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Ab initio Studies of Some Trivalent Boron Compounds with Boron–Oxygen and Boron–Nitrogen Bonds

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Minimum energy geometries, rotational barriers and charge distributions have been studied for the boranes: H_2BXH, $HB(XH)_2$ and $(H_2B)_2X$; X=O, NH. Gaussian-type basis functions, (7*s*, 3*p*) for B, N, O and (4*s*) for H, contracted to a double-zeta basis augmented with *d*-orbitals for oxygen and nitrogen were used.

Planar equilibrium structures, short B–X bonds, and high rotational barriers have been related to importance of dative π-bonding, and the results have been discussed in terms of varying degree of such bonding in the various molecules. The partial π-bond character appears larger for B–N than for B–O bonds, and larger for the monoderivatives (H_2BXH) than for the two other types. Variations in σ-bond strength, and bonding in non-planar conformations of the boron-oxygen molecules have been discussed.

The gross charge transfer is in all molecules found to be from the borane groups, *i.e.* boron is, when attached to oxygen or nitrogen, a strong σ-donor and a weaker π-acceptor so as to give polar bonds in the B^+-X^- sense. The partial moments involving hydrogens are important for the resultant dipole moments, the directions of which have been discussed.

Comparisons with experimental results for some of the molecules studied and for some of their derivatives have been included.

The trivalent boron atom, found in planar arrangements with its three ligands, seeks coordinative saturation through $p_\pi-p_\pi$ interactions with the attached atoms or groups when these are π-electron donors. Considerable amounts of π-character have been ascribed to the B–N and B–O bonds, and the π-electron donor capacity for the NH_2, NHR and NR_2 groups has been judged superior to that of the OH and OR groups as a result of numerous spectroscopic and theoretical studies summarized elsewhere.[1,2]

In connection with structural studies by electron diffraction from the vapours of trivalent boron-oxygen and boron-nitrogen compounds, we were interested in supplementary molecular orbital studies of the bonding conditions in compounds with two adjacent B–O or B–N bonds, as compared to those with isolated B–O and B–N bonds. Comparative *ab initio* calculations of the two series H_2B-OH, $HO-BH-OH$, $H_2B-O-BH_2$ and H_2B-NH_2, $H_2N-BH-NH_2$, $H_2B-NH-BH_2$ have therefore been carried out concurrently with electron-diffraction studies of several methyl derivatives of these parent molecules.[3–5] The parent molecules were selected for the MO-studies for economical reasons. Recently, structural result from microwave spectroscopy have become available for some of these metastable molecules, $HB(NH)_2$,[6] H_2BNH_2 [7] and $HB(OH)_2$.[8,9] This provides possibilities for useful comparisons with our results, both from the MO-, as well as the ED-studies, the latter giving direct information about the effects of methyl substitutions.

Several of the present molecules and some of their methyl derivatives have been subject to various types of semi-empirical[1,10–17] and *ab initio*[2,6b,17–23] molecular orbital studies. For our purpose it was essential with consistent types of calculations at a reasonably high level for all six compounds, since the results of geometry optimalizations and popula-

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tion analyses are known to be quite sensitive to the type of calculation carried out. This report contains the theoretical part of our structural studies, and its scope follows largely the *ab initio* investigations previously carried out at this institute for H_2BOH [19] and H_2BNH_2 [18] for which only complementary calculations have been added.

COMPUTATIONAL DETAILS

The Roothaan-Hall equations were solved by a computer program MOLECULE [24] which applies contracted Gaussian-type orbitals (CGTO) and utilizes the symmetry of the molecule under investigation. Various sets of basis functions have been studied for H_2BOH [19] and our calculations employ the type of basis which was judged satisfactory for H_2BOH [19] and later used for H_2BOOBH_2,[25] *i.e.* (7*s*, 3*p*) for oxygen, nitrogen and boron and (4*s*) for hydrogen, contracted to a double zeta basis, $\langle 4,2/2\rangle$, augmented by a *d*-set for oxygen and nitrogen.[26,27] A squared scale factor of 1.44 for the orbital exponents of the hydrogen functions [28] and a value for the *d*-exponents of 0.95 [29] were chosen. These values differ from the corresponding ones of 1.25 and 1.33,[30] respectively, used in the previous calculations on H_2BOH and H_2BOOBH_2,[19,25] while they are consistent with the values used for H_2BNH_2.[18]

The importance of polarization functions (*d*-orbitals) for oxygen and nitrogen, as discussed elsewhere [19,31] should be noticed, while such functions for boron have been neglected since they apparently are of lesser significance.[19,25] The chosen basis is modest. However, the Hartree-Fock theory underestimates bond lengths, and slightly better estimates of molecular geometries are actually often obtained using a basis set which falls short of that required for the Hartree-Fock limit.[31] In any case, the various failures of basis set and method, are assumed to give nearly constant errors in the calculated quantities, so as to give reliable variations throughout a series of molecules even though the absolute values cannot be trusted.

GEOMETRIES, ROTATIONAL BARRIERS AND FORCE CONSTANTS

Computational results

Molecular models with numbering of the atoms and definitions of the torsional angles used to describe the different conformations of the molecules are shown in Fig. 1. The number of energy calculations with varying nuclear positions had to be limited due to computer-time restriction. Therefore, the O–H, N–H and B–H bond lengths were maintained at values fixed or optimized in previous studies on H_2BOH, H_2BOOBH_2 [19,25] and H_2BNH_2.[18] The values are given in square brackets in Fig. 1. The energy was assumed to exhibit second order polynominal dependency upon the geometrical parameters. The minima were located by successive one-dimensional searches (3 points) or by two-dimensional searches with one correlation term (6 points). The grids for our energy calculations were designed with the main purpose of determining the geometries and rotational barriers and they were therefore not always sufficiently closely spaced and symmetrical about the minima to yield accurate force constants. However, diagonal force constants were computed for all three-points variation of a parameter.

The units employed throughout this paper are: a.u. (Hartree) for total energies, kcal mol^{-1} for relative energies, and aJ $Å^{-2}$ or aJ rad^{-2} for force constants. The conversion factors are: 1 a.u. = 4.359828 aJ = 2625.47 kJ mol^{-1} = 627.51 kcal mol^{-1}; 1 Å = 10^{-10} m; 1 aJ = 10^{-18} J = 1 mdyn Å. Some of the results of the energy calculations for various conformers and for optimized geometries of the molecules are comprised in Tables 1 and 2, respectively, for the oxygen and nitrogen compounds. Relative energies and thereby the rotational barriers are included in these tables. The obtained geometrical parameters for the equilibrium structures are also given in Fig. 1, whereas the force constants for stretch and torsions about the B–X bonds are given in Table 3. Additional results are available upon request, and the six subsections given below contain details on the calculations and comparisons with previous theoretical results for each of the six compounds under investigation. In general, our values for the total energies are lower than those obtained in minimal STO-3G [20,22] and split-valence 4–31G [6b,21,22] and 4–21* (* polarization functions on oxygen) [23] level calculations, and comparable to the energy for aminoborane using the most extensive GTO-set (9, 3, 3).[17] They are, however, about 0.1 a.u. above the energies obtained when larger numbers of gaussian functions are used to construct the double zeta (9*s*, 5*p*) or split-valence (6–31G*) basis sets,[18,19,21] which are comparable with respect to the computed total energies, although the 6–31G*

