

## Nonrigid molecular behaviour of beryllium borohydride I. INDO study

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MS received 6 November 1979; revised 16 January 1980

**Abstract.** Potential barriers of internal motions in three different structures of beryllium borohydride have been calculated by the INDO method. INDO results show that only two structures can be optimised along the path of interconversion.

**Keywords.** Internal motion; potential barrier; INDO; beryllium borohydride.

### 1. Introduction

The structure of beryllium borohydride has been a puzzle to the chemists from time to time. Available experimental data indicate the presence of more than one structure undergoing rapid interconversions among themselves (Almerningen *et al* 1967; Burg and Schlesinger 1940; Cook and Morgan 1969; Marynick and Lipscomb 1971, 1972; Nibler 1972; Silbiger and Bauer 1946; Stosick 1952; Nibler and McNabb 1969; Nibler and Dyke 1970). *Ab initio* Hartree-Fock Self-Consistent-Field Configuration-Interaction (HFSCF/CI) studies by Marynick and Lipscomb (1973) show that three possible structures may coexist and undergo a rapid intermolecular hydrogen tautomerism. These three structures belong to the  $D_{2d}$ ,  $C_4$  and  $D_{3d}$  point group symmetry, the second one being primarily responsible for the observed dipole moment of  $2.1 D$  (Nibler and McNabb 1969; Nibler and Dyke 1970).

If beryllium borohydride is to be considered as a fluxional molecule, a permutational group-theoretical analysis using the notion of proper generators (Trindle and Bouman 1975) may be carried out in order to evaluate the properties of the system. Such a study requires the knowledge of potential barriers to various internal motions, and interconversions among different possible structures. In this work we report the INDO results for these potential barriers.

### 2. Calculations

We choose the three optimised structures of Marynick and Lipscomb (1973) and call the  $D_{2d}$ ,  $C_4$  and  $D_{3d}$  structures as structures 1, 2 and 3. We investigate the

following internal motions: (i) Internal rotations of  $H_2^1B$ ,  $-BH_2^2Be-$  and  $H_2^3BH_2^4Be-$  groupings in structures 1 and 2 and of  $H^1-BH_2^2Be$  group of structure 3; (ii) (3, 6) permutations and simultaneous (3, 6), (4, 5) permutations of hydrogens in structure 1, (3, 6) permutation in structure 2 and (3, 7) permutation in structure 3. More simultaneous multiple permutations are not considered since the potential barriers in single and double pair permutations in structure 1 turn out to be nearly equal and quite high so that these motions may not significantly contribute to the non-rigidity of the species. The structures 1, 2 and 3 are shown in figure 1.

Since structure 2 appears as a stable intermediate between structures 1 and 3 we investigate only 1-2 and 2-3 interconversions. The paths of these interconversions are chosen in accordance with the McIver-Stanton symmetry rules (McIver and Stanton 1972; Stanton and McIver 1975) and are shown in figure 1.

### 3. Discussion

We show the relative stabilities of the three structures in table 1a. Although the INDO results show a reverse order of stability, the trend is quite inconclusive since all the three structures are comparable in stability. Table 1b shows the valence orbital energies for the three structures. The lowest virtual orbital in the  $D_{2d}$  structure degenerates giving rise to the possibility of the existence of a low-lying Jahn-Teller excited state of distorted molecular symmetry which may contribute to the ground state dipole moment.

The potential barriers in various internal rotations and permutations are shown in table 2. Most of the processes involve high energy barriers and are not expected to contribute to the non-rigidity of the species. Internal rotations of the  $H_2^1BH_2^2Be-$  group in structure 2 and that of the  $H^1BH_2^2Be$  group in structure 3 are associated with relatively small barriers. These motions are important in determining the flexibility of each individual structure.

