

## *Ab initio* study of boron hydroxy species: $B(OH)_4^-$ , $B(OH)_4$ and $B(OH)_3O^-$ †

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*Ab initio* SCF studies at STO-3G and 4-31G levels have been performed on  $B(OH)_4^-$  as well as on the recently reported radicals  $B(OH)_4$  and  $B(OH)_3O^-$ . The RHF calculations for  $B(OH)_4^-$  lead to  $T_d$  structure, which is in agreement with the experimental results. The  $B(OH)_4$  radical is found to prefer a  $C_{2v}$  geometry rather than  $T_d$  or  $D_{2d}$  structures according to UHF calculations. The  $T_d$  and  $D_{2d}$  structures are 23.7 and 12.6 kcal/mol higher respectively in energy than the  $C_{2v}$  structure at the STO-3G level. STO 4-31G calculations show that the corresponding values are 16.3 and 11.5 kcal/mol respectively for the  $T_d$  and  $D_{2d}$  structures. The UHF calculations using both the basis sets indicate that the two geometries considered for the  $B(OH)_3O^-$  radical anion,  $T_d$  and  $C_{3v}$ , are very close energetically.

Boron chemistry is interesting for many reasons<sup>1</sup>. It is a semi-conductor and has properties intermediate between metals and non-metals, making the bonding in its compounds very unusual<sup>2</sup>. Thus when a hitherto unknown boron radical  $B(OH)_4$  was reported recently<sup>3</sup> and a subsequent paper<sup>4</sup> reported the existence of another radical  $B(OH)_3O^-$  which is supposed to be in equilibrium with  $B(OH)_4$ , we were interested in elucidating their probable structures about which little is known. Ramakrishnan and coworkers studied the reactivity and rates of reaction of these species with a number of aromatic and aliphatic substrates and found that they are fairly good one-electron oxidants and react with organic substances either by electron-transfer or hydrogen atom abstraction<sup>3-5</sup>.

However, as these species are very short lived, it is difficult to arrive at their structures experimentally. Some preliminary semiempirical SINDO1<sup>6-8</sup> investigations on these structures have been undertaken<sup>5</sup>. These results however need to be confirmed by more extensive studies. In this work we report a more detailed *ab initio* study of the various probable structures of these compounds and their energies.

### Computational details

*Ab initio* SCF molecular orbital calculations were carried out using Gaussian basis sets. As

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$B(OH)_4^-$  is a closed shell system, Restricted Hartree-Fock (RHF) calculations were carried out, whereas for  $B(OH)_4$  and  $B(OH)_3O^-$  Unrestricted Hartree-Fock (UHF) calculations were done using the STO-3G minimal and 4-31G split valence basis sets<sup>9,10</sup>. The SIEMENS 7.580-E main frame computer of IIT, Madras was used for the computations. Energy optimisations were performed via the analytical gradient techniques included in the Gaussian 70 program<sup>11</sup>.

The UHF calculations using semiempirical SINDO1 method<sup>6-8</sup> were also carried out on  $B(OH)_4$  for  $T_d$  and  $D_{2d}$  geometries and on  $B(OH)_3O^-$  for  $T_d$  geometry which were not reported earlier<sup>5</sup>. Molecular geometries were optimised in the SINDO1 method by Newton-Raphson procedure using the energy difference method<sup>6</sup>. All bond lengths, bond angles and energies reported in this work are in Angstroms, degrees and atomic units respectively unless mentioned otherwise. It may be noted that the SINDO1 energies are not comparable to the *ab initio* values because of their semi-empirical nature. However, the relative energies are comparable and have significance (Table 4).

### Results and Discussion

#### $B(OH)_4^-$

The  $B(OH)_4^-$  anion occurs in many minerals. The structure of the ground state of the ion (Fig. 1) has been established experimentally using

Table 1—Geometry parameters and energies for  $B(OH)_4^-$  anion

Symmetry	Parameter <sup>a</sup>	Exptl. <sup>b</sup>	SINDO1 <sup>c</sup>	RHF/STO-3G	RHF/4-31G
$T_d$	$r_1$	1.470	1.469	1.466	1.480
	$r_2$	—	0.959	0.9885	0.952
	$\theta_1$	109.5	109.5	109.5	109.5
	$\theta_2$	—	109.5	104.8	111.09
	$E$	—	-70.1782	-322.0774	-326.1837

<sup>a</sup>See Fig. 1; <sup>b</sup>from ref. 9; <sup>c</sup>from ref. 5.

