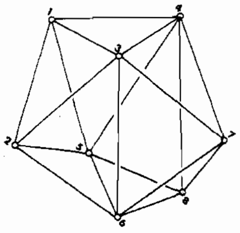
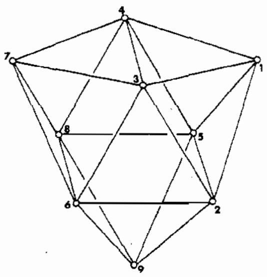
(24) Grimes, R. N. *J. Organomet. Chem.* **1967**, *8*, 45.
(25) Lipscomb, W. N. *Science* **1966**, *153*, 373.
(26) Camp, R. N.; Marynick, D. S.; Graham, G. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6781.
(27) Armstrong, D. R. *Rev. Roum. Chim.* **1975**, *20*, 883.



1,7-$C_2B_6H_8$

C^1B^3	**1.773**	1	-.05	.10
C^1B^4	**1.569**	2	-.14	.06
C^1B^2	**1.576**	3	-.05	.06
C^1B^5	**1.825**	5	-.04	.06
B^2B^5	**1.884 (1.843)**			
B^3B^4	**1.993 (1.886)**			
B^2B^3	**1.871 (1.813)**			
B^3B^6	**1.967 (1.880)**			
B^5B^6	**1.991 (1.999)**			
B^2B^6	**1.642 (1.685)**			

Figure 8. Microwave structure by: Rogers, H. N.; Lau, K. K. L.; Beaudet, R. A. *Inorg. Chem.* **1976**, *15*, 1775.

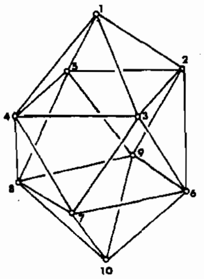


1,7-$C_2B_7H_9$

C^1B^2	**1.674 (1.61)**	1	-.08	.10
C^1B^3	**1.643 (1.60)**	2	-.07	.06
B^3B^4	**1.910 (1.76)**	3	-.06	.07
B^3B^2	**1.983 (1.97)**	9	-.11	.07
B^2B^5	**1.853 (1.78)**			
B^2B^6	**1.980 (1.98)**			
B^2B^9	**1.731 (1.70)**			

Figure 9. X-ray structure of 1,7-$(CH_3)_2$-$C_2B_7H_7$ (symmetrically averaged) by: Koetzle, T. F.; Scarbrough, F. E.; Lipscomb, W. N. *Inorg. Chem.* **1968**, *7*, 1076.

$C_3B_3H_7$, $C_2B_4H_8$, CB_5H_9. MNDO predicts these three hydrides to have pentagonal-pyramidal structures **5**–**7** with apical boron and the carbon atoms adjacent to one another (Figures 4–6). The structure for **7** was reported in ref 11 but is repeated here for comparison. The crystallographic[28] geometry for **6** agrees well with that predicted, and spectroscopic evidence[29] suggests that **5** also has a pentagonal-pyramidal structure with adjacent carbon atoms. The MNDO orbital energies for **6** agree well with those calculated by Marynick and Lipscomb,[30] and both calculations predict the most negative atom to be B^1, followed by $B^4 > B^5$ (MNDO) or $B^5 > B^4$ (PRDDO[30]).



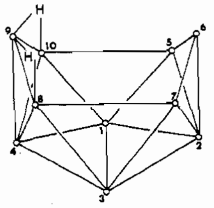
1,6-$C_2B_8H_{10}$

C^1B^2	1.633	1.597	1	-.10	.11
C^1B^4	1.680	1.600	2	-.08	.07
B^2C^6	1.748	1.751	4	-.06	.07
B^2B^3	1.972	1.861	6	.01	.10
B^2B^5	1.911	1.812	7	-.08	.08
B^4B^5	1.881	1.831	8	-.05	.07
C^6B^7	1.900	1.776	10	-.19	.08
C^6B^{10}	1.622	1.632			
B^9B^2	1.808	1.789			
B^9B^5	1.801	1.798			
B^9B^8	1.894	1.841			
B^8B^{10}	1.740	1.681			
B^8B^4	1.842	1.828			
B^7B^{10}	1.739	1.694			

1,10-$C_2B_8H_{10}$

C^1B^2	1.655	1	-.066	.11
B^2B^3	1.927	2	-.073	.06
B^2B^6	1.821			

Figure 10. 1,6-$C_2B_8H_{10}$ X-ray structure of 1,6-$(CH_3)_2$-$C_2B_8H_8$ (symmetrically averaged) by: Koetzle, T. F.; Lipscomb, W. N. *Inorg. Chem.* **1970**, *9*, 2279.



5,7-$C_2B_8H_{12}$

B^1B^2	1.731	1	-.01	.07
B^1B^3	1.842	2	-.10	.07
B^1B^4	1.795	4	-.26	.06
B^1C^5	1.803	5	-.13	.08
B^1B^{10}	1.862	6	.02	.03
B^2C^5	1.801	8	.02	.03
B^2B^6	1.926	9	-.14	no H_t
B^4B^8	1.883	H_b	.07	
B^4B^9	1.753			
B^6C^5	1.562			
C^5B^{10}	1.637			
B^9B^{10}	1.878			
B^9H_b	1.288			
$B^{10}H_b$	1.476			

Figure 11.

Chlorination of **6** in fact takes place at the 5 position; Marynick and Lipscomb have discussed this apparent anomaly.

These hydrides can be regarded as analogues of $C_6H_6^{2+}$ which (in the form of derivatives) apparently[31] has the

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(28) Boer, F. P.; Streib, W. E.; Lipscomb, W. N. *Inorg. Chem.* **1964**, *3*, 1666.
(29) "Gmelin Handbuch", Springer-Verlag: New York, 1974; Band 15, Borverbindungen Teil 2, pp 153, 154.
(30) Marynick, D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1972**, *94*, 8699.