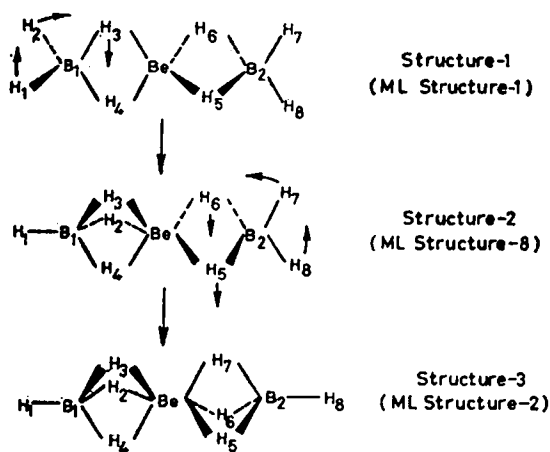


Figure 1. Structures of beryllium borohydride and the interconversion routes.

Table 1a. Relative energies of the structures of beryllium borohydride.

Structure	Relative energy in kcal. mol <sup>-1</sup>	
	INDO calculation	<i>Ab initio</i> / CI*
1	0.00	0.00
2	-33.67	6.5
3	-76.62	7.3

\* From Merynick and Lipscomb (1973).

Table 1b. INDO valence orbital energies for the structures of beryllium borohydride.

Structure 1		Structure 2		Structure 3	
<i>D</i> <sub>2d</sub>	A.u.	<i>C</i> <sub>s</sub>	A.u.	<i>D</i> <sub>3d</sub>	A.u.
<i>A</i> <sub>1</sub>	-1.3621	<i>A'</i>	-1.3975	<i>A</i> <sub>1g</sub>	-1.4198
<i>B</i> <sub>1</sub>	-1.2513	<i>A'</i>	-1.2532	<i>A</i> <sub>2u</sub>	-1.2669
<i>E</i>	-0.7934	<i>A''</i>	-0.8516	<i>E</i> <sub>u</sub>	-0.8387
<i>A</i> <sub>1</sub>	-0.7345	<i>A'</i>	-0.7864	<i>A</i> <sub>1u</sub>	-0.7344
<i>B</i> <sub>1</sub>	-0.6587	<i>A'</i>	-0.7385	<i>A</i> <sub>2u</sub>	-0.6645
<i>E</i>	-0.6372	<i>A'</i>	-0.6538	<i>E</i> <sub>g</sub>	-0.5920
<i>E</i>	0.2596	<i>A'</i>	-0.6291	<i>A</i> <sub>1g</sub>	0.1878
<i>A</i> <sub>1</sub>	0.1890	<i>A''</i>	-0.5891	<i>E</i> <sub>w</sub>	0.2206
		<i>A'</i>	0.1492		
		<i>A'</i>	0.1845		
		<i>A'</i>	0.2200		

Table 1c. Choice of INDO parameters.

	H	Be	B
$-\beta_A^0$ (eV)	9	13	17
<i>G</i> <sup>1</sup> (Au)	..	0.1407	0.199265
<i>F</i> <sup>3</sup> (Au)	..	0.089125	0.13041
<i>Z'</i> (STO exponent)	1.2	1.95	2.6
$\frac{1}{2}(I + A)$ (eV)	13.06 (1s)	9.32 (2s)	14.05 (2s)
		5.96 (2p)	8.30 (2p)

The various terms are as denoted in the reference by Pople *et al* (1967).

Table 1d. Atomic coordinates in Å.

	x	y	z
I. $D_{3d}$			
H <sup>f</sup>	1.0389	0.0	2.4988
H <sup>b</sup>	0.0	1.0227	1.0790
B	0.0	0.0	1.9182
Be	0.0	0.0	0.0
II. $C_s$			
H <sup>f</sup>	0.0	0.0	-2.9202
H <sup>b</sup>	1.1529	0.0	-1.1618
H <sup>b</sup>	-0.5716	0.9921	-1.2453
H <sup>b</sup>	-0.5716	-0.9921	-1.2453
H <sup>f</sup>	1.0391	0.0	2.5044
H <sup>f</sup>	-1.0391	0.0	2.5031
H <sup>b</sup>	0.0	1.0206	1.1132
H <sup>b</sup>	0.0	-1.0206	1.1132
B	0.0	0.0	1.9227
B	0.0	0.0	-1.7436
Be	0.0	0.0	0.0
III. $D_{3d}$			
H <sup>f</sup>	0.0	0.0	2.9217
H <sup>b</sup>	-1.1458	0.0	1.2290
B	0.0	0.0	1.7437
Be	0.0	0.0	0.0

Reference : Marynick and Lipscomb (1973).

