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# Beryllium Borohydride, LCAO-MO Calculations

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The results of simple LCAO—MO calculations on $BeB_2H_8$ and $B_2H_6$ are reported. They indicate that in $BeB_2H_8$ binding between Be and H(3) may be neglected and the Be atom considered to be bonded to the B atoms through H(2) bridge bonds. H(4) is found to carry negative charge, B positive, and the dipole moment to be considerable.

We present in this paper the results of some simple LCAO—MO calculations on beryllium borohydride and diborane. Both the calculations and analysis of the results have been modeled after Hoffmann and Lipscombs studies on the boron hydrides.[1]

## COMPUTATION

The determination of the molecular structure of $BeB_2H_8$ by electron diffraction is described in the preceding paper.[2] Our LCAO—MO calculations were based on the structure parameters listed in Table 2, column a. The structure parameters of diborane were taken from a recent electron diffraction investigation by Bartell and Carroll.[3]

The oribital exponents for Be and B were selected according to Slater's rules.

All overlap intergrals,[4] $S_{ij}$, between hydrogen (1*s*) and beryllium and boron (2*s*) and (2*p*) orbitals were included. The resonance intergrals, $H_{ij}$ ($i \neq j$), were set equal to $H_{ij} = KS_{ij}$. All results listed in Tables 1 and 2 were obtained with $K = -21$ eV.[1c] The Be and B Coulomb intergrals, $H_{ii}$, were set equal to minus valence state ionization potentials:[5]

$\alpha(Be,2s) = -9.76$ eV  $\alpha(Be,2p) = -5.81$ eV
$\alpha(B,2s) = -15.02$ eV  $\alpha(B,2p) = -8.33$ eV

Hoffmann and Lipscomb [1c] found that computations made with

$$\alpha(H,1s) = -13.53 \text{ eV} \qquad \text{(Method I)}$$

failed to reproduce the charge distribution found in diborane by less approximative calculations.[6] The disagreement could be removed by using different

*Table 1.* Overlap populations and bond lengths.

| | B–B | B–H(1) | B–H(2) | B–H(3) | Be–B | Be–H(2) | Be–H(3) | Be–H(4) |
|---|---|---|---|---|---|---|---|---|
| $BeB_2H_8$ | 1.74 Å | 1.16 Å | 1.23 Å | 1.31 Å | 1.84 Å | 1.99 Å | 1.73 Å | 1.61 Å |
| I | 0.356 | 0.888 | 0.652 | 0.396 | 0.264 | 0.196 | 0.116 | 0.652 |
| II | 0.228 | 0.920 | 0.672 | 0.396 | 0.236 | 0.212 | 0.080 | 0.740 |
| $B_2H_6$ | 1.78 Å | 1.20 Å | 1.20 Å | 1.34 Å | | | | |
| I | 0.388 | 0.856 | 0.856 | 0.452 | | | | |
| II | 0.192 | 0.904 | 0.904 | 0.420 | | | | |

*Table 2.* Atomic charges and dipole moment.

| | B | H(1) | H(2) | H(3) | Be | H(4) | $\mu$(D) |
|---|---|---|---|---|---|---|---|
| $BeB_2H_8$ | | | | | | | |
| I | + 0.420 | −0.144 | −0.038 | + 0.150 | + 0.200 | −0.490 | 9.2 |
| II | + 0.348 | + 0.002 | + 0.120 | −0.072 | −0.088 | −0.358 | 8.7 |
| $B_2H_6$ | | | | | | | |
| I | + 0.278 | −0.176 | −0.174 | + 0.064 | | | 0.0 |
| II | + 0.212 | −0.026 | −0.026 | −0.156 | | | 0.0 |

values for the Coulomb intergrals of terminal and bridge hydrogen atoms. Following these workers we have therefore also performed calculations with

$$\alpha(H^b,1s) = -11.60 \text{ eV}$$
$$\alpha(H^t,1s) = -15.75 \text{ eV} \qquad \text{(Method II)}$$

In $BeB_2H_8$ H(3) and H(3′) were regarded as bridge atoms, the others as terminal.

The secular equations,

$$\sum_j c_j(H_{ij} - ES_{ij}) = 0 \; ; \qquad \text{all i,}$$

were solved on a computer, and total energies, atomic charges,[1b] and subtotal overlap populations[1b] ("bond orders") computed.

## RESULTS AND DISCUSSION

The computations in $BeB_2H_8$ gave eight strongly bonding orbitals (accomodating sixteen binding electrons) the highest of which had the energy −13.35 eV (Method I) or −12.38 eV (Method II). The lowest empty orbital was found at −4.17 eV by either method. The transition would be allowed for electromagnetic radiation. The high excitation energy is in agreement with the fact that the compound is colorless. No UV absorbtion spectrum has been reported.

The total energy is −252.60 eV (I) or −245.84 eV (II).

The bond distances and overlap populations of $BeB_2H_8$ and $B_2H_6$ are given in Table 1.

It is seen that the overlap population of Be—H(2) is roughly twice that of Be—H(3). This is particularly surprising since the computations are based on a model in which the Be—H(2) bond is 0.26 Å longer than the Be—H(3) bond and the overlap intergrals correspondingly smaller. The relative magnitude of the two overlap populations is not sensitive to changes in the constant K when the latter is varied from −17 eV to −29 eV.

This — taken along with the considerable Be—B overlap population — suggests that as a first approximation Be—H(3) bonding may be neglected and the beryllium atom regarded as being bonded to the two boron atoms through H(2) and H(2′) hydrogen bridge bonds.

This view in turn suggests that the Be—H(2) distance should be shorter than the Be—H(3) distance. As pointed out in the preceding paper (Table 2, column b) this is quite possible.

The atomic charges and dipole moments obtained are shown in Table 2.

It is seen that the B atoms should carry a large positive charge, the H(4) atoms a large negative charge, and that the dipole moment should be nearly 10 Debye. Again it is found that the results are not very sensitive to changes in $K$. The magnitude of the charges and hence the dipole moment is certainly too big, the reason being that electron-electron repulsion in no way has been included in the calculations. But one may hope that their sign is correct.

No attempt to measure the dipole moments has been reported, but the very low volatility and high melting point of $BeB_2H_8$ compared to $Al(BH_8)_3$ [4] (the difference in melting point is at least 180°) indicate that it is considerable.

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