# *Ab initio* MO Studies of Boric Acid, B(OH)$_3$, Tris(amino)borane, B(NH$_2$)$_3$, and Tris(boryl)amine, N(BH$_2$)$_3$

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The results of *ab initio* molecular orbital calculations on (H$_2$B)$_3$N, B(NH$_2$)$_3$ and B(OH)$_3$ are presented in this paper. These results complement those already published for (H$_2$B)$_2$NH, H$_2$BNH$_2$, HB(NH$_2$)$_2$ and for (H$_2$B)$_2$O, H$_2$BOH and HB(OH)$_2$.[1] Taken together the results provide a basis for discussion of structural and bonding trends in the two series of molecules:

(H$_2$B)$_3$N, (H$_2$B)$_2$NH, H$_2$BNH$_2$, HB(NH$_2$)$_2$, B(NH$_2$)$_3$

—   (H$_2$B)$_2$O , H$_2$BOH , HB(OH)$_2$, B(OH)$_3$
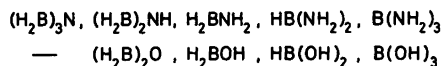
In both series the number of π-acceptor atoms (B) to π donor atoms (N or O) decreases monotonically on going from left to right, and on either side of H$_2$BNH$_2$ or H$_2$BOH the formal possibility for π-bonding decreases symmetrically as the central acceptor (left) or donor (right) atoms are shared between an increasing number of donor or acceptor atoms respectively.

The minimum energy geometries of HB(OH)$_2$ and HB(NH$_2$)$_2$ have previously been shown[1] to compare favourably with microwave structural results.[2,3] Similarily, recent MW results for H$_2$BNH$_2$[4] and H$_2$BOH[5] give further evidence for the good correspondence between results obtained by *ab initio* calculations at the present level and those obtained experimentally by MW spectroscopy.

Methyl derivatives of each molecule in the two series of molecules except trisaminoboranes have been subject to gas electron-diffraction studies[6-11] and their molecular structures have been related to those of the parent molecules.[1,8,10]

A recent publication by Pople and coworkers contains results, including minimum energy geometries, obtained for H$_2$BNH$_2$, HB(NH$_2$)$_2$, H$_2$BOH, HB(OH)$_2$ and B(OH)$_3$ by *ab initio* MO calculations at various levels.[12] These results are generally in good agreement with ours. In particular it is pleasing that full geometry optimization on the perpendicular forms confirms that a 90° rotation about the B−O bonds results in a very modest

elongation of the B−O bonds, while rotation about the B−N bonds to perpendicular conformations results in a substantial elongation of the B−N bonds.

Computational details and results. The calculation procedure followed strictly that employed for the previous series of molecules,[1] *i.e.* the computer program MOLECULE[13] and Gaussian-type orbitals [(7s, 3p) for boron, oxygen and nitrogen and (4s) for hydrogen] contracted to a double-zeta basis augmented with polarization functions for oxygen and nitrogen were used. The results are comprised in Table 1.

The minimum energy geometries were obtained for fixed B−H, O−H and N−H bond lengths (see Table 1) by six-points variations of the parameters r(BO) and ∠ BOH; r(BN) and ∠ BNH; and r(NB) and ∠ NBH, assuming the molecules to be planar (C_{3h}-symmetry). In subsequent calculations one group in each molecule was rotated about the bond to the central atom. Torsional angles of $\phi = 5°$ gave increased energies in all cases by amounts as reflected by the reported torsional force constants (Table 1) computed by assuming harmonic torsional behaviour about $\phi = 0°$. The barriers to rigid rotation were computed using the energies obtained when one group was rotated to the $\phi = 90°$ positions. From the Mulliken population analyses the gross atomic population (N_k) for B, O, and N and the overlap populations ($n_{k,l}$) for the B−O and B−N bonds are given in Table 1 for the planar structures of the molecules, and these quantities are split into their σ- and π-contributions. The formal charges, Q, of all the atoms of the molecules are easily deducted from the given gross atomic populations by considering the number of electrons of the free neutral atom, and for the hydrogens also implementing the neutrality and the symmetry of the molecules.