Table II. Calculated Orbital Energies (eV) for Neutral Carboranes[a]

1,5-$C_2B_3H_5$			1,2-$C_2B_3H_5$		1,3-$C_2B_3H_5$	
orbital	MNDO	ab initio[b]	orbital	MNDO	orbital	MNDO
1e''	11.49	12.57	3a''	10.95	5b	10.13
2e'	12.63	13.71	8a'	11.50	6a	11.62
$2a_2''$	12.99	15.78	7a'	12.74	5a	12.14
$3a_1'$	16.51	16.46	2a''	12.77	4b	13.23
$2a_1'$	17.44	19.81	6a'	13.49	3b	13.65
1e'	19.78	19.02	5a'	16.72	4a	16.18
$1a_2''$	27.76	25.17	4a'	16.97	3a	17.96
$1a_1'$	40.47	32.87	1a''	19.84	2b	17.97
			3a'	21.82	2a	21.61
			2a'	25.57	1b	29.13
			1a'	41.47	1a	36.96

$C_3B_3H_7$		2,3-$C_2B_4H_8$			CB_5H_9	
	MNDO		MNDO	ab initio[c]		MNDO
5a''	10.52	5a''	10.57	9.44	9a'	11.18
9a'	10.95	9a'	11.60	11.24	5a''	11.44
8a'	12.32	8a'	12.90	12.49	8a'	12.88
4a''	13.45	4a''	13.39	13.25	4a''	13.17
7a'	13.48	3a''	13.63	13.60	7a'	13.36
6a'	13.92	7a'	13.75	13.47	6a'	13.86
3a''	14.25	6a'	13.97	14.23	3a''	14.13
5a'	17.48	5a'	17.24	16.49	5a'	16.81
2a''	18.17	4a'	18.13	17.22	2a''	18.12
4a'	19.50	2a''	19.56	18.37	4a'	19.02
3a'	20.26	3a'	19.76	18.80	3a'	19.83
2a'	26.40	1a''	26.88	22.96	1a''	24.72
1a''	29.94	2a'	26.99	24.05	2a'	27.50
1a'	42.83	1a'	40.77	30.37	1a'	37.51

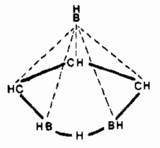
2,4-$C_2B_5H_7$			2,3-$C_2B_5H_7$		1,7-$C_2B_5H_7$	
	MNDO	ab initio[d]		MNDO		MNDO
$3b_1$	11.61	10.13	$4b_1$	11.47	$2e_2$	11.14
$7a_1$	11.98	11.14	$1a_2$	11.68	$1e_1''$	12.68
$1a_2$	12.38	12.37	$3b_2$	12.03	$2a_2''$	13.73
$4b_2$	12.70	12.44	$2b_2$	12.97	$2e_1'$	14.04
$2b_1$	12.99	12.93	$7a_1$	13.06	$1e_2'$	17.19
$6a_1$	13.96	13.86	$3b_1$	14.06	$3a_1'$	17.74
$3b_2$	14.30	14.98	$6a_1$	14.22	$2a_1'$	19.27
$5a_1$	17.01	15.33	$5a_1$	17.06	$1e_1'$	24.10
$4a_1$	17.64	16.28	$4a_1$	17.82	$1a_2''$	28.53
$2b_2$	17.96	16.80	$3a_1$	18.23	$1a_1'$	43.88
$3a_1$	19.00	19.49	$2b_1$	18.82		
$1b_1$	21.86	19.53	$1b_2$	21.79		
$2a_1$	24.71	21.68	$2b_1$	27.13		
$1b_2$	30.74	25.66	$1b_1$	27.27		
$1a_1$	43.02	31.90	$1a_1$	43.32		

$C_2B_6H_8$		$C_2B_7H_9$		1,6-$C_2B_8H_{10}$		1,10-$C_2B_8H_{10}$	
	MNDO		MNDO		MNDO		MNDO
8b	11.65	$5b_2$	11.07	7a''	11.35	$2e_2$	12.09
9a	11.71	$8b_1$	11.48	14a'	11.81	$3e_1$	12.26
7b	12.12	$4b_1$	12.18	13a'	12.34	$4a_1$	13.16
8a	12.52	$2a_2$	13.08	6a''	12.45	$2e_3$	13.22
7a	13.34	$7a_1$	13.16	12a'	13.00	$2e_1$	13.94
6b	13.73	$4b_2$	13.16	11a'	13.27	$3b_2$	15.30
6a	13.81	$3b_1$	13.34	5a''	13.32	$2b_2$	16.95
5b	14.71	$6a_1$	14.63	4a''	14.10	$3a_1$	18.17
5a	17.54	$3b_2$	15.07	10a'	14.26	$1e_2$	18.27
4a	17.83	$5a_1$	17.03	9a'	15.26	$1e_3$	19.54
4b	17.84	$2b_1$	18.24	8a'	16.30	$2a_1$	23.66
3b	18.43	$1a_2$	18.34	7a'	18.25	$1e_1$	25.91
3a	19.60	$4a_1$	18.41	3a''	18.45	$1b_2$	35.54
2b	24.13	$3a_1$	19.86	6a'	18.72	$1a_1$	43.06
2a	24.87	$2b_2$	20.07	2a''	19.38		
1b	32.23	$1b_1$	23.84	5a'	20.37		
1a	42.79	$2a_1$	28.09	4a'	21.67		
		$1b_2$	33.10	1a''	26.09		
		$1a_1$	43.29	3a'	27.86		
				2a'	33.95		
				1a'	43.50		

