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Ground States of Molecules. 47.[1] MNDO Studies of Boron Hydrides and Boron Hydride Anions

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MNDO calculations were included for some of the boron hydrides in a previous paper describing the parametrization of MNDO for boron. Here we report MNDO calculations for the rest of the known boron hydrides up to $B_{10}H_{16}$ and for the known boron hydride dianions up to $B_{12}H_{12}^{2-}$. Calculations for one or two unknown species of potential interest are included. While the results confirm the previously noted tendency of MNDO to underestimate the strengths of three-center bonds, they are in sufficiently good agreement with experiment to suggest that MNDO may prove useful in studies of boron hydride chemistry.

Introduction

Thirty years have elapsed since Longuet-Higgins[2] first interpreted the structures of diborane and other "electron-deficient" molecules (e.g., $Al_2(CH_3)_6$) in terms of the novel and fruitful concept of a two-electron bond linking three atoms, the electrons occupying a three-center MO formed by σ-type overlap of three AO's. Lipscomb[3] has shown how this concept can lead to a general theory of the structures of the boron hydrides (and hence also of related carboranes) and similar three-center bonds also occur in other inorganic and organometallic compounds.

In 1945 Dewar[4] suggested the existence of another type of multicenter bond, formed by interaction of a filled π MO with the empty orbital of an acceptor, and he subsequently pointed out[5] that such a π complex, formed by an olefin with a transition metal as acceptor, could be stabilized by back-coordination of metal d electrons into the empty antibonding π MO. This idea was confirmed experimentally 3 years later by Chatt and Duncanson[6] and has proved the key to extensive areas of organometallic chemistry.

Since three-center bonds thus play a major role in the chemistry of inorganic elements, a quantitative theoretical treatment of such compounds would be of major value, and a number of calculations of this kind have been reported. Most of these have been based on the Roothaan[7]–Hall[8] (RH; "ab initio SCF") SCF LCAO MO method, but Lipscomb et al. have also carried out extensive calculations for the boron hydrides,[9] using a semiempirical SCF method (PRDDO[10]), parametrized to reproduce the results of RH calculations. Calculations have also been carried out by other more primitive procedures but these are of no interest in the present connection.

Since the errors in the absolute energies calculated by the RH method, even with CI, are very large in a chemical sense, the results can be useful only in connections where empirical tests have shown that the errors cancel. Extensive studies by Pople et al.[11] have shown that the geometries of molecules containing only two-center bonds are well reproduced, even using a minimum basis set, and the same is also the case for charge distributions and for heats of reaction of isodesmic[12] processes. The relative energies of isomers with different types of bonding are, however, not well reproduced unless a very large basis set is used. This is true in particular of isomeric "classical" and "nonclassical" carbocations where the latter contain three-center bonds,[13] so the use of PRDDO in this connection presents uncertainties since it has been tested only by comparison with RH calculations using a moderate-sized basis set.

Lipscomb et al. have been mainly concerned with details of the bonding and electron distribution in boron hydrides and have therefore naturally carried out their calculations mostly with experimental geometries. In the cases where they have optimized geometries, they have been following the course that has been until recently traditional in RH calculations, i.e., varying one coordinate at a time, an optimization procedure which, however, is open to criticism, as is likewise an analogous procedure commonly used to locate transition states. Since this problem is of general importance, a discussion is given in the Appendix. For reasons indicated there, it is essential to use derivative optimization procedures (e.g., Murtagh–Sargent[14] or Davidon–Fletcher–Powell (DFP)[15]) to locate minima on potential surfaces and to characterize all stationary points by calculating force constants.[16] The calculation of derivatives of the energy in the RH method presents problems but these have been solved.[17] The only remaining difficulty is the large amount of computation required to determine them. The calculation of derivatives in semiempirical methods is very much simpler, providing a further advantage over ab initio procedures in terms of computing time.

We have been concerned for some time now with the problem of carrying out analogous calculations for organic compounds and their reactions. Our first generally successful treatment (MINDO/3[18]) was a semiempirical method based on the INDO approximation[19] but parametrized to reproduce experimental quantities (heats of formation and geometries) rather than to mimic the results of ab initio calculations. MINDO/3 has proved remarkably successful, reproducing the energies and geometries, and a variety of other properties, of a wide range of molecules with reasonable accuracy.[20] In particular, it has given good results for the relative energies of isomeric "classical" and "nonclassical" carbocations,[13] the latter being species containing three-center bonds (usually π complexes[21]). In view of this success, we were naturally interested in extending MINDO/3 to boron in the hope that it might prove equally effective for the study of boron hydrides and carboranes. Unfortunately all our attempts to parametrize MINDO/3 for boron failed,[22] due we believe to the inadequacies of the INDO approximation on which it is based. Recently, however, an analogous treatment (MNDO[23]) has been developed here, based on the NDDO approximation,[24] and we have been able to parametrize this successfully for boron.[25] The errors in the calculated heats of formation are generally larger than for compounds of the later second period elements (C–F), suggesting that the parameters are still not optimal. This is not surprising in view of the dearth of accurate thermochemical data for boron compounds needed to determine the parameters.

While MNDO seemed superior to MINDO/3 in almost every respect, there were some indications that it might underestimate the strengths of three-center bonds. Thus calculations[13c] for the isomeric $C_3H_7^+$ ions indicated that it

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Table I. Calculated Properties of the Boron Hydrides

Molecule	ΔH_f/ kcal mol^{-1}	Dipole moment/ D	ϵ_{HOMO}/ eV	Mol sym
B_3H_7	8.6	0.79	12.49	C_{2v}
B_3H_9	20.5	0.37	13.63	D_{3h}
B_4H_8[a]	15.6	0.39	11.72	C_s
B_4H_8[b]	8.1	1.13	12.56	C_1
B_4H_8[b]	21.1	0	12.12	D_{2h}
B_6H_{12}	7.6	1.14	12.56	C_2
B_8H_{12}	26.2	3.63	10.80	C_s
B_9H_{15}	25.9	3.61	11.24	C_s
$B_{10}H_{16}$	64.8	0	10.00	D_{4h}

[a] Double bridged. [b] Single bridged. [c] No bridge.

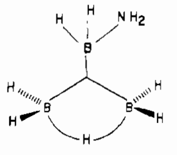
underestimated the relative stabilities of the nonclassical "protonated cyclopropanes" and our previous calculations[25] for boron hydrides and carboranes led to incorrect structures of lower symmetry in one or two cases where the observed symmetrical structures contain unusual numbers of multicenter bonds (e.g., B_5H_9). It seems unlikely, on the other hand, that the errors in the calculated multicenter bond energies can be large because the heats of formation calculated for the boron hydrides agreed with experiment to within the same bounds[25] as those for other boron compounds and without any systematic tendency to too positive values. In order to obtain further information concerning this and concerning the potential usefulness of MNDO in this area of chemistry, we have carried out calculations for a number of additional boron hydrides and boron hydride anions. Here we report our results.

Procedure

The calculations were carried out using the standard MNDO procedure[23] with the parameters for boron reported in part 41[25] of this series. All geometries were optimized by the standard DFP procedure[15] used in MINDO/3[18] and MNDO.[23] No assumptions were made other than that of specific elements of symmetry in calculations for structures with specified symmetry. Transition states were located approximately by the usual reaction coordinate method and refined by minimizing the scalar gradient of the energy.[16] All stationary points were characterized by calculating and diagonalizing the matrix of second derivatives of the energy[16] (Hessian or force constant matrix). (See Appendix.) In cases where an unwanted negative eigenvalue was present, the required stationary point was located by distorting the molecule in a manner corresponding to the eigenvector for the unwanted negative eigenvalue (see Appendix).

Results and Discussion

A. Neutral Boron Hydrides. Table I lists the heats of formation, dipole moments, and molecular symmetries calculated for the boron hydrides studied here. Table II shows their calculated geometries and distributions of formal charge. Table III gives the calculated orbital (Hartree–Fock) energies, which should, according to Koopmans' theorem,[26] be approximately equal to *minus* the corresponding ionization energies. Values from other calculations and experiment are included for comparison. The individual compounds are discussed in detail below.