Discussion. The quantities of major interest in connection with bond strength variations are compared graphically for both series of molecules in Fig. 1. The fact that the B−O bond elongation in the series H$_2$BOH, BH(OH)$_2$ and B(OH)$_3$ is not pronounced and that the B−O bonds in the *syn* and *anti* moieties of HB(OH)$_2$ are comparable in length to those in B(OH)$_3$ and H$_2$BOH, respectively, is in agreement with the other *ab initio* molecular orbital results for these molecules.[12] It is seen from Fig. 1 that the bond length (r) increases on either side of H$_2$BNH$_2$ and H$_2$BOH as expected from the decreased possibilities for π-bonding, but the distance distributions are not symmetrical, the bonds being longer when the donors (N or O) are the central atoms, *i.e. r* is longer for B/X equal to 3/1 and 2/1 than for B/X values of 1/3 and 1/2, respectively.

Further inspection of Fig. 1 reveals that the π-bond order is greater in the B−N than in the B−O

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Table 1. Total energies (E_{tot}, in a.u.), minimum energy geometries[a] (distances, r, in Å and angles, $\angle$, in degrees), barriers to rigid rotation (ΔE, in kcal mol^{-1}), force constants (stretch, k_r, in aJ Å^{-2} and torsion, k_ϕ, in aJ rad^{-2}), charge distributions (net overlap populations, $n(k,l)$, and gross atomic population, $N(k)$) for $B(OH)_3$, $B(NH_2)_3$ and $N(BH_2)_3$.

$B(OH)_3$		$B(NH_2)_3$		$N(BH_2)_3$	
E_{tot}	−250.88452	E_{tot}	−191.43727	E_{tot}	−131.93389
$r(OH)$	0.95 (fixed)	$r(NH)$	1.006 (fixed)	$r(BH)$	1.200 (fixed)
$r(BO)$	1.378	$r(BN)$	1.439	$r(NB)$	1.461
$\angle BOH$	111.36	$\angle BNH$	123.26	$\angle NBH$	119.61
ΔE	9.04	ΔE	10.53	ΔE	11.97
$k_r(BO)$	8.1	$k_r(BN)$	7.32	$k_r(NB)$	6.22
$k_\phi(BO)$	0.10	$k_\phi(BN)$	0.13	$k_\phi(NB)$	0.15
$n(B,O)$	0.73	$n(B,N)$	0.76	$n(N,B)$	0.64
σ	0.58	σ	0.59	σ	0.48
π	0.15	π	0.17	π	0.16
$N(B)$	3.93	$N(B)$	3.92	$N(B)$	4.58
σ	3.52	σ	3.46	σ	4.42
π	0.41	π	0.46	π	0.17
$N(O)$	8.78	$N(N)$	7.97	$N(N)$	8.02
σ	6.92	σ	6.13	σ	6.52
π	1.86	π	1.84	π	1.50

[a] C_{3h}-symmetry assumed. See text.

bonds, and that the variation in n^π throughout the series of molecules is less pronounced for the boron −oxygen than for the boron−nitrogen compounds. According to the present calculations the π-bonding is reduced by approximately equal amounts within each of the pairs $(H_2B)_2NH$, $HB(NH_2)_2$; $(H_2B)_3N$, $B(NH_2)_3$; and $(H_2B)_2O$ and $HB(OH)_2$ as compared to H_2BNH_2 and H_2BOH. Thus the unsymmetrical variations of the B−X bond lengths appear to be caused by changes in the σ-bond strength which increases throughout both series of molecules so as to amplify the effect from the decrease in π-bonding as the number of borane groups attached to a central π-donor increases, and to oppose the effect as the number of π-donors attached to a central π-accepting boron atom increases. In fact, the opposing variations of n^σ and n^π in the H_2BOH, $HB(OH)_2$ and $B(OH)_3$ series result in a slight decrease only in n_{tot} and consequently in the B−O bond length. The present calculations suggest that the σ-bond becomes stronger when the number of electronegative ligands attached to a central atom increases as also established experimentally, whereas the σ-bond is weakened as an electronegative central atom is bonded to an increasing number of electropositive ligands.