$C_2B_8H_{12}$		$C_2B_7H_{13}$		$C_2B_9H_{11}$		$C_2B_9H_{13}$	
	MNDO		MNDO		MNDO		MNDO
14a'	10.98	13a'	10.73	b_1	11.25	9a''	11.25
8a''	11.69	8a''	11.65	a_2	11.85	15a'	11.87
13a'	12.20	12a'	12.25	a_1	12.23	14a'	12.03
7a''	12.43	7a''	12.43	b_2	12.53	8a''	12.15
6a''	12.48	11a'	12.65	a_2	12.78	13a'	12.56
12a'	12.91	10a'	13.24	a_1	12.89	7a''	12.71
11a'	13.56	6a''	13.85	b_2	13.47	12a'	13.20
10a'	14.08	5a''	14.00	b_1	13.59	6a''	13.87
5a''	14.36	9a'	14.35	b_1	14.42	11a'	14.20
4a''	14.65	4a''	14.56	a_1	14.49	10a'	14.62
9a'	14.82	8a'	15.18	b_2	15.79	5a''	14.87
8a'	16.49	7a'	16.59	b_2	16.29	9a'	15.10
7a'	17.50	6a'	17.65	a_1	16.64	8a'	16.32
6a'	18.08	5a'	18.55	a_1	18.50	4a''	16.67
3a''	19.03	3a''	19.01	b_1	18.80	7a'	18.41
5a'	20.09	4a'	20.50	a_1	19.66	6a'	18.91
4a'	21.25	2a''	22.16	a_2	20.57	3a''	20.88
2a''	21.85	3a'	25.43	a_1	21.45	5a'	21.12
3a'	26.07	2a'	29.21	b_2	22.12	4a'	21.65
2a'	29.59	1a''	32.89	b_1	26.82	2a''	22.61
1a''	32.42	1a'	39.44	a_1	28.97	3a'	27.85
1a'	41.66			b_2	35.52	1a''	30.38
				a_1	42.79	2a'	31.43
						1a'	42.82

1,2-$C_2B_{10}H_{12}$			1,7-$C_2B_{10}H_{12}$			1,12-$C_2B_{10}H_{12}$		
	MNDO	ab initio[e]		MNDO	ab initio[e]		MNDO	ab initio[e]
$6b_2$	12.18	11.43	$10a_1$	12.12	11.18	$2e_{2u}$	12.12	11.29
$6b_1$	12.20	11.21	$3a_2$	12.30	11.54	$2e_{2g}$	12.69	11.51[f]
$3a_2$	12.36	11.48	$6b_2$	12.47	11.70	$1e_{1g}$	13.11	13.14
$10a_1$	12.37	11.43	$6b_1$	12.69	12.16	$3e_{1u}$	13.20	13.28
$9a_1$	12.71	12.19	$9a_1$	12.77	12.49	$4a_{1g}$	13.89	13.66
$5b_2$	12.93	12.43	$5b_2$	12.88	12.57	$2e_{1u}$	15.07	15.10
$5b_1$	13.16	13.17	$8a_1$	13.12	13.06	$3a_{2u}$	15.61	15.43
$2a_2$	13.23	13.39	$2a_2$	13.43	13.50	$1e_{2u}$	16.21	14.61
$8a_1$	13.68	13.96	$5b_1$	13.50	13.90	$2a_{2u}$	17.43	18.39
$4b_1$	15.10	14.58	$4b_2$	15.13	14.61	$3a_{1g}$	18.80	18.29
$4b_2$	15.40	15.07	$7a_1$	15.15	15.24	$1e_{2g}$	20.89	18.26[g]
$7a_1$	15.43	14.83	$4b_1$	15.55	14.91	$1e_{1g}$	21.12	19.56
$3b_1$	16.25	15.37	$3b_2$	16.23	15.18	$2a_{1g}$	24.23	22.69
$6a_1$	16.57	16.00	$3b_1$	16.55	16.98	$1e_{1u}$	28.86	24.84
$3b_2$	17.10	16.73	$6a_1$	16.97	15.95	$1a_{2u}$	35.45	29.01
$5a_1$	18.96	18.53	$5a_1$	18.86	18.38	$1a_{1g}$	44.00	32.33
$1a_2$	20.96	18.86	$2b_2$	20.95	18.58			
$2b_1$	21.01	19.21	$4a_1$	21.00	18.94			
$4a_1$	21.06	19.59	$1a_2$	21.09	19.37			
$3a_1$	21.70	20.73	$3a_1$	22.23	21.44			
$2b_2$	23.18	21.33	$2b_1$	22.40	20.71			
$1b_1$	28.72	25.06	$1b_2$	28.94	24.87			
$2a_1$	31.83	26.75	$2a_1$	30.22	25.63			
$1b_2$	31.90	27.32	$1b_1$	34.52	28.65			
$1a_1$	44.87	33.74	$1a_1$	44.16	32.65			

[a] Orbitals for valence shell electrons only. [b] Armstrong, D. R. *Rev. Roum. Chim.* 1975, *20,* 883. [c] Marynick, D.; Lipscomb, W. N. *J. Am. Chem. Soc.* 1972, *94,* 8699. [d] Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* 1972, *94,* 8692. [e] "Boron Hydride Chemistry"; Muetterties, E. L., Ed.; Academic Press: New York, 1975; pp 72–73. [f] Originally assigned e_{1g}. [g] Originally assigned a_{2u}.



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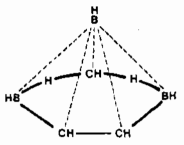

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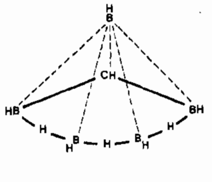

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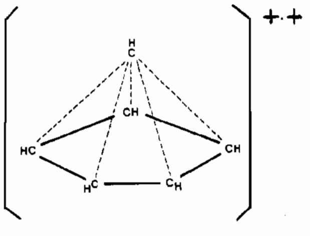

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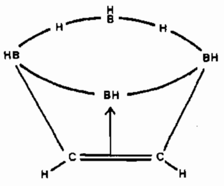

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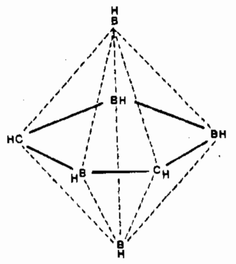