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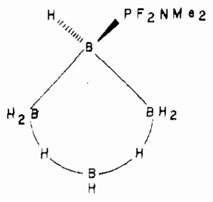

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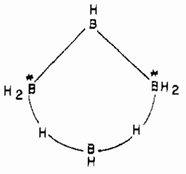

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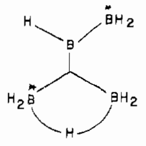

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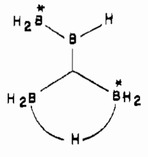

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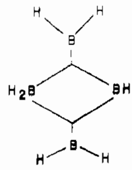
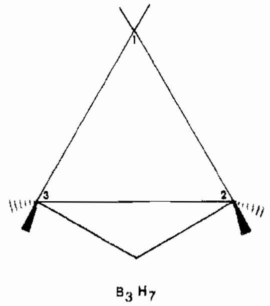


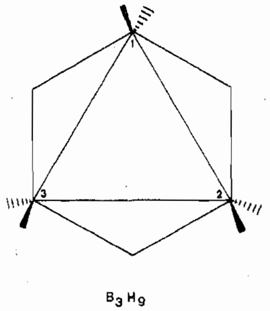
6

B_3H_7. While the structure of the $B_3H_7 \cdot NH_3$ complex is known[27] (i.e., **1**), that of the free boron hydride is not. MNDO predicts only a structure with a single hydrogen bridge and with the apical BH_2 group coplanar with the B_3 system to be stable (structure Ia), in agreement with a PRDDO study by Lipscomb et al.[28] and similar to the structure of the B_3H_7 moiety in **1**. The planarity of the apical BH_2 group implies sp^2 hybridization. This is confirmed by the MNDO calculation which indicates the LUMO to consist of an empty 2p AO of the apical atom. This AO is used to bind ammonia in the adduct **1**.



Ia

B_3H_9. This species has not been detected as such, but it is probably[29] formed as a transient intermediate in the pyrolysis of diborane. The structure predicted by MNDO (Ib) cor-



Ib

Table II. Geometries and Charges for the Boron Hydrides[a]

Structure no.	Atom	Distance, Å	Atom no.	Charges B	Charges H
Ia	B^1B^2	1.779	1	0.14	0.01, 0.01
	B^2B^3	1.731	2	−0.09	−0.01, −0.01
	B^1H	1.167	H_b		0.07
	B^2H	1.170			
	B_2H_b	1.355			
Ib	B^1B^2	2.27	1	0.05	−0.02, −0.02
	B^1H	1.165	H_b		−0.01
Ic	B^1B^2	1.813	1	0.01	0.01
	B^1B^3	1.895	2	0.01	0.09
	B^2B^3	1.650	3	−0.08	0.00, −0.01
	B^1H	1.171	H_b		0.04
Id	B^1B^2	1.761	1	−0.10	−0.01, −0.01
	B^1B^3	1.763	2	0.00	0.06
	B^2B^3	1.776	3	−0.06	−0.01, −0.01
	B^1B^4	2.629	4	0.14	−0.02, −0.02
	B^2H	1.180	H_b		0.07
	$B'B'$	1.170			
	$B'H''$	1.170			
	B^3H''	1.169			
	B^3H''	1.169			
	B^4H'	1.159			
	$B'H_b$	1.343			
Ie	B^1B^2	1.696	1	−0.16	0.00
	B^1B^3	1.798	3	0.19	−0.01
	B^1H	1.175			
	B^3H	1.167			
If	B^1B^2	1.795	1	−0.03	−0.01, −0.01
	B^2B^3	2.695	2	0.05	0.05
	B^2B^5	1.570	3	−0.11	0.00, 0.01
	B^1B^6	1.766	H_b		0.07
	B^2B^6	1.765			

Structure no.	Atom	Distance, Å MNDO	Distance, Å Obsd[b]	Atom no.	Charges B	Charges H
Ig	B^1B^2	1.697	1.83	1	0.14	0.03
	B^1B^3	1.948	1.81	2	−0.31	0.03
	B^1B^4	1.800	1.72	3	0.02	0.02
	B^3B^4	1.718	1.79	5	−0.10	0.04
	B^4B^5	1.688	1.81	7	0.02	0.04
	B^2B^8	1.754	1.70	H_b^{38}		0.10
	B^7B^8	1.841	1.71	H_b^{78}		−0.02
	B^3B^8	1.829	1.67	H_b^{45}		0.03
	B^2B^3	1.947	1.82			
Ih	B^1B^2	1.766	1.77	1	0.08	0.07
	B^1B^4	1.817	1.76	2	−0.28	0.07
	B^1B^5	1.779	1.75	3	0.06	−0.02, −0.07
	B^2B^5	1.880	1.82	4	−0.24	0.02
	B^2B^6	1.745	1.76	5	−0.01	0.04
	B^6B^7	1.845	1.78	6	0.01	0.05
	B^5B^6	1.851	1.84	H_b^{34}		0.10
	B^4B^5	1.883	1.95	H_b^{56}		0.05
	B^4B^3	1.820	1.86	H_b^{67}		0.01
	B^4B^9	1.855	1.80			
	$B^4H_b^{34}$	1.232				
	$B^3H_b^{34}$	1.635				
	$B^5H_b^{56}$	1.387				
	$B^6H_b^{56}$	1.396				
	$B^6H_b^{67}$	1.376				
Ii	$B^1B^{1'}$	1.617		1	−0.16	. . .
	B^1B^2	1.727		2	0.02	0.05
	B^2B^3	1.854		H_b		−0.03
	B^2H_b	1.384				

[a] The figures are drawn to provide a visual representation and are not intended to indicate a bonding scheme. [b] For symmetrized distances see ref 14.

responds to a very loose aggregate of three borane units, the BB distances being very large (2.27 Å) and the energy changing little when the molecule is distorted even to quite large extents. The geometry is similar to that from a PRDDO calculation by Lipscomb et al.[3b] (BB distance, 2.32 Å). The first ionization energy calculated by MNDO is also the same as that for BH_3 (13.63 eV). The dissociation into (BH_3 + B_2H_6) is moreover predicted to be exothermic, by 14.7 kcal/mol. It seems likely that B_3H_9 can indeed at best exist as a transient intermediate.

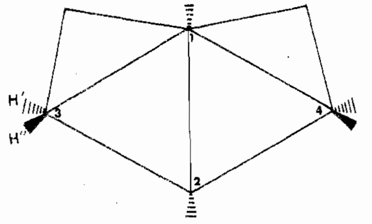
B_4H_8. This hydride is known only as its adduct with dimethylaminodifluorophosphine which has been shown[30] to have the structure **2**. Analogy with B_3H_7 suggests that the free hydride should have an analogous structure **3**, of C_s symmetry,

Table III. MNDO Orbital Energies (eV) for Boron Hydrides

				B_8H_{12} C_s		B_9H_{15} C_s		
B_3H_7 C_{2v}	B_3H_9 D_{3h}	B_4H_8 C_s	B_6H_{12} C_s	MNDO	Ab initio[a]	MNDO	Ab initio[a]	$B_{10}H_{16}$ D_{4h}
12.49 $1a_2$	13.63 $1e''$	11.72 $4a''$	12.56 7b	10.80 $12a'$	9.20	11.24 $14a'$	9.61	10.00 $3e_u$
13.12 $4a_1$	13.64 $2a_1'$	12.78 $6a'$	12.68 8a	11.74 $6a''$	11.65	11.97 $7a''$	11.43	11.62 $4a_{1g}$
13.66 $2b_1$	14.40 $2e'$	13.15 $3a''$	12.70 7a	12.19 $11a'$	12.35	12.57 $6a''$	12.60[b]	12.01 $3e_g$
13.70 $3a_1$	14.90 $1a_2''$	14.02 $5a'$	13.33 6a	12.79 $10a'$	12.90	12.58 $13a'$	12.41	13.05 $2e_u$
15.00 $1b_2$	21.51 $1e'$	14.32 $2a''$	13.41 6b	12.95 $5a''$	12.65	12.74 $12a'$	12.41	13.13 $2e_g$
19.88 $1b_1$	28.27 $1a_1'$	15.49 $4a'$	13.76 5b	13.37 $9a'$	13.33	13.39 $11a'$	13.41	14.73 $3a_{2u}$
20.68 $2a_1$		17.67 $3a'$	13.81 5a	14.37 $4a''$	14.34	13.48 $5a''$	13.69	14.88 $1b_{1u}$
28.95 $1a_1$		20.69 $2a'$	15.16 4b	14.54 $8a'$	13.88	13.88 $10a'$	13.66	14.92 $1b_{2g}$
		23.19 $1a''$	15.25 4a	14.68 $7a'$	15.07	14.44 $9a'$	14.34	15.94 $3a_{1g}$
		30.51 $1a'$	17.43 3b	16.36 $3a''$	15.13	14.91 $4a''$	14.69	16.76 $1b_{2u}$
			20.17 3a	17.05 $6a'$	16.52	15.05 $8a'$	15.26	16.88 $1b_{1g}$
			20.35 2b	18.35 $5a'$	17.50	17.13 $7a'$	16.19	18.04 $2a_{2u}$
			22.81 2a	19.86 $2a''$	17.31	17.47 $6a'$	16.87	21.15 $2a_{1g}$
			28.33 1b	20.18 $4a'$	18.20	17.84 $3a''$	16.90	22.59 $1e_u$
			30.15 1a	23.03 $3a'$	21.03	20.12 $5a'$	18.77	23.20 $1e_g$
				25.98 $1a''$	22.50	20.81 $4a'$	19.05	33.07 $1a_{2u}$
				28.12 $2a'$	24.57	21.27 $2a''$	19.62	33.93 $1a_{1g}$
				35.04 $1a'$	28.11	25.13 $3a'$	22.61	
						26.32 $1a''$	23.32	
						29.40 $2a'$	25.22	
						35.43 $1a'$	28.05	

[a] J. H. Hall, Jr., D. S. Marynick, and W. N. Lipscomb, *J. Am. Chem. Soc.*, 96, 770 (1974). [b] Misassigned in original paper (ref 14). Reassigned on p 69 of ref 3a.