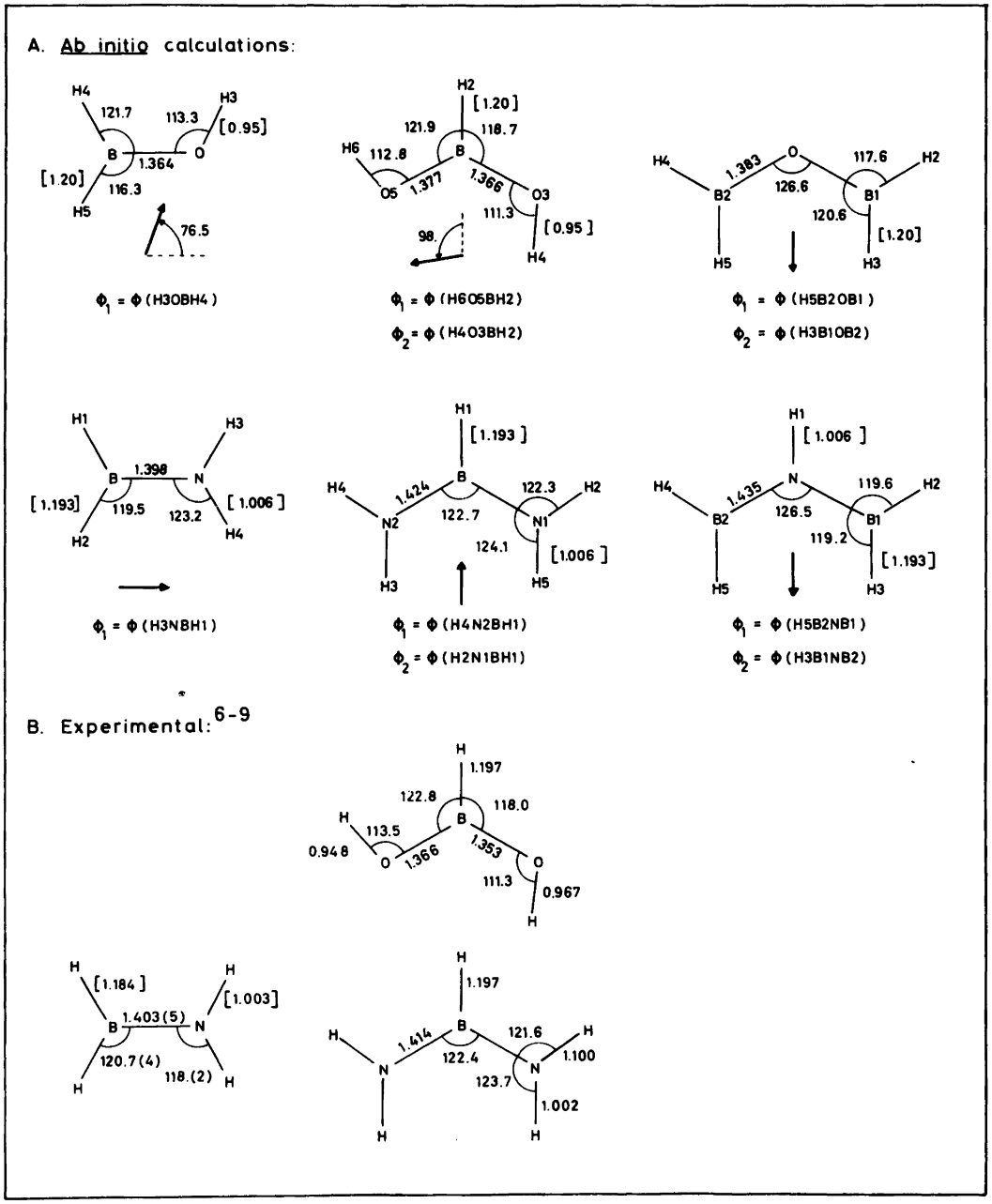

Fig. 1. (A) Atomic numbering and torsional angles (ϕ) defined relative to 0° for *syn*. Geometrical parameters (distances in Å, angles in degrees) for the minimum energy structures, all of which are found to be coplanar ($\phi = 0°$). Parameters in square brackets are assumed values. (B) Corresponding experimental results from microwave spectroscopic studies for three of the molecules.[6-9] The arrows in section A indicate the directions of the calculated dipole moments, defined in the direction of the line joining negative to positive charge.

Table 1. Geometries (distances in Å, angles in degrees), total energies (E_{tot}, in a.u.) and relative energies (ΔE, in kcal mol^{-1}) for the boron-oxygen series.

Conformations[a] Sym. (ϕ_1, ϕ_2)	E_{tot}[b]	ΔE[b]	Geometrical parameters[a]
H_2BOH			
C_s (0)	−101.20642	0.	BO = 1.36; BOH = 115.; OBH4 = OBH5 = 120.
C_s (90)[c]		15.10	
C_s (0)[c]	−101.20685	–	BO = 1.364; BOH = 113.3; OBH4 = 121.7; OBH5 = 116.3
$HB(OH)_2$			
C_s (0,180)	−176.04704	0.	BO5 = BO3 = 1.38; BO5H6 = BO3H4 = 112.9; H2BO5 = H2BO3 = 121.2
C_{2v}(0,0)		2.20	
C_{2v}(180,180)		4.81	
C (0,90)[c]		10.62	
C (90,180)		10.40	
C_2 (90,90)		22.16	
C_{2v}(180,180)		3.31	BO5 = BO3 = 1.376; BO5H6 = BO3H4 = 115.0; H2BO5 = H2BO3 = 117.2
C_{2v}(0,0)		2.48	BO5 = BO3 = 1.370; BO5H6 = BO3H4 = 112.9; H2BO5 = H2BO3 = 121.2
C_s (0,180)[c]	−176.04766	0.	BO5 = 1.377; BO3 = 1.366; BO5H6 = 112.8; BO3H4 = 111.3; H2BO5 = 121.9; H2BO3 = 118.7
$(H_2B)_2O$			
C_{2v}(0,0)	−126.48244	0.	B2O = B1O = 1.37; OB2H4 = OB1H2 = 120; OB2H5 = OB1H3 = 120; BOB = 130[d]
D_{2h}(90,90)		10.16	BOB = 180[d]
D_{2d}(0,90)		3.48	
C_{2v}(90,90)		12.68	BOB = 130[d]
C_s (0,90)[c]		3.70	
C_{2v}(0,0)	(−126.48256)	0.	BOB = 127.4
C_{2v}		9.91	BOB = 167.4
C_s (0,90)		2.87	BOB = 149.2
C_2 (45,45)		2.92	BOB = 152.0
C_s (0,90)	(−126.47683)	–	B2O = 1.371; B1O = 1.389; BOB = 130;
C_2 (45,45)	(−126.47789)	–	B2O = B1O = 1.367; BOB = 150[d]
D_{2d}(0,90)	(−126.47734)	–	B2O = B1O = 1.359; OB2H4 = OB2H5 = OB1H2 = OB1H3 = 119.1; BOB = 180[d]
C_{2v}(0,0)[c]	−126.48347	–	B2O = B1O = 1.383; OB2H4 = OB1H2 = 117.6; OB2H5 = OB1H3 = 120.6; BOB = 126.6

[a] Definitions of torsional angles, ϕ, and labelling of the atoms are given in Fig. 1. Parameter values are given only when they differ from those given in the previous set. The last values given for each molecule correspond to the minimum energy geometries also given in Fig. 1. [b] Parenthesized energy quantities were obtained in potential surface minimalizations. Conversion factor for the units are given in the text. [c] Population analyses are given in Table 4. [d] Symmetry determined or otherwise fixed angle.

is in many respects claimed to be comparable to the (7*s*,3*p*) double zeta basis as the effects from more functions in 6 − 31G* should be partly cancelled by a stronger contraction scheme.

(*i*) *Hydroxyborane (boronic acid), H_2BOH.* In order to check the effects of the changes in the orbital exponents, to obtain the barrier to rigid rotation for the chosen basis set, and to include the OBH angles in the optimization scheme, a few calculations, supplementary to the ones already reported,[19] were carried out.

The final energy for the (7*s*,3*p*,1*d*/7*s*,3*p*/4*s*) basis was reported to be −101.19330 a.u. for the planar model with assumed OBH angles of 120° and optimized r(BO)- and ∠BOH-values of 1.36 Å and 115°, respectively.[19] For these geometrical param-

Table 2. Geometries (distances in Å, angles in degrees), total energies (E_{tot}, in a.u.) and relative energies (ΔE, in kcal mol^{-1}) for the boron-nitrogen series.