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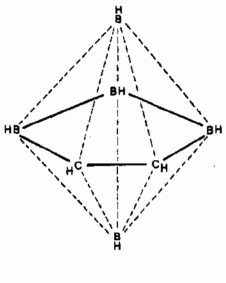

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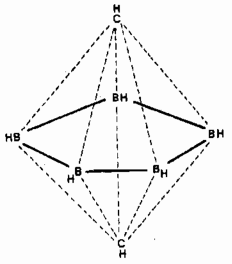

12

analogous pentagonal-bipyramidal structure **8**. This can be derived by combination of the pentadienate anion, $C_5H_5^-$, with HC^{3+}, the two units being linked by a triple dative μ bond in which the three filled π MO's of $C_5H_5^-$ act as donors and the three empty AO's of CH^{3+} as acceptors. $C_3B_3H_7$ is derived from **8** by replacing the apical carbon and one basal carbon by B^- (isoelectronic with C) and then one basal C–B unit by the isoelectronic B–H–B, with a three-center BHB bond. The other two hydrides are obtained by replacement of additional C–B units by B–H–B. The geometries calculated for **5** and **7** correspond well to this description. In each case the distances from the apical atom to the basal atoms are similar and the CC bond lengths in **5**, while small (1.455 Å), are greater than those expected in the aromatic ring of $C_5H_5^-$. Dative bonding with the apical atom in **8** should of course reduce the strengths of the CC bonds in the C_5H_5 moiety. In the case of **6**, Marynick and Lipscomb[30] claim on the basis of a localized orbital transformation of their PRDDO wave functions that the molecule is best represented as an ethylene derivative, i.e., **9**. The distances from the apical bond in **6** to the basal atoms do show much more variation than those in **5** or **7**, and the variations are in the direction expected on the basis of this suggestion.

$C_2B_5H_7$. Of the four possible geometric isomers of $(CH)_2(BH)_5$, based on a pentagonal bipyramid, only the 2,4[32] (**10**) and 2,3[33] (**11**) are known. The carbon atoms have been shown to occupy equatorial positions by a microwave study.[34] The MNDO calculations were carried out assuming C_{2v} geometries for **10** and **11** and D_{5h} for **12**. Calculation of force constants indicated **10** and **11** to be minima on the potential surface, but the D_{5h} structure for **12** had a Hessian matrix with two negative eigenvalues. We did not try to optimize the geometry of **12** further since it seemed likely that this would be another case where MNDO gives an incorrect structure and since no derivatives of **12** are known. The 1,2 isomer did not correspond to a minimum on the MNDO potential surface.

MNDO predicts the stabilities of the three stable isomers to fall in the order **10** > **11** > **12**, implying that the tendency of carbon atoms to occupy positions of low coordination is more important here than their tendency to keep apart. The MNDO geometries and charges for **10**, **11**, and **12** are shown in Figure 7. The orbital energies for **10** are compared with those from a minimum basis set RH calculation by Marynick and Lipscomb[35] in Table II.

$C_2B_6H_8$. In the larger carboranes, we have not tried to study all possible species and all possible isomers. We have confined ourselves to examining structures that have been determined experimentally, to see if MNDO in fact predicts corresponding minima on the potential surfaces. The known form of this hydride ($C_2B_6H_8$) has been shown[36] to have a structure intermediate between a square antiprism and a dodecahedron. MNDO reproduces the observed geometry very nicely, including its C_2 symmetry (the symmetry axis bisects the 3–4 and 5–6 bonds; Figure 8). No experimental data are available for comparison. The dipole moment and ionization potential (but not the formal charges) agree with those from a PRDDO calculation by Dixon et al.,[37] using an assumed geometry.

$C_2B_7H_9$. An X-ray study[38] of the 1,7-dimethyl derivative of this hydride has shown it to be a triangular prism with one of the three square faces capped by boron and two by carbon atoms. This structure was reproduced by a MNDO calculation assuming C_s symmetry (Figure 9). However, the corresponding Hessian matrix had a negative eigenvalue. This again appears to be a case where MNDO fails to reproduce the correct geometry. The carbon atoms in the C_s structure of Figure 9 seem to have a stabilizing effect because MNDO predicted the corresponding structure for the analogous negative ion, $B_9H_9^{2-}$, to be unstable, even when C_s symmetry was enforced. It has been found[38] that electrophilic attack takes place preferentially at B_9 in $C_2B_7H_7(CH_3)_2$. MNDO (Figure 9) predicts this to be the most negatively charged position.

$C_2B_8H_{10}$. Pyrolysis of the *C,C'*-dimethyl derivative of $C_2B_9H_{13}$ (see below) gives a *C,C'*-dimethyl derivative of $C_2B_8H_{10}$ which is indicated by NMR[38] and X-ray[39] studies

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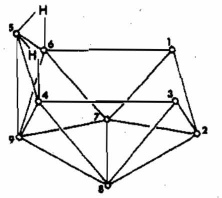
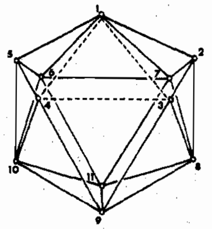


1,3-$C_2B_7H_{13}$

C^1B^2	1.651	1.704
C^1B^6	1.695	1.706
C^1B^7	1.830	1.672
B^2B^7	1.840	1.730
B^4B^5	1.917	1.819
B^4B^8	1.816	1.779
B^4B^9	1.887	1.823
B^5B^9	1.695	1.725
B^7B^8	1.712	1.714
B^7B^9	1.804	1.777
B^5H_b	1.321	1.18
B^6H_b	1.420	

1	-.07	$.06_{ax}/.03_{eq}$
2	-.20	.02
4	-.04	.03
5	-.06	.05
7	.03	.07
9	-.27	.07
H_b		.03

Figure 12. X-ray structure of 1,3-$(CH_3)_2$-$C_2B_7H_{11}$ (symmetrically averaged) by: Voet, D.; Lipscomb, W. N. *Inorg. Chem.* **1967**, *6*, 112.