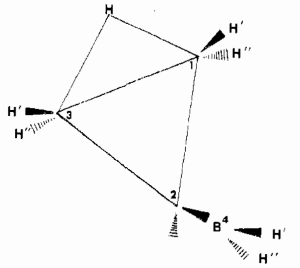
with two BHB bridges. This structure was in fact reproduced by a MNDO calculation in which C_s symmetry was enforced and the resulting geometry (Ic) corresponded quite closely to that from a similarly constrained PRDDO calculation.[31] When, however, we calculated the force constants for this structure, we found to our surprise that one of them was negative. The C_s structure is therefore, according to MNDO, not a minimum on the potential surface but a saddle point or transition state. Distorting the molecule along the corresponding eigenvector and renormalizing, we obtained a true minimum corresponding to **4** (Id), lower in energy than **3** by 7.5 kcal/mol. Thus **3** is the transition state for the degenerate interconversion of **4** and an identical species **5** in which the two boron atoms with asterisks change places.



B_4H_8

Double bridged

Ic



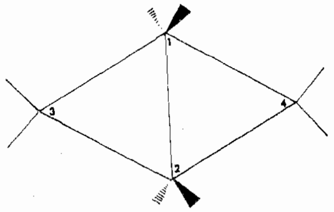
B_4H_8

Single bridged

Id

Lipscomb et al.[31] do not seem to have considered **4** (**5**) as a possible structure for B_4H_8. Instead they studied (PRDDO) another isomer, **6**, with D_{2d} symmetry, finding it to be lower than **3** in energy by 7 kcal/mol. They also carried out RH calculations for **6**, using the PRDDO geometry. Here **6** appeared to be marginally higher in energy than **3** (by 2.3 kcal/mol when CI was included).

A MNDO calculation for **6**, with imposed D_{2d} geometry, led to a structure (Ie) very similar to the PRDDO one. We checked that it was a genuine minimum on the potential surface by calculating the force constants, all of which were positive. According to MNDO, **6** is higher in energy than **3** by 5.5 kcal/mol, in good agreement with the RH calculations by Lipscomb et al.[31] (which, however, were not based on optimized geometries).



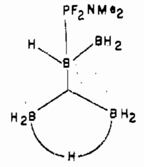
B_4H_8

No bridge

Ie

The formation of adducts such as **2** can easily be explained on the basis of structure **4** for B_4H_8. According to MNDO, the LUMO of **4** is almost entirely (84%) composed of a 2p AO of B^2, the atom adjacent to the exocyclic BH_2 group. Coordination of a donor should therefore take place at B^2, making the latter quadricovalent and hence weakening the BBB three-center bond. Such adducts might then be expected to rearrange to corresponding derivatives of **3**, e.g., **7** → **2** (cf. **4** → **3**).

Lipscomb et al.[31] have suggested that **3** should be represented not by the depicted structure but rather as a symmetrical hybrid of the two mirror image structures **8** and **9**. Each of these has an extra three-center bond compared with **3**, **4**, or **6**, so the hybrid of **8** and **9** might be especially stable. Since MNDO underestimates the strengths of multicenter bonds, it might then underestimate the stability of the species we have written as **3**. However, as we have already pointed out, MNDO agrees with the RH calculations reported by Lipscomb et al. in making **3** marginally more stable than **6**.



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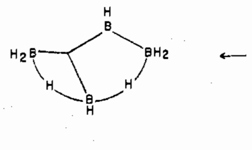

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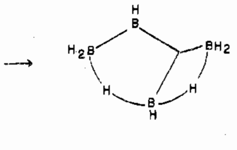

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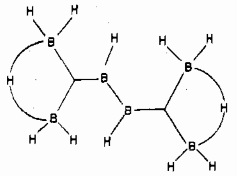

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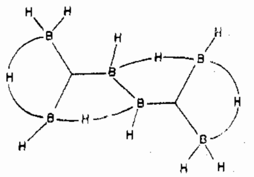
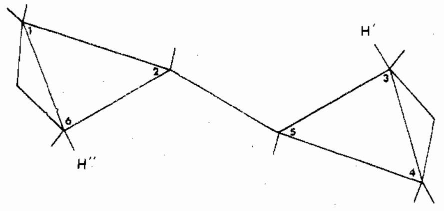


11

Indeed, MNDO gives a larger estimate for the difference in energy between them. Since **3**, **4**, and **6** resemble one another in each having two three-center bonds and two coordinately unsaturated boron atoms, there is no reason to suppose that MNDO will not reproduce the energy of **4** relative to **3** and **6** in a satisfactory manner. The conclusion that the most stable isomeric form of B_4H_8 is **4** must therefore be taken seriously. In any case, right or wrong, our calculations emphasize the need for proper geometry optimization and a thorough search of the potential surface in studies of this kind.

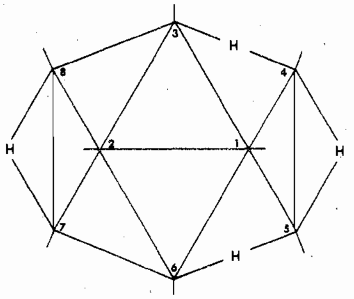
B_6H_{12}. The structure of this hydride has not yet been determined. MNDO predicts it to be derived from two molecules of B_3H_7 by linkage through the apical positions (B^1,$B^{1'}$) with loss of hydrogen (**10**; Ic). An analogous structure, **11**, has been proposed[32] on the basis of ^1H and ^{11}B NMR studies. **10** and **11** differ only by the replacement of two BH two-center bonds in **10** by three-center BHB bonds in **11**. Since MNDO underestimates the relative strengths of three-center bonds, **11** is probably correct. It should, however, be noted that our calculated geometry for **10** is not inconsistent with the NMR evidence.

B_8H_{12}. MNDO correctly[3] predicts B_8H_{12} to have the C_s structure shown in If and the calculated geometry agrees quite well with experiment.[33] Lipscomb et al.[34] have reported a minimum basis set RH calculation for B_8H_{12}, using the experimental geometry. Their calculated dipole moment (3.75 D) is close to the MNDO value (3.63 D) and the orbital energies also agree quite well (Table III). The charge distributions (Ig) also agree qualitatively. In particular, the boron atom with the smallest electron density (B^2) is the one at which nucleophilic attack seems to take place most easily.[35] We also studied the C_{2v} structure **4**, by imposing the appropriate symmetry, finding it to lie 12.4 kcal/mol above the C_s one. This is likely to be a lower limit since the C_{2v} structure has only two BHB bridges whereas the C_s structure has four.



B_6H_{12}

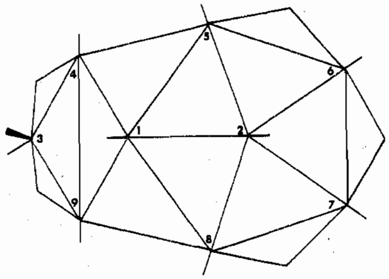
If



B_8H_{12}

Ig

B_9H_{15}. Here again MNDO reproduces the experimental[36] structure reasonably well (Ih). The MNDO dipole moment (3.61 D) agrees well with that (3.70 D) from a minimum basis set RH calculation,[34] using the experimental geometry. While the latter calculation was based on (assumed) symmetrical BHB bridges, the results indicated that each bridging hydrogen is bonded more strongly to one boron atom than to the other. The MNDO optimized geometry has BHB bridges that are unsymmetrical in this sense. Indeed, the B^3HB^4 bridge is the most unsymmetrical so far given by a MNDO calculation, the BH distances being 1.232 and 1.635 Å. The MNDO orbital energies agree quite well with the ab initio[34] ones (Table III) and both procedures predict B^2 to be the most negative site (Ih).



n-B_9H_{15}

Ih

$B_{10}H_{14}$. This molecule was discussed in part 41[25] where MNDO was shown to give a good account of its geometry. Here we report some further results.

The first concerns the energy of an isomeric form of $B_{10}H_{14}$ with a topology (2802) corresponding to that (2632) of the dianion (which will be discussed presently). We calculated the energy of this species by enforcing appropriate symmetry, finding it to be less stable than the "normal" 4620 isomer by 16.7 kcal/mol. Two minimum basis set calculations have led to similar conclusions but larger estimates of the energy difference (59[37] and "about 50"[34] kcal/mol).

