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Quantum mechanical studies of distortions and polymerization of borate polyhedra

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Abstract

Ab initio self-consistent-field (SCF) molecular orbital (MO) theory has been used to calculate energy optimized B–O bond lengths (R(B–O)) for BO_3^{3-} and optimized R(B–O) and ∠B–O–B for $B(OH)_3$ (D_{3h} and C_{3v} symmetry), H_2BOBH_2, $(OH)_2BOB\ (OH)_2$, $H_2BOHBH_2^+$, $B_3O_6^{3-}$, $B_3O_6H_3$ and AlO_2BO. At the STO-3G minimum basis set level calculated R(B–O) for the neutral clusters differ from experiment by no more than 0.04Å. STO-3G calculations on H_2BOBH_2 and $(OH)_2BOB(OH)_2$ predict ∠B–O–B of 126° and 130°, respectively, with the predicted value for H_2BOBH_2 being in good agreement with values predicted using larger basis sets and with values for both molecules being near the range of values (128–133°) observed in crystalline B_2O_3. Protonation of the oxygen in H_2BOBH_2 causes almost no change in calculated ∠B–O–B but does produce a calculated increase in R(B–O) which is in agreement with observed bond length–bond strength sum systematics. For the $(OH)_3BOSi(OH)_3^-$ cluster the calculated STO-3G value of ∠B–O–Si is 125°, in good agreement with average observed values of 125–128° for such angles. STO-3G calculations on the $B_3O_6H_3$ ring reproduce the ordering of R(B–O) observed in $K_3B_3O_6$, with distances internal to the ring larger than those external, and give a ∠B–O–B in good agreement with the experimental value of 122.7°. The $(OH)_2BOB(OH)_2$ results also indicate that smaller valence electron charge buildup occurs in bridging than in nonbridging B–O bonds.

Introduction

Many features of mineral structure and spectra have recently been explained using molecular quantum mechanical methods (Tossell and Gibbs, 1977; Tossell, 1979). Early investigations were limited to the use of semiempirical molecular orbital (MO) methods such as extended Huckel and complete neglect of differential overlap (CNDO). Calculations were carried out on discrete molecular clusters chosen to model the solid minerals. The extended Huckel calculations demonstrated correlations between experimental bond lengths, bond angles and Mulliken overlap populations consistent with observed trends (Tossell and Gibbs, 1977 and references therein; Schlenker *et al.*, 1978). CNDO calculations on the model molecule $H_3SiOSiH_3$ (Tossell and Gibbs, 1978; Meagher *et al.*, 1979) yielded an energy optimized Si–O–Si angle of 150° in good agreement with those observed in gaseous $H_3SiOSiH_3$ (144°) and the $H_3SiOSiH_3$ molecular crystal (142°, Barrow *et al.*, 1979) and with the average value (148°) observed for a number of crystalline SiO_2 polymorphs. Although later *ab initio* self-consistent-field (SCF) MO calculations have generally substantiated the semiempirical calculations (*e.g.*, Newton and Gibbs, 1980; Geisinger and Gibbs, 1981), it has sometimes been found (*e.g.*, in $(SiH_3)_2O$) that calculated bond angles show significant variation with the choice of expansion basis set (Ernst *et al.*, 1981).

A serious limitation of semiempirical MO methods is their poor prediction of equilibrium bond lengths. This, however, has been one of the major achievements of *ab initio* SCF MO methods; bond distances and bond angles for small molecules have regularly been reproduced within a few percent of their experimental values (Thomson, 1978; Collins *et al.*, 1976; Schmiedekamp *et al.*, 1979; Wallmeier and Kutzelnigg, 1979). *Ab initio* theory has also been reasonably successful in the calculation and assignment of vertical ionization potentials for both core and valence electrons (Schwartz, 1977). In the area of quantum mineralogy, *ab initio* SCF MO methods have yielded accurate values for: (1) equilibrium bond distances and vibrational frequencies in triangular borate (Gupta and Tossell, 1981), carbonate and nitrate ions (Radom, 1976; Julg and Letoquart, 1978); (2) equilibrium bond lengths in four coordinated hydroxy anions of first row elements (Gupta *et al.*, 1981); (3) X-ray emission and photoelectron spectra for quartz and vitreous silica (Gilbert *et al.*, 1973; Newton and Gibbs, 1979); (4) tetrahedral bond length and bridging angle variations for framework silicates (Newton and Gibbs, 1980); and (5) the bulk modulus of low quartz (O'Keefe *et al.*, 1980).