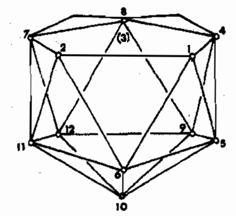
2,5-$C_2B_9H_{11}$

	C_s	C_{2v}	obs
B^1C^2	1.612	1.638	1.67
B^1B^3	2.447	2.127	2.06
B^1B^6	1.998	2.127	2.06
C^2B^3	1.568	1.604	1.60
C^2B^7	1.709	1.604	1.60
B^3B^4	2.191	1.863	1.87
B^6B^7	1.713	1.863	1.87
C^2B^8	1.796	1.790	1.70
B^3B^8	1.861	1.857	1.82
B^7B^8	1.812	1.857	1.82
B^3B^9	1.725	1.818	1.78
B^7B^{11}	1.942	1.818	1.78
B^8B^9	1.918	1.785	1.80
B^8B^{11}	1.699	1.785	1.80
B^9B^{11}	1.949	1.966	1.85

	C_s	
1	.02	.04
2	-.10	.09
3	.04	.05
7	-.11	.05
8	-.04	.06
9	-.21	.06
11	-.05	.06

	C_{2v}	
1	.00	.06
2	-.03	.11
3	-.11	.06
8	-.08	.07
9	-.06	.06

Figure 13. X-ray structure of 2,5-$(CH_3)_2$-$C_2B_9H_9$ (symmetrically averaged) by: Tebbe, F. N.; Garrett, P. M.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 869.



1,2-$C_2B_9H_{13}$

C^1C^2	1.557
C^1B^4	1.609
C^1B^5	1.862
C^1B^6	1.756
B^4B^8	1.981
B^4B^5	1.860
B^4B^9	1.878
B^5B^6	1.786
B^5B^9	1.779
B^5B^{10}	1.790
B^6B^{10}	1.879
B^8B^9	1.853
B^9B^{12}	1.828
B^9B^{10}	1.805
B^4H_b	1.324
B^8H_b	1.402

1	-.03	.09
4	-.19	.04
5	.02	.06
6	-.16	.06
8	.00	.06
9	-.14	.06
10	-.09	.08
H_b		.12

Figure 14.

to be a symmetrical bicapped square antiprism with the carbon atoms in the 1,6 positions.

When C_s symmetry was enforced, MNDO reproduced this structure nicely (Figure 10), but the corresponding Hessian matrix had one negative eigenvalue. The corresponding eigenvector suggested that a bicapped cube might prove to be a minimum on the MNDO potential surface, but this was not the case. We also carried out calculations for the 1,10 isomer, with both carbon atoms in apical positions. Here we found a local minimum corresponding to a bicapped square antiprism, analogous to the experimental structure for the 1,6 isomer. This structure is consistent with the NMR spectrum[38,40] which shows both the carbon atoms to be equivalent and all eight boron atoms to be equivalent. MNDO predicts the 1,10 isomer to be lower in energy than the 1,6 by 26 kcal/mol. The 1,6-dimethyl derivative of the 1,6 isomer indeed rearranges to the 1,10-dimethyl derivative of the 1,10 isomer on heating to 300–350 °C.[38,40]

It has been reported[41] that 1,6-$C_2B_8H_{10}$ is rapidly hydrolyzed by acid or base at room temperature whereas the 1,10 isomer was almost unchanged after heating for 12 h with base. This behavior can be understood in terms of the charges predicted by MNDO (see Figure 10). The negative charge at the apical boron atom (B^{10}) in the 1,6 isomer is more than double that at any other position in either molecule while C^6 in the 1,6 isomer is the only atom in either molecule that has a net positive charge.

PRDDO calculations by Lipscomb et al.[37] predicted B^2, not B^{10}, to be the most negative position. This difference could well be due to their failure to optimize geometries.

$C_2B_8H_{12}$. Very little work has been reported for this carborane, which is supposed to have the structure indicated in Figure 11, i.e., part of an icosahedron. As indicated, MNDO reproduces this nicely. The boron atom between the two carbon atoms B^6 is thought[44] to have an empty 2p AO available for coordination with electron donors. According to MNDO, the LUMO is extensively delocalized, but it does have a large contribution (22%) from the expected orbital of B^6.

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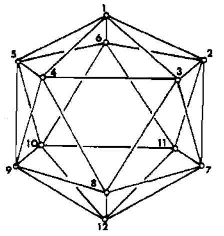


$1,2\text{-}C_2B_{10}H_{12}$

C^1C^2	1.749	1.653	1	-.02	.11
C^1B^4	1.749		3	-.12	.07
C^1B^3	1.750	1.711	4	-.08	.07
B^3B^4	1.835	1.803	8	-.08	.07
B^3B^8	1.806		9	-.07	.07
B^4B^9	1.821				
B^4B^8	1.821				
B^9B^{12}	1.803				
B^9B^8	1.842				
B^4B^5	1.818	1.789			

7-C-B H

C^1B^2	1.731	1.720	1	-.01	.11
C^1B^4	1.791		2	-.13	.08
C^1B^5	1.731		4	-.08	07
B^2B^3	1.868		5	-.10	.07
B^2B^6	1.804	1.791	9	-.09	.07
B^4B^5	1.813				
B^4B^8	1.817	1.817			
B^4B^9	1.820				
B^9B^{10}	1.822				
B^9B^5	1.829				

$1,12\text{-}C_2B_{10}H_{12}$

C B	1.759	1.710	1	.00	.11
B B	1.832	1.792	2	-.10	.08
B B	1.806	1.772			

$CB_{11}H_{12}^-$

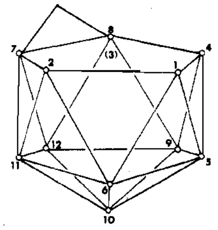
C^1B^2	1.755	1	.01	.06
B^2B^3	1.816	2	-.13	.02
B^2B^7	1.812	7	-.11	.02
B^7B^8	1.820			
B^7B^{12}	1.821			

Figure 15. $C_2B_{10}H_{12}$ electron gas diffraction of *o*-, *m*-, and *p*-$C_2B_{10}H_{12}$ by: Bohn, R. K.; Bohn, M. D. *Inorg. Chem.* **1971**, *10*, 350.