Table IV compares the MNDO orbital energies for the normal 4620 geometry with orbital energies using an ab initio calculation and ionization energies determined by photoelectron spectroscopy. As usual in the case of boron compounds, the MNDO orbital energies for the first few MO's are too large by ca. 1 eV. The agreement with the observed ionization energies is otherwise very satisfactory.

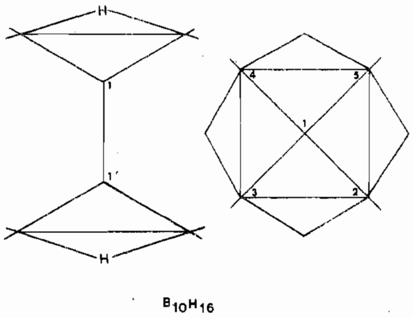
$B_{10}H_{16}$. Several isomers of $B_{10}H_{16}$ are possible,[3a] derived from two molecules of B_5H_9 by loss of two hydrogen atoms

Table IV. Comparison of MNDO, PES, and ab Initio Orbital Energies (eV) for $B_{10}H_{14}$

Assignment	MNDO	PES[a]	Ab initio[a]	Ab initio[b]
$5b_2$	11.29	10.15	10.97	10.58
$6b_1$	12.11 sh	10.91	11.58	11.65
$8a_1$	12.28	11.66	11.62	11.89
$3a_2$	12.35		11.97	12.38
$5b_1$	12.69		12.44	12.95
$7a_1$	13.07		13.02	12.79
$2a_2$	13.65	13.02	13.24	13.96
$4b_2$	13.67		12.71	13.06
$3b_2$	14.40 sh	13.64	13.53	14.61
$6a_1$	14.52 sh	14.38	13.72	14.58
$4b_1$	15.01		14.33	15.24
$3b_1$	16.73		14.76	15.73
$5a_1$	17.20		15.28	16.22
$4a_1$	17.69	15.21	16.32	17.14
$2b_2$	19.24		17.63	18.12
$3a_1$	20.57	15.92	17.35	17.93
$2b_1$	20.87	16.73	18.53	19.46
$1a_2$	21.84 sh	17.20	19.40	20.24
$2a_1$	25.75	19.6	22.22	23.21
$1b_2$	27.37		22.68	23.51
$1b_1$	29.67 sh	20.70	24.94	25.80
$1a_1$	36.72	23.2	27.92	28.84

[a] D. R. Lloyd, N. Lynaugh, P. J. Roberts, and M. F. Guest, *J. Chem. Soc., Faraday Trans. 2*, 1382 (1975).

and formation of a BB bond. We carried out calculations for the known 11′ isomer, i.e., the one linked through the two apical atoms of the B_5 units. Since MNDO incorrectly attributes a lower symmetry to B_5H_9 than that observed,[22] we assumed C_{4v} symmetry for each B_5 unit with the units eclipsed, the whole molecule having D_{4h} symmetry. The corresponding optimized geometry (Ii) differs from that calculated[22] for C_{4v} B_5H_9 in having somewhat longer BB bonds and the new $(B^1B^{1'})$ bond is long (1.617 Å). The negative charges at B^1 and $B^{1'}$ are also smaller than in B_5H_9 and the energy of the HOMO (e symmetry) is numerically smaller (10.00 vs. 11.48 eV).



Ii

B. Boron Hydride Anions. Table V lists the heats of formation, HOMO and LUMO energies, and molecular symmetries calculated by MNDO for a number of boron hydride anions while Table VI shows the calculated geometries and distributions of formal charge. It will be seen that the HOMO–LUMO energy gaps are very large for all these ions, implying large excitation energies. Indeed, B_9H_9 alone among them shows absorption in the UV region.[38,39]

The ease of oxidation should be greater, the higher the energy of the HOMO. Polarographic data[38] indicate that ease of oxidation increases in the order $B_{12}H_{12}^{2-} < B_{10}H_{10}^{2-} < B_{11}H_{11}^{2-} \ll B_8H_8^{2-} < B_9H_9^{2-} < B_6H_6^{2-}$.

The order of the MNDO–HOMO energies agrees with this, viz., $B_{12}H_{12}^{2-} < B_{10}H_{10}^{2-} \sim B_{11}H_{11}^{2-} < B_7H_7^{2-} < B_8H_8^{2-} < B_9H_9^{2-} < B_6H_6^{2-} < B_5H_5^{2-}$. The order from other theoretical calculations[38] is less satisfactory. For example they predict $B_8H_8^{2-}$ to be oxidized more readily than $B_6H_6^{2-}$, in disagreement with experiment and MNDO.

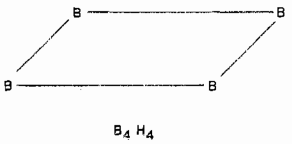
Table V. Boron Hydride Anions

	ΔH_f/kcal mol^{-1}	ϵ_{HOMO}/eV	ϵ_{LUMO}/eV	Mol sym
BH_4^-	−35.9	−5.41	−10.78	T_d
$B_4H_4^{2-}$	91.5	−1.94	−13.22	D_{4h}
$B_4H_4^{2-}$	178.9	−5.38	−11.78	T_d
$B_4H_4^{2-}$	88.1	−2.28	−13.60	D_{2d}
$B_5H_5^{2-}$	76.3	−1.73	−12.09	D_{3h}
$B_6H_6^{2-}$	33.0	−0.62	−11.65	O_h
$B_6H_6^{2-}$	103.8	−1.21	−10.53	D_{3h}
$B_7H_7^{2-}$	1.9	0.34	−10.42	D_{5h}
$B_7H_7^{2-}$	37.3	−0.91	−9.92	C_{2v}
$B_7H_7^{2-}$	78.3	−2.56	−8.44	C_{3v}
$B_8H_8^{2-}$	−19.5	0.07	−10.41	D_{2d}
$B_8H_8^{2-}$	−17.7	0.35	10.86	C_{2v}
$B_8H_8^{2-}$	1.1	−0.15	−9.70	D_{4d}
$B_8H_8^{2-}$	37.1	0.51	−8.83	D_{3h}
$B_8H_8^{2-}$	74.4	−1.01	−8.93	D_{3d}
$B_8H_8^{2-}$	184.9	−1.23	−7.32	O_h
$B_9H_9^{2-}$	−19.4	−0.04	−9.81	C_{2v}
$B_{10}H_{10}^{2-}$	−58.5	0.90	−9.48	D_{4d}
$B_{10}H_{10}^{2-}$	−37.5	0.70	−8.11	C_{2v}
$B_{10}H_{14}^{2-}$ 2632	−42.6	0.85	−8.40	C_{2v}
$B_{10}H_{14}^{2-}$ 4450	65.1	−3.18	−7.76	C_{2v}
$B_{11}H_{11}^{2-}$	−66.3	0.85	−8.19	C_{2v}
$B_{11}H_{11}^{2-}$	−65.8	1.02	−8.16	C_s
$B_{11}H_{11}^{2-}$	−19.8	−0.34	−5.85	C_{5v}
$B_{11}H_{11}^{2-}$ (UHF)	−26.4			C_{5v}
$B_{12}H_{12}^{2-}$	−137.5	2.59	−8.69	L_h
$B_{12}H_{12}^{2-}$	−28.2	1.31	−7.15	D_{5h}
$B_{12}H_{12}^{2-}$	−47.6	1.08	−7.98	D_{3h}
$B_{12}H_{12}$	−10.9	1.04	−8.18	O_h
$B_{12}H_{12}^{2-}$	−7.5	0.85	−7.40	D_{3h}

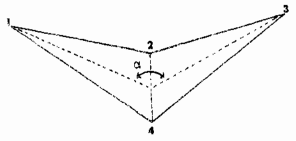
A discussion of the individual ions follows.

BH_4^-. This ion is widely used in organic chemistry as a reducing agent and has therefore attracted a good deal of attention from theoreticians. The calculated formal charges (B, −0.32 e; H, −0.17 e) agree with those from ab initio calculations[40] although a strong basis set dependence was noted. The MNDO heat of formation (−35.9 kcal/mol) is in fair agreement with a rather poorly defined experimental value (−23.5 ± 5 kcal/mol[41]).

$B_4H_4^{2-}$. The main interest of this still unknown species concerns its geometry. The corresponding neutral species has been obtained as its tetrachloro derivative, B_4Cl_4, whose structure in a crystal is a distorted tetrahedron.[42] MNDO predicts $B_4H_4^{2-}$ to have a similar nonplanar D_{2d} structure (IIa), more stable than the square-planar one by 3.4 kcal/mol. This result is unexpected because $B_4H_4^{2-}$ is isoelectronic with the dication of cyclobutadiene, $C_4H_4^{2+}$.

