

A Floating Spherical Gaussian Orbital Model of Molecular Structure

VII. Borazane and Diborane

ARTHUR A. FROST

Department of Chemistry, Northwestern University, Evanston, Illinois

Received March 18, 1970

The FSGO model has been used to make *ab initio* calculations of the geometrical structures of borazane and diborane. Where experimental data are available there is good agreement between calculated and observed values.

Für *ab initio*-Rechnungen zur geometrischen Struktur des Borazans und Diborans wurde das FSGO-Modell benutzt. Soweit experimentelle Werte vorhanden sind, stimmen die berechneten und beobachteten Werte gut überein.

La méthode FSGO a été utilisée pour effectuer des calculs *ab-initio* sur les structures géométriques du borazane et du diborane. Un bon accord est obtenu entre les valeurs calculées et les valeurs expérimentales existantes.

1. Introduction

The floating spherical Gaussian orbital (FSGO) model is discussed in detail in Paper I of this series [1–6]. As currently applied, the model predicts the electronic and geometric structure of singlet ground states of molecules with localized orbitals without the use of any arbitrary or semiempirical parameters. The localized orbitals are constructed by using single normalized spherical Gaussian functions,

$$\varphi_i(\mathbf{r} - \mathbf{R}_i) = \left(\frac{2}{\pi q_i^2} \right)^{3/4} \exp[-(\mathbf{r} - \mathbf{R}_i)^2/q_i^2] \quad (1)$$

with orbital radius, q_i , and position \mathbf{R}_i . A single Slater determinant represents the total electronic wave function. If \mathbf{S} is the overlap matrix of the set of non-orthogonal localized orbitals $\{\varphi_i\}$ and $\mathbf{T} = \mathbf{S}^{-1}$, then the electronic energy expression for a molecule is

$$E = 2 \sum_{j,k} (j|k) T_{jk} + \sum_{k,l,p,q} (kl|pq) [2T_{kl}T_{pq} - T_{kq}T_{lp}] \quad (2)$$

where $(j|k) = \int \varphi_j h \varphi_k dv$; $h = 1$ electron operator and

$$(kl|pq) = \int \varphi_k(1) \varphi_l(1) \frac{1}{r_{12}} \varphi_p(2) \varphi_q(2) dv_1 dv_2.$$

The nuclear repulsion energy is added to the electronic energy and the total energy is minimized by a direct search procedure with respect to all parameters: orbital radii, q_i , orbital positions, \mathbf{R}_i , and nuclear positions.

Papers II, III, and IV presented the results of calculations for many hydrides of first-row atoms and other simple molecules. Paper V described one version of the computer program. Paper VI presented results using double Gaussian orbitals.

Although the use of double Gaussians [6] improves the total energy of a molecule there is only a slight effect on the geometry. Therefore it is desirable to make further calculations with the simpler single Gaussian model inasmuch as much less computer time is required. It was shown [3] that the best bond lengths were obtained with elements in the middle of the first row. Accordingly many hydrocarbons were calculated with success [4]. Therefore, it would also be supposed that the model would do well when applied to boron and nitrogen compounds.

These calculations can be considered as approximate SCF calculations with an absolute minimum basis set, that is, a set of n orbitals for n electron pairs.

Borazane ($\text{BH}_3\text{—NH}_3$, Ammonia Borane)

Energy calculations have been made on borazane by Hoffman [7] using the extended Hückel method and by Veillard *et al.* [8] and by Tinland [9] using the SCF-LCAO-MO method with Gaussian orbitals. In the latter strictly *ab initio* calculations the geometry was fixed and attention was paid to the energy levels, the total energy, and the electron population analysis. No attempt was made to find the equilibrium geometry by minimization.

Peyerimhoff and Buenker [10] carried out SCF-MO as well as CI calculations. By minimizing the total energy with respect to the B–N internuclear distance while keeping the remaining bond distances and angles fixed they predict an equilibrium distance of 3.275 bohr compared with experimental value of 2.95 bohr obtained by Hughes [11].

The present FSGO calculation of borazane was done in the simplest manner by assuming an ethane-like staggered C_{3v} symmetrical structure. The 18 electrons were placed in 9 doubly-occupied orbitals of which 2 were assumed to be inner shell orbitals centered on the B and N nuclei, 3 orbitals for B–H bonds, 3 for N–H bonds and the ninth for the B–N bond. With the above constraints a full minimization was carried out requiring variation of 15 nonlinear parameters. These included 5 nuclear coordinates, 5 orbital radii and 5 orbital position parameters. The final variation in the search for the minimum determined the parameters to within about 0.1%. Table 1 shows the resulting geometry as indicated by bond distances and bond angles as well as the energy and dipole moment. Table 2 gives the coordinates of each nucleus and of each orbital center as well as the orbital radii. The nitrogen nucleus was arbitrarily fixed at the origin and the x -axis as the three-fold axis.