Boron displays either three- or four-fold coordination

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with oxygen in borate minerals as expected from boron–oxygen radius ratio considerations (Pauling, 1929). Our earlier calculations (Gupta and Tossell, 1981) using *ab initio* SCF MO theory and minimum STO-3G basis sets for the molecular clusters $B(OH)_3$ and $B(OH)_4^-$ yielded energy optimized B–O bond lengths within .04Å of the average values observed in borate minerals. *Ab initio* calculations employing larger basis sets have also yielded accurate geometric parameters for a number of gaseous molecules containing B–O bonds (Fjelding *et al.*, 1980), but no application of the results to solid materials has been made. Our previous 4-31G calculation on BO_3^{3-} in its equilibrium geometry was also used to predict the X-ray emission spectra (XES) and photoelectron spectra (PES) of crystalline B_2O_3. The present paper is a continuation of our effort to understand bonding and electronic structure of borate minerals quantum mechanically. We have first repeated our calculations on BO_3^{3-} and $B(OH)_3$ monomeric units, using larger expansion basis sets and less severe symmetry constraints. We have also fully optimized the geometry of H_2BOBH_2, a simple model for corner sharing triangular borate, using a number of different expansion basis sets in order to evaluate the reliability of small basis set results for this species. The effect of bond strength sum on R(B–O) is modeled by calculations on $H_2BOHBH_2^+$ and AlO_2BO, borate ring geometries are studied through calculations on the trimeric cluster $B_3O_6H_3$ and the optimum value of the ∠B–O–Si in $(OH)_3BOSi(OH)_3^-$ is calculated. For the dimer $(OH)_2BOB(OH)_2$ calculations at the valence double zeta level are used to obtain valence electron difference density maps.

Computational details

The SCF MO theory on which this paper is based was developed by Roothaan (1951). A comprehensive introduction to this theory has been given by Schaefer (1972). The *ab initio* SCF MO calculations were carried out using the programs HONDO (Dupuis *et al.*, 1977) or an extended version of HONDO called GAMESS (Dupuis *et al.*, 1980). The STO-3G bases (Hehre *et al.*, 1969, 1970) employed standard molecular exponents for the Slater type atomic orbitals, *e.g.*, a H1s exponent of 1.24 compared to the optimum value of 1.0 in free H. Our earlier studies with optimum atomic exponents (Stewart, 1969) yielded H–H distances (and consequently ∠B–O–B in H_2BOBH_2) which were considerably larger than experiment. 4-31G basis sets of valence double zeta quality were also employed for some of the geometry and electron distribution studies. For H and O 4-31G bases were obtained directly from the tabulation of Ditchfield *et al.* (1971). For B the 4-31G basis of Hehre and Pople (1972) was employed. We also carried out calculations on H_2BOBH_2 with a d polarization function of exponent 0.95 on O. It is known that such polarization functions can significantly affect calculated angles at divalent oxygen (Pople, 1977; Bader and Gangi, 1975). The exponent value of 0.95 for O3d was chosen to make our calculations compatible with those of Fjeldberg *et al.*, (1980). In construction of valence electron density difference maps we have used double zeta quality Slater orbital wavefunctions for the neutral spherical atoms (Clementi and Roetti, 1974). The lack of strict comparability of molecular (4-31G) and atomic (double zeta Slater) basis sets makes accurate calculation of absolute difference densities impossible. Indeed, inclusion of polarization functions and corrections for thermal motion would be necessary for this purpose (Coppens and Stevens, 1977). Rather, we are interested in changes in valence electron difference density between our present calculations on dimers and previous ones on monomers (Gupta and Tossell, 1981) employing the same combination of molecular and free atom bases as in the present case. For molecular clusters with high symmetry, small numbers of non-H atoms and using small basis sets (*e.g.*, H_2BOBH_2, $B_3O_6H_3$) complete geometry optimizations were done using the GRADSCF procedure (Komornicki *et al.*, 1977) implemented in the GAMESS program. In other cases, certain geometric parameters were held fixed (*e.g.*, R[B–O] in $[OH]_2BOB[OH]_2$) and optimized parameters were determined by parabolic interpolation.

