Ab initio Molecular Orbital Calculations on the Acidic Properties of Boralite

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The ability to characterise the acidic and geometric properties of boron substituted zeolites using *ab initio* molecular orbital calculations is demonstrated; the acidity of the bridged hydroxy group in boralite is predicted to lie between that of terminal and bridged aluminium forms.

Isomorphous substitution of aluminium by various other elements into zeolite frameworks provides an important method to vary acidic and hence catalytic properties. The stabilities and variation in the acidic properties of these new materials are in most cases a matter for experiment. *A priori* prediction of the properties of such altered zeolite forms would therefore be of considerable advantage. It has been known for some time that accurate geometrical information can be obtained using *ab initio* molecular orbital calculations on silica and aluminosilicate structures.[1,2] An especially encouraging finding from these studies is that simple discrete molecular clusters [*e.g.* $(SiH_3)_2O$ or SiH_3OHAlH_3] can give a good quantitative account of related crystalline materials. In this report we use *ab initio* calculations to predict the geometrical and electronic (particularly acidic) properties of boralites using silicon–boron units representative of the boralite framework. The close correspondence between theoretical and experimental observations leads us to conclude that such calculations can be valuable as *a priori* guides to the synthetic zeolite chemist.

The units investigated are represented in Figure 1 where (a) is taken to represent a terminal hydroxy group, (b) and (c) correspond to bridged hydroxy groups of the aluminium and boron forms respectively, and (d) represents the unprotonated boron form. The prohibitive cost of *ab initio* type calculations limits the size of the clusters that can be investigated. As shown previously[1,3] and as demonstrated here, such simple units can lead to quite accurate agreement with experimental observations. The M.O. calculations were performed at the restricted Hartree–Fock–Roothaan level using the 3–21 G basis set. The calculations including geometry optimisation (within the symmetry constraints of Table 1) and force constant evaluation were performed using the GAMESS quantum chemistry package as implemented on the CYBER 205 computer at the University of Manchester Regional Computer Centre. For the basis set used typical bond length errors are ±1 pm whereas force constants are generally overestimated by 5—20%.[2,4] Timings for optimization and force constant evaluation varied from 300 to 1200 s.

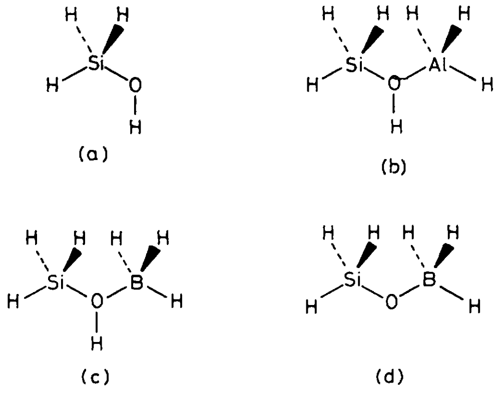

Figure 1. Molecular models for quantum chemical calculations.

An outline of the geometrical data and relevant properties so obtained for units of Figure 1 are presented in Tables 1 and 2. The data are similar to those obtained recently by Mortier *et al.*[2] From Tables 1 and 2 it can be seen that the calculated OH bond length and the OH stretching frequency of the bridged boron form are intermediate in value between that of the terminal and bridged aluminium forms. The $|q_H q_O|$ value, which can be taken as a measure of the ionicity of the O–H bond,[5] and the deprotonation energy (ΔH_D) are also intermediate in value for the boron unit. All these calculated properties suggest an intermediate acidity for the boron unit compared with the terminal and bridged aluminium forms. The acidic properties of boralites have been characterised experimentally by i.r.[6] and ^1H magic angle spinning (m.a.s.) n.m.r. spectroscopy, and temperature programmed desorption of ammonia.[6] In all three cases, it is demonstrated that the acidic properties of the bridged hydroxy group of boralite lie between those of terminal (SiOH) and bridged aluminium hydroxy groups in agreement with the present theoretical predictions (Table 1). Additionally, the increase in the Si–O and B–O bond lengths on protonation (Table 1) is similar to that found both experimentally[8] and theoretically[2] for the aluminium form. Recent ^{11}B m.a.s. n.m.r. results[9] have been interpreted to indicate that considerable lengthening of the B–O bond occurs in the protonated form of boralite resulting in a severe distortion of the BO_4 tetrahedron. Although our theoretical model is concerned with the OBH_3 tetrahedron, the observed increase in the B–O bond length of 14.6 pm on protonation, plus the significant variations in the OBH and HBH bond angles (Table 1) is in qualitative agreement with a distortion of the tetrahedral symmetry around the boron atom on protonation. ^{27}Al M.a.s. n.m.r. results[10] also suggest that a distortion of the Al tetrahedron occurs in the protonated form