Conformations[a] Sym. (ϕ_1, ϕ_2)	E_{tot}[b]	ΔE[b]	Geometrical parameters[a]
H_2BNH_2			
$C_{2v}(0)$	−81.40853	0.	BN = 1.398; BNH = 123.4; NBH = 119.5
$C_{2v}(90)$		38.41	
$C_{2v}(90)$		35.47	BN = 1.479
$C_{2v}(0)$	(−81.40853)	–	BN = 1.398; BNH = 123.2; NBH = 119.5
$HB(NH_2)_2$			
$C_{2v}(0,0)$	−136.42764	0.	BN1 = BN2 = 1.424 · NBN = 122.7; BN1H2 = BN2H4 = 122; BN1H3 = BN2H5 = 122.
$C_{2v}(90,90)$		55.06	
C_s (0,90)[c]		19.11	
C_s (0,90)		17.54	BN1 = 1.404; BN2 = 1.481
$C_{2v}(0,0)$[c]	−136.42805	–	BN1 = BN2 = 1.424; NBN = 122.7; BN1H2 = BN2H4 = 122.3; BN1H3 = BN2H5 = 124.1
$(H_2B)_2NH$			
$C_{2v}(0,0)$	−106.67867	0.	NB1 = NB2 = 1.435; BNB = 126.5; NB1H2 = NB2H4 = 119.5; NB1H3 = NB2H5 = 119.5
$C_{2v}(90,90)$		55.16	
C_s (0,90)[c]		21.72	
C_s (0,90)		20.17	NB1 = 1.409; NB2 = 1.492
$C_{2v}(0,0)$[c]	−106.67868	–	NB1 = NB2 = 1.435; BNB = 126.5; NB1H2 = NB2H4 = 119.6; NB1H3 = NB2H5 = 119.2

[a–c] See corresponding footnotes of Table 1.

Table 3. Stretch (k, in aJ Å^{-2}) and torsional (τ, in aJ rad^{-2}) diagonal force constants for the B–X bonds.

Molecule[a]	Sym. (ϕ_1,ϕ_2)	k(BX)	τ(BX)
H_2BOH	C_s (0)	7.68	–
$HB(OH)_2$	$C_{2v}(0,0)$	7.47	0.10
	$C_{2v}(180,180)$	7.58	–
	C_s (0,180)	7.02,6.93[b]	0.15
$(H_2B)_2O$	$C_{2v}(0,0)$	7.43	0.045[c]
	C_2 (45,45)	7.41	0.082[d]
	$D_{2d}(0,90)$	7.90	–
	C_s (0,90)	7.08,6.65[b]	–
H_2BNH_2	$C_{2v}(0)$	7.52	0.40
	$C_{2v}(90)$	5.45	–
$HB(NH)_2$	$C_{2v}(0,0)$	6.81	0.15
	C_s (0,90)	7.08,5.30[b]	–
$(H_2B)_2NH$	$C_{2v}(0,0)$	5.99	0.28
	C_s (0,90)	6.43,5.00	–

[a] See Fig. 1 for definitions of the torsional angles (ϕ) and Tables 1 and 2 for corresponding geometrical parameters. [b] The two values refer to the moieties with ϕ_1 and ϕ_2, respectively. [c] For ∠BOB = 130°; τ = 0.08 for ∠BOB = 120°. [d] For ∠BOB = 150°; τ = 0.028 for ∠BOB = 140°.

eters the change in the scale factor for the hydrogen exponents to 1.44 and subsequently the oxygen *d*-exponent to 0.95 lowered the energy to −101.20192 and −101.20642 a.u., respectively. The change in the *d*-exponent caused approximately the same effect on the energy for the orthogonal form so as to give insignificantly different rotational barriers. For the combination 1.44/0.95 the energies are given for the planar and perpendicular forms in Table 1. The barrier to rigid rotation is seen to be 15.1 kcal mol^{-1}, as compared to 17.5 kcal mol^{-1} obtained with the larger (9,5,1/4) basis [19] which gave a geometry optimized barrier of 16.4 kcal mol^{-1}. The non-rigid barriers reported for 6−31G* and STO-3G-level calculations [20] are 14.4 and 21.7 kcal mol^{-1}, respectively. When accounting for an expected 1 kcal mol^{-1} drop in the barrier upon optimization, our value corresponds best to the result from the claimed comparable 6−31G* level calculations.

The planar structure was optimized by multivariate searches, first for the two OBH angles and consecutively for *r*(BO) and ∠BOH. The results are given in Table 1 and Fig. 1. The obtained asymmetry for the OBH_2-group agrees well with that obtained both by MINDO [16] and by STO-3G [20] and 4−21* [23] level *ab initio* calculations. The variations in ∠BOH and *r*(BO) of 113−121° and 1.33−1.38 Å, respectively dependent on the basis set chosen, have been discussed previously.[19] Our results are within these ranges and an overall good agreement is obtained for the optimized parameters with those of the on the 4−21* level fully optimized structure.[23]

The previous *ab initio* calculations showed an increase by 0.02 Å [19] and 0.037 Å [20] in the BO bond for the orthogonal form, which in our case was not optimized. However, a rather modest lengthening was corroborated by some of our results for H_2BOBH_2 as described in section (*iii*).

(ii) Dihydroxoborane (boronic acid), $HB(OH)_2$. By variations of the two torsional angles ϕ_1 and ϕ_2 (see Fig. 1), energies were calculated for various conformations of $HB(OH)_2$ for a fixed set of values for the bond distances and valence angles as given in Table 1. Energy minima were found for the three types of coplanar structures among which the *syn,anti* form ($\phi_1 = 0°$, $\phi_2 = 180°$) was favoured over the *syn,syn* ($\phi_1 = \phi_2 = 0°$) and *anti,anti* ($\phi_1 = \phi_2 = 180°$) forms by, respectively, 2.2 and 4.8 kcal mol^{-1}. The barriers of rigid rotation from the *syn,anti* form are similar for rotation about either B−O bond, being 10.6 and 10.4 kcal mol^{-1} for rotation into the *syn,syn* and *anti,anti* forms, respectively. Simultaneous rotation of both groups yields an insignificantly different barrier (11.1 kcal mol^{-1}), *i.e.* the required energy is approximately doubled as seen from Table 1. By analogy to H_2BOH (previous section) only a minor drop in the barriers upon optimization of the perpendicular from is expected.

Each of the three coplanar structures were optimized with respect to the B−O bond and the valence angles. For the two forms of C_{2v}-symmetry (*syn,syn* and *anti,anti*) this was a three parameter problem which was solved by two-dimensional variations of ∠OBH and ∠BOH and consecutive one-dimensional optimization of *r*(BO). The results are given in Table 1. The interdependencies between the angles were found to be of minor importance and the six variables of the *syn,anti* form were optimized by successive one-dimensional searches. The results are given in Table 1 and Fig. 1. The *syn,anti* form was favoured over the *syn,syn* and *anti,anti* forms by 2.4 and 3.3 kcal mol^{-1}, respectively, in very good agreement with the 4−21* results [23] and as compared to 3.5 and 8.4 kcal mol^{-1} obtained in 4−31G calculations in which $E_{tot} = -175.998206$ a.u. was obtained for the favoured *syn,anti* form.[21] The reported MINDO-results [16] for $HB(OH)_2$ are reversed with respect to the relative magnitude of the two B−O bonds and do not show differences for the corresponding valence angles in the *syn* and *anti* moiety of the molecule, features which were, however, also shown by the concurrent 4−21* level calculation [23] which gives overall good agreements with our structural results for all three planar conformers. As compared to the structural results for the *syn,syn* and *syn,anti* forms, the *anti,anti* form suffers large distortions in the OBO- and BOH-angles as seen from Table 1. This is probably due to hydrogen, hydrogen repulsions as optimization of the *anti,anti* form was accompanied by an increase in the H4---H6 distance from 2.09 to 2.38 Å, corresponding to a preferred interatomic distance of about twice the van der Waals radius for hydrogen.