The only comparison with experiment is that for the B–N internuclear distance which was calculated to be 3.041 bohr. This is closer to the experimental value of 2.95 than the value 3.275 of Peyerimhoff and Buenker referred to above. Perhaps the improvement in the present calculation resulted from the relaxation of the whole molecule as opposed to the rigid treatment of the NH_3 and BH_3

Table 1. Borazane calculated results

Bond distances (bohr)			
BN	3.041	✕ BNH	116.0°
BH	2.423	✕ NBH	105.4°
NH	1.884	✕ HNH	102.2°
		✕ HBH	113.2°
Total Energy	-69.852 hartree		
Dipole Moment	5.46 D		

Table 2. Borazane parameters

Nucleus	Charge	Coordinates (bohr)		
		X	Y	Z
N	7.0	0.0	0.0	0.0
B	5.0	3.041	0.0	0.0
H	1.0	-0.826	0.846	1.466
H	1.0	-0.826	0.846	-1.466
H	1.0	-0.826	-1.693	0.0
H	1.0	3.684	2.336	0.0
H	1.0	3.684	-1.168	2.023
H	1.0	3.684	-1.168	-2.023
Orbital ^a	Radii	X	Y	Z
SN	0.277	0.0	0.0	0.0
SB	0.400	3.041	0.0	0.0
HN	1.498	-0.381	0.373	0.646
HN	1.498	-0.381	0.373	-0.646
HN	1.498	-0.381	-0.746	0.0
HB	1.889	3.492	1.749	0.0
HB	1.889	3.492	-0.874	1.514
HB	1.889	3.492	-0.874	-1.514
BN	1.533	0.487	0.0	0.0

^a Orbital notation: SN, SB, inner shell orbitals; HN, HB, BN, corresponding bond orbitals.

portions by them. Of course the present calculated total energy of -69.852 hartree is well above their calculated SCF value of -82.5754 because of the poor representation of the inner shells with simple Gaussians. This result agrees with other FSGO calculations in that about 85% of the Hartree-Fock limit is obtained [3]. The calculated dipole moment, 5.46 D, compares with 5.72 D computed by Peyerimhoff and Buenker and the experimental value, 4.9 D, obtained by Weaver *et al.* [12].

The B-H and N-H distances are close to the FSGO values calculated for the free BH₃ and NH₃ molecules [3], for B-H, 2.423 as compared with 2.353, and for N-H, 1.884 compared with 1.910 bohr. The total energy of -69.852 hartree may be compared with the sum of the FSGO energies of NH₃ (-47.568) and BH₃ (-22.297). The difference, which should represent a dissociation energy,

indicates that the borazane molecule is unstable by 0.013 hartree. This is probably unreliable because of the large errors in the total energies as compared with Hartree-Fock values.

Diborane

B_2H_6 has been the subject of many theoretical calculations on account of its unusual structure. Recent *ab initio* calculations are the SCF calculations of Buenker *et al.* [13], Palke and Lipscomb [14], Burnelle and Kaufman [15], and Switkes *et al.* [16]. In all of these the geometry was fixed at experimental values.

Hensen [17] applied an ionic model calculation to determine the geometrical parameters theoretically. The present FSGO model is more closely related to Hensen's than to the typical SCF-LCAO-MO calculation.

In the present calculations the 16 electrons were placed in pairs in 8 floating spherical Gaussian orbitals. Two of these orbitals were assumed to be inner shell orbitals nearly centered on the boron nuclei. The remaining 6 orbitals were considered bonding orbitals and were initially placed at appropriate positions depending upon what was assumed about the nuclear geometry. Several calculations were performed both with the accepted geometry and with distorted geometries. Upon minimization of the energy an initial distorted structure invariably relaxed to the D_{2h} symmetrical structure. In this symmetrical structure 4 orbitals are B-H bonding orbitals to terminal H's and 2 are so-called three-center bonding orbitals located towards each of the bridge H's. In determining the final geometrical bond distances and bond angles for the symmetrical structure 11 non-linear parameters or combinations were varied. These included 4 nuclear position parameters, 3 orbital radii, and 4 orbital position parameters. One of the latter, which allowed the inner shell orbitals to float off their respective nuclei, could have been omitted as the effect is almost negligible. In searching for the minimum energy the parameters were varied down to about 0.001% of their values. The final results are in Tables 3 and 4.

