Supplementary Material Available. Tables containing the experimental $1/T_1{}^0$, $1/T_{1,\mathrm{obsd}}$, and $1/T_{1\mathrm{P}}$ data corresponding to Figure 4 as well as the line width data corresponding to Figure 5 and the chemical shift and contact shift data corresponding to Figure 6 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-6962.

References and Notes

(1) (a) University of Copenhagen; (b) University of Utah.
(2) (a) A. S. Mildvan and M. Cohn, *Adv. Enzymol. Relat. Areas Mol. Biol.*, **33,** 1 (1970), and references therein; (b) M. Cohn, *Q. Rev. Biophys.*, **3,** 61 (1970).
(3) A. S. Mildvan and J. L. Engle, *Methods Enzymol.*, **26,** 654 (1972).
(4) C. H. Fung, A. S. Mildvan, A. Allerhand, R. Komoroski, and M. C. Scrutton, *Biochemistry,* **12,** 620 (1973).
(5) Y.-F. Lam, G. P. P. Kuntz, and G. Kotowycz, *J. Am. Chem. Soc.*, **96,** 1834 (1974).
(6) A. F. Crockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73,** 553 (1973), and references therein.
(7) C. D. Barry, R. J. P. Williams, and A. V. Xavier, *J. Mol. Biol.*, **84** 471 (1974), and references therein.
(8) A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, London, 1961, Chapter VIII.
(9) M. O. Dayhoff, "Atlas of Protein Sequence and Structure", Vol. 5, National Biomedical Research Foundation, Georgetown University Center, 1972.
(10) H. C. Freeman, *Adv. Protein Chem.*, **22,** 257 (1967).
(11) H. Kroll, *J. Am. Chem. Soc.*, **74,** 2034 (1952).
(12) R. H. Carlson and T. L. Brown, *Inorg. Chem.*, **5,** 268 (1966).
(13) I. L. Givot, A. S. Mildvan, and R. H. Abeles, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **29,** 531 (1970).
(14) B. R. McGarvey, *Transition Met. Chem.*, **3,** 89 (1966).
(15) M. Tinkham, R. Weinstein, and A. F. Kip, *Phys. Rev.*, **84,** 848 (1951).
(16) R. S. Codrington and N. Bloembergen, *J. Chem. Phys.*, **29,** 600 (1958).
(17) Z. Luz and R. G. Shulman, *J. Chem. Phys.*, **43,** 3750 (1965).
(18) A. R. Peacocke, R. E. Richards, and B. Sheard, *Mol. Phys.*, **16,** 177 (1969).
(19) J. A. McMillan, "Electron Paramagnetism", Reinhold, New York, N.Y., 1968, p 27.
(20) I. Solomon, *Phys. Rev.*, **99,** 559 (1955).
(21) N. Bloembergen, *J. Chem. Phys.*, **27,** 572 (1957).
(22) R. E. Connick and D. Fiat, *J. Chem. Phys.*, **44,** 4103 (1966).
(23) J. Reuben, G. H. Reed, and M. Cohn, *J. Chem. Phys.*, **52,** 1617 (1970).
(24) T. R. Stengle and C. H. Langford, *Coord. Chem. Rev.*, **2,** 349 (1967).
(25) M. Eigen and R. G. Wilkins, *Adv. Chem. Ser.*, **No. 49,** 55, (1965).
(26) N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34,** 842 (1961).
(27) M. Rubinstein, A. Baram, and Z. Luz, *Mol. Phys.*, **20,** 67 (1971).
(28) B. R. McGarvey, *J. Phys. Chem.*, **61,** 1232 (1957).
(29) H. Eyring, *Chem. Rev.*, **17,** 65 (1935).
(30) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40,** 2686 (1964).
(31) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37,** 307 (1962).
(32) N. Bloembergen, *J. Chem. Phys.*, **27,** 595 (1957).
(33) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28,** 107 (1958).
(34) R. R. Ernst, *Adv. Magn. Reson.*, **2,** 1 (1966).
(35) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(36) J. L. Deutsch and S. M. Poling, *J. Chem. Educ.*, **46,** 167 (1969).
(37) C. C. McDonald and W. D. Phillips, *J. Am. Chem. Soc.*, **85,** 3736 (1963).
(38) E. V. Raju and H. B. Mathur, *J. Inorg. Nucl. Chem.*, **31,** 425 (1969).
(39) R. Hausser and F. Noack, *Z. Phys.*, **182,** 93 (1964).
(40) W. L. Purcell and R. S. Marianelli, *Inorg. Chem.*, **9,** 1724 (1970).
(41) R. H. Henson, D. Phil. Thesis, Oxford 1972.
(42) F. F. Brown, I. D. Campbell, R. H. Henson, C. W. J. Hirst, and R. E. Richards, cited in R. A. Dwek, "Nuclear Magnetic Resonance in Biochemistry", Clarendon Press, Oxford, 1973, p 206.
(43) G. H. Reed, J. S. Leigh, Jr., and J. E. Pearson, *J. Chem. Phys.*, **55,** 3311 (1971).
(44) G. H. Reed and M. Cohn, *J. Biol. Chem.*, **247,** 3073 (1972).
(45) G. H. Reed and M. Cohn, *J. Biol. Chem.*, **245,** 662 (1972).
(46) A. W. Nolle and L. O. Morgan, *J. Chem. Phys.*, **36,** 378 (1962).
(47) C. C. Hinckley and L. O. Morgan, *J. Chem. Phys.*, **44,** 898 (1966).
(48) J. Reuben and M. Cohn, *J. Biol. Chem.*, **245,** 6539 (1970).
(49) K. A. Fraser and M. M. Harding, *J. Chem. Soc. A*, 415 (1967).
(50) E. Willstadter, T. A. Hamor, and J. L. Hoard, *J. Am. Chem. Soc.*, **85,** 1205 (1963).