The 1-2 interconversion has a small potential barrier of 1.132 kcal mol<sup>-1</sup> with respect to structure 1, but the 2-3 process does not have any barrier at all. Structures 2 and 3 appear to be related by large amplitude vibrational motions. This result casts serious doubt on the geometry optimisation of Marynick and Lipscomb (1973). The conventional procedure of geometry optimisation involves optimisation along a few symmetry coordinates without disturbing the gross symmetry of the species, thus giving rise to the possibility of overlooking optimisation along a possible interconversion path. Our calculation shows that either structure 2 or structure 3 (but not both at the same time) is to be considered as the stable isomer. After considering correlation effects (HFSCF/CI) one may choose structure 2 as the more stable configuration.

The reverse order of stability in table 1 casts serious doubt on the quantitative reliability of the INDO method in dealing with the fluxional behaviour related to the interconversion mechanism. This work uses results from a standard CNINDO program of the Quantum Chemistry Program Exchange (QCPE No. 194) of Indiana University, based on the work of Pople and co-workers (Pople *et al* 1965, 1967; Pople and Segal 1965, 1966). We also include the INDO parameters, the

Table 1e. Calculated Coulomb integrals in Å.

Structure 1		Structure 2		Structure 3	
H <sub>4</sub> -H <sub>4</sub>	0.7500	H <sub>4</sub> -H <sub>4</sub>	0.7500	H <sub>4</sub> -H <sub>4</sub>	0.7500
H <sub>2</sub> -H <sub>2</sub>	0.4723	B <sub>4</sub> -B <sub>4</sub>	0.4723	B <sub>4</sub> -B <sub>4</sub>	0.473
Be-Be	0.3542	Be-Be	0.3542	Be-Be	0.3542
H <sup>t</sup> -H <sup>t</sup>	0.2538	H <sub>2</sub> <sup>t</sup> -H <sub>2</sub> <sup>t</sup>	0.2537		
(different)		(different)			
H <sup>t</sup> -H <sup>b</sup>	0.2590	H <sub>2</sub> <sup>t</sup> -H <sub>2</sub> <sup>b</sup>	0.2616	H <sup>t</sup> -H <sup>b</sup>	0.2579
H <sup>t</sup> -H <sup>b'</sup>	0.1479	H <sub>2</sub> <sup>t</sup> -H <sub>2</sub> <sup>b'</sup>	0.1443	H <sup>t</sup> -H <sup>b'</sup>	0.1229
	0.1281		0.1260		
H <sup>t</sup> -H <sup>t'</sup>	0.1016	H <sub>2</sub> <sup>t</sup> -H <sub>1</sub> <sup>t'</sup>	0.0958	H <sup>t</sup> -H <sup>t'</sup>	0.0906
H <sup>b</sup> -H <sup>b</sup>	0.2577	H <sub>2</sub> <sup>b</sup> -H <sub>3</sub> <sup>b</sup>	0.2583	H <sup>b</sup> -H <sup>b</sup>	0.2654
(different)		(different)		(different)	
H <sup>b</sup> -H <sup>b'</sup>	0.2036	H <sub>2</sub> <sup>b</sup> -H <sub>3</sub> <sup>b</sup>	0.2178, 0.1926, 0.1678	H <sup>b</sup> -H <sup>b'</sup>	0.1951, 0.1575
		H <sub>2</sub> <sup>b</sup> -H <sub>1</sub> <sup>t'</sup>	0.1272		
		H <sub>3</sub> <sup>b</sup> -H <sub>3</sub> <sup>b</sup>	0.2655 0.2646		
		(different)			
		H <sub>3</sub> <sup>b</sup> -H <sub>1</sub> <sup>t'</sup>	0.1607, 0.1571		
H <sup>t</sup> -B	0.3897	H <sub>2</sub> <sup>t</sup> -BH <sub>3</sub>	0.3896	H <sup>t</sup> -B	0.3921
H <sup>t</sup> -B'	0.1166	H <sub>1</sub> -BH <sub>3</sub>	0.3923	H <sup>t</sup> -B'	0.1134
H <sup>t</sup> -Be	0.1941	H <sub>2</sub> -BH <sub>3</sub>	0.1210	H <sup>t</sup> -Be	0.1803
		H <sub>1</sub> -BH <sub>2</sub>	0.1093		
		H <sub>2</sub> -Be	0.1937		
		H <sub>1</sub> -Be	0.1804		
H <sup>b</sup> -B	0.3644	H <sub>2</sub> <sup>b</sup> -BH <sub>2</sub>	0.3682	H <sup>b</sup> -B	0.3770
H <sup>b</sup> -B'	0.1670	H <sub>3</sub> -BH <sub>3</sub>	0.3784, .3705	H <sup>b</sup> -B'	0.1661
H <sup>b</sup> -Be	0.3133	H <sub>2</sub> -BH <sub>3</sub>	0.1744	H <sup>b</sup> -Be	0.2895
		H <sub>3</sub> -BH <sub>2</sub>	0.1571, .1607		
		H <sub>3</sub> -Be	0.3103		
		H <sub>3</sub> -Be	0.2948, .2881		
B-B'	0.1379	B-B'	0.1443	B-B'	0.1517
B-Be	0.2556	B(H <sub>2</sub> )-Be	0.2552	B-Be	0.2724
		B(H <sub>3</sub> )-Be	0.2724		
Electronic Energy					
-43.903078		-44.516312		-45.172854	
Total Energy					
-15.966898		-16.020566		-16.089011	