Table 3. *Diborane results*

Bond ^a	Hensen ^b calculation	This calculation	Experimental ^c
Bond distances (bohr)			
B-B	4.31	3.47	3.35
B-H _t	1.89	2.34	2.25
B-H _b	2.48	2.61	2.53
Angles (degrees)			
B-B-H _t	118.2	117.2	119.9
H _b -B-H _b	61.1	96.7	97.0
H _t -B-H _t	123.6	125.6	120.2

^a Atom notation: H_t, terminal H; H_b, bridge H.

^b Ref. [17].

^c Ref. [18] values converted to atomic units.

Table 4. *Diborane parameters*

Nucleus	Charge	Coordinates (bohr)		
		X	Y	Z
B	5.0	0.0	0.0	1.733
B	5.0	0.0	0.0	-1.733
H _t	1.0	2.082	0.0	2.801
H _t	1.0	-2.082	0.0	2.801
H _t	1.0	2.082	0.0	-2.801
H _t	1.0	-2.082	0.0	-2.801
H _b	1.0	0.0	1.947	0.0
H _b	1.0	0.0	-1.947	0.0
Orbital	Radius	Coordinates (bohr)		
		X	Y	Z
S	0.400	0.0	0.0	1.732
S	0.400	0.0	0.0	-1.732
BR	1.900	0.0	1.257	0.0
BR	1.900	0.0	-1.257	0.0
HB	1.850	1.468	0.0	2.485
HB	1.850	-1.468	0.0	2.485
HB	1.850	1.468	0.0	-2.485
HB	1.850	-1.468	0.0	-2.485

The bond distances and bond angles agree with the experimental results of Bartell and Carroll [18] within two or three per cent which is typical of previous FSGO calculations. The total energy of -44.592 hartree is small in magnitude as compared with the best SCF result, -52.7551 , of Buenker *et al.* [13]. Again the fraction is about 85%, the defect being mostly in the poor representation of the inner shell. In principle the dissociation energy of B_2H_6 into $2BH_3$ can be calculated. The result $2(-22.297) + 44.592 = -0.002$ is probably not significant on account of the poor total energies.

The present calculation differs from most others in predicting the complete geometry of the diborane molecule. In comparison with the Hensen [17] calculation which also predicts geometry the FSGO method not only produces more accurate geometry but also does it by a strictly *ab initio* quantum mechanical calculation.

Acknowledgements. Miss Virginia Fiedler kindly assisted in the computations. The research was supported by a grant from the National Science Foundation.

References

1. Frost, A. A.: *J. chem. Physics* **47**, 3707 (1967), Paper I.
2. — *J. chem. Physics* **47**, 3714 (1967), Paper II.
3. — *J. physic. Chem.* **72**, 1289 (1968), Paper III.
4. — Rouse, R. A.: *J. Amer. chem. Soc.* **90**, 1965 (1968), Paper IV.
5. — — Vesceilius, L.: *Int. J. quant. Chemistry* II S, 43 (1968), Paper V.
6. Rouse, R. A., Frost, A. A.: *J. chem. Physics* **50**, 1705 (1969), Paper VI.
7. Hoffmann, R.: *J. chem. Physics* **40**, 2474 (1964).

8. Veillard, A., Levy, B., Daudel, R., Gallais, F.: *Theoret. chim. Acta (Berl.)* **8**, 312 (1967).
Moireau, M.-Cl., Veillard, A.: *Theoret. chim. Acta (Berl.)* **11**, 344 (1968).
9. Tinland, B.: *J. molecular Structure* **3**, 244 (1968).
10. Peyerimhoff, S. D., Buenker, R. J.: *J. chem. Physics* **49**, 312 (1968).
11. Hughes, E. W.: *J. Amer. chem. Soc.* **78**, 502 (1956).
12. Weaver, J. R., Shore, S. G., Parry, R. W.: *J. chem. Physics* **29**, 1 (1958).
13. Buenker, R. J., Peyerimhoff, S., Allen, L. C., Whitten, J. L.: *J. chem. Physics* **45**, 2835 (1966).
14. Palke, W. E., Lipscomb, W. N.: *J. Amer. chem. Soc.* **88**, 2384 (1966).
15. Burnelle, L., Kaufman, J. J.: *J. chem. Physics* **43**, 3540 (1965).
16. Switkes, E., Stevens, R. M., Lipscomb, W. N.: *J. chem. Physics* **51**, 2085 (1969).
17. Hensen, K.: *Theoret. chim. Acta (Berl.)* **14**, 273 (1969).
18. Bartell, L. S., Carroll, B. L.: *J. chem. Physics* **42**, 1135 (1965).

Professor Arthur A. Frost
Department of Chemistry
Northwestern University
Evanston, Illinois 60201, USA