Ab Initio Calculation Including Electron Correlation of the Structure and Binding Energy of BH_5 and $B_2H_7{}^-$

Claus Hoheisel and Werner Kutzelnigg*

Contribution from the Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum,
Bochum-Querenburg, Germany.

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Abstract: Quantum chemical ab initio calculations with and without the inclusion of electron correlation are performed for five possible structures of BH_5 and four possible structures of $B_2H_7{}^-$. In the SCF approximation BH_5 is not stable with respect to $BH_3 + H_2$; with correlation it has a binding energy of −2 kcal/mol in a C_s geometry. Isomerization is possible via the C_{2v} structure, the energy of which is 9 kcal/mol higher. For $B_2H_7{}^-$ previous SCF results are confirmed and with correlation the experimental binding energy (with respect to $BH_3 + BH_4{}^-$) is reproduced. The ion is symmetric with one linear B-H-B bond.

I. Introduction

The molecule BH_5 is isoelectronic to the ion $CH_5{}^+$ that has been studied both experimentally[1-3] and theoretically.[4-8] Since $CH_5{}^+$ is quite stable as an "ion in space" (its binding energy with respect to $CH_4 + H^+$ is −125 kcal/mol and with respect to $CH_3{}^+ + H_2$ −40 kcal/mol),[6-8] one could guess that BH_5 should be a stable species as well. Recent experimental studies of the protolysis or hydrolysis[9-11] of $BH_4{}^-$ led to the postulate of BH_5 as an intermediate in these reactions. A CNDO/2 calculation[9] of four possible structures of BH_5 (belonging to the symmetry groups D_{3h}, C_{3v}, C_{4v}, and C_s) led to the prediction that BH_5 should have C_s symmetry (like $CH_5{}^+$) with a binding energy of −1.531 au (∼−40 eV or −900 kcal/mol) with respect to B + 5H. Since this value of the binding energy is rather unrealistic (something similar was observed for other boron hydrides like B_2H_6[12]) the result from the CNDO calculation could not be regarded as definite and we therefore performed a refined ab initio calculation, including electron correlation, with the CEPA-PNO and PNO-CI methods described elsewhere.[14-19]

The ion $B_2H_7{}^-$ that is well-known from experiment[20-23] is interesting insofar as a structure with a single linear symmetric B-H-B bond has been proposed for this ion. Ab initio studies including correlation of B_2H_6[13,24,25] that has two B-H-B bonds, of $BeBH_5$[26] that is held together by three Be-H-B bonds, and BeB_2H_8[26] where structures with two

Table I. Optimum Geometry and Binding Energy of BH_5 in Different Structures in SCF Approximation[a]

Configuration	Symmetry group	R_{B-H}, a_0	r_{B-H}, a_0	σ_{B-H}, a_0	α, deg	β, deg	γ, deg	E_{BIND},[b] kcal/mol
I	C_s	(5.55)	(2.25)		(5.0)	(14.8)	(119.5)	(1.4)
II	C_{3v}							
III	D_{3h}	2.27	2.27				60.0	56.5
IV	C_{4v}	2.25	2.35		30.0		75.5	38.5
V	C_{2v}	2.40	2.25	2.40	51.0		60.0	19.3

[a] The structures and the geometrical parameters are illustrated in Figure 1. The values for configuration I are in parentheses because they do not correspond to a (symmetry-restricted) minimum in the proper sense (see text). [b] $E_{BIND} = E_{SCF}(BH_5) - E_{SCF}(BH_3) - E_{SCF}(H_2)$.

and three hydrogen bonds compete have shown that the correlation energy has a marked influence on the binding energy in those systems. We therefore regard a calculation of $B_2H_7^-$ on the same level of approximation as worthwhile, even though good SCF results have already been published.[25] We also decided to compare competitive structures for $B_2H_7^-$ with one, two, and three hydrogen bonds, respectively.

II. Method and Basis Set

We used the IEPA-PNO, PNO-CI, and CEPA-PNO methods[14-19] that were recently described in detail[18] and applied to first row[27] and second row hydrides[28] as well as to other molecules.[29] We always start with an SCF calculation and then transform the SCF-MO's to localized ones according to Boys,[30] before the calculation of the correlation effects is performed.

In the IEPA (independent electron pair approximation) scheme the correlation energy of the different electron pairs is computed independently, in CEPA (coupled electron pair approximation) the interaction of the electron pairs is taken into account, and CI means configuration interaction in the usual sense, limited to double substitutions. In all three schemes the pair correlation functions are calculated in a PNO (pair natural orbital) expansion. The CEPA values are usually closest to the exact ones.[17,27-29] The basis set consists of Gaussian lobes from which p and d functions are constructed as described in ref. 31. A "small basis"[33] was used for the geometry optimizations. It consists of the (8s,4p) Huzinaga basis[32] in the contraction (5,1,1,1; 3,1) for B and the 4s basis in the contraction (3,1) for H.