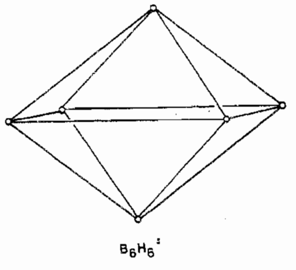


IIa



IIa′

$B_6H_6^{2-}$. This ion is known[43] to have an octahedral (O_h) geometry. MNDO reproduces this quite well (IIb). The



IIb

Table VI. Geometries and Charges for the Boron Hydride Anions

				Charges	
Structure no.	Atom	Distance, Å	Atom no.	B	H
IIa	BB	1.556	1	−0.31	−0.19
	BH	1.188			
IIa′	B^1B^2	1.547	1	−0.34	−0.15
	B^1B^3	2.143			
	BH	1.178			
	α'	147.6			
IIb	BB	1.733	1	−0.28	−0.06
IIc	$B_{eq}B_{eq}$	1.645	B_{eq}	−0.28	−0.06
	$B_{ax}B_{eq}$	1.837	B_{ax}	−0.08	−0.06
IId	B^1B^2	1.669	1	−0.28	−0.06
	B^1B^3	1.848	3	−0.06	−0.09
	B^1B^5	1.627			
	B^3B^5	2.008			
IIe	B^1B^2	1.609	1	−0.23	−0.04
	B^1B^3	1.911	2	−0.15	−0.06
	B^2B^6	1.730	3	−0.15	−0.05
	B^3B^6	1.893	6	−0.15	−0.08
	B^2B^3	1.921	7	−0.15	−0.08
	B^6B^9	1.978			
	B^6B^7	1.584			
IIf	B^1B^2	1.717	1	−0.32	−0.02
	B^2B^3	1.900	2	−0.02	−0.04
	B_2B_6	1.823			
IIg	B^1B^2	1.740	1	0.07	−0.03
	B^1B^3	2.061	2	−0.26	−0.03
	B^2B^3	1.661	3	−0.26	−0.05
	B^2B^8	1.823	8	−0.13	−0.04
	B^3B^4	1.846	9	−0.13	−0.04
	B^3B^8	1.861			
	B^8B^9	1.776			
	B^9B^{11}	1.914			
IIh	B^2B^3	1.733	2	−0.11	−0.06
	B^2B^7	1.823	7	−0.15	−0.04
	B^7B^8	1.805	12	−0.09	−0.04
	B^7B^{12}	1.819			

		Distance, Å			Charges	
Structure no.	Atom	MNDO	Obsd[a]	Atom no.	B	H
IIi	B^1B^2	1.761	1.78	1	−0.27	−0.03
	B^1B^3	1.945	1.81	2	0.06	−0.04
	B^1B^5	1.808	1.78	5	−0.11	−0.07
	B^2B^5	1.813	1.75	6	−0.28	−0.10[c] −0.04[d]
	B^2B^6	1.823	1.75			
	B^5B^6	1.807	1.88	H_b		0.06
	B^5B^{10}	2.000	1.89			
	B^5H_b	1.361	1.35			
IIj	BB	1.817	1.77[b]		−0.14	−0.03

[a] D. S. Kendall and W. N. Lipscomb, *Inorg. Chem.*, **12**, 546 (1973). [b] J. A. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.*, **82**, 4427 (1960). [c] Outer. [d] Inner.

Table VII. Comparison of Orbital Energies for $B_6H_6{}^{2-}$

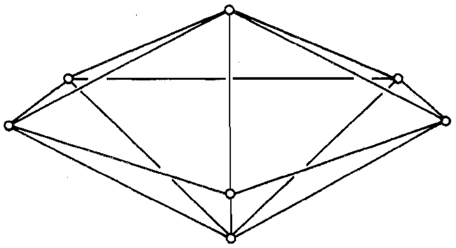
	MNDO[a]	Ab initio[b]	Xα[c]
$1t_{2g}$	−0.62	−3.92[d]	3.21
$2t_{1u}$	1.59	−0.65[d]	2.17
$1e_g$	6.08	2.94	4.63
$2a_{1g}$	6.10	3.65	5.81
$1t_{1u}$	11.60	5.66	8.12
$1a_{1g}$	24.33	13.55	13.84

[a] All energies in eV. [b] Reference 14. [c] Reference 5. [d] These values were switched in the original paper,[14] presumably in error, since the present version appears in E. L. Muetterties, "Boron Hydride Chemistry", Academic Press, New York, N.Y., 1975, p 70.

ordering of MO's given by MNDO agrees better with that from an Xα calculation[44] than does an RH one by Lipscomb et al.[34] (Table VII). Note that the HOMO has a positive energy (Table V), implying that electrons in it are not bound. This problem often occurs in SCF MO calculations for ions and has been discussed by Lipscomb et al.[34] We also carried out calculations for a triangular prism (D_{3h}) geometry. The calculated heat of formation was greater by 70.8 kcal/mol than that for the octahedron.

$B_7H_7{}^{2-}$. Three reasonable structures can be written for this ion: a pentagonal bipyramid (D_{5h}) and a triangular prism with the extra boron atom capping either a square (C_{2v}) or triangular (C_{3v}) face. As Table V shows, MNDO predicts the D_{5h} structure (IIc) to be the most stable, followed by the square-capped prism (C_{2v}) and triangular-capped prism (C_{3v}) with energies relative to D_{5h} of 25.4 and 76.4 kcal/mol, respectively.

The ^{11}B NMR spectrum[45] of the ion shows two peaks with areas in the ratio 5:2, as would be expected for the D_{5h} structure. It is, however, possible that the spectrum could arise from a structure of lower symmetry, through accidental degeneracies. The calculated negative charges on the apical boron atoms (D_{5h} structure) are less than those on the other boron atoms (0.08 e vs. 0.28 e; IIc). MNDO calculations indicate that the negative charge at a given boron atom in a



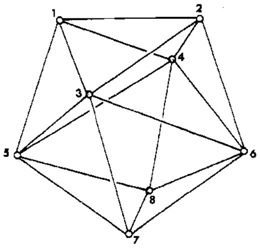
$B_7H_7^=$

IIc

boron hydride anion is smaller, the greater the connectivity of the atom.

$B_8H_8^{2-}$. Structures that have been considered for this ion include a dodecahedral species (D_{2d}), a cube (D_h), a square antiprism (D_{hd}), a triangular prism capped on two square faces (C_{2v}) or both ends (D_{3h}), and a triangular antiprism capped at both ends (D_{3d}). Table VIII compares the energies calculated for all these species, using MNDO. For comparison, we also calculated their energies by the RH method, using the STO-6G basis set. These calculations were carried out using the MNDO geometries, since geometry optimization by this procedure would have been impracticable. The results are also shown in Table VIII. Finally, the last column of the table shows the corresponding energies calculated by Muetterties,[39,45a] using a Hückel-type procedure.

MNDO and STO-6G predict the dodecahedron to be the most stable form of the ion, in agreement with an x-ray crystal structure[45a] of the corresponding tetraaminozinc salt (IId).



$B_8H_8^=$

IId

The ^{11}B NMR spectrum of the cesium salt in water showed only a single line,[45a] which at the time was attributed to accidental degeneracy. Later, however, a study of the ^{11}B NMR spectrum of the sodium salt in glyme at lower temperatures showed[45b] that the ion is in fact fluxional, the spectrum splitting into three peaks with intensity ratios 2:4:2, a pattern that would be expected for the square-capped triangular prism (C_{2v}) but not for the dodecahedral structure. Thus the equilibrium structure of the ion in solution differs from that in the crystal, a most unusual phenomenon. Clearly the two isomers must be very similar in energy, their orders of stability therefore depending on the environment. The fluxional behavior in solution must then be attributed to rapid interconversion. (It should be added that a later paper[45c] implies that the measurements in solution were for the tetra-*n*-butylammonium salt, but this does not, of course, alter the situation.)

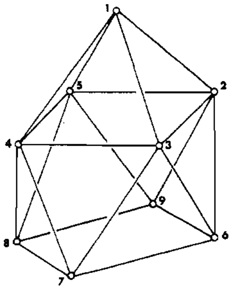
All three calculations agree in predicting the D_{2d} and C_{2v} ions to have very similar energies, much lower than those of the other isomers. Possibly MNDO is nearest to the truth since it gives the smallest difference in energy. The calculations of course refer to the gas phase, so no definite conclusions can be drawn concerning the relative energies of the ions in solution or in the crystal. The ^{11}B NMR spectrum indicates that their interconversion requires appreciable activation but gives no definite information concerning their relative energies.

Table VIII. Calculated Relative Energies of $B_8H_8^{2-}$

		MNDO^a	STO-6G^b	Hückel type MO^c
Dodecahedron	D_{2d}	0	0	0
Square bicapped prism	C_{2v}	1.8	3.4	−6.0
Square antiprism	D_{4d}	20.6	47.4	−48.4
Bicapped trigonal prism	D_{3h}	56.6	144.4	55.6
Bicapped trigonal antiprism	D_{3d}	93.9	116.8	44.7
Cube	O_h	204.4	490.5	39.2

^{a} All energies in kcal/mol. ^{b} This work. ^{c} References 2 and 7.

