Theoret. chim. Acta (Berl.) 26, 381—386 (1972)

The Electronic Structure of the $B_2H_5^+$ Ion

B. J. DUKE and D. G. STEPHENS
Department of Chemistry, University of Lancaster, England

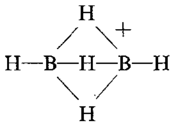
Received January 4, 1972

The $B_2H_5^+$ ion has been studied using the *ab initio* SCF method employing a basis set of Gaussian orbitals and various semi-empirical methods. The most stable structure appears to be a planar structure with two vacant *p* orbitals rather than a triply bridged structure suggested by analogy with acetylene with which it is isoelectronic. The semi-empirical results reinforce earlier conclusions that inclusion of charges from neighbouring atoms in iterative Extended Hückel methods is necessary to satisfactorily treat ionic molecules.

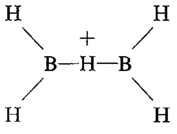
Das $B_2H_5^+$-Ion ist mit Hilfe der *ab initio* SCF-Methode unter Benutzung eines Basissatzes von Gaußorbitalen und mit verschiedenen semiempirischen Methoden untersucht worden. Die stabilste Struktur scheint eine planare Struktur mit zwei leeren *p*-Orbitalen und nicht eine dreifach verbrückte Struktur zu sein, wie sie durch Analogiebetrachtungen am Acetylen nahegelegt wird. Durch die semiempirischen Resultate werden die bereits früher erhaltenen Ergebnisse bestätigt, daß zur zufriedenstellenden Behandlung von Molekülionen mit iterativen erweiterten Hückel-Methoden die Berücksichtigung der Ladungen benachbarter Atome nötig ist.

The mass spectrum of diborane is interesting in that it shows a particularly large peak at mass number corresponding to the $B_2H_5^+$ ion. Indeed the appearance potentials for $B_2H_6^+$ and $B_2H_5^+$ are reported to be identical at 11.9 eV [1]. This suggests an unusually stable structure for the $B_2H_5^+$ ion. This species is also interesting in that it is the borane isoelectronic to acetylene. One of us [2] has already commented on this using a simple Extended Hückel Method with the parameters proposed by Hoffmann and Lipscomb [3] for boranes. Diborane is isoelectronic with ethylene and has a structure with the same symmetry and a similar electronic spectrum. The diborohydride ion $B_2H_7^-$ is isoelectronic with ethane and is thought [4, 5] to have a structure with the same symmetry containing one B—H—B bridge.

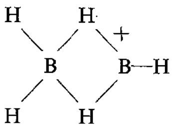
In the course of developing and testing empirical methods based on the Extended Hückel Method it is important to correct the difficiences of the simple methods of this type for charged species and to test methods for these species against more accurate *ab initio* wave functions. The several possible structures for the $B_2H_5^+$ ion are ideal for this purpose. *Ab initio*, and semi-empirical methods for this species have been studied. Three possible structures have been considered two of which are identical to those discussed earlier [2].



I



II



III

Structure I has D_{3h} symmetry with three B–H–B bridges. It has the same structural relation to acetylene as diborane has to ethylene and involves no vacant orbitals. Structure II is planar with only one B–H–B bridge. There are two vacant *p* orbitals on the boron atoms. The twisted form with the terminal groups normal to each other is likely to be the preferred conformation. Semi-empirical calculations described later indicate that this is so but the planar form has been used for the main calculations. Structure III is the simplest structure arising from the removal of one hydrogen atom. Geometries were chosen in a simple manner. All terminal B–H bonds were taken as 1.19 Å and all bridge B–H bonds as 1.33 Å. In structure II the bond angles are 120°. In structure III the structure is identical to that of diborane with the odd terminal bond moved down into the line of the boron atoms. In structure III the angles and thus the B–B length were calculated assuming a *sp* hybrid pointing to the terminal bond and three equivalent hybrids pointing to the bridge atoms. This gives a B–B distance of 1.53 Å. It should be noted that a similar argument using sp^2 hybrids closely predicts the structure of the bridge region of diborane.