chosen coordinates and the calculated Coulomb integrals in tables 1c, 1d and 1e. Because of the smallness of the related potential barriers and the presence of a low-lying empty  $E_u$  orbital in structure 3 one does not expect an elaborate CI calculation to alter significantly the gross conclusions achieved in this work.

In summary our INDO results predict the species to be described by two interconverting isomers (structure 1 and, for example, 2) with a small potential barrier

Table 2. INDO potential barriers of internal motions in beryllium borohydride.

Structure	Internal motion	Potential barrier in kcal. mol <sup>-1</sup>
<i>Internal rotation</i>		
1	H <sub>2</sub> <sup>1</sup> B group	200.8
1	-BH <sub>2</sub> <sup>2</sup> Be- grouping	238.4
1	H <sub>2</sub> <sup>1</sup> BH <sub>2</sub> <sup>2</sup> Be group	37.16
2	H <sub>2</sub> <sup>2</sup> B group	248.0
2	-BH <sub>2</sub> <sup>1</sup> Be- grouping	245.8
2	H <sub>2</sub> <sup>2</sup> BH <sub>2</sub> <sup>1</sup> Be group	2.468
3	H <sup>3</sup> BH <sub>2</sub> <sup>2</sup> Be group	1.875
<i>Permutations</i>		
1	(3, 6)	356.6
1	(3, 6) and (4, 5)	355.9
2	(3, 6)	326.4
3	(3, 7)	370.0
<i>Interconversions</i>		
1-2	Interconversion	1.132 <sup>a</sup>
2-3	Interconversion	Nil <sup>b</sup>

<sup>a</sup> Potential barrier with respect to structure 1.

<sup>b</sup> No barrier between the two structures along this route.

in their interconversion. There is a large amplitude vibrational motion associated with the second isomer. It has also an internal rotation of comparatively small barrier. A permutational group-theoretical analysis is being published soon.

### Acknowledgement

One of the authors (SND) acknowledges financial support from the University of Burdwan.

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