It is important to note that some of the molecular clusters employed here are not stable gas phase molecules but merely model systems. Thus, a complete optimization of their geometry to high precision is meaningless. Rather, we are concerned with the development of a simple modeling procedure which will enable us to understand average values and ranges of geometric parameters in complex solids. The modeling aspect of our calculations must constantly be borne in mind while assessing the results. We have also restricted the basis set size in our calculations to reduce computer expense and because we are mainly concerned with the geometric and electronic trends observed in large systems rather than with the accurate reproduction of the properties of small gas phase molecules.

Although our work is to a large extent a computer "experiment" designed to define the nature of appropriate cluster models for minerals, previous experience suggests several principles to be used in generating the clusters and interpreting the results. First, the cluster model works best for the study of geometries if bonds internal to the cluster are stronger and more covalent than the external bonds. For example, in $B(OH)_3$(S) the B–O bonds are stronger than the H bonds holding the solid structure together. Second, bonds near the middle of the cluster are more accurately described than those on the periphery. Thus B–O bond distances would be more accurate than O–H distances in $B(OH)_3$. Third, proper coordination number is very important for metal atoms and less critical for anions. Fourth, the total cluster charge must be kept small. A qualitative analysis (Tossell, 1981) indicates that for a simple $M(OH)_n$ anion calculated bond distances will be exaggerated by an amount varying as (cluster charge)^2/metal cation charge. A simple way to obtain nearly neutral clusters is by profonation, *e.g.*, by converting BO_3^{3-} into H_3BO_3. However, OH^- is probably less polarizable than O^{2-} within most crystals so such a procedure may introduce a systematic error. Finally, geometric parameters obtained from the cluster calculation are at best representative of the average values of such parameters in a range of solids. For example, the calculated B–O distance in H_3BO_3 should be compared with average distances between (three-coordinate) B and O in solids. Even this correspondence will not be obtained if forces outside the cluster unit are large and/or are biased in one direction (*e.g.*, to increase the B–O distance) rather than being randomly distributed when a range of solids is considered.

Results of computations

Triangular borate monomers

As shown in Table 1, the calculated equilibrium geometry of BO_3^{3-} is of D_{3h} symmetry and has R(B–O) = 1.419Å using an STO-3G basis set and 1.435Å for the 4-31G basis, both of which are longer than the experimental values of 1.34–1.40Å. The increase in calculated R(B–O) with basis set expansion is surprising since 4-31G calculated bond distances are generally smaller than STO-3G values. For the isoelectronic ions NO_3^- and CO_3^{2-} calculated distances decrease from STO-3G to 4-31G by 0.059 and 0.025Å, respectively (Radom, 1976). It thus appears that the change in bond distance with basis set is a function of total charge. As the total charge becomes more negative the calculated 4-31G bond distance increases more rapidly than the STO-3G. A similar result was observed for C_2^{2-} by Radom (1976) with the calculated 4-31G bond distance being longer than the STO-3G value by .059Å. Ahlrichs (1975) has noted that if a SCF MO calculation gives positive eigenvalues for any of the occupied MO's the calculated energy may be lowered by admixture of continuum functions into these MO's. The highest energy occupied MO's of NO_3^- have negative eigenvalues while those of CO_3^{2-} are slightly positive and those of BO_3^{3-} strongly positive ($\epsilon \simeq +11$ eV for the highest energy occupied MO). Thus, basis set expansion for anions may lead to different results than for neutral molecules. Of course, both STO-3G and 4-31G distances are considerably larger than the observed experimental distances as expected for highly negative ions (Tossell, 1981). This problem is easily corrected by protonation of the cluster leading to STO-3G and 4-31G values for R(B–O) and ∠B–O–H in good agreement with experiment (Table 1; STO-3G and 4-31G calculated O–H distances are 0.98 and 0.95Å, respectively, also consistent with expected values). Calculations on $HB(OH)_2$ (Fjeldberg *et al.*, 1980) employing 3d functions on O yield an average predicted B–O distance of 1.371Å which is almost identical to our 4-31G calculated value for $B(OH)_3$ and is in good agreement with the gas phase electron diffraction result of 1.359 (quoted in Fjeldberg *et al.*, 1980).