Calculational Methods

a) Ab initio Method

A basis set of 5*s*-type and 2*p*-type Gaussian orbitals on the boron atom and 2*s*-type Gaussian orbitals on the hydrogen atoms was used. This gives a total of 32 orbitals. All integrals were calculated, the SCF equations solved and a Mulliken population density matrix analysis carried through using the POLYATOM program [6] obtained from QCPE [7] and modified to run on the ICL 1909 Computer. Since these calculations on this computer are slow only a limited number were made. The Gaussian orbital exponents used were

B *s*	0.216	1.076	5.367	26.677	132.85
B *p*	0.149	0.878			
H *s*	0.27	1.8			

This basis set is identical to the smaller basis set used by Burnelle and Kaufmann [8] for diborane.

b) Semi-Empirical Methods

Five semi-empirical methods have been employed – EHM, IEHM, NCC, CNDO-A and CNDO-B. EHM is the simple Extended Hückel Method. IEHM is an iterative variant in which the diagonal *H* matrix elements are modified by the atomic charge of the same atom. NCC is a further variant in which the diagonal H matrix elements are also modified by the atomic charge on all other atoms. The NCC method has been studied in detail by Duke and Stephens [9] and an outline of the method published by Armstrong, Duke and Perkins [10]. CNDO-A and CNDO-B are variants in the original Complete Neglect of Differential Overlap (CNDO) method proposed by Pople and Segal [11]. The five methods are identical in all respects including the choice of parameters to methods 1, 3, 4, 5 and 6 used by Armstrong, Duke and Perkins [10] for Aminoborane.

Results and Discussions

Results of the *ab initio* method will be discussed first as this allows a prediction of the most stable structure and a basis for judging the empirical or semi-empirical methods.

a) Ab initio Total Energies

Structure II has the lowest energy. Since Structure I is rather restricted in the bridge region and has a high nuclear repulsion energy this calculation was repeated with the geometry of the bridge region expanded by 5%, the terminal bonds remaining at 1.19 Å. This will be described as Structure I(b) with the original structure as I(a). Results are shown in Table 1. All energies are expressed in the atomic unit of energy (1 Hartree 27.21 eV).

Orbital energies and atomic population charges are reported in Tables 2, 3 and 4 for comparison with other methods. The total energies are close. Relative to the energy of the lowest Structure II these are (in Kcals).

I(a)	18.83
I(b)	12.68
III	19.36

Table 1

Structure	I(a)	I(b)	II	III
$E_{electronic}$	−80.799	−79.6961	−74.4034	−78.7818
$E_{nuclear}$	29.3718	28.2586	22.9457	27.3550
E_{total}	−51.4277	−51.4375	−51.4577	−51.4269

Table 2. $B_2H_5^+$ structure I(a)—D_{3h}

	Orbital energies and atomic charges					
	SCF	EHM	IEHM	NCC	CNDO-A	CNDO-B
A_1'	−0.8377	−0.5146	−0.5910	−0.7816	−1.0238	−0.9048
E'	−0.8498	−0.5152	−0.6225	−0.8216	−1.1358	−0.9727
A_2''	−0.8932	−0.6258	−0.6961	−0.8936	−1.1595	−1.0310
A_1'	−1.2870	−0.8064	−0.9218	−1.1484	−1.8148	−1.6138
q_B	0.163	0.577	0.265	0.273	0.041	0.256
q_{H-t}	0.167	−0.126	0.030	0.019	0.124	0.071
q_{H-b}	0.113	0.033	0.137	0.139	0.223	0.116

Table 3. $B_2H_5^+$ structure II – D_{2h}

	Orbital energies and atomic charges					
	SCF	EHM	IEHM	NCC	CNDO-A	CNDO-B
B_{3g}	−0.7454	−0.5078	−0.5942	−0.7539	−0.9656	−0.8392
B_{2u}	−0.7604	−0.5180	−0.6095	−0.7731	−1.0220	−0.8824
A_g	−0.8045	−0.5179	−0.6296	−0.7993	−1.0595	−0.9209
B_{1u}	−0.9312	−0.7063	−0.7985	−0.9720	−1.1929	−1.0746
A_g	−1.0444	−0.7697	−0.8879	−1.0777	−1.4245	−1.2888
q_B	0.512	0.739	0.335	0.425	0.421	0.516
q_{H-t}	0.085	−0.126	0.047	0.013	0.043	0.005
q_{H-b}	−0.366	0.026	0.141	0.097	−0.012	−0.049

Table 4. Total energy

	I	II	III	
"Correct" total energy				
SCF	−51.428	−51.458	−51.427	III > I > II
CNDO-A	−11.524	−10.847	−11.291	II > III > I
CNDO-B	− 5.844	− 6.543	− 6.071	I > III > II
"Sum of orbital" total energy				
EHM	− 5.953	− 6.036	− 5.978	I > III > II
IEHM	− 6.905	− 7.036	− 6.927	I > III > II
NCC	− 8.931	− 8.749	− 8.846	II > III > I
SCF	− 9.435	− 8.572	− 9.110	II > III > I
CNDO-A	−12.539	−11.329	−12.051	II > III > I
CNDO-B	−10.990	−10.012	−10.595	II > III > I