A "large basis" [33] was taken for the final calculations at the computed equilibrium geometries. It differs from the "small basis" by the addition of polarization functions, namely a d set (η = 0.61) for B and a p set (η = 0.61) for H. The p basis of B was tentatively used in the contraction (2,1,1), but pilot calculations indicated, in agreement with the findings of Ahlrichs,[13] that the p function with the smallest η could be left out without affecting the results for the binding energies and the energy differences between the isomers of BH_5.

The computer times with the "large basis" were by about a factor 5-10 larger than those with the "small basis." One SCF point for BH_5 needed ~3.5 min with the small and ~32 min with the large basis, one point including correlation needed 82 min. For one SCF point of $B_2H_7^-$ in the small basis 50 min and in the large basis 220 min were necessary. The calculation of correlation with the large basis is in principle possible for B_2H_7, but we chose a less time-consuming compromise as described in section VIII that needed only 2 × 150 min. These values of computer time are for the Telefunken TR 440.

III. Search for the Equilibrium Structure of BH_5 in the SCF Approximation

Five types of structures as illustrated in Figure 1 were considered. They are the same as in the study of CH_5^+.[6,8]

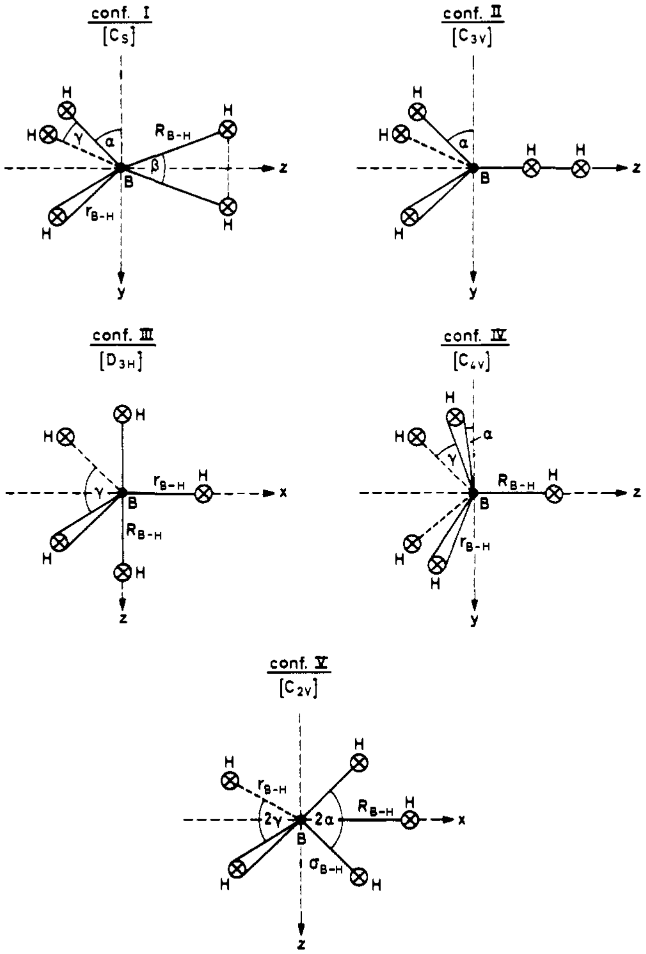

Figure 1. Five possible structures of BH_5.

Starting values for the geometrical parameters were those of BH_3.[34] The following structural parameters were varied (see Figure 1): (configuration I) r_{BH}, R_{BH}, α, β (for the BH_3 subunit local C_{3v} symmetry was retained); (configuration II) R_{BH}, R_{HH}, α; (configuration III) r_{BH}, R_{BH}; (configuration IV) r_{BH}, R_{BH}, α; (configuration V) r_{BH}, σ_{BH}, R_{BH}, α.

The results of the geometry optimization for the different structures are collected in Table I. The energies given in Table I were calculated with the "large basis", but the "small basis" was used for the geometry optimization. For structure II there was a continuous increase of the energy on approach of the H_2 to BH_3 and no minimum could be found by relaxation of the other geometrical parameters. The same was true for structure I, but here one could force the energy to go through a minimum if one constrained the out-of-plane angle α of the BH_3 subunit to be constant and to be larger than 5°. The energy curve for α = 8° as a function of the distance R between the B atom and the midpoint of the H_2 subunit is illustrated in Figure 2. The relative

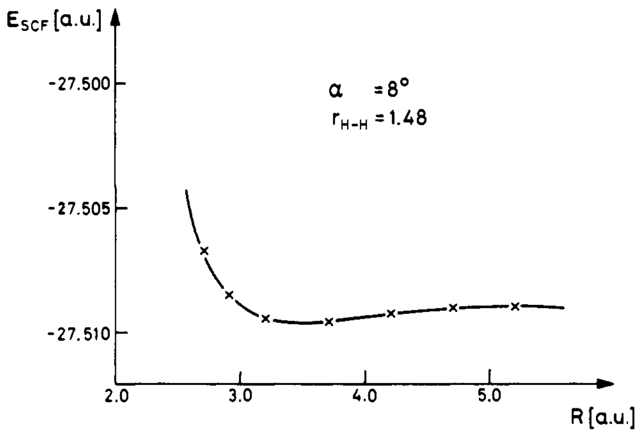

Figure 2. SCF energy of BH_5 in configuration I for α and r_{H-H} fixed.