Similarily to the close relationsships between the changes in n_{tot} and r for both series of molecules it is seen that the variations of ΔE_{rot} and n^π are closely related for the boron−nitrogen series as expected since the barriers to rigid rotation in these molecules should express the energy needed to break the π-bonds. However, the results for $B(OH)_3$ conform to the trend suggested by the previous results for H_2BOH and $HB(OH)_2$,[1] *i.e.* ΔE_{rot} for $B(OH)_3$ is not as low as expected from considerations of ΔE_{rot} for H_2BOH and the difference between the n^π values for the two molecules. This has, together with the small elongation of the B−O bond upon rotation to perpendicular forms, been discussed previously,[1] and related to the possibility that due to a second lone pair of electrons of the oxygen it may act as a π-electron donor to boron even in perpendicular forms as also suggested in connection with interpretations of NMR data for boranes with boron−oxygen bonds.[14]

Crystal structure data are available for some more complex tris(boryl)amines. In tris(1,3,2-benzodioxaborol-2-yl)amine the boron atoms have bonded interactions with two oxygens in addition to the nitrogen. The molecule is planar in the solid state and has an average B−N bond length of 1.438 Å[15] which appears short according to the trends established by the present calculations. During the preparation of the present manuscript X-ray structural studies have shown that $N[B(SCH_3)_2]_3$ and three other trisborylamines possess C_2 symmetry with two different N−B bond lengths in
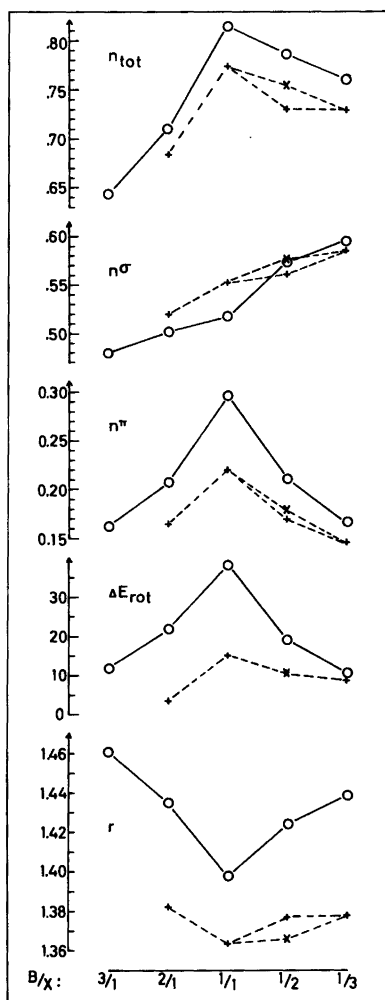
for some of the molecules, approaches the single bond estimate for B−N of 1.50 Å and the value calculated for perpendicular forms of aminoborane (1.479 Å).[1] These results seem to warrant more serious treatment of nonplanar models for $(H_2B)_3N$ and this will be considered in connection with further structural studies of tris(boryl)amines.

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Fig. 1. Bond distances (*r*, in Å), barriers to rigid rotation (ΔE_{rot}, in kcal mol^{-1}) and total, σ- and π overlap populations (n_{tot}, n^π and n^σ, respectively) for the B−X bonds as a function of the number of boron atoms per π-electron donor (B/X), *i.e.* for $(H_2B)_3N$, $(H_2B)_2NH$, H_2BNH_2, $HB(NH_2)_2$ and $B(NH_2)_3$ (○, and full lines) and for $(H_2B)_2O$, H_2BOH, $HB(OH)_2$ and $B(OH)_3$ (+, and broken lines; for $HB(OH)_2$, + refers to *syn,* and × to *anti* HBOH arrangements).

the solid state.[16] The short bonds vary between 1.42 −1.44 Å and the longer bond to the group more or less perpendicular to the B_3N-plane varies between 1.46−1.48 Å. Thus, the two shorter B−N bonds in each molecule are comparable in length to those of bis(boryl)amines[11] whereas the bond for which effects from π-bonding should be negligible, at least