(iii) Diboryloxide (borinic anhydride), $(H_2B)_2O$. Various conformations of H_2BOBH_2 were investigated by variations of the BOB angle and the torsional angles, ϕ_1 and ϕ_2, defined in Fig. 1. Some of the results are given in Table 1, which also includes values for the remaining geometrical parameters.

A planar model of C_{2v} symmetry emerged from a

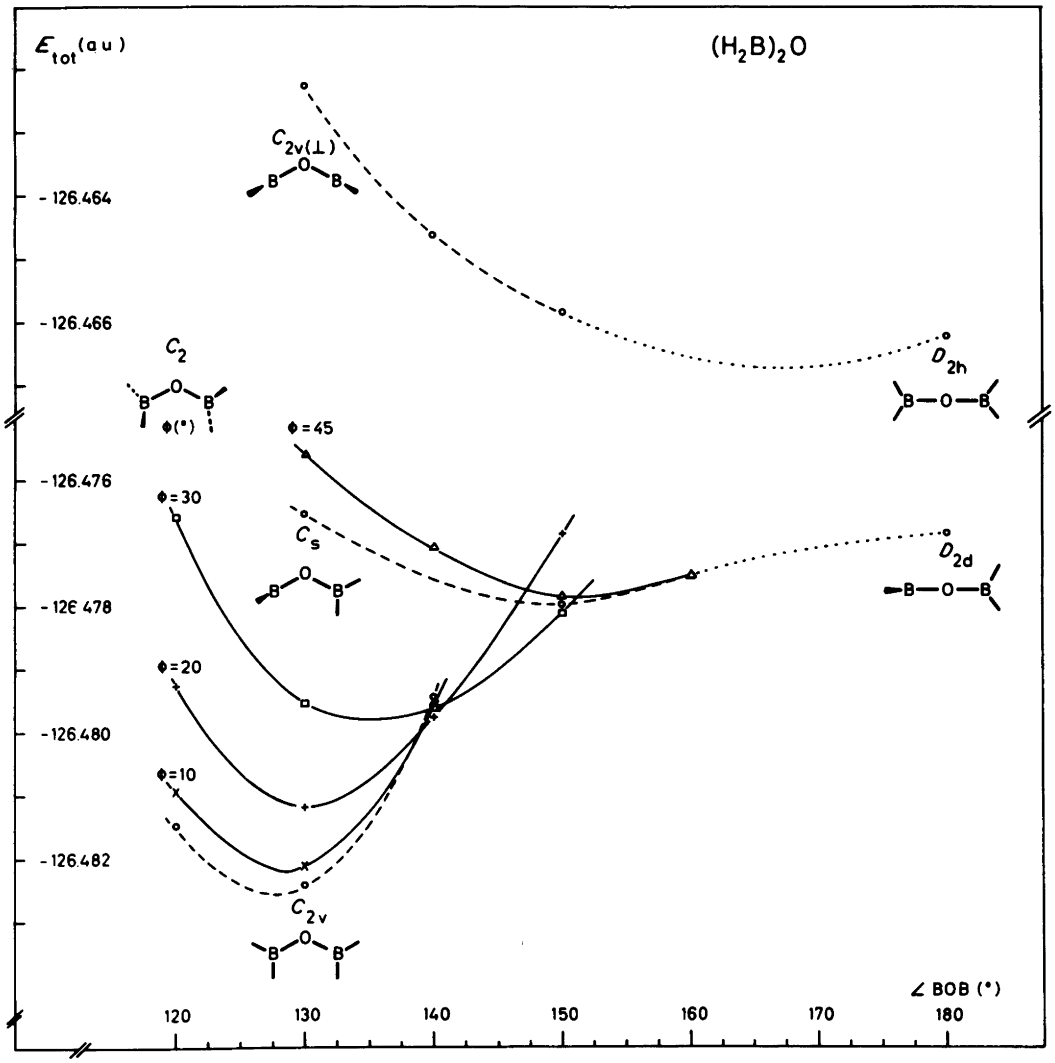

Fig. 2. Total energies calculated for various conformers of oxo-bisborane. The dashed curves (– – –) show the energies for the planar (C_{2v}) and the perpendicular forms (C_s and $C_{2v}(\perp)$) from which barriers to rigid rotation at ∠BOB=130° and to ∠BOB-optimized rotation of one, respectively two, H_2B-groups may be deduced. The dotted lines (...) extrapolate the C_s and $C_{2v}(\perp)$ curves into their linear counterparts (D_{2d} and D_{2h}, respectively). The full lines (——) give the energy curves for various C_2-models, and they demonstrate the interdependencies between ∠BOB and ϕ.

C_2-model, by a six-points coupled variation of ∠BOB and $\phi=\phi_1=\phi_2$. The BOB angle was approximately 130°, and its energy relative to that of the C_s-model and that of the perpendicular C_{2v}-model (⊥) gives the barrier to rigid rotation of one, respectively two BH_2-groups. See the dashed curves in Fig. 2, which show that optimization of ∠BOB yields energy minima at 127.4, 149.4 and 167.4°, respectively, for the C_{2v} ($\phi=0$)-, C_s- and C_{2v} (⊥)-models. Rotation of both groups approximately triples the energy required for rotation of one group, and the barriers for the latter are 3.70 and 2.87 kcal mol^{-1}, respectively, for rigid and ∠BOB-optimized rotation as also seen from Table 1. The

obtained planar C_{2v}-model is favoured over the planar linear counterpart (D_{2h}-symmetry) by 10.2 kcal mol^{-1} and over the linear "allene-like" structure (D_{2d}-symmetry) by 3.5 kcal mol^{-1}. The enlargement to 149.4° for ∠BOB upon rotation of one H_2B-group to the perpendicular C_s-form is consistent with the results for H_2BOH [19] for which rotation to the orthogonal form is accompanied by an angle opening to 121°, *i.e.* in both cases rotation is favoured over inversion (∠BOB = 180°).

In the optimization of the C_2-model large interdependencies were encountered for ϕ and ∠BOB as seen from the full lines of Fig. 2. The ultimate change to non-planarity for increasing BOB-angles and *vice versa* should be noticed, and these results will later be discussed in relation to the bent, twisted form experimentally determined [4] for $[(CH_3)_2B]_2O$. They could also suggest that torsions where C_2-symmetry is maintained could go through a linear D_{2d}-form. However, for $\phi = 45°$ the preferred BOB-angle was 152° and this C_2-model and the C_s-model exhibit similar BOB-angles and total energies (Table 1 and Fig. 2).