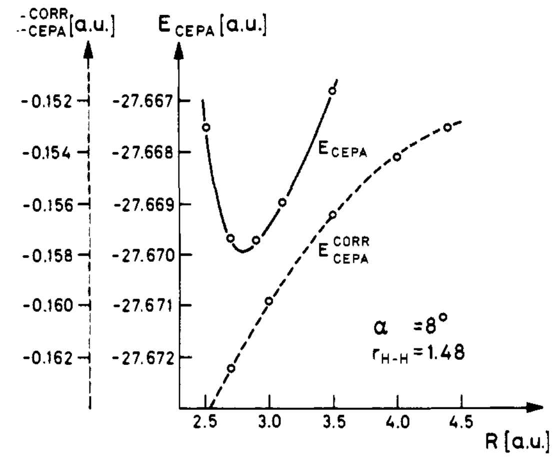

Figure 3. Correlation energy and total energy of BH_5 in configuration I for α and r_{HH} fixed.

Table II. Total Energies in Different Approximations (in au) for Optimized Structures (Large Basis)

Molecule	$-E_{SCF}$	$-E_{IEPA}$	$-E_{CEPA}$	$-E_{PNOCI}$
H_2	1.129086	1.163913	1.163913	1.163913
BH_3	26.387012	26.512176	26.503314	26.498504
BH_5 [C_s]	(27.507790)[a] 27.513797[b]	27.683820	27.669950	27.660190
BH_5 [C_{2v}]	27.485058	27.672980	27.656191	27.645422

[a] For the minimum of the CEPA calculation. [b] For the constrained SCF minimum (see text).

minimum (i.e., the binding energy of BH_5 with respect to H_2 and bent BH_3) increases with α (for $5° < \alpha < 30°$) which means that pyramidal BH_3 with an sp^3-type unoccupied AO is better able to bind H_2 via a three-center two-electron bond than is planar BH_3 with a p-type unoccupied AO. However, the energy required to deform BH_3 by the out-of-plane angle α increases faster with α so that the absolutely lowest of the constrained minima occurs for the smallest possible value of α, i.e., for $\alpha = 5°$. The energy corresponding to this constrained minimum is, as can be seen from Table I, only 1.4 kcal/mol above the sum of the energies of BH_3 and H_2. For structure II not even a constrained minimum of this kind could be found. For the structures III, IV, and V one does find minima but they are energetically much above BH_3 and H_2. Note that all values for E_{bind} in Table I are positive, which means that BH_5 has a higher energy than $BH_3 + H_2$. It is unlikely that for any of these structures there exists a real local minimum; we rather expect that the energy goes down in any case if one relaxes the symmetry restrictions. We conclude that in the SCF approximation BH_5 is not bound with respect to $BH_3 + H_2$.

All the energy differences quoted in this paper refer to the minima of the potential curves and not to the zero-point vibrational levels.

IV. The Correlation Energy of BH_5

We have computed the correlation energy for the structures I (C_s) and V (C_{2v}) and, of course, of BH_3 and H_2 in the same basis. There was no reason to expect that structures III or IV would become competitive if electron correlation is taken care of. Inclusion of correlation in the CEPA scheme stabilizes the C_{2v} structure by 12.4 kcal/mol with respect to $BH_3 + H_2$ so that with inclusion of correlation BH_5 in C_{2v} symmetry lies only 7 kcal/mol above the energy of the separated systems $BH_3 + H_2$. We did not reoptimize the geometry (obtained from SCF calculations) of this C_{2v} structure. Pilot calculations indicate that such a reoptimization can only lower the energy by 1 or at most 2 kcal/mol.

The C_s structure becomes stable with respect to $BH_3 + H_2$ if electron correlation is included. Since there was no minimum of the SCF potential surface in C_s geometry we had to optimize the geometry with correlation (see section III). The equilibrium structure was found for the following values (see Figure 1): $R_{B-H} = 2.90\ a_0$, $r_{B-H} = 2.25\ a_0$, $r_{H-H} = 1.48\ a_0$, $\alpha = 8°$, $\beta = 29.6°$. In Figure 3 the total energy as well as the correlation contribution to the binding energy is plotted as a function of the distance R between B and the midpoint of H_2. At the equilibrium geometry the binding energy is ~ -2 kcal/mol, the correlation contribution is ~ -7 kcal/mol, and the SCF repulsion $\sim +5$ kcal/mol. The pertinent total energies for the equilibrium geometries are collected in Table II.

Obviously the fact that BH_5 is bound with respect to $BH_3 + H_2$ is exclusively due to correlation. Before we comment on this somewhat unusual case of a chemical bond we want to say a few words about the individual contributions to the correlation energy in BH_5, BH_3, and H_2.

The correlation energy of a molecule computed in the coupled electron pair approximation (CEPA) can be decomposed into independent electron pair (IEPA) contributions ϵ_μ and coupling correlation terms $\Delta\epsilon_{\mu\nu}$, where μ,ν count the pairs. The bulk of the change in correlation energy is in the IEPA contributions ϵ_μ which are collected in Table III. The localized MO's in BH_5 can directly be compared with those of BH_3 and H_2 since BH_5 in structure I contains rather distinct BH_3 and H_2 subunits. One sees from Table III that the contributions of the BH_3 subunit in BH_5 to the correlation energy are smaller in absolute value than in isolated BH_3 by $0.12480 - 0.12270 = 0.0021$ au but that the correlation energy of the H_2 subunit is larger in BH_5 by 0.00182 in absolute value so that the intrasubsystem correlation energy changes by only 0.0004 au. The intersubsystem correlation energy amounts to $0.01828 \approx 13$ kcal/mol and equals practically the total change in the IEPA correlation energy. The pair coupling terms reduce this difference to the CEPA value of ~ 7 kcal/mol.