Table 1. Optimised geometries for model units.

System (point group)	H_3SiOH (C_s)	$H_3SiOHAlH_3$ (C_s)	$H_3SiOHBH_3$ (C_s)	$H_3SiOBH_3^-$ (C_s)
r(SiH)	148.5[a]	147.5	147.5	150.7
∠OSiH	110.6	107.2	107.7	114.5
∠HSiH	107.9	110.7	110.2	104.5
r(SiO)	167.3	173.4	172.2	162.4
r(OH)	95.8	96.7	96.3	
∠SiOH	127.7	120.4	125.5	
∠SiOAl		126.8		
∠SiOB			122.6	139.8
r(AlO)		192.8		
r(BO)			168.1	153.5
r(AlH)		161.9		
r(BH)			120.5	123.9
∠OAlH		100.5		
∠OBH			103.6	110.0
∠HAlH		117.1		
∠HBH			114.3	108.7

[a] Bond distances in pm; angles in degrees.

Table 2. OH bond characteristics and deprotonation energies.[a]

	q_H	q_O	$\lvert q_H q_O \rvert$	ν_{OH}/cm^{-1}	$\Delta H_D/kJ\,mol^{-1}$
H_3SiOH	0.4156	−0.8859	0.3682	3995[b]	1640[b]
$H_3SiOHBH_3$	0.4670	−0.8649	0.4040	3964	1460
$H_3SiOHAlH_3$	0.4727	−0.9341	0.4415	3931[b]	1429[b]

[a] q_H, q_O, Mulliken charges on bridging H and O; ΔH_D deprotonation energy; ν_{OH}, calculated OH stretching wavenumber; for absolute comparison with experimental values appropriate scaling factors are necessary, ref. 2. [b] From ref. 2.

of ZSM5, although the distortion is predicted to be less than that observed for the boron substituted form.[9] The theoretical data presented here, however, do indicate that the OBH_3 and $OAlH_3$ tetrahedra are similarly distorted. The bridged aluminium unit in Figure 1 can be interpreted in terms of an electron donor (AlH_3)–electron acceptor (H_3SiOH) interaction.[5] A similar situation can be put forward for the bridging boron unit with BH_3 acting as the electron donor unit and the degree of perturbation of the H_3SiOH unit can be taken as a measure of the strength of this interaction. The similar SiOH angle calculated for the H_3SiOH and the bridged boron unit (Table 1) plus the similar oxygen charges (Table 2) suggest a weaker perturbation of H_3SiOH by BH_3 compared with perturbation by AlH_3. Thus the bridged boron hydroxy group is predicted by *ab initio* calculations to be more silanol in character than the bridged aluminium form which, as outlined above, has been verified experimentally.

We conclude that *ab initio* M.O. calculations can predict variations that occur in the acidic and geometric properties of zeolitic materials upon isomorphous substitution of aluminium. The range of elements capable of being substituted into zeolite frameworks continues to grow and it is clear that M.O. calculations, at the *ab initio* level, can be a valuable and reliable indicator of the properties of such materials.

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