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ON THE BONDING AND ELECTRONIC STRUCTURE OF BORON—OXYGEN COMPLEXES. AB INITIO MO-CALCULATIONS ON BH_3OH_2, $(BH_2OH)_2$ AND RELATED COMPOUNDS

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Summary

Ab initio molecular orbital calculations have been carried out on H_3BOH_2, $(H_2BOH)_2$ and some related species, and the bonding and energies of reaction are discussed within the HF-approximation. It is concluded that the bonding in these species is very similar to that in the related aluminium compounds, and that the reorganisation energy due to conjugation in BH_2OH is responsible for a very low dissociation energy for the $(BH_2OH)_2$ molecule.

Introduction

A previous paper [1] presented the results of a study of monomeric hydroxyborane by ab initio calculations which indicated the presence of a partial π-bond superimposed on the σ-bond between B and O in the planar form. An interesting reaction possibility for this compound is dimerisation via bridging oxygen atoms, but as far as we know no compounds of the type $(R_2BOR)_2$ exist, and some analogous nitrogen compounds do not dimerise while others exhibit what appears to be reversible dissociation on melting [2].

Related aluminium compounds, however, form rather stable dimers of the type concerned [3], and the reasons for this difference are not known with certainty. It has been claimed that reorganisation energy due to p_π—p_π conjugation governs the dissociation energy of R_2BX dimers, whereas this effect is of minor importance in the aluminium compounds. The suggested p_π—d_π conjugation in the aluminium dimers has been ruled out by a recent ab initio study [4]. The present ab initio molecular orbital calculations on BH_3OH_2 and $(BH_2OH)_2$ were undertaken to provide insight into the nature of the B—O

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bonds in such molecules, and to compare the results with those for related aluminium compounds [4,5]. It is also of interest to compare the results of calculations on the $CH_3OH_2^+$ [6] ion with those from the BH_3OH_2 molecule.

Computational details

The calculations were carried out with the programme MOLECULE [7] which solves the Roothaan—Hall equations for a Gaussian-type basis. A [9, 5, 1/4] basis set contracted to ⟨4, 2, 1/2⟩ was used [8]. The exponents of the hydrogen *s*-functions were multiplied by 1.25, whereas the *d*-functions were given the exponent 0.95 for both oxygen and boron.

Calculations

H_3BOH_2

The H_3BO fragment was assumed to have C_{3v} symmetry, and the B—H and O—H bond distances in this and all other species mentioned below taken as 1.20 and 0.96 Å respectively. The B—O bond distance, the HOH valence angle; the angle ϕ between the B—O bond and the plane of the water molecule and the OBH angle were varied to minimize the energy. All calculations were carried out on a model of C_s symmetry with the H_2O plane perpendicular to the symmetry plane (see Fig. 1).

First the angles ϕ and HOH were fixed at 180 and 110 degrees, respectively, and the B—O bond distance and OBH angle varied simultaneously. The results were fitted to a second order potential surface, and the minimum energy occurred for a B—O bond distance and a OBH angle equal to 1.83 Å and 100° respectively. Some of the energies calculated during the optimisation are listed in Table 1, which shows that there is a strong coupling between these two parameters and that the potential surface is rather shallow. Accordingly B—O bond distances from 1.67 to 1.91 Å cannot be ruled out.

Using the obtained values for these two parameters the energy was calculated for values of 180, 150, 120 and 90 degrees for the angle ϕ. The results were fitted to a fourth degree polynomial assuming the derivative of the polynomial to be zero for the value zero of the angle ϕ. The minimum energy was then found for $\phi = 128°$.

Finally the B—O bond distance, the OBH angle and the angle ϕ were fixed at 1.83 Å, 100° and 120° respectively, and calculations carried out for three values of the angle HOH. Assuming that the energy can be expressed as a second degree polynomial in the angle HOH, we found the minimum at 107°.

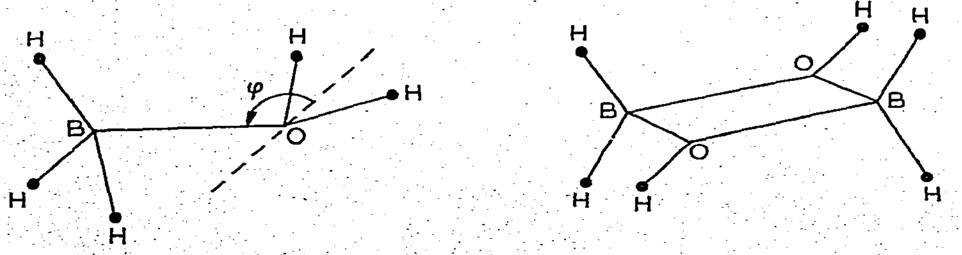

Fig. 1. Geometry of BH_3OH_2 and $(BH_2OH)_2$ and definition of the angle ϕ.