The planar C_{2v}-model was optimized by a multivariate search for the two OBH-angles and successive one-dimensional variations of r(BO) and ∠BOB. The two parameters r(BO) and ∠OBH of the D_{2d}-model were found in a combined optimization. The results are given in Table 1, and the C_{2v} model is favoured over the allene-type structure by 3.85 kcal mol^{-1}. The linear form (D_{2d}) exhibits a shorter B–O bond than the favoured C_{2v} model, 1.359 Å as compared to 1.383 Å. An intermediate value of 1.367 Å was obtained for the C_2-model with $\phi = 45°$ and ∠BOB = 150°. Finally, it should be noticed that rotation of one H_2B-group of the C_{2v}-model is accompanied by small shifts only in the B–O bond distances. For the C_s-model with ∠BOB = 130° the BO bond lengths are 1.371 and 1.389 Å, respectively, for the in-plane and out-of-plane moieties, whereas rotation to the orthogonal form for H_2BOH was accompanied by an elongation of the B–O bond by about 0.02 Å.[19]

(iv) Aminoborane (boraneamine), H_2BNH_2. The planar equilibrium structure for H_2BNH_2 is well-established by theoretical calculations, and the structure has been fully optimized in two *ab initio* calculations.[18,20] Our calculations for this molecule, therefore, had the main purpose of obtaining comparable quantities to the ones calculated for the five other molecules in the series. A one-dimensional search for the B–N bond, sensitive to the chosen basis set, in the planar model, was carried out. The energies for the orthogonal form with unchanged and optimized B–N bond were computed and, as compared to the planar form, this gave rotational barriers of 38.4 and 35.4 kcal mol^{-}, respectively, for rigid and partially optimized (BN bond, only) rotation. The corresponding values reported previously are: 40.7 and 38.0 kcal mol^{-1} for GTO (2*p*,3*s*/3*s*) calculations;[17] 42.7 and 39.7 kcal mol^{-1} for the extended (9*s*,5*p*,1*d*/9*s*,5*p*/4*s*) double zeta calculations,[18] and 43.1 kcal mol^{-1} for the rigid rotation on the minimal STO-3G level. The reported fully optimized barriers are on the minimal (STO-3G),[20] split-valence (6–31G*),[20] and double zeta (9*s*,5*p*)[18] levels 35.6, 29.4 and 33.3 kcal mol^{-1}, respectively. Expansion of the B–N bond in the perpendicular form represents a gain in energy of about 3 kcal mol^{-1}, consistent with previous results [17,18] cited above. The pyramidal conformation of the nitrogen in the perpendicular form is well-established,[15,18,20] and accounts for the remaining difference of the rigid and non-rigid rotational barriers which are seen to be 9.4 and 7.5 kcal mol^{-1}. It appears that when accounting also for this latter flexibility, our results would again be in best agreement with the 6–31G*-level value [20] of 29.4 kcal mol^{-1} for non-rigid rotation.

The obtained bond length of 1.397 Å for the planar form is longer than the ones previously reported: 1.355 Å for GTO-basis;[17] 1.378 for the CGTO-basis;[18] and 1.372 Å for STO-3G level calculations.[20] A substantial lengthening of the B–N bond upon rotation has been obtained in all four calculations, which are, however, not consistent with respect to the magnitude of this increase, the B–N bond length of the perpendicular form being 1.479, 1.42,[17] 1.469,[18] and 1.490[20] Å, respectively.

The previous results [18,20] for the BNH and NBH angles were consistent. However, due to a large discrepancy with an experimental result for ∠BNH,[7] these angles were also varied. The optimization did not result in significant changes and the final structure is given in Table 2 and Fig. 1.

The possible pyramidal shape of the aminogroup was considered for $\phi = 15°$. This gave higher total energies and significant deviation from planarity was not observed. These calculations also showed an increase in energy upon rotation from $\phi = 0$ to $\phi = 15°$.

(v) Diaminoborane (boranediamine), $HB(NH_2)_2$. The BNB angle was determined by a multivariate search together with r(BN) for a planar structure

of C_{2v} symmetry. Subsequent optimization of r(BN) and $\phi=\phi_1=\phi_2$ in a model of C_2-symmetry yielded a planar model which subsequently was optimized with respect to the BNH-angles (see Table 2 and Fig. 1). The barriers to rigid and partially optimized (the BN bonds only) rotation were calculated relative to this planar structure. Rigid rotation of two groups (C_{2v} symmetry, $\phi_1=\phi_2=90°$) more than doubled the energy difference obtained for one group (C_s-symmetry, $\phi_1=\phi_2=90°$) as seen from Table 2. According to 4−31G calculations,[21] the energy difference between these two orthogonal forms is 25.4 kcal mol^{-1} as compared to our result of 36.0 kcal mol^{-1}. The optimization of the B−N bond caused a drop in the rotational barrier of 2.6 kcal mol^{-1}. It should be noted that analogy to aminoborane [18,20] suggests a further drop in the barrier if allowance were made for the expected pyramidal nitrogen in the perpendicular (to the NBN-plane) moiety of the molecule. The two BN bonds of the planar and perpendicular moieties of the molecule approach the values obtained respectively for planar and orthogonal forms of aminoborane itself (1.398 and 1.479 Å).

*(vi) Diborylamine (*N*-boryl-boraneamine), $(H_2B)_2NH$.* The calculations for $(H_2B)_2NH$ were analogous to those carried out for $HB(NH_2)_2$ and the results are given in Table 2 and Fig. 1. The total energy for the planar form was found to be −106.620862 a.u. in 4−31G-calculations,[21] which gave a rotational barrier of 22.1 kcal mol^{-1} as compared to the barriers of 21.7 and 20.2 kcal mol^{-1} for rigid and partial optimized rotation in our calculations. Further optimization is assumed to have little effect on the value for the rotational barrier, contrary to the situation for bisaminoborane. The two BN bonds in the planar and perpendicular part of the C_s-model approach the corresponding values in the planar and orthogonal forms of aminoborane itself, although not as closely as found for bisaminoborane.

On the geometrical parameters

The minimum energy geometries for all six molecules are given on molecular models in Fig. 1 which also includes corresponding experimental results, available for three of the molecules.[6-9] Comparisons between calculated and experimental bond lengths show good agreements. The magnitude of the discrepancies is about 0.01 Å with $r_s<r_e$ for $HB(OH)_2$ and $HB(NH_2)$ and $r_o>r_e$ for H_2BNH_2. Moreover, a difference in the B−O bonds of the *syn* and *anti* moieties of bishydroxyborane have been reproduced, and also an increase in the B−N bond length from aminoborane to diaminoborane, although it appears less pronounced in the experimental data. The angle parameters of $HB(OH)_2$ and $HB(NH_2)_2$ also show pleasing agreements. For aminoborane a discrepancy for ∠BNH appears particularly disturbing, but it should be noted that it was stated in the microwave study [7] that rotational constants of more isotopic species would give a more reliable structure for H_2BNH_2. For $HB(NH_2)_2$ a similar discrepancy for ∠BNH indicated by the preliminary experimental results [6a] is removed as compared to the final structural parameters.[6b] Altogether the agreements seem close enough to justify discussions under the assumption that the theoretical and experimental results are approximately on the same scale.

The B−X bonds in hydroxyborane and in aminoborane are both shorter by approximately 0.1 Å than the estimated single bond lengths obtained from the sum of covalent radii corrected for σ-bond polarization (B→X), due to electronegativity differences of the bonded pair of atoms. Using a covalent radius of 0.85 Å for boron [3,32] and the other quantities in accordance with those given by Pauling,[33] the single bond estimates are 1.46 (*i.e.* 1.58−0.12) Å and 1.50 (*i.e.* 1.58−0.08) Å for B−O and B−N, respectively. Since both oxygen and nitrogen have lone pairs of electrons available for back donation into the formally empty p_z orbital of boron, the shortening of the bonds may be ascribed to partial double bond character, *i.e.* $p\pi-p\pi$ interactions. The coplanar conformations obtained for all six molecules are probably related to the importance of such π-bonding, since these give the most favourable overlap between the lone pairs and the boron p_z-orbital.