$B_9H_9^{2-}$. This ion is known[38] to form a tricapped prism, three boron atoms capping the square faces of a triangular prism (symmetry D_{3d}). Each of the capped faces is a square pyramid, similar to that in B_5H_9. As we have already noted,[22] MNDO fails to predict the structure of B_5H_9 correctly, probably because of its tendency to underestimate the energies of three-center bonds. The D_{3h} situation for $B_9H_9^{2-}$, like C_{4v} B_5H_9, contains an abnormally large number of such bonds. The structure predicted by MNDO for $B_9H_9^{2-}$ is of C_{2v} symmetry, derived by distorting a capped square antiprism (IIe). The D_{3h} structure is not a stationary point on the MNDO potential surface, lying 23.4 kcal/mol above the C_{2v} one.

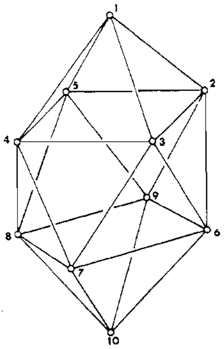


$B_9H_9^=$

IIe

$B_{10}H_{10}^{2-}$. This is one of the most stable and most studied of the boron hydride anions and many derivatives are known. While the most stable structure is of D_{4d} symmetry, polyhedral rearrangement takes place at temperatures above 300 °C, probably[42,43] via a C_{2v} transition state. The experimental activation energy for rearrangement of the related species $B_{10}H_8(NMe_3)_2$ in tetrachloroethane is 37 kcal/mol.[46]

The structure found by MNDO with D_{4d} constraint is shown in IIf. This structure, however, had one negative eigenvalue.



$B_{10}H_{10}^=$

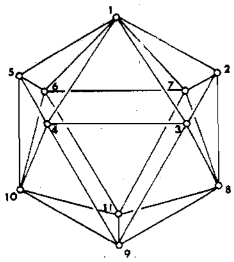
IIf

The numerical value of this (45 cm^{-1}) was, however, very small,[48] suggesting that the true minimum is very close to the

D_{4d} structure. We were also able to locate a transition state of C_{2v} structure, similar to that proposed by Muetterties et al.[46,47] and higher in energy than the D_{4d} structure by 21 kcal/mol. The agreement with experiment seems satisfactory, given that the parent ion should rearrange faster than the derivative. Another possible intermediate for scrambling would be the D_{4h} structure, a bicapped square prism corresponding to the D_{4d} bicapped square antiprism. The D_{4h} structure was, however, higher in energy than the C_{2v} transition state by 3 kcal/mol.

The charges given by MNDO for the D_{4d} structure, IIf, agree with those from an RH calculation by Lipscomb et al.,[34] predicting electrophilic attack to be easiest at the apical boron atoms and nucleophilic attack at the equatorial ones, as appears to be the case.[46]

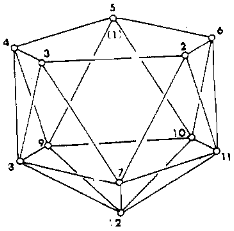
$B_{11}H_{11}^{2-}$. Since the analogous carborane $C_2B_9H_{11}$ has a C_{2v} structure, it seems likely that the same is true also for $B_{11}H_{11}^{2-}$ MNDO indeed predicts the most stable form of $B_{11}H_{11}^{2-}$ to have this geometry, IIg.



$B_{11}H_{11}^{=}$ C_{2v}

IIg

Recently Tolpin and Lipscomb[49a] have examined the ^{11}B NMR spectrum of $(Et_4N)_2B_{11}H_{11}$ in glyme and found it to imply fluxional behavior at ambient temperatures involving interconversion of pairs of equivalent C_{2v} species via isomers of different symmetry. They suggested as a candidate a C_{5v} structure, which had already been considered for the ion itself, IIh. However, MNDO predicts this to be higher in energy by no less than 40 kcal/mol, which would seem to eliminate it from consideration. It is true that the symmetry of the C_{5v} ion implies that it must be a biradical, two electrons occupying a degenerate HOMO. Species of this kind cannot be reliably treated by the usual spin-restricted version of MNDO. UMNDO[50] is now available; we used it to calculate the C_{5v} structure. However, the total energy found in this way was only 6.6 kcal/mol lower than that given by the restricted treatment.



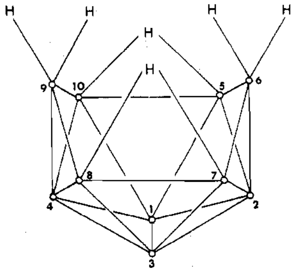
$B_{11}H_{11}^{=}$ C_{5v}

IIh

Another possible structure that has been suggested[49b] is one of C_5 type. MNDO predicts this to be a saddle point, i.e., the transition states for interconversion of equivalent C_{2v} isomers, and furthermore predicts it to be very little higher in energy (by only 0.5 kcal/mol) than the C_{2v} structure. This therefore seems the most likely intermediate in the fluxional rearrangement observed by Tolpin and Lipscomb. At higher temperatures, other rearrangements may occur. Indeed Muetterties and Knoth[38] have estimated the activation energy for such processes to be ca. 30 kcal/mol, which would fit our calculations nicely if here the C_{5v} species is involved. Muetterties and Knoth were unaware of the fluxional behavior that the ion has now been shown to exhibit, at lower temperatures.

It is interesting to note that the C_{2v} structure is unusual in containing a heptacoordinated boron atom. The fact that fluxional behavior is observed a low temperatures suggests that if MNDO underestimates the stability of such bonding, the error cannot be large. On the other hand, the calculated activation energy for the fluxional process is certainly too low so the calculated energy of the C_{2v} species is presumably somewhat too positive.

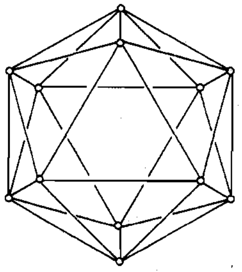
$B_{10}H_{14}^{2-}$. This ion could exist in structures with 2632 or 4450 topologies, analogous respectively to the 2802 and 4620 topologies for $B_{10}H_{14}$ (vide supra). Guest and Hillier[37] predict the 2632 structure to be the more stable by 134 kcal/mol and Lipscomb et al[34] by 150 kcal/mol. MNDO leads to a somewhat smaller difference, 108 kcal/mol. The geometry calculated by MNDO agrees well with experiment (IIi) and the MNDO formal charges parallel those reported by Lipscomb et al.[34] (IIi).



$B_{10}H_{14}^{=}$

IIi

$B_{12}H_{12}^{2-}$. This ion was first reported by Hawthorne[51] in 1960 and its icosahedral symmetry was established in the same year by x-ray analysis of the potassium salt.[52] It and its perhalo derivatives are the only molecular species as yet reported to have I_h symmetry. Its extreme stability is indicated by the lack of any apparent change of a salt containing the $1,2\text{-}B_{12}Br_2Cl_{10}^{2-}$ ion after 2.5 h at 500 °C.[38] MNDO reproduces the observed structure (IIj) and the orbital ordering (Table IX) agrees with that reported by Lipscomb (see ref 3a, p 70).



$B_{12}H_{12}^{=}$

IIj

A topic of current interest is the possibility of degenerate rearrangement in symmetrical species. The $B_{12}H_{12}^{2-}$ ion, as the only representative of the I_h symmetry group, is an obvious target. No rearrangements have been observed in the ion itself (where the reactions could be followed only by isotopic labeling), but the isoelectronic 1,2-dicarbadecaborane $C_{12}B_{10}H_{12}$

Table IX. Orbital Energies for $B_{12}H_{12}^{2-}$ I_h

	MNDO[a]	PRDDO[b]
$1g_u$	2.59	1.82
$2h_g$	3.42	2.75
$2t_{1u}$	5.79	5.17
$1t_{2u}$	7.37	5.93
$2a_g$	9.68	7.67
$1h_g$	11.62	9.11
$1t_{1u}$	19.25	14.56
$1a_g$	29.91	18.56

[a] All energies in eV. [b] Reference 19.

Table X. Stationary Points on the $B_{12}H_{12}^{2-}$ Potential Surface[a]

Symmetry		Energy/kcal mol^{-1}
I_h, icsohedron		−137.5
D_{5h}, bicapped pentagonal prism		−28.2
O_h, cubic octahedron		−10.9
D_{3h}, stationary point in triangle rotation of icsohedron		−47.6
D_{3h}, stationary point in triangle rotation of cubic octahedron		−7.5

[a] In all figures except D_{5h} the icsohedron is viewed down a threefold axis and can be thought of as a prism (or antiprism) surrounded by a belt of borons (except for I_h all borons in the belt are coplanar).

rearranges on heating first to the 1,7- and then to the 1,12-isomer. The former reaction takes place around 425 °C and the second at about 600 °C.[38]

Several possible mechanisms have been suggested for rearrangements of this kind. In the case of the carboranes, no one process alone can account for the observed course of the reaction. The first proposal, by Lipscomb et al.,[53] was the diamond-square-diamond (dsd) mechanism which, in the case of the icosahedron, would involve a cubic-octahedral transition state. Grafstein and Dvorak[54] have suggested that the halves of the icosahedron may rotate in opposite directions, leading to a D_{5h} transition state. A third possibility, suggested by Muetterties and Knoth,[38] is the rotation of triangular faces in the icosahedron, involving D_{3h} transition states. These mechanisms have been examined for the corresponding rearrangements of $B_{12}H_{12}^{2-}$ using MNDO, with results summarized in Table X.