$C_2B_7H_{13}$. The structure of this hydride has been determined[45] by X-ray analysis of a dimethyl derivative. MNDO reproduces this well (Figure 12). Note that the BHB bridges are correctly predicted to be asymmetric, with the hydrogen atoms nearer B^5 than B^4 or B^6.

The axial hydrogen of the methylene group has been shown to exhibit enhanced acidity.[38] This result has been explained[45] by a calculation which implied that the overall electron densities follow the order axial CH > bridge BHB > equatorial CH. MNDO predicts the axial hydrogens to be the most positive (Figure 12) but inverts the order of the bridge and equatorial hydrogens.

$C_2B_9H_{11}$. The structure of the 2,5-dimethyl derivative of this carborane (2,5-$C_2B_9H_{13}$) has been shown[46] by an X-ray study to be nearly octadecahedral (Figure 13). A geometry optimization starting with this geometry led to a more open structure in which the heptacoordinate boron had become pentacoordinate by breaking two bonds. A similar problem arose[4] in the case of the analogous dianion $B_{11}H_{11}^{2-}$.



$1,7\text{-}C_2B_9H_{12}^-$

C^1B^2	1.605	1	-.02	.03
C^1B^4	1.624	2	-.15	-.02
C^1B^5	1.801	4	-.11	-.01
C^1B^6	1.767	5	-.06	.01
B^2B^6	1.909	6-	-.15	.01
B^4B^8	1.928	9	-.24	.01
B^4B^5	1.894	10	-.11	.03
B^4B^9	1.829	H_b		.08
B^5B^6	1.792			
B^5B^9	1.813			
B^5B^{10}	1.744			
B^6B^{11}	1.728			
B^6B^{10}	1.861			
B^9B^{10}	1.871			
B^4H_b	1.365			

Figure 16.

When C_{2v} symmetry was enforced, the energy calculated was only 5.2 kcal/mol higher than that for the C_s minimum and the geometry calculated for the C_{2v} structure agreed well with experiment (Figure 13). Bases are known[39] to react with $C_2B_9H_{11}$ very easily by opening of the polyhedral cage, probably by attacking the heptacoordinate boron; this suggests that the structure with lower coordination number, predicted by MNDO, is probably close in energy to the C_{2v} one. It therefore seems likely, as we have suggested elsewhere,[4] that MNDO underestimates the relative stabilities of such symmetric structures by only small amounts. Possible isomeric structures with higher symmetry should always be studied as well as that corresponding to a given MNDO potential minimum. If the MNDO energy of a given symmetric structure is only a little higher, it may very well in fact represent the true minimum.

$C_2B_9H_{13}$. This carborane is believed to have the structure of an icosahedron with one apex missing. Only the 1,2 isomer has been characterized, the 1,7 isomer being very unstable. Both isomers lose hydrogen on heating, forming $C_2B_9H_{11}$ (see above). MNDO reproduces the geometry of the 1,2 isomer nicely (Figure 14) and predicts the reaction

$$1,2\text{-}C_2B_9H_{13} \rightarrow 1,7\text{-}C_2B_9H_{11} + H_2$$

to be exothermic by 29 kcal/mol. The positions of the two extra hydrogen atoms in 1,2-$C_2B_9H_{13}$ have not been established, but it seems likely that they form bridges opposite the carbon atoms, in agreement with the MNDO structure. Electrophilic attack is expected at $B^4 > B^6 > B^9$ and nucleophilic attack at $B^5 > B^8$.

$C_2B_{10}H_{12}$. The icosahedral *o*-, *m*-, and *p*-carboranes are noted for their exceptional thermal and chemical stabilities and are almost the only "nonclassical" boron compounds (other than diborane) with possible industrial applications.[47] The MNDO geometries of all three isomers (Figure 15) agree quite

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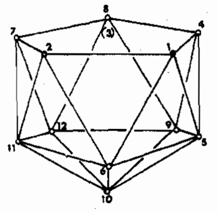
(45) Voet, D.; Lipscomb, W. N. *Inorg. Chem.* **1967**, *6*, 113.

(46) Tsai, C. C.; Streib, W. E. *J. Am. Chem. Soc.* **1966**, *88*, 4513.

(47) See ref 32.



$1,2\text{-}C_2B_9H_{11}$

C^1C^2	1.572	1	.00	-.02
C^1B^4	1.610	4	-.16	-.09
C^1B^5	1.777	5	-.19	-.04
C^1B^6	1.790	6	-.20	-.04
B^4B^8	1.686	8	-.16	-.08
B^4B^5	1.891	9	-.12	-.05
B^4B^9	1.922	10	-.16	-.02
B^5B^6	1.808			
B^5B^9	1.747			
B^5B^{10}	1.819			
B^6B^{10}	1.749			
B^8B^9	1.886			
B^9B^{12}	1.759			
B^9B^{10}	1.847			

$1,7\text{-}C_2B_9H_{11}^=$

C^1B^2	1.608	1	.09	-.03
C^1B^4	1.606	2	-.27	-.07
C^1B^5	1.797	4	-.18	-.08
C^1B^6	1.835	5	-.17	-.03
B^2B^6	1.846	6	-.17	-.05
B^4B^8	1.682	9	-.18	-.05
B^4B^5	1.894	10	-.16	-.02
B^4B^9	1.923			
B^5B^6	1.801			
B^5B^9	1.744			
B^5B^{10}	1.822			
B^6B^{11}	1.762			
B^6B^{10}	1.785			
B^9B^{10}	1.854			

Figure 17.