TABLE 1

CALCULATED ENERGIES FOR H_3BOH_2 OBTAINED FOR DIFFERENT VALUES OF HBO AND R(B—O) WITH HOH = 110° AND $\phi = 0°$

R(B—O)	HBO	Energy [a]	HBO	Energy [a]	HBO	Energy [a]
1.58	105	1.30	100	3.02	95	
1.67	105	3.68	100	0.79	95	5.50
1.75			100	0.06	95	3.32
1.83			100	0.00	95	2.13
1.91			100	0.48	95	1.57

[a] kcal mol^{-1} relative to the minimum value.

$(H_2BOH)_2$

Calculations were carried out on models of C_{2v} symmetry with the H_2B planes perpendicular to the B_2O_2 ring plane (see Fig. 1). Both the angles OBO and BOB were taken as 90°, which is very close to the optimized ring angles in dimer aminoborane [9]. Further we used 120° for the HBH angles in accordance with the electron-diffraction structure for diborane [10]. The B—O bond distance was optimized to 1.53 Å.

H_2BOH

Recent ab initio calculations on this molecule predicted the most stable form to be the planar one [1], and the barrier to internal rotation around the BO bond to be 16.4 kcal mol^{-1}. The basis used in that calculation was identical to ours except for using three contracted gaussian *s*-functions on hydrogen instead of two as in the present investigation. This difference in basis will probably not influence the rotation barrier [1].

We performed two calculations on this molecule using our less extended hydrogen basis. Using the optimized geometry parameter the total energy increased with 4.28 kcal mol^{-1}, relative to the earlier results [1]. Further we expanded the BO bond from 1.33 to 1.53 Å with all the other geometry parameters unchanged. Compared to the first calculation the energy increased with 16.2 kcal mol^{-1}.

B_2H_6

For this molecule the geometry parameters were taken from the electron-diffraction investigation of Bartell and Carroll [10]. These values were 1.196, 1.339, 1.775 Å and 120° for the BH_a, BH_b, BB bond distances and H_aBH_a angle respectively.

BH_3

Calculations were carried out on a planar model of D_{3h} symmetry, an in order to estimate the reorganization energy on a model of C_{3v} symmetry with different values for the angle HBH. The results are presented in Table 2.

TABLE 2

CALCULATED TOTAL ENERGIES FOR BH_3 FOR DIFFERENT VALUES OF THE HBH ANGLE

HBH	E_{tot} (a.u.)
120.0	−26.384 624
119.3	−26.382 095
117.1	−26.374 472
113.6	−26.361 485
109.4	−26.345 711

H_2O

Calculations were carried out on H_2O using 105° for the HOH angle and 0.96 Å for the R(O—H).

Results and discussion

The energies obtained by the calculations on the lowest energy conformations of H_3BOH_2 and $(H_2BOH)_2$ as well as the energies obtained by calculations on H_2BOH, BH_3, B_2H_6, H_2O and H_2 are listed in Table 3 along with some of the results obtained from the population analysis.

H_3BOH_2

The energy of reaction 1 can be calculated from energies listed in Table 4 to

$$BH_3 + H_2O \rightarrow BH_3OH_2 \qquad (1)$$

$\Delta E_1 = -12.1$ kcal mol^{-1}. Since the present calculations do not include electron correlation, this value as well as those of other reaction energies calculated below, must be regarded with some reservation. But since reaction 1 involves very little change of charge distribution, the omission is probably not serious.

The available experimental information for these compounds is rather scarce. The heat of formation for reaction 2 is, however, estimated to be −16.71 kcal

$$BF_3 + H_2O \rightarrow BF_3OH_2 \qquad (2)$$

mol^{-1} and calculated to be −24.8 kcal mol^{-1} [11], whereas the value 13.1 has been measured for the reaction 3 [12]. In the light of this comparison our

$$Me_2O + BF_3 \rightarrow BF_3OMe_2 \qquad (3)$$

results may be considered reasonable.

The estimated B—O bond distance in the present calculation (1.83 Å) is almost 0.3 Å longer than that determined for BF_3OMe_2 (1.52) by electron diffraction [13], and also much longer than the B—O length in BH_3OH_2 (1.61) predicted by ab initio calculations using the STO-3G basis [14]. However, as mentioned above our results indicate that bond distances from 1.67 to 1.91 Å cannot be excluded.