The first four rows of Table X show the heats of formation calculated for the parent ion and for the three structures indicated above. We also located another stationary point which corresponded to triangular rotations in the cubic octahedron. This is also shown in Table X.

The lowest barrier is clearly that for the triangle rotation in the icosahedron, with an activation energy of 90 kcal/mol. This is consistent with an estimate[38] from thermal studies of >80 kcal/mol. The D_{5h} transition state is higher in energy by 19 kcal/mol and that for the dsd (cubic octahedron) mechanism higher again, 36 kcal/mol above the triangle rotation.

Conclusions

The main purpose of this investigation was to obtain further information concerning the apparent tendency of MNDO to underestimate the stabilities of compounds containing multicenter bonds and to investigate the possible utility of MNDO as a practical aid in the study of boron hydride chemistry.

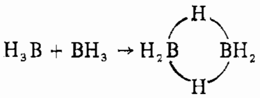
In the majority of cases examined, MNDO has reproduced the observed geometries in a satisfactory manner. We have also previously shown[25] that the heats of formation of boron hydrides are predicted with reasonable accuracy in cases where these are known experimentally (B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, $B_{10}H_{14}$). Since all these species contain multicenter bonds, it seems clear that if MNDO systematically underestimates the energies of such bonds, the errors must be small.

Several additional cases have appeared where MNDO leads to incorrect geometries, of lower symmetry than those observed and with fewer multicenter bonds. The energies calculated for the former are, however, only a few kilocalories per mole lower than those for structures with the correct symmetry. In view of the general overall success of MNDO, it seems fairly clear that the errors arise only in the case of unusually "soft" molecules, corresponding to very flat minima on the corresponding potential surfaces, where small errors in the relative energies calculated for points at and near the minimum can lead to significant displacements of the minimum from its true position. It should be noted that other properties of these molecules are very well reproduced by calculations in which the appropriate symmetry is enforced; cf. the ionization energies of B_5H_9.

It might appear at first sight that MNDO is inferior to the procedures used by Lipscomb and his collaborators in that the latter have not reported any such failings. However, as we have already pointed out, Lipscomb et al. have carried out most of their calculations assuming experimental geometries, and in cases where they did optimize geometries, the methods they used were inadequate to show up deficiencies of the kind reported here. MNDO of course also gives correct structures in all cases if the appropriate symmetry is enforced. Its lack of success in certain cases may well be due simply to our use of a better optimization procedure, able to reveal such deficiencies.

There is in fact reason to believe that the RH method itself may also underestimate the strengths of three-center bonds, particularly if a moderate-sized basis set is used.

Consider the dimerization of borane to diborane



$$H_3B + BH_3 \rightarrow H_2B\overset{H}{\underset{H}{\quad}}BH_2$$

This reaction involves the replacement of two two-center BH bonds by two three-center BHB bonds, so the heat of reaction is a direct measure of the relative energies of two- and three-center bonds of analogous type. As Lipscomb et al.[56] have pointed out, three recent RH calculations, using enormous basis sets and believed to be close to the Hartree–Fock limit, have led to values of the heat of reaction (−19.0,[56] −19.9,[55] −20.6[57] kcal/mol) which are only about half the observed value (−39 kcal/mol[58]). As one might expect, the result from a minimum basis set RH calculation was even worse (−7.3 kcal/mol). While MNDO also gives too small a value (−25.2 kcal/mol[25]), this is in better agreement with experiment than even the most elaborate RH calculations. Since PRDDO was parametrized to reproduce the results of RH calculations, it too would presumably be inferior to MNDO in this case.

Another example is provided by comparisons[13] of the energies of isomeric "classical" and "nonclassical" carbocations, the latter being distinguished by the presence of multicenter bonds. Here the RH method again underestimates the stability of the latter unless a vary large basis set (6-31G*) is used. Even then the error may still persist.[13c] The MNDO results for these ions seem to parallel those given by the RH method with an intermediate basis set (4-31G).

We therefore feel justified in claiming that MNDO provides the most promising procedure for studying the chemical behavior of boron hydrides, having been thoroughly tested and giving results of at least equal accuracy at less cost.[60] However, even if this is the case, the question remains as to whether it is good enough to be of practical value.

The errors in the MNDO heats of formation for the boron hydrides are similar to those for other boron compounds but about double those for typical organic compounds composed of the later second period elements (C, N, O, F) and hydrogen.[23] However, the errors for organic molecules in MINDO/3 were about double those in MNDO and yet MINDO/3 has proved very useful in mechanistic studies of a very wide variety of organic reactions.[18] There is therefore good reason to expect MNDO to prove equally effective in studies of the boron hydrides. We have indeed obtained promising results from calculations of the hydroboration of olefins by boranes[61] and of borohydride reduction of carbonyl compounds.[62]

The lesser accuracy of MNDO in the case of boron compounds is undoubtedly due to less effective optimization of the parameters, due in turn to the dearth of accurate thermochemical data for boron compounds. Here, as in so many connections involving "inorganic" elements, there is a desperate need for accurate experimental values for the heats of formation of molecules and strengths of bonds.

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Appendix. The Calculation of Geometries and Characterization of Stationary Points on Potential Surfaces

Cyclic variation of parameters (CVP) is the oldest and most primitive of optimization procedures, whose use is acceptable only in cases where the number of parameters is small. This condition was met in the calculation of molecular geometries in early RH studies because these were necessarily confined to very small molecules, involving only a few geometric parameters, and use of CVP had the advantage of needing no special programming. Unfortunately it continued to be used for larger molecules when developments in computers made them accessible to the RH method and similar remarks apply to an analogous procedure used to locate transition states, i.e., calculation of sections of potential surfaces obtained by varying one coordinate at a time.

The CVP method is liable to converge at points on the potential surface which are not true minima and to converge very slowly at points where the gradient is small. The number of function evaluations needed for proper optimization also becomes very large as the number of parameters increases. In the RH method, each function evaluation involves a complete SCF calculation, including recalculation of all integrals. Since the CVP method provides no reliable criterion for convergence and since convergence can be slow, there is also a temptation to terminate the iterative procedure before a true minimum has been reached.

The first problem arises from the use of fixed search directions, parallel to the coordinate axes. Unless the expression for the energy is diagonal, or nearly diagonal, in the coordinates used, other types of stationary point can be mistaken for minima. This is even possible in principle in systems defined by only two geometrical variables. An example is the potential surface defined in polar coordinates by the following equation:

$$E = r^2(\cos 4\theta - 0.5 \cos 8\theta) \qquad (1)$$

The origin is a minimum for motion in the directions $\theta = 0$ and $\theta = \pi/2$ but a maximum for motion in the directions $\theta \pm \pi/4$. If we use Cartesian coordinates with axes parallel to $\theta = 0$ (y) and $\theta = \pi/2$ (x) and minimize the energy by the CVP method, with an initial geometry represented by a point near[63] the x or y axis, we will quickly arrive at the origin and conclude it to be a true minimum although in fact, it is a maximum in two orthogonal directions ($\theta = \pm\pi/4$).

This situation is unlikely to arise in small molecules involving only a few coordinates, particularly if internal coordinates are used, because the off-diagonal terms in the expression for the potential energy are small compared with the diagonal ones. In large molecules, however, the increasing number of off-diagonal terms can easily outweigh individual diagonal ones so that there is then no guarantee that the CVP "minima" will be true minima rather than stationary points of other types.

This difficulty can be avoided by use of more sophisticated optimization procedures in which the search is not carried out in fixed directions. The problems of slow convergence and excessive cost still remain, however, in procedures based only on values of the function being optimized (e.g., Brent,[64] Simplex[65]). Procedures that use derivatives of the function (e.g., Murtagh–Sargent,[14] DFP[15]) are far more efficient in these and other respects and are now being adopted in RH studies.[17] The only problem here is a technical one. The calculation of derivatives of the energy is quite complicated and also involves a great deal of computation. Since the calculation of derivatives in MINDO/3 or MNDO is relatively trivial and requires very little computing time, this further increases the cost differential between these methods and the ab initio ones.

There is, however, one situation where the derivative optimization methods also fail, i.e., when the optimization is carried out using a starting geometry that corresponds to a stationary point on the potential surface. Since the condition for convergence is that the scalar gradient should vanish and since this criterion is met at *any* stationary point, the optimization then terminates before it has properly begun. It is moreover insufficient to displace the system in an arbitrary manner and then repeat the optimization, because unless the displacement lowers the energy, optimization will normally lead back to the starting point. It is necessary to displace the molecule along a normal coordinate on which the initial structure is a maximum. In the case of a polyatomic molecule, it is usually impossible to guess the form of this coordinate with sufficient accuracy.