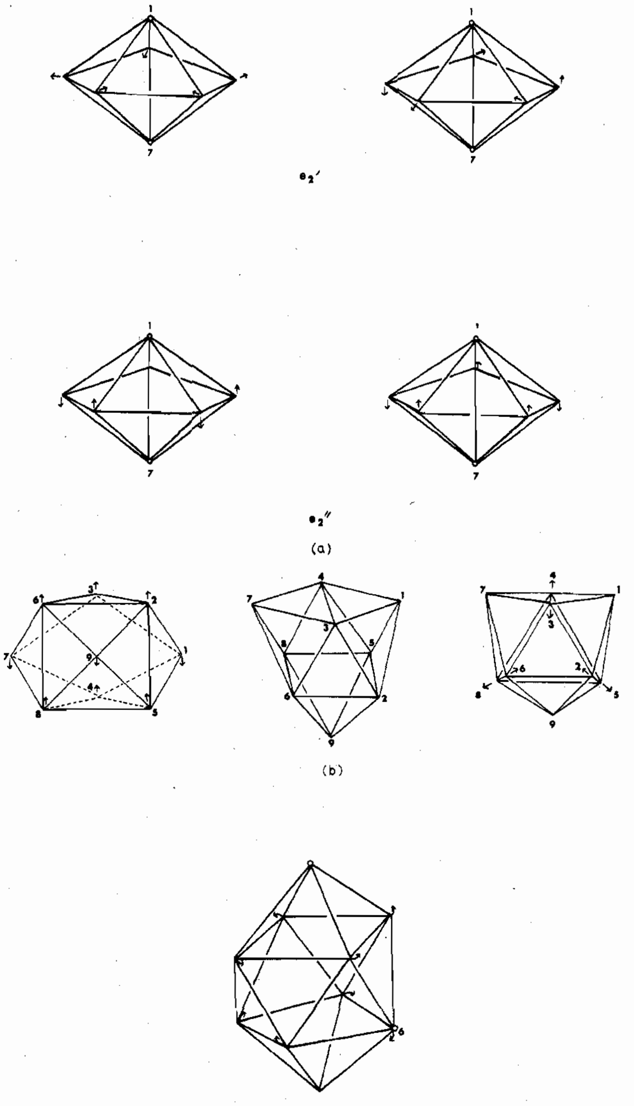


Figure 18. Eigenvectors corresponding to the imaginary vibrations: (a) eigenvectors for the imaginary vibrations of e_2' and e_2'' symmetry of $1,7\text{-}C_2B_5H_7$ (Figure 7); (b) projections of the eigenvector corresponding to the imaginary vibration of $1,7\text{-}C_2B_7H_9$ (Figure 9); (c) the eigenvector for the imaginary vibration of $1,6\text{-}C_2B_8H_{10}$ (Figure 10).

well with those determined by electron diffraction.[48] The MNDO charge distributions (Figure 15) are in fair agreement with the results of recent PRDDO calculations by Dixon et al.,[37] those from MNDO being systematically more negative.

The order of orbital energies given by MNDO (Table II) agrees quite well with those from earlier RH calculations.[49]

$CB_{11}H_{12}^-$. The ^{11}B NMR spectrum[50] of this ion supports, Lipscomb's[51] suggestion that it has an icosahedral structure. MNDO finds a stable minimum for such a geometry (Figure 15) with bond lengths similar to those in $C_2B_{10}H_{12}$. The carbon atom is predicted to be the most positively charged position and indeed has been observed[52] to be the point of nucleophilic attack by *n*-butyllithium.

$C_2B_9H_{12}^-$. Both 1,2- and $1,7\text{-}C_2B_{10}H_{12}$ react with ethoxide ion to form the corresponding 1,2- and $1,7\text{-}C_2B_9H_{12}^-$ ions,[53] by loss of one vertex from the icosahedron. The structures seem to be similar to those of $C_2B_9H_{11}$ (see below) with the extra proton in a bridging position in the five-membered ring forming the truncated face.

MNDO predicts the 1,7 isomer to be more stable than the 1,2 by 20 kcal/mol. It has indeed been reported[54] that the latter rearranges to the former at 300 °C. The MNDO structure for the 1,7 isomer (Figure 16) agrees with that previously suggested.[53] No structure determination has yet appeared. The MNDO structure for the 1,2 isomer (Table IIIA) is similar to that for the 1,7 with edge-bridging hydrogen. It has, however, been claimed[55] on the basis of an X-ray study of a derivative that this compound has a more symmetrical structure with face bridging hydrogen. MNDO reproduces this if the additional symmetry is enforced (Table IIIC); according to MNDO, this is the transition state for interconversion of two mirror image isomers of lower symmetry. The

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(50) Wiersema, R. J.; Hawthorne, M. F. *Inorg. Chem.* **1973**, *12*, 785.

(51) Lipscomb, W. N. "Boron Hydrides"; W. A. Benjamin: New York, 1963.

(52) Reference 32, p 201.

(53) (a) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642. (b) Hawthorne, M. F.; Young, D. C.; Garrett, P. M.; Owen, D. A.; Schwerim, S. G.; Tebbe, F. N.; Wagner, P. A. *Ibid.* **1968**, *90*, 862.

(54) Garrett, P. M.; Tebbe, F. N.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 5016.