Table 1. Calculated and experimental geometries of triangular borate monomers (distances in Å)

		R(B-O)			<B-O-H		
		exp	STO-3G	4-31G	exp	STO-3G	4-31G
BO_3^{3-}		1.34-1.40[a]	1.419	1.435			
$B(OH)_3$	D_{3h}		1.454	1.364	assumed 120°		
	C_{3h}	1.361[b]	1.364	1.364	114[b]	110	121

a. Gurr et al., 1970

b. Zachariasen, 1954

An examination of bond lengths and bond angles in borate minerals containing distorted triangular BO_3^{3-} groups reveals that usually longer B–O bond lengths involve narrower O–B–O bond angles. Schlenker *et al.*, (1978) using extended Huckel calculations and the resulting Mulliken bond overlap populations have drawn the same conclusion. To find out whether an energy minimum exists corresponding to the bond angle–bond length correlation described above the procedure of Schlenker *et al.* (1978) for defining apical and basal bonds and α and β angles was adopted. For an XY_3 group with all atoms in the same plane and C_{2v} point symmetry there is one apical X–Y bond and two equivalent equatorial X–Y bonds. The α angle is defined as the ^{Y}apical $^{-X-Y}$basal angle while β is one of the equivalent ^{Y}basal $^{-X-Y}$basal angles. STO-3G calculations with α fixed at 115° and basal bond lengths at 1.398Å (the STO-3G equilibrium bond distance for ∠B–O–H = 114°) were performed at a number of different apical B–O bond lengths. The minimum energy geometry was found for an elongated apical B–O bond distance of 1.403Å. These results thus are consistent with the observed bond angle–bond length correlation, with narrower O–B–O bond angles generating longer B–O bonds. However, the effect of bond angle upon bond length is smaller than that observed experimentally (Schlenker *et al.*, 1978). Similar results have been obtained from *ab initio* SCF calculations on distorted $Si(OH)_4$ by Newton and Gibbs (1980), *i.e.*, the trend of Si–O bond length with O–Si–O angle was in the correct direction but was smaller than observed experimentally. These results suggest that consideration of larger clusters will be necessary to accurately reproduce the experimental results.

Corner sharing triangular borate dimers

Crystalline B_2O_3 (Gurr *et al.*, 1970) and the pyroborates (Wells, 1975) possess corner sharing triangular borate units with bridging angles, ∠BOB, in the range of 128–153°. In order to model such B–O–B linkages, calculations were performed on the molecular clusters H_2BOBH_2 and $(OH)_2BOB(OH)_2$. Results are presented in Table 2. A C_{2v} geometry was chosen, with all atoms lying

Table 2. Calculated and experimental geometries of triangular borate dimers (distances in Å)

		STO-3G	4-31G	4-31G+O3d
H_2BOBH_2	R(B-O)	1.353	1.375	1.370
	<B-O-B	126.4°	134.5°	125.8°
		STO-3G	4-31G	
$(OH)_2BOB(OH)_2$	<B-O-B	130	144	
B_2O_3(c)	<B-O-B	128 - 133°		
all B-O-B linkages	<B-O-B	128 - 153°		

in the B–O–B plane. Such planar groupings are observed in B_2O_3 (Gurr *et al.*, 1970) and have been identified as the minimum energy conformations in more extensive geometry studies (Fjeldberg *et al.*, 1980).