From the experience with other systems we conclude that the CEPA scheme predicts energy differences with chemical accuracy, i.e., with an error of the order of magnitude of 1 kcal/mol or possibly less. In the present case refinement of the calculation is likely to increase the value of the binding energy.

V. Analysis of the Binding in the BH_5

In view of the small binding energy of only -2 kcal/mol between BH_3 and H_2 one wonders whether BH_5 should be

Table III. Pair Contributions (Localized) to the Correlation Energy (Large Basis) (in au) for BH_5, BH_3, and H_2 in Their Equilibrium Geometries

Molecule	Subunit	Pair symbol[a]	No. of equivalent pairs	Pair contribution	Sum
H_2		$-\epsilon_h$	1	0.03483	0.03483
BH_3		$-\epsilon_b$	3	0.03129	0.09386
		$-\epsilon_{bb'}$	3	0.01032	0.03094
					0.12480
BH_5	H_2	$-\epsilon_h$	1	0.03665	0.03665
BH_5	BH_3	$-\epsilon_b$	1	0.03077	0.03077
		$-\epsilon_{b'}$	2	0.03055	0.06110
		$-\epsilon_{bb'}$	2	0.01020	0.02040
		$-\epsilon_{b'b''}$	1	0.01043	0.01043
					0.12270
BH_5	Inter	$-\epsilon_{bh}$	1	0.00550	0.00550
	H_2/BH_3	$-\epsilon_{b'h}$	2	0.00639	0.01278
					0.01828

[a] Subscript h refers to a H–H bond and b to a BH bond.

Table IV. Mulliken Gross Charges and Overlap Populations for the Localized MO's in BH_5

	B	H(1)	H(2)	H(3)	H(4)	H(5)
	BH(2) Two-Center Bond					
B	0.77					
H(1)	−0.05	−0.03				
H(2)	0.86	−0.07	1.27			
H(3)	−0.04	0.01	−0.06	−0.02		
H(4)	−0.06	0.02	−0.08	0.02	−0.02	
H(5)	0.04	−0.01	0.05	0.00	−0.02	0.03
	BH(5)H(6) Three-Center Bond					
B	0.18					
H(1)	0	−0.01				
H(2)	0	0	−0.01			
H(3)	0	0	0	−0.01		
H(4)	0.12	−0.02	−0.02	−0.03	0.93	
H(5)	0.12	−0.02	−0.03	−0.02	0.74[a]	0.93

[a] For comparison: the overlap population of isolated H_2 in the same basis is 0.83.

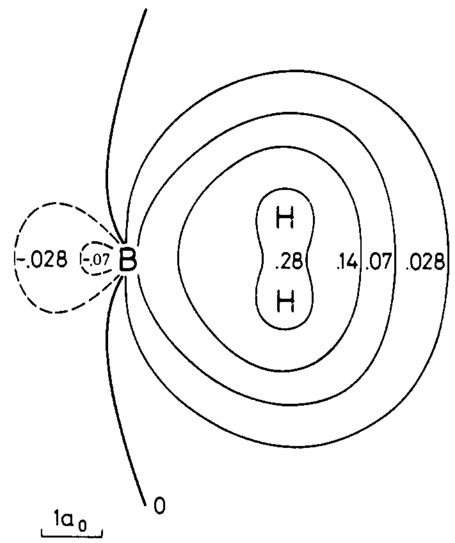

Figure 4. Contour line diagram in the BHH plane of the localized MO of BH_5 (equilibrium structure) that represents the three-center BHH bond.

Table V. Compounds in C_s Symmetry with Three-Center Two Electron Bonds[a]

	R, a_0	r_{H-H}, a_0	E_{BIND}, kcal/mol	ΔE_{CORR}, kcal/mol
LiH_2^+	3.75	1.41	−5.1	0
BeH_3^+	3.04	1.47	−24.7	0
BH_5	2.80	1.48	−2.0	7.0
CH_5^+	2.24	1.67	−43.0	21.0
H_3^+	1.43	1.65	−107.1	4.0

[a] K = Li, Be, B, C; R = distance of nucleus K from the center of mass of H_2; r_{H-H} = distance between the H atoms in the H_2 subunit; $E_{BIND} = E_{KH_n}{}^{total} - E_{KH_{n-2}}{}^{total} - E_{H_2}{}^{total}$; ΔE_{CORR} = correlation contribution to the binding energy.

regarded as a van der Waals complex rather than a chemically bound molecule. Like in genuine van der Waals complexes the intersystem correlation energy (dispersion) is mainly responsible for the existence of a stable BH_5. We nevertheless prefer to look at BH_5 as a chemically bound molecule and this for the following reasons: (1) A van der Waals bond between H_2 and BH_3 should have a still much smaller binding energy (the well depth of the van der Waals minimum of the system He-H_2 is, e.g., 0.04 kcal/mol;[35] other typical van der Waals minima are of the same order of magnitude). (2) The distance between the two subunits is much smaller than typical van der Waals distances (the distance between He and the midpoint of H_2 at the van der Waals minimum is 6.3 a_0[35]). (3) The BH_3 and H_2 subunits in BH_5 are appreciably deformed compared with the isolated BH_3 and H_2. The out-of-plane angle in the BH_3 subunit is 8° and the bond distance of the H_2 subunit is 1.48 a_0 compared with 1.40 a_0 in isolated H_2.