As compared to the lengths of the isolated B−X bonds of the monosubstituted boranes, it is seen (Fig. 1, Tables 1 and 2) that elongations are encountered in the two types of molecules with two adjacent B−X bonds. This is consistent with the reduced possibility for π-bonding in each bond: for X−B−X bonding, two π donors compete for the one empty p_z-orbital of the central boron atom; and for B−X−B bonding, two π accepting boron atoms share one π donor. The results may, therefore, be taken as evidence for the presence of double bond character in the B−O and B−N bonds of the

present series of molecules. The elongations appear to be largest for the B–X–B type of bonding, and more pronounced for the nitrogen than for the oxygen series. However, these variations cannot without ambiguity be used to judge the amount of π-character of the B–O bond relative to the B–N bond, nor for the B–X–B relative to the X–B–X bonding, due to potential effects from possible σ-bond variations throughout the series of molecules. For example, changes in the valence angles affect the hybridizations and consequently the strength of the σ-bond. Such changes appear to be most important for the oxygen in H_2BOBH_2, relative to that of H_2BOH, and should cause a shortened B–O σ-bond in H_2BOBH_2, due to larger *s*-character. More important is possibly the more direct substitution effect such as the known tendency for a bond to a central atom to become shorter when more electronegative atoms are joined to it. This suggests that σ-bond shortening should appear in X←B→X relative to B→X bonding. Correspondingly, σ-bond differences in B→X←B relative to B→X bonding may be expected, but definite trends do not appear to be experimentally established. Since both oxygen and nitrogen are σ-acceptors of electrons, it is most likely that σ-bond variations would make rigorous conclusions about relative amounts of π-character dubious, when based upon the bond-length variations alone.

With an apparent exception for $(H_2B)_2O$, the results of electron-diffraction studies of methyl derivatives of the present series of molecules and those of $B(OH)_3$ and $B(NH_2)_3$[3–5] corroborate the variations in the bond lengths as obtained in the calculations for the parent molecules. For $[(CH_3)_2B]_2O$ the B–O bonds were found to be shorter than the B–O bonds in $B(OCH_3)_3$[3] and in $CH_3B(OCH_3)_2$[5] and comparable to that in $(CH_3)_2BOCH_3$.[5] According to our calculations this discrepancy may be related to the different conformations of $(H_2B)_2O$ and its permethylated derivative. Steric repulsions between the methyl groups in H3 and H5-positions (see Fig. 1) would introduce strain in planar conformations with small (*i.e. ca.* 130°) BOB-angles for $[(CH_3)_2B]_2O$. A correlated torsion and BOB-widening would occur and the obtained values,[4] $\phi = 38°$ and $\angle BOB = 144°$, seem reasonable compared to the potential energy curves (full lines) shown for $(H_2B)_2O$ in Fig. 2. Also, the rather wide potential curves in the ranges $\phi = 30-45°$ and $\angle BOB = 140-150°$ for $(H_2B)_2O$ and the force constant variations for torsions (Table 3) and bending (0.55 and 0.16 aJ rad^{-2} for $\phi = 0°$ and $\phi = 45°$, respectively) are consistent with the suggested flexibility[4] and the reported low torsional and bending fundamental frequencies[35] for the permethylated compound. Furthermore, the calculated B–O bond lengths of the twisted ($\angle BOB = 150°$, $\phi = 45°$) form of $(H_2B)_2O$ and the planar H_2BOH are 1.367 and 1.364 Å, respectively. The electron-diffraction results of 1.359 and 1.355 Å for the corresponding methyl derivatives[4,5] are seen to be entirely consistent with these results.

The B–O bonding conditions are probably complex in the twisted form of H_2BOBH_2 as compared to the planar conformation in which one of the oxygen lone pairs may be considered unengaged, while the other participates in $p\pi - p\pi$ interactions with both borane groups, and to the allene-type structure (D_{2d}-symmetry) in which maximal utilization of both oxygen lone pairs would be possible. The short B–O bond in the D_{2d}-model as compared to that in the C_{2v}-model and the intermediate value of the twisted form (C_2, $\phi = 45°$, $\angle BOB = 150°$) could equally well be ascribed to hybridization changes of the oxygen, to participation in backdonation to boron by both oxygen lone pairs in non-planar conformers of the molecule, and to cooperative involvement of both effects. Increased possibility for backdonation is consistent with interpretations of NMR-results for $[(CH_3)_2B]_2O$.[36] Furthermore, based on ^{11}B NMR results for several three coordinated boron-oxygen compounds, it has been stated that BO π-bonding will not be much reduced in a non-planar conformation due to the existence of two free electron pairs per oxygen atom.[34] In this context it is interesting to note the different elongations encountered for the B–N and B–O bonds upon rotation to the perpendicular forms. The B–N bonds (Table 2) obviously suffer a substantial weakening and the bond lengths of the perpendicular forms approach that of single-bond estimate, whereas minor elongations only have been obtained for the B–O bonds (Table 1 and Ref. 19). This may suggest that π-bonding is of lesser importance for the B–O bonds. However, since the B–O bond lengths remain clearly short of the single bond-length estimate in the non-planar forms, this could also support the above conclusion of maintained acceptor behaviour of the boron p_z orbitals in these forms.

Predictions and rationalizations of molecular configurations may be based upon repulsions between the valence-shell electron pairs surrounding

an atom: lone pairs, double bonds and single bonds cause decreased repulsions in the mentioned order, and polarity of the bonds would account for angle openings around a more electronegative atom. Thus, by the VSEPR method, double bond character together with σ-bond polarity, B−N, could predict $\angle$NBN > 120°, $\angle$BNB > $\angle$NBN and $\angle$BNH > 120°, whereas the polarity could cancel the effect of the double bonding for the NBH_2-group giving $\angle$NBH ≈ 120°. This qualitatively accounts for our results (Fig. 1) and similar considerations could be applied on the oxygen series. Each oxygen is surrounded by one unengaged electron pair and two bonds. The last oxygen lone pair gives partial double bond character to one or both (as for $(H_2B)_2O$) of the bonds. For $(H_2B)_2O$ the large (>120°) BOB-angle would suggest that the effects of polar B−O bonds overrule the repulsion from the lone pair. However, the VSEPR method neglects effects from various non-bond repulsions. The type of H---H repulsions, described for the *anti,anti* form of $HB(OH)_2$ (section *ii*) are not important for $(H_2B)_2O$, $(H_2B)_2NH$ and $HB(NH_2)_2$, all the H---H distances in these compounds being comfortably longer than twice the van der Waals radius for hydrogen. Bartell [37] and Glidewell [38] have introduced sets of one-angle radii for the atoms. These are intermediates to the covalent and van der Waals radii and will give the closest contact between atoms over one valence angle allowed without introducing steric strain in the molecule. The geometry may be dominated by such non-bonded repulsions when larger atoms are attached to first row atoms. The effect was not expected to be a dominant factor for the present series of molecules, but it was found worthwhile to consider whether such effects could be completely neglected. The obtained large O---O, N---N, O---H, and N---H distances as compared to the estimated one-angle distances [38] suggest that the corresponding repulsions are of little importance. For interactions involving the larger boron atom the situation is not as clear, partly due to an alternative value of 1.26 Å for the boron one-angle radius [39] as compared to 1.33 Å proposed by Glidewell.[38] According to our calculations and discussion of the $[(CH_3)_2B]_2O$ structure, the large BOB-angle of 144° in this compound is caused by methyl, methyl repulsions giving a longer B---B distance than normally permitted. This observed B---B distance is 2.59 Å and the B---B distance in the minimum energy geometry (Fig. 1) of $(H_2B)_2O$ is 2.47 Å. These results favour the new r_B value [39] of 1.26 Å over the earlier reported [38] 1.33 Å and could suggest an even smaller r_B-value. The indications are that B---B repulsions are important in $(H_2B)_2O$, but not so in $(H_2B)_2NH$ where r(B---B) = 2.56 Å. In the bent-bond picture this difference could account for the presence of tilt of the BH_2-groups in the former molecule and its absence in the latter. The closest B---H contacts should be 2.18 Å [39,38] (or 2.25 Å [38]). Corresponding repulsions would be marginal for the nitrogen series, but would corroborate the VSEPR-predictions of $\angle$BNH > 120° in the H_2N-groups, which support the results of our calculations rather than the experimental results for H_2BNH_2 (Fig. 1). For the oxygen series the B---H one-angle distances are about 1.95 Å. In the same manner as tilt of the CH_3-group in methanol may be related to C---H repulsion and resulting O−C bent bond, B---H repulsions may be responsible for the tilt of H_2B in H_2BOH. However, rationalizations of the overall symmetry of $HB(OH)_2$ seem not as straightforward. It appears that an interplay between $p\pi-p\pi$ bonding theory and the non-bonded radius concept should be considered when accounting for bridging bond angles in these boranes. This is interesting in connection with the apparently not yet settled debate about $d\pi-p\pi$ bonding and non-bonded interactions for corresponding bridging angles in silicon compounds,[40] although a recent *ab initio* study [41] denounces the importance of backdonation of electrons to silicon and uses results from the population analyses to attribute the short Si-O bonds to partial ionic characters extensive of that suggested by the electronegativity differences.[33]