The geometry of H_2BOBH_2 has been previously optimized by Fjeldberg *et al.* (1980) using a double zeta basis set with an added O3d polarization function. Their values of $R(B–O) = 1.383$ and $\angle B–O–B = 126.6°$ are very similar to our 4-31G + O3d values. We find that STO-3G and 4-31G bases also give reasonable bond distances and angles. As in the case of $(SiH_3)_2O$ (Ernst *et al.*, 1981), the calculated $\angle T–O–T$ increases in going from STO-3G to 4-31G basis, but the effect is considerably smaller in magnitude than it was for $(SiH_3)_2O$.

Similar calculations have been performed for $(OH)_2BOB(OH)_2$ (with $R(B–O) = 1.379$ and $R(O–H) = 0.96$Å) yielding minimum energy $\angle B–O–B$ of 130° and 144° for STO-3G and 4-31G basis sets, respectively. Although comparison of the H_2BOBH_2 and $(OH)_2BOB(OH)_2$ results is made difficult by the use of fixed B–H and B–O(H) lengths the trend in calculated equilibrium angle is similar to that observed in CNDO and *ab initio* calculations on silicates (Tossell and Gibbs, 1978; Newton and Gibbs, 1980; G. V. Gibbs, pers. comm.) with the optimum T–O–T angle increasing slightly as the saturator is changed from H to OH.

An important property of a molecule or solid is the electron density, ρ, which is easily calculated from MO wavefunctions and may be obtained experimentally from accurate X-ray and neutron diffraction studies (Coppens and Stevens, 1977). Our previous study of BO_3^{3-} and $B(OH)_3$ (Gupta and Tossell, 1981) concentrated upon the difference electron density, $\Delta\rho$, which is the molecular density minus the sum of the densities of the neutral spherical atoms. The difference density so defined has been found to give useful information on charge transfer and covalent bond formation. For BO_3^{3-} the $\Delta\rho$ map showed charge transfer from B to O, charge buildup along the B–O bond of magnitude 0.30 electrons /Å^3 and lone pair character on O.

The $\Delta\rho$ contour maps for $(OH)_2BOB(OH)_2$ ($R(B–O) = 1.379$Å) with B–O–B angles of 130° and 180° are shown in Figure 1. The qualitative features of these maps are the same as previously described for $B(OH)_3$ but there are significant quantitative differences. The height of the $\Delta\rho$ peaks along the B–O bonds in $(OH)_2BOB(OH)_2$ are about 20% higher than in $B(OH)_3$ with the $\Delta\rho$ increase being greater for the B–O(H) bond. We also find that the B–O bridging peak is strongly dependent upon B–O–B angle, with the 180° angle case showing a substantially smaller charge buildup than the case for the 130° angle, near the observed equilibrium value. For the 130° case there is also a charge removal region separating the B–O(H) bonds and a strong polarization of lone pair density away from the B–O–B angle.

Three membered borate rings: $B_3O_6^{3-}$ and $H_3B_3O_6$

The cyclic metaborate ion $B_3O_6^{3-}$, in which three borons and three oxygens alternate within a six-membered planar ring and each boron is bonded to an additional external oxygen, is found in $K_3B_3O_6$ (Schneider and Carpenter, 1970) and other metaborates. It shows a distance from B to the internal (ring) oxygen of 1.398Å while the distance to the external oxygen is 1.331Å. Geometries for $B_3O_6^{3-}$ and $B_3O_6H_3$ have been fully optimized at the STO-3G level and results are listed in Table 3. Although the calculated trends are in agreement with experiment the B–O external distance is seriously underestimated even for the calculation on the neutral cluster, suggesting that in the solid the additional cations exert a bond lengthening effect greater than that of our H^+ saturator. Note that the $\angle B–O–B$ calculated for $B_3O_6H_3$ (121°) and that observed for $K_3B_3O_6$ (123°) are only slightly smaller than those calculated for $(OH)_2BOB(OH_2)$ (130°, STO-3G) and observed for B_2O_3 (128–133°).