The localized MO (LMO) that represents the three-center BHH bond is plotted in Figure 4. One sees from Figure 4 and also from the population analysis in Table IV that this LMO is mainly localized in the H-H bond, but that there is a nonnegligible charge transfer (0.2 electron) to the B atom and a significant B-H overlap population. The LMO's that represent ordinary B-H bonds are very much like those in BH_3.

We may compare BH_5 with other molecules which contain a H_2 subunit that form a three-center two-electron bond with an electron deficient subunit namely with LiH_2^+,[36] BeH_3^+,[37] CH_5^+,[6-8] and H_3^+.[38-40] In Table V the bond distances and binding energies of these molecules are compared with those of BH_5. As far as the distance between the heavy atom and the H_2 subunit is concerned and with respect to the change of the H-H distance BH_5 fits well in between BeH_3^+ and CH_5^+. Also the contribution of the change in correlation energy to the binding energy of BH_5 is between that of BeH_3^+ and CH_5^+. Only the binding energy of BH_5 does not fit at all. However, all the molecules to which we can compare BH_5 are ionic and their binding energies contain an appreciable amount of induction energy (interaction between the charge of, e.g., BeH^+ and the induced dipole in H_2), and electrostatic energy (between the charge and the quadrupole moment of H_2), which are not present in BH_5. The best description of binding between BH_3 and H_2 is probably to say that it is a three-center bond for which H_2 is donor and BH_3 acceptor and that this bond is effectively rather weak due to the fact that H_2 is a rather poor electron donor and to the strong electron repulsion between the subunits.

This electron repulsion is overestimated in the Hartree-Fock approximation, but taken care of correctly if electron correlation is allowed for. To conclude this section we compare the equilibrium geometry obtained for BH_5 by Olah et al. with the CNDO/2 approximation. This is done in Table VI. Although the binding energy from CNDO/2 of ∼−900 kcal/mol with respect to B + 5H is unrealistic (we get ∼−380 kcal/mol) the equilibrium geometry is not so bad, at least as far as the angle α and the (uninteresting) distance r_{BH} is concerned.

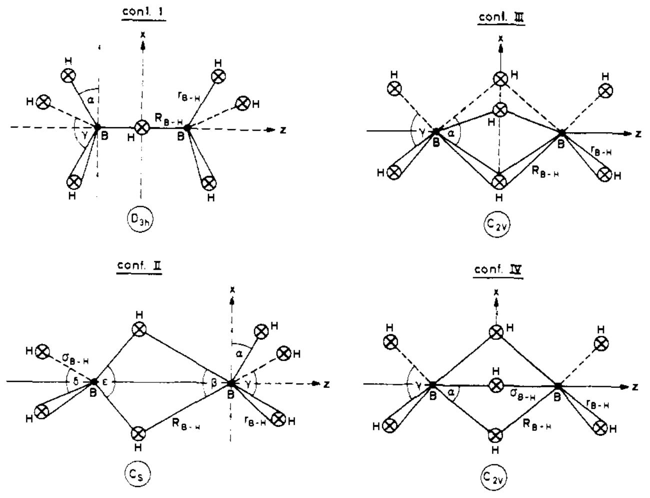

Figure 5. Four possible structures of $B_2H_7^-$

Table VI. Equilibrium Values of BH_5 in C_s Geometry

	CNDO/2	This work
γ, deg	108	119.5
r_{B-H}, Å	1.20	1.19
R_{B-H}, Å	1.31	1.53
r_{H-H}, Å	0.92	0.78

Table VII. Equilibrium Values of $B_2H_7^-$ with D_{3h} Structure

Structure I	Hall et al.[25]	This work
r_{B-H}, Å	1.223	1.225 (2.315 a_0)
R_{B-H}, Å	1.309	1.323 (2.550 a_0)
γ, deg	113.8	114.3
α, deg	14.7	14.0
E_{BIND}(SCF), kcal/mol	−25.1	−24.8
E_{BIND}(CEPA), kcal/mol		−28.1

VI. Comment on the Experiments Concerning BH_5

The existence of BH_5 as postulated from experiments[9-11] is confirmed by our calculations. To explain the isotope exchange results[9-11] it is not sufficient that BH_5 exists; one has also to postulate that the barrier for isomerization is sufficiently small. From our calculation this barrier, namely the energy difference between structures I and V, equals ~9 kcal/mol (CEPA); however, the barrier is above the dissociation limit to $BH_3 + H_2$. One would therefore expect that the decomposition of BH_5 into $BH_3 + H_2$ is much faster than the isomerization, which is in contradiction to the experimental findings.

A possible explanation of this discrepancy is that the experiments were done in solution whereas the calculations were done for molecules "in space". Both BH_4^- and the protolyzing H^+ are solvated and consequently the BH_5 formed is trapped in a solvating sphere. Thus BH_5 has probably enough energy to isomerize several times before BH_3 and H_2 can "escape" from the solvation sphere.