On the force constants

Generally force constants obtained in *ab initio* calculations with appropriate grids are higher than the valence force constants obtained from vibrational spectroscopic data by 10−20 %. In addition to these methodical problems, pure BO and BN stretch force constants (k) are difficult to obtain experimentally due to many atoms of similar masses. For a few methyl derivatives of H_2BOH, $HB(OH)_2$ and $B(OH)_3$, k(BO) is found in the range [42-45] of 4.3−5.4 aJ Å^{-2}. No specific trend for variations correlated with the number of oxygen joined to boron seems to be present, whereas for the corresponding nitrogen series, k(BN) is found to be [46-48] 7.0, 7.5 and 4.5−5.0 aJ Å^{-2}. Comparisons with the *ab initio* values given in Table 3, show that the

discrepancies vary greatly and mostly exceed the 10–20 % limit.

The *ab initio* results suggest approximately equal B–X bond strengths for H_2BOH and H_2BNH_2. For the nitrogen series the variation of k(BN), although somewhat exaggerated, seems to be consistent with the bond-length variation, including a substantial drop in the force constants of the perpendicular forms. For the oxygen series the variations in k(BO) are not pronounced, though the larger values are obtained for the shortest B–O bonds found in H_2BOH and in the D_{2d}-form of $(H_2B)_2O$. It is interesting to note that the k(BO) difference for the planar and perpendicular moieties of $(H_2B)_2O$ (C_s-form) is small (7.02 and 6.65 aJ Å^{-2}) as compared to the difference (7.08 and 5.3 aJ Å^{-2}) obtained for the isoelectronic $(H_2B)_2NH$. This is consistent with the corresponding bond-length variations, and corroborates the suggestion that the B–O bond is weakened to a smaller degree upon rotation. The variation of the torsional force constants is seen to conform to that of the rotational barriers and consequently also to the following discussion of the latter, as is consistent with the implication that both quantities deal with energies required for breaking the favourable $p\pi - p\pi$ overlap in the planar forms.

On the rotational barriers

The calculated rotational barriers are given in Tables 1 and 2. The only possibility for direct comparisons with experimental counterpart is provided for by a recent determination to 13 kcal mol^{-1} for the rotational barrier of $HB(NH_2)_2$.[6b] This experimental value compares favourably with the calculated value of 17.5 kcal mol^{-1} for the partially optimized rotational barrier, which was judged (previous subsection *v*) too high since non-planarity of the aminogroup was not accounted for in the perpendicular form.

The torsional barriers for various derivatives of monoaminoboranes are usually found in the regions about 15–20 kcal mol^{-1},[50–56] but the importance of steric factors has been stressed [53,54] in connection with observations in the 9.9–26.6 kcal mol^{-1} range.[53] For bisaminoborane the barriers seem to be found 10 kcal mol^{-1} lower than in corresponding monoaminoboranes [54] as compared to the change from 17.5 to 35.5 kcal mol^{-1} calculated for the parent molecules (Table 2). For bismethoxyphenylborane the B–O rotational barrier has been determined to 9.4 kcal mol^{-1} as compared to 13.2 kcal mol^{-1} for methoxydiphenylborane.[57] This is consistent with the variations of the calculated values from 10.6 to 15.1 kcal mol^{-1} for the corresponding parent molecules $HB(OH)_2$ and H_2BOH (Table 1). The experimental values [36] of 8.6 and 8.5 kcal mol^{-1}, respectively, for $[(CH_3)_2B]_2O$ and $(CH_3)_2BOCH_3$, indicate similarities in the B–O bond strengths as suggested by the previously discussed bond lengths. The calculated barrier for $(H_2B)_2O$ is, however, a factor of five lower than that of H_2BOH, and it could reflect the alleged differences in bonding conditions for $(H_2B)_2O$ and its permethylated derivative. The low barrier of about 3 kcal mol^{-1} for $(H_2B)_2O$ as compared to the ΔE-values for H_2BOH and $HB(OH)_2$, is also remarkable when the results for the nitrogen analogues are considered. The rotational barriers suggest about equally reduced degree of π-bonding in $HB(NH_2)_2$ and $(H_2B)_2NH$ as compared to the monoderivative, whereas for the oxygen series a more drastic reduction is implied for $(H_2B)_2O$ than for $HB(OH)_2$. The rotational barriers throughout the two series, indicate higher π-character in the B–N bonds than in the corresponding B–O bonds. It should be noted, however, that any involvement of the second lone pair of oxygen in backdonation to boron for the non-planar conformations could make estimates of π-character in the planar forms to some extent misleading when based on torsional barriers and force constants alone.

CHARGE DISTRIBUTIONS

Some results of dipole moment calculations (μ) and population analyses [58,59] for the minimum energy geometries are given in Table 4. The population analyses involved calculations of net atomic populations, n(k), overlap populations, n(k,l), gross atomic populations, N(k), and the formal atomic charges, $Q = N(k) - N°(k)$, where $N°(k)$ corresponds to the total number of electrons in the ground state of the free neutral atom. The gross charge transfers,[20] ΔQ, across each B–X bond in the direction from the borane groups were also computed. Results of Mulliken population analyses of STO-3G wave functions [20] for H_2BXH (X=O,NH), confirmed previous conclusions [10,17] that boron is a strong σ-donor and a weaker π-acceptor, the overall effect being a transfer of electrons from BH_2 towards X, and it was stated that the π donation was larger for

Table 4. Dipole moments (μ, in D) and results of Mulliken population analyses (n (k,l), N(k) and ΔQ as defined in the text) for the minimum energy geometries and in parentheses for perpendicular conformations (see footnote *c* to Tables 1 and 2).

	H_2BOH	$HO-BH-OH$	$H_2B-O-BH_2$	H_2BNH_2	$H_2N-BH-NH_2$	$H_2B-NH-BH_2$
ϕ_1,ϕ_2(°):	0 (90)	0,180 (0,90)	0,0 (0,90)	0 (90)	0,0 (0,90)	0,0 (0,90)
μ	1.705	1.646	0.629	1.995	1.420	1.228
n(k,1)						
B,O(N)	0.77	0.73,0.76	0.68	0.82	0.79	0.71
σ	0.55	0.56,0.58	0.52	0.52	0.58	0.50
$\pi(2p_z)$	0.21	0.17,0.18	0.17	0.30	0.21	0.21
B,H[a]	0.77	0.75	0.80	0.84	0.86	0.84
	0.79		0.77			0.84
O(N),H[a]	0.54	0.54,0.54	–	0.67	0.68	0.64
					0.65	
N(k)						
B	4.53 (4.44)	4.24 (4.22)	4.48 (4.47,4.43)	4.64 (4.46)	4.30 (4.31)	4.60 (4.64,4.46)
σ	4.31	3.90	4.32	4.34	3.89	4.39
$\pi(2p_z)$	0.22 (0.12)	0.34	0.17	0.30 (0.04)	0.41	0.21
O(N)	8.71 (8.75)	8.76,8.75 (8.73,8.76)	8.74 (8.75)	7.88 (7.97)	7.94 (7.89,7.96)	7.93 (7.96)
σ	6.93	6.92,6.92	7.07	6.18	6.14	6.35
$\pi(2p_z)$	1.78	1.84,1.83	1.67	1.70	1.80	1.58
H_B[a]	1.10 (1.12)	1.10 (1.13)	1.08 (1.10,1.09)	1.07 (1.12)	1.09 (1.12)	1.06 (1.06,1.08)
	1.08		1.06 (1.08)			1.05 (1.07)
$H_{O(N)}$[a]	0.58 (0.57)	0.58,0.58 (0.58,0.58)	–	0.67 (0.64)	0.68 (0.68,0.68)	0.65 (0.65)
					0.69 (0.68)	
$\Delta Q(BH_2)$	0.29 (0.32)	0.33 (0.31,0.34)	0.37 (0.35,0.40)	0.21 (0.30)	0.31 (0.24,0.32)	0.29 (0.24,0.37)
$\Delta Q^a(BH_2)$	0.51	0.50	0.54	0.51	0.50	0.50