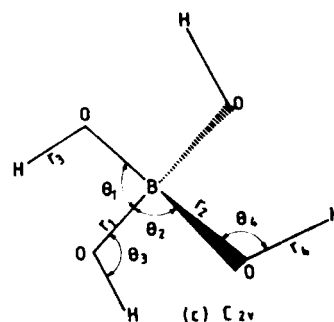
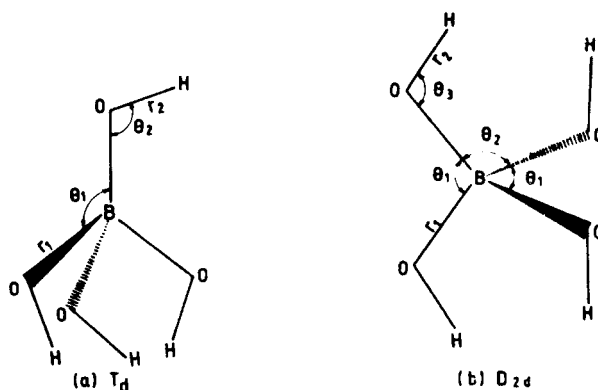
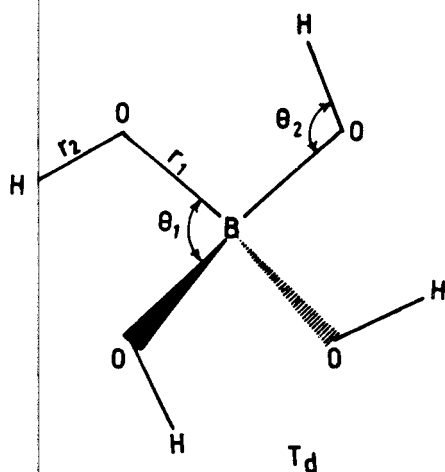


Fig. 1—Definition of geometry parameters for the  $B(OH)_4^-$  anion

Raman spectroscopy<sup>12</sup> and also by X-ray analysis<sup>13</sup> and found to be tetrahedral. Our *ab initio* (STO-3G and 4-31G) bond lengths are in very close agreement with the experimental values as can be seen from Table 1.

### $B(OH)_4$

Three possible structures have been considered as shown in Fig. 2. If we consider the symmetry of the Boron-Oxygen framework only, then the structures belong to  $T_d$ ,  $D_{2d}$  and  $C_{2v}$  point groups. The results of calculations involving these geometries are given in Table 2. Since  $B(OH)_4$  differs from  $B(OH)_4^-$  by one electron only, tetrahedral structure was tried first in the SINDO1 calculation<sup>5</sup>. The optimisation process however clearly showed the grouping of bond lengths and angles into two groups, indicating a preference for the  $C_{2v}$  structure, the two sets of B—O lengths being 1.405 and 1.520 Å<sup>5</sup>. However, *ab initio* calculations considering a  $T_d$  geometry for  $B(OH)_4$  gave optimised bond length of 1.456 and 0.986 Å for the B—O and O—H bonds respect-

Fig. 2—Definition of geometry parameters for the three different structures of the  $B(OH)_4$  radical

ively and 108.5° for the OBH angles at the STO-3G level. The corresponding energy for the equilibrium geometry was -322.0775 a.u. In the UHF/4-31G calculation, the B—O bond length was found to be close to the STO-3G value, the O—H bond was reduced by 0.03 Å and the OBH angle was found to be larger by 8 degrees and the energy was -326.0386 a.u.

In the  $D_{2d}$  structure, all the B—O bonds are equal and are found to be close to the tetrahedral bond length according to the UHF/STO-3G calculation but larger by 0.023 Å in the UHF/4-31G calculation. The O—H bond lengths for both the basis were very close to the respective tetrahedral

Table 2—Geometry parameters and energies of  $\text{B(OH)}_4$  radical

Symmetry	Parameter <sup>a</sup>	SINDO1	UHF/STO-3G	UHF/4-31G
$T_d$	$r_1$	1.47	1.456	1.464
	$r_2$	0.96	0.986	0.959
	$\theta_1$	109.5	109.5	109.5
	$\theta_2$	108.9	108.5	117.3
	$E$	-69.9154	-322.0775	-326.0386
$D_{2d}$	$r_1$	1.434	1.464	1.487
	$r_2$	0.965	0.989	0.956
	$\theta_1$	109.1	113.1	113.4
	$\theta_2$	115.0	114.4	111.4
	$\theta_3$	109.0	108.4	117.9
	$E$	-69.9290	-322.0951	-326.0462
$C_{2v}$ <sup>b</sup>	$r_1$	1.405	1.397	1.407
	$r_2$	1.52	1.525	1.579
	$r_3$	0.965	0.98	0.956
	$r_4$	0.973	0.996	0.96
	$\theta_1$	116.7	122.1	120.8
	$\theta_2$	115.0	115.5	112.5
	$\theta_3$	109.5	109.3	114.9
	$\theta_4$	112.7	105.9	115.6
	$E$	-69.9541	-322.1152	-326.0646

<sup>(a)</sup>See Fig. 2; <sup>(b)</sup>SINDO1 values from ref. 5.