Situations of this kind arise in the case of molecules believed to have symmetry. When the geometry optimization is carried out with corresponding symmetry constaints to reduce the number of independent variables and so likewise the cost of the computation, it seems at first sight sufficient to check the validity of the assumed symmetry by a final optimization without symmetry constraints. However, it is easily seen that the point in question must in any case be a stationary point of some kind on the potential surface. It cannot therefore be identified as a minimum by a further unconstrained optimization, because this will lead to it whether it is a minimum or not. The same problem also arises with nonderivative optimization methods, and analogous difficulties are commonly encountered in attempts to locate transition states. Here again it is easy to mistake stationary points of other kinds as saddle points. Evidently there is an urgent need for some procedure that will enable us to distinguish different types of stationary points from one another. Such a procedure has been provided by McIver and Komornicki,[16a,b] following an earlier suggestion by Murrell et al.[16c]

If the matrix of second derivatives of the energy (Hessian or force constant matrix) is diagonalized, the resulting eigenvalues are the force constants for the normal modes of vibration. In the case of a minimum, all must be >0, while a saddle point (transition state) has one, and only one, negative eigenvalue. We have found that use of Cartesian coordinates in this procedure also provides a very good test of convergence of the optimization. In this case six of the eigenvalues of the Hessian matrix should vanish, corresponding to the three modes of translation and three of rotation of the molecule as a whole. If the Hessian matrix is calculated at a nonstationary point on the potential surface, these modes mix with the others so the corresponding eigenvalues no longer vanish.

Furthermore, in cases where there are unwanted negative eigenvalues, the corresponding eigenvectors represent the directions in which the molecules have to be distorted in order to lead to a decrease in energy. If the molecule is distorted accordingly and the geometry optimization repeated, a true minimum can be found. Similar remarks apply in the case of "transition states" with two or more negative eigenvalues. One of these, corresponding to the required reaction coordinate, can easily be recognized from the form of the corresponding eigenvector, while the eigenvector(s) of the other negative mode(s) indicate(s) the type(s) of distortion needed to reach the true transition state.

It should be noted that the points raised here are not purely hypothetical but are based on our own very extensive experience. We now routinely check *all* stationary points on potential surfaces by the McIver–Komornicki procedure because we have encountered so many cases where its use alone has saved us from error. We feel that similar precautions should be taken in *all* future calculations of the geometries and reactions of molecules, by ab initio and semiempirical methods alike.

Registry No. B_3H_7, 12429-70-8; B_3H_9, 36350-66-0; B_4H_8 (double bridged), 65915-72-2; B_4H_8 (single bridged), 65956-97-0; B_4H_8 (no bridge), 59035-20-0; B_6H_{12}, 12008-19-4; B_8H_{12}, 19469-16-0; B_9H_{15}, 19465-30-6; $B_{10}H_{14}$, 17702-41-9; $B_{10}H_{16}$, 12430-42-1; BH_4^-, 16971-29-2; $B_4H_4^{2-}$, 12429-81-1; $B_5H_5^{2-}$, 12429-90-2; $B_6H_6^{2-}$, 12429-97-9; $B_7H_7^{2-}$, 12430-07-8; $B_8H_8^{2-}$, 12430-13-6; $B_9H_9^{2-}$, 12430-24-9; $B_{10}H_{10}^{2-}$, 12356-12-6; $B_{10}H_{14}^{2-}$, 12430-39-6; $B_{11}H_{11}^{2-}$, 12430-44-3; $B_{12}H_{12}^{2-}$, 12356-13-7.

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A Molecular Orbital Study of Rare Earth Metal Trihalide Molecules

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Self-consistent charge extended Hückel calculations on rare earth metal trihalide molecules give lower total valence electron energies for pyramidal geometries than for planar geometries in agreement with the weight of experimental evidence. A correlation diagram analysis indicates that the dominant factor is enhanced overlap between the metal $5d_{z^2}$ and the halogen p orbitals in the pyramidal geometry. Consistent with this, the charge distribution is most delocalized for the minimum energy structures, providing further indication of the importance of covalency in LnX_3 systems.

Introduction

The view that bonding in rare earth metal compounds, particularly complexes, is substantially electrostatic[1] has been challenged with respect to the lanthanide trihalide molecules on the grounds that a hard-sphere ion model fails to account for the observed bond energies.[2] Although the inclusion of polarization effects brings about agreement,[3] these corrections are sufficiently large that considerable covalency must be inferred (since polarization of the anions means a net movement of electron density into the internuclear region). Furthermore, recent evidence from infrared studies of matrix-isolated trifluoride molecules,[4] from electric deflection of molecular beams of trifluorides,[5] and from electron diffraction studies[6] strongly supports a pyramidal structure for most, if not all, of the lanthanide trihalides; this would be unlikely if the bonding were essentially ionic.

Since the experimental evidence seems to support a significant degree of covalent bonding, it was considered timely to undertake molecular orbital calculations to gain insight into the nature of the bonding and the reasons for the nonplanarity. The large number of electrons in these molecules made an approximate, semiempirical method attractive for these purposes, and it was decided to use the extended Hückel method[7] because of its recent success in applications to transition metal compounds.[8] Also, the method has the ability to illuminate features of electronic structure responsible for geometry. Since the f-electron energies appear to be similar in the free ion, crystalline trihalides,[9] and gaseous molecules,[10] f orbitals were not explicitly included in the calculations; however, the effects of f electrons will be felt in that they influence the empirical parameters used in the calculations. This is the first application of a full, albeit approximate, MO treatment to lanthanide systems.[11]

Method

The calculations were performed using the program ICON8. In this program, a Slater-type nodeless single exponential is used to represent the radial part of the wave function:

$$R(r) = Nr^{n^*-1} \exp[(Z-S)r/a_0n^*]$$

where n^* is the effective quantum number (in this case the principal quantum number), a_0 is the Bohr radius, r is the distance of the electron from the nucleus, S is a screening constant which was evaluated by the method of Burns,[12] Z is the atomic number, and N is a normalizing factor.

Coulomb integrals were derived iteratively via a quadratic self-consistent charge procedure using the valence state ionization energy (VSIE) formalism of Ballhausen and Gray.[13] In this procedure, the Coulomb integrals, H_{ii}, are given in terms of three valence configurations for each atomic orbital:

$$-H_{ss} = (2 - e_s - e_p)[e_s(\text{VSIE:}\ \ d^2s)] + (e_s - 1)[e_s(\text{VSIE:}\ \ d^{n-2}s^2)] + e_p[e_s(\text{VSIE:}\ \ d^{n-2}sp)]$$

$$-H_{pp} = (2 - e_s - e_p)[e_p(\text{VSIE:}\ \ d^{n-1}p)] + (e_p - 1)[e_p(\text{VSIE:}\ \ d^{n-2}p^2)] + e_s[e_p(\text{VSIE:}\ \ d^{n-2}sp)]$$

$$-H_{dd} = (1 - e_s - e_p)[e_d(\text{VSIE:}\ \ d^n)] + e_s[e_d(\text{VSIE:}\ \ d^{n-1}s)] + e_p[e_d(\text{VSIE:}\ \ d^{n-1}p)]$$

where e_s, e_p, and e_d are the summed orbital occupations of the s, p, and d orbitals, respectively. The VSIEs are given a quadratic charge dependence:

$$\text{VSIE(of a confign)} = AQ^2 + BQ + C$$

where Q is the charge and A, B, and C are a unique set of constants for each configuration on each atom. The values of these parameters were determined, using Brewer's energy level data,[14,15] according to the method of Basch, Viste, and Gray.[16] The initial guess for the Coulomb integrals on the lanthanides was taken as $-\text{VSIE}(Q = 0)$ for each configuration. A compilation of orbital exponents ($Z - S$) and VSIE parameters (A, B, C) for the lanthanides and the halogens is given in Tables 1–3 of the supplementary material.

A Mulliken population analysis is used to determine charge distributions. Calculations were performed for the molecules in both D_{3h} (planar) and C_{3v} (pyramidal) geometries, the latter being done at 5° intervals of out-of-plane angle. The metal–halogen distances were those used earlier.[2,3] Early calculations on LaX_3 (X = F, Cl, Br, I) included halogen d orbitals, but the results differed in no significant manner from calculations using only halogen s and p orbitals. Hence, later calculations did not include halogen d orbitals.

Results from two general procedures are discussed below. The first of these is an extended Hückel calculation with full iteration to charge self-consistency for a particular geometry (FCI), and the second is a calculation varying bond angles (BAV) but using the Coulomb integrals obtained from an FCI calculation for the planar D_{3h} configuration of the molecule.

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