VII. SCF Calculations of $B_2H_7^-$

Four possible structures of $B_2H_7^-$ are illustrated in Figure 5. Hall, Marynick, and Lipscomb[25] performed an SCF calculation of structure I of $B_2H_7^-$ with a linear B-H-B bridge, using a minimal STO basis. They obtained the structure parameters that are compared in Table VII with our results from SCF calculations with the "large" basis. We have also performed SCF calculations for structure II with two (bent) B-H-B bridges and structures III and IV with three bridges. The optimum geometries for these structures are indicated in Table VIII. We have optimized structures II, III, and IV under the contraint that they have C_s and C_{2v} symmetry, respectively, such that the two bridges in structure II and two of the three bridges in structures III and IV are symmetrically equivalent. Also the local threefold axes in structures II and IV were imposed. Under these constraints minima for these structures were found. The minimum for structure III lies 250 kcal/mol and that of structure IV 200 kcal/mol above the sum of the energies of BH_4 and BH_3, whereas both structures I and II are bound with respect to $BH_3 + BH_4^-$, namely structure I by 25 kcal/mol and structure II by 6 kcal/mol. This clearly indicates that bonding through a single B-H-B bond is most effective. In structure II one recognizes BH_3 and BH_4^- subunits, whereas in structure I two equivalent BH_3 subunits and a H^- in the bridge are found. The ion in structure I turns out to be stable with respect to asymmetric deformations, in agreement with Hall et al.,[25] i.e., it has D_{3h} symmetry although only C_{2v} symmetry was imposed. (We did not investigate the possible difference in energy between a "staggered" and "eclipsed" structure; this difference is probably very small.) While the B-H-B bond in structure I prefers to be symmetric, the two B-H-B bonds in structure II are definitely asymmetric. If one forces them to be symmetric the energy is raised by ~60 kcal/mol. We did not investigate whether in going from structure II to structure I there is a barrier, but we think that this is unlikely and that structure II does not represent a local minimum. Structures III and IV have unexpectedly high energies and unexpectedly large BH distances in the bridges.

VIII. Correlation Energy of $B_2H_7^-$

For $B_2H_7^-$ a full calculation with the "large" basis and with inclusion of correlation is possible but somewhat time consuming. We therefore performed the calculation of the correlation energy "in pieces". For structure I we performed a calculation with the large basis for the "left" half of the molecule plus the B-H-B bond and the small basis

Table VIII. Equilibrium Values of $B_2H_7^-$ in C_s Symmetry and C_{2v} Symmetry

Structure II	SCF-optimized values C_s symm	Structure III	SCF-optimized values C_{2v} symm	Structure IV	SCF-optimized values C_{2v} symm
r_{B-H}, a_0	2.30	r_{B-H}, a_0	2.30	r_{B-H}, a_0	2.30
R_{B-H}, a_0	4.00	R_{B-H}, a_0	3.15	R_{B-H}, a_0	3.22
τ_{B-H}	2.30			τ_{B-H}, a_0	2.60
α; β; γ, deg	10.0; 57.0; 110.0	α, deg	65	α, deg	72
δ; ε	110.0; 112.0	γ, deg	120	γ, deg	120
E_{BIND}(SCF), kcal/mol	−6.3	E_{BIND}(SCF), kcal/mol	+250[a]	E_{BIND}(SCF), kcal/mol	+196
E_{BIND}(CEPA), kcal/mol	−10.0				

[a] This value was obtained with the small basis, the corresponding values for structures I, II, and IV are −25.6, −7.4, and 187 kcal/mol, respectively.

Table IX. Energies (in au) of B_2H_7 in Four Different Structures

	Large basis			Small basis
Molecule	$-E_{SCF}$	$-E_{IEPA}{}^a$	$-E_{CEPA}{}^a$	$-E_{SCF}$
BH_3	26.3870	26.5121	26.5033	26.3757
BH_4^-	26.9689	27.1475	27.1297	26.9560
$B_2H_7^-$ [I]	53.3953	53.7080	53.6778	53.3725
$B_2H_7^-$ [II]	53.3659	53.6779	53.6489	53.3435
$B_2H_7^-$ [III]				52.9341
$B_2H_7^-$ [IV]	53.0331			53.0331

[a] For $B_2H_7^-$ see text.

for the "right" half. For the left half plus the bridge the full correlation energy in the IEPA-PNO, CEPA-PNO, and PNO-CI schemes was calculated. From twice this correlation energy the contribution of the B-H-B bond was subtracted. In doing so one ignores the interaction terms between BH bonds on different sides of the ion and also some nonadditivity corrections. The error is, as calculations on comparable molecules have shown, at most of the order of 1 kcal/mol. For structure II where the "left" and the "right" half of the molecule are not equivalent, two calculations had to be performed. The total energies with and without correlation are collected in Table IX. Some test calculations indicated that the geometries are not affected appreciably by correlation, we therefore did not reoptimize the geometries. The binding energies which in SCF approximation were ∼−25 and ∼−6 kcal/mol or structures I and II, respectively, are found by CEPA to be −28 and −10 kcal/mol; the experimental value is −30 kcal/mol,[15] so the agreement is rather good. The contribution of the change in correlation energy to the binding energy is not so spectacular as in B_2H_6 or in BH_5.

In spite of the noticeable binding energy of ∼−30 kcal/mol of $B_2H_7^-$ with respect to $BH_3 + BH_4^-$ the B-H-B bond turns out to be very "soft", in the sense that the energy is very insensitive to changes in the B-B distance. Variation of this distance by $\pm 0.1\ a_0$ raises the energy by only 0.002 au. This is found both in calculations with and without correlation.

IX. Conclusion

BH_5 is stable in a C_s structure (analogous to that of CH_5^+) by as little as 2 kcal/mol with respect to $BH_3 + H_2$. Isomerization of BH_5 (i.e., scrambling of the nonequivalent H atoms via a C_{2v} structure) requires 9 kcal/mol. Binding in BH_5 is essentially due to the electron correlation; in the SCF approximation no stable BH_5 is found. Although a previous CNDO calculation predicted qualitatively the equilibrium structure of BH_3, it could not reveal that BH_5 is hardly bound with respect to $BH_3 + H_2$. For $B_2H_7^-$ the symmetric structure with a single B-H-B bond turns out to be the most stable. The calculated binding energy is ∼−25 kcal/mol in SCF approximation and ∼−28 kcal/mol with correlation, in good agreement with the experimental value of −30 kcal/mol. The change in correlation energy is less important than in other boron hydrides.