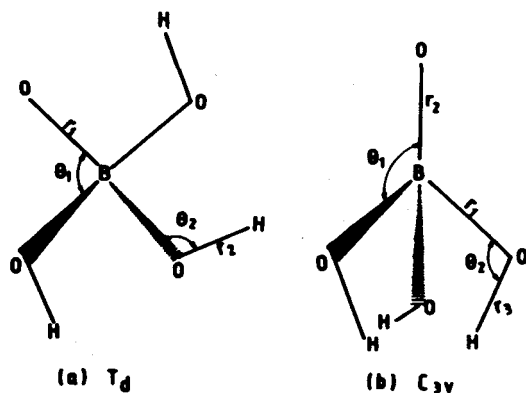


Fig. 3—Definition of geometry parameters for the two different structures of the  $\text{B(OH)}_3\text{O}^-$  radical anion

O—H lengths. The  $D_{2d}$  structure has two sets of bond angles  $\theta_1$  and  $\theta_2$  which are 113.1 and 114.4° respectively by STO-3G calculations and 113.4 and 111.4° by STO 4-31G calculations. Table 2 shows that the energy of the  $D_{2d}$  structure is lower than the corresponding  $T_d$  value: because of relaxation in bond lengths and angles.

The  $C_{2v}$  structure on optimisation gave two sets of bond lengths and bond angles, where a pair of

bonds was shortened and another pair was elongated. The shorter pair of bonds was 1.397 Å at the STO-3G level, the 4-31G value being very close to this value. The longer one was found to be 1.525 Å at the STO-3G level and 1.579 Å at the 4-31G level. The bond angles  $\theta_1$  and  $\theta_2$  are larger than the  $T_d$  and  $D_{2d}$  angles. At the 4-31G level, their values are ~2.5° lower than the STO-3G level,  $\theta_1$  being very close to 120°. Angles  $\theta_3$  and  $\theta_4$  at the 4-31G level are relatively larger than the STO-3G values like all BOH angles obtained in this work.

The removal of one electron from the tetrahedral  $\text{B(OH)}_4^-$  anion is expected to lower the symmetry due to Jahn-Teller distortion<sup>14</sup>. Our studies reveal that both  $D_{2d}$  and  $C_{2v}$  symmetries have lower energies than the  $T_d$  structure. The  $C_{2v}$  geometry has lowest energy as seen from the relative energies given in Table 4. Paddon-Row and Wong recently reported *ab initio* study<sup>15</sup> of the potential energy surface of the  $\text{BH}_4$  radical at the UHF and UMP2 levels with 6-31G(d) and 6-31G(d,p) basis sets followed by single point refinements on the optimised structures at the

Table 3—Geometry parameters and energies of  $B(OH)_3O^-$  radical anion

Symmetry	Parameter <sup>a</sup>	SINDO1	UHF/STO-3G	UHF/4-31G
$T_d$	$r_1$	1.455	1.474	1.491
	$r_2$	0.959	0.988	0.951
	$\theta_1$	109.5	109.5	109.5
	$\theta_2$	110.5	103.7	112.3
	$E$	-69.4663	-321.4785	-325.5687
$C_{2v}^b$	$r_1$	1.473	1.473	1.483
	$r_2$	1.443	1.491	1.459
	$r_3$	0.959	0.988	1.002
	$\theta_1$	109.1	109.3	108.4
	$\theta_2$	108.9	105.6	109.6
	$E$	-69.4674	-321.4772	-325.5613

<sup>(a)</sup>See Fig. 3; <sup>(b)</sup>SINDO1 values are from ref. 5.