The arrangement around the oxygen atom is similar to that in the related compounds $CH_3OH_2^+$ and AlH_3OH_2 as shown in Table 4. It is seen that the inversion angle ϕ is only 153° for the aluminium compound compared to 137.5 and

TABLE 3

ENERGIES, GROSS ATOMIC POPULATIONS, OVERLAP POPULATIONS, AND TOTAL *d*-ORBITAL POPULATION

	$(H_2BOH)_2$	H_2BOH	H_3BOH_2	H_2O	BH_3	B_2H_6	H_2
Total energies	−202.64578	−101.32849	−102.42745	−76.02349	−26.38462	−52.790204	−1.126905
Gross B	4.50	4.76	5.05		5.06	5.32	
Gross O	8.89	8.75	8.80	8.67			
Gross H(B)	1.06	1.01	1.03		0.98	0.89 [a]	
Gross H(B)	1.06	0.96	1.04			0.90 [b]	
Gross H(O)	0.49	0.53	0.52	0.67			
Overlap B—O	0.32	0.72	0.18				
Overlap B—B	−0.16					0.25	
Overlap O—O	−0.12						
Overlap B—H	0.82	0.87	0.84		0.82	0.36 [a]	
Overlap B—H	0.82	0.83	0.83			0.86 [b]	
Overlap O—H	0.52	0.53	0.53	0.57			
Total *d*-orb. pop. B	0.067	0.08	0.029		0.018	0.09	
Total *d*-orb. pop. O	0.012	−0.026	0.016	0.056			

[a] Bridge. [b] Terminal.

TABLE 4

CALCULATED QUANTITIES FOR $CH_3OH_2^+$, BH_3OH_2 AND ALH_3OH_2

	∠HOH (°)	φ_{min} (°)	$E_{\phi=\phi} - E_{\phi=0}$ (kcal mol^{-1})	Reference
$CH_3OH_2^+$	110.0	137.5	2.2	6
BH_3OH_2	107.0	128.0	3.4	This work
BH_3OH_2	105.3	180.0		14
AlH_3OH_2	109.3	153.0	0.20	4

128° for the two other species. The calculated energy minimum for the aluminium compound is, however, very shallow, the energy of the planar configuration being only 0.2 kcal mol^{-1} higher, and only when ϕ becomes less than —50° or greater than +50° does the energy increase rapidly [4].

The equilibrium geometry obtained with the STO-3G basis [14] predicted a planar arrangement around the oxygen atom. This is in agreement with calculations on the $CH_3OH_2^+$ ion when *d*-orbitals are excluded [6]. The conclusion was drawn from these calculations that *d*-orbitals are necessary in describing the geometry around the oxygen atom [6].

The gross atomic populations listed in Table 3 indicate that the B atom in H_3BOH_2 carries a net positive charge of +0.05 and the O atom a net negative charge of —0.80, while the H(B) atoms carry a negative charge and the H(O) atoms a positive charge. They further indicate that the formation of the complex is accompanied by a transfer of —0.17 electrons from donor to acceptor. Comparison with the gross atomic populations of BH_3 and H_2O indicates that charge is taken from the H(O) atoms and ends up on the H(B) atoms, while the negative charge on O increases while it decreases on boron. The numbers taken from the population analysis should, however, be handled with some care as the partitioning used in the population analysis may be too coarse to reflect the real redistribution of charge.

The rather low value obtained for the overlap population for this compound (0.18) as for H_3AlOH_2 (0.095) and BH_3NH_3 (0.177) reflects the weakness of the dative bond.

H_2BOH and $(H_2BOH)_2$

The calculated energies of reaction are:

$$H_3BOH_2 \rightarrow H_2BOH + H_2 \qquad \Delta E_2 = -17.5 \tag{4}$$

$$2H_2BOH \rightarrow (H_2BOH)_2 \qquad \Delta E_3 = +7.0 \tag{5}$$

$$B_2H_6 \rightarrow 2BH_3 \qquad \Delta E_4 = +13.15 \tag{6}$$

$$B_2H_6 + 2H_2O \rightarrow 2H_2BOH + 2H_2 \qquad \Delta E_5 = -46.15 \tag{7}$$

The sum of reaction 1 and reaction 4 may in fact be considered as a reaction of borane with water forming hydroxyborane and hydrogen. This is the first step in the reaction of borane with water to form hydrogen and boric acid. The calculated energy for this step in —29.6 kcal mol^{-1} compared to the dimerisation energy of borane (—6.58 kcal/mol). The second step in this process is estimated to be of the same magnitude [15].