All known stable molecules with three-center two-electron bonds that involve a H_2 subunit are positive ions. BH_5 is the first neutral molecule of this kind; its very small binding energy results mainly from the poor electron donor properties of H_2. Both in BH_5 and in the "hypothetical" structures II and III of $B_2H_7^-$ B is coordinated by five H atoms. Such a BH_5 coordination is rather unfavorable and if it is present it is very unsymmetric, with three close and two distant H atoms.

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References and Notes

(1) V. L. Tal'rose and A. Lyubimova, *Dokl. Akad. Nauk SSSR*, **86**, 909 (1962).
(2) G. A. Olah and R. H. Schlosberg, *J. Am. Chem. Soc.*, **90**, 2726 (1968).
(3) M. D. Sefcik, J. M. S. Henis, and P. P. Gaspar, *J. Chem. Soc.*, **61**, 4321 (1974).
(4) A. Gamba, G. Morosi, and M. Simonetta, *Chem. Phys. Lett.*, **3**, 20 (1969).
(5) H. Kollmar and H. O. Smith, *Chem. Phys. Lett.*, **5**, 7 (1970).
(6) V. Dyczmons, V. Staemmler, and W. Kutzelnigg, *Theor. Chim. Acta*, **5**, 361 (1970).
(7) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972).
(8) V. Dyczmons and W. Kutzelnigg, *Theor. Chim. Acta*, **33**, 239 (1974).
(9) F. A. Olah, P. W. Westermann, Y. K. Mo, and G. Klopman *J. Am. Chem. Soc.*, **94**, 7859 (1972).
(10) M. M. Kreevoy and J. E. C. Hutchins, *J. Am. Chem. Soc.*, **94**, 6371 (1972).
(11) R. E. Mesmer and W. C. Jolly, *Inorg. Chem.*, **1**, 608 (1962).
(12) R. Ahlrichs, unpublished results, related to ref 13.
(13) R. Ahlrichs, *Theor. Chim. Acta*, **35**, 59 (1974).
(14) R. Ahlrichs and W. Kutzelnigg, *J. Chem. Phys.*, **48**, 1819 (1968).
(15) M. Jungen and R. Ahlrichs, *Theor. Chim. Acta*, **17**, 339 (1970).
(16) R. Ahlrichs, *Theor. Chim. Acta*, **33**, 157 (1974).
(17) W. Meyer, *J. Chem. Phys.*, **5**, 1017 (1973).
(18) R. Ahlrichs, H. Lischka, V. Staemmler, and W. Kutzelnigg, *J. Chem. Phys.*, **62**, 1225 (1975).
(19) R. Ahlrichs and F. Driessler, *Theor. Chim. Acta*, **36**, 275 (1957).
(20) H. Brown, P. Stehle, and P. Tierney, *J. Am. Chem. Soc.*, **79**, 2020 (1957).
(21) D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963).
(22) W. G. Evenas, C. E. Halloway, K. Sukumarabandhu, and D. McDaniel, *Inorg. Chem.*, **7**, 1746 (1968).
(23) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, N.Y., 1963.
(24) M. Gelus, R. Ahlrichs, V. Staemmler, and W. Kutzelnigg, *Chem. Phys. Lett.*, **7**, 503 (1970).
(25) J. H. Hall, Jr., D. S. Marynick, and W. N. Lipscomb, *Inorg. Chem.*, **11**, 1326 (1972).
(26) R. Ahlrichs, *Chem. Phys. Lett.*, **19**, 174 (1973).
(27) R. Ahlrichs, F. Driessler, H. Lischka, V. Staemmler, and W. Kutzelnigg, *J. Chem. Phys.*, **62**, 1235 (1975).
(28) R. Ahlrichs, F. Keil, H. Lischka, W. Kutzelnigg, and V. Staemmler, *J. Chem. Phys.*, **63**, 455 (1975).
(29) R. Ahlrichs, H. Lischka, B. Zurawski, and W. Kutzelnigg, *J. Chem. Phys.*, in press.
(30) J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 303 (1960).
(31) F. Driessler and R. Ahlrichs, *Chem. Phys. Lett.*, **23**, 571 (1973).
(32) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).
(33) The names "small basis" and "large basis" do not have the same meaning as in ref 27–29.
(34) M. Gelus and W. Kutzelnigg, *Theor. Chim. Acta*, **28**, 103 (1973).
(35) B. Tsapline and W. Kutzelnigg, *Chem. Phys. Lett.*, **23**, 173 (1973).
(36) W. Kutzelnigg, V. Staemmler, and C. Hoheisel, *Chem. Phys.*, **1**, 27 (1973).
(37) M. Jungen and R. Ahlrichs, *Mol. Phys.*, **28**, 367 (1974).
(38) W Kutzelnigg, R. Ahlrichs, I. Labib-Iskander, and W. A. Bingel, *Chem. Phys. Lett.*, **1**, 447 (1967).
(39) I. G. Csizmadia, R. E. Kari, J. C. Polanyi, A. C. Roach, and *M. A. Robb, J. Chem. Phys.*, **52**, 6205 (1970).
(40) L. Salem and R. D. Poshusta, *J. Chem. Phys.*, **59**, 3497 (1973).