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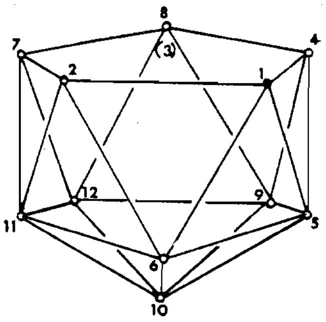
Table III. Geometry and Formal Charges in 1,2-$C_2B_9H_{12}^-$



1,2-$C_2B_9H_{11}$

atom pair	internuclear distance[a] calcd A[b]	internuclear distance[a] calcd B[c]	internuclear distance[a] calcd C[d]	internuclear distance[a] obsd
C^1C^2	1.574	1.574	1.584	1.553
C^1B^4 (C^2B^7)	1.615 (1.596)	1.606	1.584	1.620
B^4B^8 (B^7B^8)	1.937 (1.719)	1.828	1.867	1.821
C^1B^6 (C^2B^6)	1.754 (1.815)	1.785	1.826	1.729
C^1B^5 (C^2B^{11})	1.816 (1.785)	1.801	1.783	1.712
B^4B^5 (B^7B^{11})	1.873 (1.860)	1.867	1.859	1.783
B^4B^9 (B^7B^{12})	1.840 (1.890)	1.865	1.774	1.761
B^8B^9 (B^8B^{12})	1.830 (1.877)	1.854	1.829	1.770
B^6B^5 (B^6B^{11})	1.794 (1.787)	1.791	1.760	1.765
B^5B^9 ($B^{11}B^{12}$)	1.792 (1.743)	1.768	1.782	1.758
B^9B^{12}	1.827	1.827	1.922	1.815
B^5B^{10} ($B^{11}B^{10}$)	1.760 (1.854)	1.807	1.820	1.773
B^9B^{10} ($B^{12}B^{10}$)	1.861 (1.791)	1.829	1.824	1.794
B^6B^{10}	1.806	1.806	1.808	1.772
B^4H_b	1.349	1.349	1.923	1.631
B^8H_b	1.376	1.376	1.218	1.331
C^1H_b (C^2H_b)	2.343 (2.666)	2.504	2.551	1.993

atom	calculated formal charges[e] A[b]		calculated formal charges[e] B[c]		calculated formal charges[e] C[d]	
C^1/C^2	−0.07/0.04	0.04/0.04	−0.02	0.04	−0.02	0.04
B^4/B^7	−0.14/−0.22	−0.01/−0.02	−0.18	−0.02	−0.13	−0.01
B^8	−0.11	−0.01	−0.11	−0.01	−0.22	−0.01
B^6	−0.15	0.01	−0.15	0.01	−0.11	0.01
B^5/B^{11}	−0.06/−0.16	0.02/0.01	−0.11	0.02	−0.17	0.02
B^9/B^{12}	−0.21/−0.03	0.00/0.01	−0.12	0.01	−0.10	0.01
B^{10}	−0.11	0.03	−0.11	0.03	−0.10	0.02
H_b	0.12		0.12		0.12	

[a] The bridging hydrogen is between B^4 and B^8 in structure A and between B^4, B^8, and B^7 in structure B. [b] Structure calculated for the local minimum on the MNDO potential surface. [c] Mean of structure A and its mirror image. [d] Structure calculated with enforced C_s symmetry. [e] First column gives heavy atom charges; second column gives hydrogen charges.

X-ray evidence did not exclude this possibility. Indeed, the authors favored the symmetrical (single minimum) solution only because of the apparent lack of (spurious) thermal motion in this bridging hydrogen (which migrates in the interconversion of the two MNDO structures). As will be seen from Table III, a mean of the latter is in somewhat better agreement with experiment than the calculated symmetrical structure; note in particular the CC internuclear distance which is usually well reproduced by MNDO. In any case, the MNDO energies for the two structures differed by only 2.2 kcal/mol.

The bridging hydrogen is acidic in both the 1,2 and 1,7 isomers but more so in the former. This is consistent with the calculated formal charges (+0.12 and +0.08, respectively; Table III).

A PRDDO calculation for 1,2 isomer has been reported.[56]

$C_2B_9H_{11}^{2-}$. This dianion is derived by loss of the bridging proton from $C_2B_9H_{12}^-$. It is well-known for its ability to complex metal ions, forming η^5 derivatives via the exposed five-membered ring.[57] MNDO reproduces the expected structures for the 1,2 and 1,7 isomers (Figure 17).

As in the case of the monoanion, the 1,7 isomer is predicted to be the more stable, this time by 18 kcal/mol.

The HOMO of the isoconjugate ion, $B_{11}H_{11}^{4-}$, is of E_1 symmetry and concentrated on the open face of the truncated icosahedron, as Lipscomb[58] has predicted. The two highest occupied MO's in both 1,2- and 1,7-$C_2B_9H_{11}^{2-}$ are very similar to the pair of degenerate HOMO's in $B_{11}H_{11}^{4-}$. These results account nicely for the exceptional facility with which these ions form metal complexes.

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Registry No. **1**, 20693-66-7; **2**, 30396-61-3; **3**, 23777-70-0; **4**, 73688-24-1; **5**, 23732-88-9; **6**, 21445-77-2; **7**, 12385-35-2; **10**, 20693-69-0; **11**, 30347-95-6; **12**, 25036-79-7; 1,7-$C_2B_6H_8$, 23732-90-3; 1,7-$C_2B_7H_9$, 26894-16-6; 1,6-$C_2B_8H_{10}$, 23704-81-6; 1,10-$C_2B_8H_{10}$, 23653-23-8; 5,7-$C_2B_8H_{12}$, 31387-16-3; 1,3-$C_2B_7H_{13}$, 17653-38-2; 2,5-$C_2B_9H_{11}$ (C_s), 61815-17-6; 2,5-$C_2B_9H_{11}$ (C_{2v}), 17764-84-0; 1,2-$C_2B_9H_{13}$, 34721-46-5; 1,2-$C_2B_{10}H_{12}$, 16872-09-6; 1,7-$C_2B_{10}H_{12}$, 16986-24-6; 1,12-$C_2B_{10}H_{12}$, 20644-12-6; $CB_{11}H_{12}^-$, 73758-08-4; 1,7-$C_2B_9H_{12}^-$, 11093-02-0; 1,2-$C_2B_9H_{12}^-$, 11130-95-3; 1,2-$C_2B_9H_{11}^{2-}$, 56902-43-3; 1,7-$C_2B_9H_{11}^{2-}$, 39469-99-3.

Supplementary Material Available: MNDO Cartesian coordinates for the carboranes studied (14 pages). Ordering information is given on any current masthead page.

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(58) Reference 32, p 389.