On the basis of bond dissociation energies, Koski *et al.* [1] predicted that $B_2H_5^+$ would be formed by removal of a terminal hydrogen atom from diborane. This would suggest Structure III for the ion. This *ab initio* calculation suggests that the structure has a higher energy than the planar form. It is not of course possible from this limited calculation to predict the energy necessary for Structure III to rearrange to Structure II. Structure III may therefore be the actual structure involved in the mass spectra results, even though energy would be gained in a rearrangement to the planar form. The triple bridge structure both on energy criteria and on the basis of its lack of similarity to the parent molecule seems unlikely. However since this structure is an electronic closed shell this structure is a possibility if the $B_2H_5^+$ could ever be stabilised by a suitable solvent and anion in solution. There is however no evidence for this species in solution.

b) Semi-Empirical Methods

Results for the semi-empirical methods are given in Tables 2 and 3 for structures I and II as examples. Results for structure III show similar features. The Extended Hückel methods and its two variants show similar results to those obtained for other positive ions such as the ammonium ion [9]. The orbital energies are too high unless neighbouring atom charges are included. The CNDO results are similar to those obtained for aminoborane [10]. Orbital energies are too low, but the charges are predicted with more accuracy than by the Extended Hückel methods. Similar results are obtained for all three structures. Within the Extended Hückel approach it is clearly necessary to include neighbouring atom terms. The NCC method gives overall better results than EHM or IEHM for both orbital energies and charges. The CNDO methods give good charges but with the parameters used in this work they give poor orbital energies.

Table 4 gives estimates for the total energy for the three structures. EHM, IEHM and CNDO-B agree with the SCF results in predicting structure II to be the most stable. NCC and CNDO-A however give the reverse of the order of stability predicted by the SCF method. No semi-empirical method studied here predicts the same order of stability as the SCF method. These results should however be viewed with caution. The CNDO methods by using the full Hamiltonian, use the correct expression for the energy within the framework of the CNDO approximations. The total energy results, in conjunction with the orbital energies, clearly show CNDO-B to be better than CNDO-A. The total energy term for the Extended Hückel methods is a simple sum of orbital energies. Inclusion of the additional terms in IEHM and NCC is however equivalent to the inclusion of electron repulsion terms and these should perhaps be included in the total energy expression. There is however no unique division between one-electron and two-electron terms within the IEHM and NCC methods. Work is in hand on testing various total energy expressions which include the additional parameters used in IEHM and NCC along with nuclear repulsion terms. The simple sum of orbital energies is however used for the IEHM and NCC method in Table 4 and there is therefore no reason to expect these methods to be better than EHM.

It is interesting to note that the sums of orbital energies for the NCC method and both CNDO methods, are in the same order as those from the SCF functions. The sum of orbital energies for the SCF function does not predict the same order of stability as the correct total energies. This supports the view that a better energy expression needs to be derived for the iterative methods.

This study of semi-empirical methods confirms earlier work that the NCC method gives the best overall agreement with SCF results and that within the Extended Hückel method inclusion of terms from neighbouring atoms is essential for ionic species.

Acknowledgement. We wish to thank the Peel Studentship Trust of the University of Lancaster for the award of a scholarship to one of us (D.G.S.).

References

1. Koski, W. S., Kaufmann, J. J., Pachucki, C. F., Shipko, F. J.: J. Amer. chem. Soc. **80**, 3202 (1958).
2. Duke, B. J.: Nature **209**, 1234 (1966).
3. Hoffmann, R., Lipscomb, W. N.: J. chem. Physics **37**, 2872 (1962).
4. Gaines, D.: Inorg. Chem. **2**, 523 (1963).
5. Duke, B. J., Howarth, O. W., Kenworthy, D. G.: Nature **202**, 81 (1964).

6. Czismadia, I. G., Harrison, M. C., Moskowitz, J. W., Sutcliffe, B. T.: Theoret. chim. Acta (Berl.) **6**, 191 (1966).
7. — — — Seling, S., Sutcliffe, B. T., Barnett, M. P.: Q.C.P.E. Program 14 (Polyatom), Indiana University, Indiana, USA.
8. Burnelle, L., Kaufmann, J. J.: J. chem. Physics **43**, 3540 (1965).
9. Duke, B. J., Stephens, D. G.: Unpublished work.
10. Armstrong, D. R., Duke, B. J., Perkins, P. G.: J. chem. Soc. (A), 2566 (1969).
11. Pople, J. A., Segal, G. A.: J. chem. Physics **44**, 3289 (1966).

Dr. B. J. Duke
Department of Chemistry
University of Lancaster
Lancaster, England