Perturbation of B–O bond lengths by changes in bond strength sum to oxygen

To model bond length perturbation of the BO_3 unit produced by neighboring cations we have considered two systems: protonated H_2BOBH_2 (*i.e.*, $H_2BOHBH_2^+$); and AlO_2BO. All calculations were performed at the STO-3G level. We find a R(B–O) in $H_2BOHBH_2^+$ which is .086Å longer than in H_2BOBH_2 (the <B–O–B is 127.8°, essentially unchanged from H_2BOBH_2). For AlO_2BO in C_{2v} symmetry with Al bonded to two oxygens we find R(B–O) of 1.480Å for O bonded to B and Al and 1.212Å for O bonded to B alone. The average R(B–O) in AlO_2BO is thus 1.391Å, somewhat smaller than the 1.419Å value calculated for the BO_3^{3-} anion. The elongation of the B–O bonds by Al^{3+} is then either 0.09Å or 0.06Å depending upon whether the AlO_2BO average or BO_3^{3-} is taken as reference.

Although the AlO_2BO species are probably purely hypothetical, related species do exist in the gas phase. For example, Moore and Devlin (1978) studied gaseous LiO_2NO by calculation and experiment and concluded that it possessed a C_{2v} geometry of the type assumed for AlO_2BO and had an inequivalency of the N–O bond

