A Theoretical Study of Beryllium Borohydride BeB_2H_8

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ON the basis of electron diffraction measurements a novel structure has been suggested[1] for gaseous beryllium borohydride which is strikingly different from the previously accepted "diborane-like" structure. Both are shown in the Figure and it is suggested that, in the new structure (II), the Be and the two B atoms are situated at the apices of an isosceles triangle and interconnected by three-centre hydrogen-bridge bonds.

To investigate features of the bonding in this system and to confirm that the new structure is indeed more stable than the classical one, we have carried out a series of non-empirical calculations on the two models of the molecule. Gaussian-type atomic orbitals (G.T.O's) have been employed using first a minimum- then an extended-basis set totalling 43 orbitals. The latter comprised three G.T.O's for the 1*s* and 2*s* orbitals of B and Be, two for their 2*p* orbitals, and two for each hydrogen 1*s* orbital. The orbital exponents were taken from the work of Moskowitz and his co-workers[2] and the input data subjected to a modified version of the Polyatom self-consistent routine.[3] Bond-lengths and angles for model (I) were those given in ref. **4**, and for model (II) they were abstracted from ref. 1.

The results of the calculations on both models are summarised in the Table which lists the Mulliken atomic and overlap populations (*i.e.* the bond orders), the total electronic energies, and the dipole moments. A consideration of the total energies reveals that model (II) is less stable than the classical structure by 5·48 ev. However, this does not preclude the existence of a yet more stable form based essentially on the pattern of Almenningen *et al.*, but having different bond-lengths and angles. In an optimum situation the nuclear and electronic energies might contribute differentially to produce lower total energy.

In a later paper Almenningen, Gundersen, TABLE

Quantities calculated for BeB_2H_8

Model (I)

Net atomic populations			
Be	B	H_1	H_2
2·413	3·836	0·579	0·779
Gross atomic populations			
3·214	5·224	0·980	1·104
Overlap populations			
Be–H_2	B–H_1	B–H_2	Be–B
0·185	0·714	0·538	0·305

Model (II)

Net atomic populations							
Be	B	H_1	H_2	H_3	H_4		
2·925	4·085	0·475	0·481	0·837	0·911		
Gross atomic populations							
3·474	5·168	0·879	0·871	1·059	1·283		
Overlap populations							
Be–H_2	Be–H_3	Be–H_4	B–H_1	B–H_3	B–H_2	B–B	Be–B
0·042	−0·141	0·743	0·665	0·370	0·692	0·384	−0·100

Energies (ev)	Model (I)	Model (II)
Electronic	−3221·537	−3361·273
Nuclear repulsion	+1429·409	+1574·622
Total	−1792·128	−1786·652

$\Delta = 5{\cdot}477$

Dipole moment	Model (I)	Model (II)
	0	6·894 D

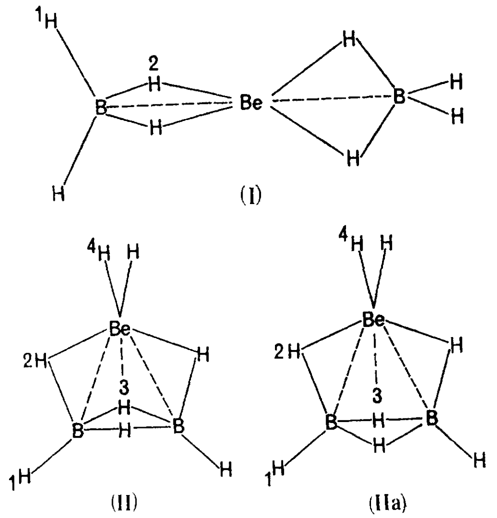

FIGURE. *Structures for BeB_2H_8.*

Haaland, and Nilsson[5] suggested that the original bond-lengths and angles of model (II) should be modified and proposed a new set of molecular parameters. The chief differences in these are (a) the Be–B distance is shortened to 1·818 Å and (b) the Be–H_2 distance is shortened to 1·89 Å, so becoming less than the Be–H_3 distance (now 2·04 Å).

Using these data we calculated the total electronic energy of the new model (IIa) using a minimum-basis set only of Gaussian functions. The total energies of all three models obtained using the minimum-basis set calculation are: (I) −1770·850; (II) −1765·950; (IIa) −1750·960 ev. On this evidence the third structure (IIa) is less stable than either of the previous two and this situation is not expected to change on proceeding to the extended-basis set calculation. If the molecular parameters of model (II) were varied further, then a minimum in total energy below that of (I) might be discovered. We have not yet undertaken an investigation of this because of the very large number of possible permutations in bond-lengths and angles.

Some insight as to how the parameters could be altered is gained by examining the population-analysis figure for models (I) and (II) which clearly illustrate the marked difference in electronic structure between the two. The classical structure possesses both substantial Be–B cross-ring and bridging B–H bonds (orders 0·305 and 0·538 respectively). Moreover the Be–H bridge bond is also quite strong. On the other hand, in (II) the Be–B bonds have overall, weak, antibonding character as has the Be–H(3) bond. In addition the remaining Be–H bridge bonds are of low order (0·042). To compensate, the B–B, B–H (terminal) and Be–H (terminal) bonds are strong and hence the overall picture of the structure is of two internally strongly-bonded units, one of which is essentially B_2H_6 and the other BeH_2.

It is interesting that both models exhibit similar charge-separation between the Be and B atoms. The former atom has a fairly strong positive charge (0·5—0·8 units) and the latter is weakly negative (*ca.* 0·2 units). The electron-distribution results suggest that a more stable form of (II) might result from further reduction of the Be–B and Be–H_2 distances. This would tend to decrease the negative overlap charge-density between these atom pairs.

A further useful calculated quantity is the dipole moment. This is zero for structure (I), but large for (II) and thus an experimental determination of its value could be diagnostic.

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[5] A. Almenningen, G. Gundersen, A. Haaland, and J. E. Nilsson, 3rd International Symposium on Organometallic Chemistry, München, 1967.