The estimated HF-energy for the similar reaction of alane with water is —26.5 kcal mol^{-1} [4], which is rather close to the results for borane. The hydroxyalane, however, dimerise with a reaction energy of —58.6 kcal mol^{-1}, compared to an energy of dissociation of +7.0 kcal mol^{-1} for the dimer hydroxyborane.

This dimerisation energy indicates that the bond energy for the two "new" dative O—B bonds is positive. It is well known however that the reorganization energy of an acceptor molecule has an important influence on the thermodynamics of donor—acceptor complex formation. In the case of the hydroxyborane monomer, the reorganization energy incorporates the energy required to extend the O—B bond from 1.33 to 1.53 Å (16.2 kcal mol^{-1}), the energy required to the internal rotation around the B—O bond (16.4 kcal mol^{-1}) and the inversion of the BH_2 group (ca. 10 kcal mol^{-1} estimated from the calculations on BH_3). Concomitant bending and stretching of the BH and NH bonds are assumed to cause only a small reduction in the stabilization energy. Thus for two molecules of BH_2OH, 85.2 kcal mol^{-1} are needed for the reorganization process. Addition of the calculated dissociation energy yields an overall figure of 78.2 kcal. The intrinsic mean bond dissociation energy of each new B—O bond formed on dimerisation is therefore 39.1 kcal mol^{-1}.

This bond energy should be compared to the calculated bond energy for the dative B—O bond (12.1 kcal mol^{-1}). The great discrepancy may be partly explained by the reorganisation of the BH_3 group, and probably partly by the introduction of a electronegative hydroxy group on the borane part in the dimerisation. The metal—metal bond in the ring is discussed below, with the conclusion that it is of minor importance in $(BH_2OH)_2$.

In a study on the dimerisation of the BH_2NH_2 the mean BN bond dissociation energy was calculated to be 66.0 kcal mol^{-1} [9].

The reorganization of the AlH_2OH molecule in the dimerisation process should be similar to that of the boron compound, and the contribution from the rotation around the Al—O bond, the lengthening of the Al—O bond and the inversion of the H_2Al group will be 4.2, 8.4 and 10 kcal mol^{-1} respectively [4, 5]. Including the dissociation energy, —58.6 kcal mol^{-1}, this adds up to 103.8 kcal mol^{-1}, giving an intrinsic mean Al—O bond dissociation energy of 51.9 kcal mol^{-1}. This led to the conclusion that the Al—O dative bond is about 12.8 kcal mol^{-1} stronger than the B—O bond in these compounds. This difference in bonding energy between the aluminium and boron compounds represents only 50% of the difference in the dissociation energy. We thus conclude that the main reason why the R_2AlX compounds, X being NR_2, OR and SR, form stabil dimers while the related boron dimers are scarcely possible of existence, is the difference in reorganization energy. The main contribution to this energy results mostly from misalignment of the p_π orbitals on the oxygen and boron atoms.

While gross atomic populations indicated that formation of the complex H_3BOH_2 was accompanied by a charge transfer of —0.18 from donor to acceptor, the dimerisation of H_2BOH appears to be accompanied by a transfer of —0.10 from the acceptor part (BH_2) to the donor part (OH). But the process must be considered in two steps, first the deformation of the BH_2OH fragment and then the association, and therefore the results from the population analysis should be regarded with caution.

The B—O overlap population in $(H_2BOH)_2$, 0.32 is somewhat less than the average of the B—O overlap population in BH_3OH_3 and BH_2OH, viz. 0.45. But if the average is calculated using only the σ overlap population in H_2BOH, it is reduced to 0.32, similar to the overlap population in $(BH_2OH)_2$.

It is noteworthy that both the O—O and B—B overlap populations are negative, in contrast to the B—B overlap population in B_2H_6. This indicates that there is no bonding across the ring.

Metal—metal bonding was also negligible (0.036) in the dimerization of BH_2NH_2 [9], and it is reasonable to conclude that metal—metal bonding is rather unimportant when there are sufficient electrons in the bridges to give rise to four electron-pair bonds.

Finally to point out that contrary to expectation the contribution of p_π—d_π bonding is very similar to that in the aluminium compounds.

Conclusion

The calculations show that the bonding in the BH_3OH_2 and $(BH_2OH)_2$ is quite similar to the related aluminium compounds, wheras the BH_2OH molecule shows a much stronger conjugation than the AlH_2OH molecule. The results also predict that within the relevant approximation it is the reorganisation energy that prevents the BH_2OH from forming dimer and polymers and diverts it towards formation of boric acids and a series of conjugated systems. This is in contrast to the behaviour of the aluminum compounds, in which the reorganisation energies are of minor importance, and very few conjugated aluminum systems exist.

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