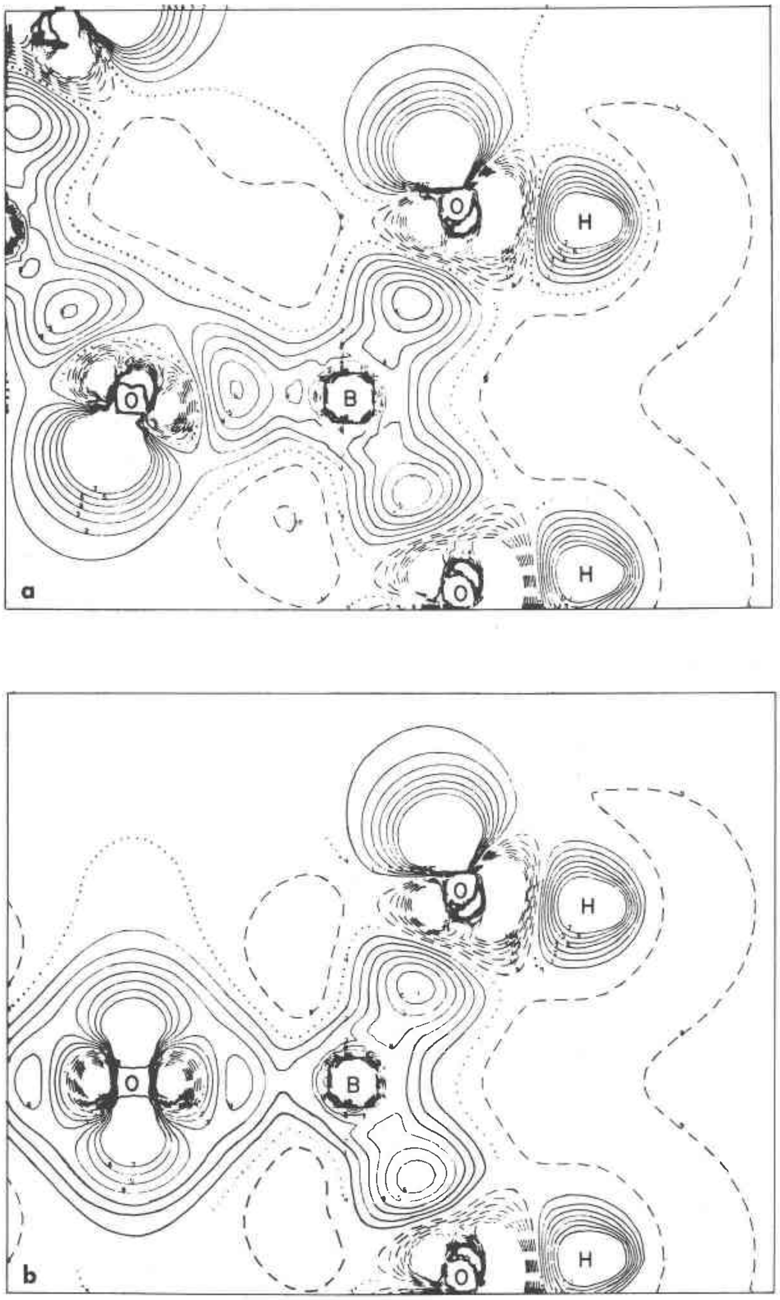

Fig. 1. Electron density differences, $\Delta\rho$, between molecule and superimposed neutral spherical atoms for $(OH)_2BOB(OH)_2$ in the plane of the molecule. Negative contours are dashed, zero contours dotted and positive contours solid. Contours change by intervals of ±0.05 electrons $(\text{Å})^{-3}$. (a) angle BOB = 130° (b) angle BOB = 180°

distances. The bond to oxygen coordinated by Li was found to be longer than that for the uncoordinated oxygen by 0.09Å, consistent with qualitative bond length–bond strength sum systematics.

The effect of second neighbor cations upon bond length is often described in terms of their electrostatic bond strength which is defined as their formal charge divided by their coordination number (Pauling, 1929). The bond strengths to oxygen from H and Al in the clusters considered are thus 1 and 3/2, respectively. A linear relationship between bond strength received and bond length has been noted by Baur (1970) and Ferraris and Catti (1973) have shown that this approach yields the expression $\Delta R = k\Delta p$ for distorted oxide polyhedra, in

Table 3. Calculated STO-3G equilibrium geometries for $B_3O_6^{3-}$ and $B_3O_6H_3$ compared with experimental geometries in $K_3B_3O_6$ and $Na_3B_3O_6$

	$B_3O_6^{3-}$	$B_3O_6H_3$[a]	exp[b,c]
R(B-O internal) (Å)	1.430	1.374	1.398,1.433
R(B-O external) (Å)	1.279	1.289	1.331,1.280
<B-O internal-B (°)	125	121	122.7,114.5

[a] optimum R(O-H) = 0.95Å

[b] Schneider and Carpenter (1970)

[c] Marezio, et al. (1963)

which ΔR is the difference of the inequivalent M–O bond distances, Δp the difference in bond strength sums received by the oxygens and k an empirical parameter. For B–O bonds they give a k value of 0.082Å per bond strength unit. Clearly our calculated bond elongations are of approximately the expected magnitude.

Corner-sharing silicate and borate tetrahedra

In borosilicates boron may exist either in three or four coordination in the presence of tetrahedral silicon (Ghose and Wan, 1976). The bridging bond angle B–O–Si between tetrahedral B and Si varies from 120° to 135° (Finney and Kumbasak, 1970), but the mean value usually has a very narrow range of 125–128° (Ghose and Wan, 1976; Wells, 1975). Calculations on the protonated cluster $(OH)_3SiOB(OH)_3^-$, using the STO–3G basis set and holding Si–O, B–O and O–H bond length at values of 1.61Å, 1.472Å and 0.96Å, respectively, angles around B and Si at 109.5 and B–O–H or Si–O–H angles at 114° gave a minimum energy angle at 125°. The variation of energy with variation in bridging bond angle is rather steep at both very small and very large angle but is small in the range 120–131°. The calculated average and range of bridging angle are thus consistent with experiment. Since 4–31G calculations on the $(OH)_3SiOB(OH)_3^-$ cluster would have been quite expensive, it was fortunate that the STO–3G calculations yielded reasonable results. These were not an artifact of the fixed geometric parameters since a full STO–3G optimization of $(OH)_3SiOB(OH)_3^-$ also yielded a <Si–O–B of 125 (and R(Si–O) = 1.60, R(B–O) = 1.44; Chakoumakos and Gibbs, 1981; Gibbs, pers. comm.).

Conclusions

The present results indicate that small basis set *ab initio* SCF MO calculations on small molecular clusters are adequate for reasonable prediction of bond angles and bond distances in borate minerals. The appropriateness of such model calculations for solids is further supported by the similarity of observed gas phase and solid geometric parameters. It is, therefore, possible to obtain both absolute values of geometric parameters and trends in such parameters with very modest computational effort for borate systems.

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