Table 4—Relative energies of the various geometries of  $B(OH)_4$  and  $B(OH)_3O^-$ 

Species	Symmetry	Energy in a.u.		$\Delta E^a$ in kcal/mol		
		STO-3G	4-31G	SINDO1	STO-3G	4-31G
$B(OH)_4$	$T_d$	-322.0775	-326.0386	26.0	23.7	16.3
	$D_{2d}$	-322.0951	-326.0462	17.5	12.6	11.5
	$C_{2v}$	-322.1152	-326.0646	0.0	0.0	0.0
$B(OH)_3O^-$	$T_d$	-321.4785	-325.5687	0.7	0.0	0.0
	$C_{3v}$	-321.4772	-325.5613	0.0	0.8	4.6

<sup>(a)</sup>difference in energy with respect to the lowest energy geometry

UMP4<sup>16-19</sup> level using the 6-31G(df,p) basis set. Their studies reveal that  $BH_4$  has only two stable structures,  $C_{2v}$  symmetry and  $C_{3v}$  symmetry, of which the  $C_{2v}$  structure is the global minimum. The  $C_{2v}$  structure is predicted to be kinetically stable to dissociation at 77°K, in agreement with the ESR data for  $BH_4$ . Since  $B(OH)_4$  is similar to  $BH_4$  in the sense that in the former boron is attached to four O-H groups instead of four hydrogens and both being radicals, a  $C_{2v}$  structure for  $B(OH)_4$  seems justifiable.

#### $B(OH)_3O^-$

As in the case of the earlier species, we started with a tetrahedral geometry for  $B(OH)_3O^-$ . SINDO1 and *ab initio* STO-3G and 4-31G results are in agreement with each other (Table 3). The B-O bond length at the 4-31G level is 0.017 Å longer than the STO-3G value whereas the O-H bond length is shorter at the 4-31G level by 0.037 Å. This trend is similar to all the geometries studied for  $B(OH)_4^-$  and  $B(OH)_4$  (Fig. 3).

Since the SINDO1 calculations had already been reported for the  $C_{3v}$  geometry<sup>5</sup>, we have carried out *ab initio* calculations for this geometry using both STO-3G and 4-31G basis sets (Fig. 3b and Table 3). It is interesting to note that though the trends in general are similar, the STO-3G basis gives a value of  $r_2$  much larger than  $r_1$ , whereas the 4-31G basis gives a value of  $r_2$  lower than  $r_1$ . The 4-31G result is in accordance with our expectation because the extra electron resides mainly on the lone oxygen and is available for  $\pi$ -bonding with the boron giving rise to a partial double bond character and thereby shortening it. The SINDO1 results<sup>5</sup> also reflected this shortening.

The energy difference between the  $C_{3v}$  and the  $T_d$  structures is so small (less than 5 kcal/mol) both at the STO-3G and the 4-31G levels (Table 4), that it is difficult to say without refined calculations as to which of these is the favoured geometry.

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### References

- 1 Cotton F A & Wilkinson G, *Advanced inorganic chemistry*, (John Wiley, New York), 1972.
- 2 Elschenbroich C & Salzer A, *Organometallics* (VCH Publishers, New York), 1989.
- 3 Padmaja S, Ramakrishnan V, Rajaram J & Kuriacose J C, *Proc Indian Acad Sci (Chem Sci)*, 100 (1988) 297.
- 4 Padmaja S, Ramakrishnan V, Rajaram J & Kuriacose J C, *J chem Soc Faraday Trans 1*, 85 (1989) 2249.
- 5 Padmaja S, *Generation, characterization and reactions of the borate radical, a new transient species*, Ph.D. thesis, I.I.T. Madras, 1990.
- 6 Nanda D N & Jug K, *Theoret chim Acta*, 57 (1980) 95.
- 7 Jug K, Iffert R & Schultz J, *Int J Quantum Chem*, 32 (1987) 265.
- 8 Iffert R & Jug K, *Theoret chim Acta*, 72 (1987) 373.
- 9 Pople J A & Nesbet G, *J chem Phys*, 22 (1954) 571.
- 10 Hehre W J, Stewart R F & Pople J A, *J chem Phys*, 51 (1969) 2657.
- 11 Hehre W H, Lathan W A, Dichfield R, Newton M P & Pople J A, *GAUSSIAN 70 PROGRAM*, Q.C.P.E. no. 236.
- 12 Edwards J O, Morrison G C, Ross V F & Schultz J W, *J Am chem Soc*, 77 (1955) 266.
- 13 Fornasier M, *Periodica Mineral, Rome*, 18 (1949) 103.
- 14 Jahn H A & Teller E, *Proc Roy Soc (London) Ser A*, 161 (1937) 220.
- 15 Paddon-Row M N & Wong S S, *J molec Struct (Theochem)*, 180 (1988) 353.
- 16 Moller C & Plesset M S, *Phys Rev*, 46 (1934) 618.
- 17 Pople J A, Binkley J S & Seeger R, *Int J Quantum Chem*, S10 (1976) 1.
- 18 Krishnan R & Pople J A, *Int J Quantum Chem*, 14 (1978) 91.
- 19 Krishnan R, Frisch M J & Pople J A, *J chem Phys*, 72 (1980) 4244.