[a] For symmetrically different hydrogens the ones *syn* to the skeleton or in H_2BOH *syn* to the OH are given first.

nitrogen than for the more electronegative oxygen.[20] Thus, in order to gain more detailed insight into the effects of various substituents on the electronic charge distributions, the calculated quantities involving boron, nitrogen and oxygen were split into their σ- and $\pi(2p_z)$-contributions. It was shown that the various quantities calculated were not significantly affected by valence-angle optimalization for the planar form of H_2BOH nor by optimalization of r(BN) for the orthogonal form of H_2BNH_2. This was judged to justify comparisons of results for the minimum energy geometries with those for various non-planar conformations in spite of optimalization inconsistencies. Some results for the perpendicular forms ($\phi=90°$ or $\phi_1=0°$ and $\phi_2=90°$, see Tables 1 and 2) are included in parentheses in Table 4. The populations of the boron p_z orbital were extracted from the total populations, when this was judged suitable for discussions of bond length variations, in particular for the different elongations encountered for B–O and B–N bonds upon rotation.

For H_2BOH, effects due to variations in the basis functions were studied. The computed populations appeared to be only slightly affected by the described (previous section, *i*) variations in the *d*-exponent and the scale factor of the hydrogen orbital exponents, as compared to the more major effects encountered for the (7*s*,3*p*) to (9*s*,5*p*) basis-set enlargements. It appears that the previously reported comparisons of populations of H_2BOH and H_2BOOBH_2,[25] suffer from the more serious type of basis-set inconsistency. Notwithstanding the small effects from exponent discrepancies, our results for H_2BOH (Table 4) should, therefore, rather be used for comparisons with the reported quantities[25] for H_2BOOBH_2. This yields smaller differences in the calculated quantities for the H_2B-O groups except for the total B–O overlap population. The comparable r(BO), n^{π}(B,O) and n^{σ}(B,O) values would be for H_2BOH, 1.364 Å, 0.22 a.u. and 0.55 a.u.; and for H_2BOOBH_2, 1.415 Å, 0.21 a.u. and 0.45 a.u., which indicate that the longer B–O bond in the peroxide may be related primarily to weaker σ-bonding.

Our results for H_2BOH and H_2BNH_2 confirm the conclusions of the earlier STO-3G calculations[20] although the difference between n^{π}(B,O) and n^{π}(B,N) has become more pronounced. As seen from Table 4, a small opposing effect in the σ contributions compensates some of the π difference so as to give a somewhat reduced but still larger total overlap population for the B–N bonds as compared to the B–O bond. Population analyses of the methyl derivatives $(CH_3)_2BZ$, $Z=OCH_3$, $N(CH_3)_2$, based on STO-3G wave functions,[2] show that the above conclusions from the STO-3G study of H_2BOH and H_2BNH_2,[20] are valid also for the relative π donor capacity of OCH_3 and $N(CH_3)_2$. The relative magnitudes of n^{σ}(B,O) and n^{σ}(B,N) for these methyl derivatives were reversed as compared to our results in Table 4. Comparative studies of BZ_3 showed[2] that $N(CH_3)_2$ is a stronger π donor than OCH_3 also in the trisubstituted boranes, and that increasing substitution (1→3) results in decreased n^{π}(B,Z) and n^{tot}(B,Z) values, whereas n^{σ}(B,Z) would be unchanged for $Z=OCH_3$ and slightly increased for $Z=N(CH_3)_2$. According to our results, these trends may be extended to the mono- and di-substituted species H_2BXH and $HB(XH)_2$, (X=O,NH). This is demonstrated by the values of Table 4 which show that the decrease for n^{π}(B,O) is smaller than for n^{π}(B,N), and that this in part is compensated for by a larger increase in n^{σ}(B,X) for the aminoseries. The total overlap population is further decreased for B→X←B bonding as compared to the described X←B→X bonding. However, the π contributions to n(B,X) are not significantly changed, and variations in n^{σ}(B,X) appear to be responsible for the overall drop in the overlap population. The n^{σ}(B,X) values for the B→X←B bonding are also slightly lower than those of the isolated bond, *i.e.* for H_2BXH. The relative magnitudes of the n^{π}(B,X) values seem to parallel the ranging of the π-bond order in the methyl derivatives as based on ^{11}B, ^{17}O, and ^{14}N NMR data,[60] with the exception of the diboryloxides. Discrepancies in structural results between the parent molecule $(H_2B)_2O$, and its permethylated derivative have been discussed in the previous section, and it appears that the short B–O bond in $[(CH_3)_2B]_2O$ may indeed be related to strong π-bonding, the NMR results suggesting a decreased π bond order along the series $[(CH_3)_2B]_2O > (CH_3)_2BOCH_3 > CH_3B(OCH_3)_2$.

The gross atomic populations give information about the polarizations in the molecule. The formal charges of the hydrogens ($Q(H_B)$, $Q(H_O)$ and $Q(H_N)$), easily deductable from the N(k) values of Table 4, show that the hydrogens act as weak electron acceptors when attached to the electropositive boron, and as electron donors when attached to the electronegative oxygen and nitrogen. The magnitudes of $Q(H_O)$ and $Q(H_N)$ are substantial, and they are in relative order as expected from the differences

in electronegativity of oxygen and nitrogen. Correspondingly, the $Q(B_O)$-values are larger than the $Q(B_N)$-values, but in this case the charges are affected by differences in backdonation of electrons from oxygen and nitrogen into the formally empty boron p_z-orbital and in the σ-interactions with the hydrogens. The importance of considering the effects of all substituents on the central atoms of H_2BNH_2 has been stressed previously,[17] and is most easily seen from the Q(O)- and Q(N)-values. Although nitrogen is the better π-donor and presumably the poorer σ-acceptor, it carries invariably larger negative charges than the corresponding oxygens, and this is caused by the presence of one more σ donating hydrogen. A major part of the charges on the oxygens and nitrogens originates from the hydrogens, but there is also a gross charge transfer (ΔQ, Table 4) from the borane groups in all molecules. This is also demonstrated by the calculated contribution from boron to the σ-populations of oxygen and nitrogen (ΔQ^σ), which in all cases are larger than the π-backdonation. This causes the bonds to be polar in the $B^+ - X^-$ sense. The ΔQ^σ-values do not show obvious trends in the relative strength of the σ-donor behaviour of boron to oxygen and to nitrogen in these compounds.

Calculations on H_2BNH_2[17] have shown that the dipole moments are quite sensitive to the various basis sets employed in that study, giving results in the range 1.78 – 2.52 D. The preferred value of 2.071 D is, however, in good agreement with our result, given in Table 4. Experimental dipole moments are available from Stark splitting data for $HB(OH)_2$,[8] H_2BNH_2,[7] and $HB(NH_2)_2$:[6] 1.47(2), 1.844(15) and 1.25 ± 0.01 D, respectively. These results are all lower than the calculated counterparts (see Table 4) as expected for good SCF-MO wave functions.[59] The obtained discrepancies of 8 – 12 % are reasonable when considering that Hartree-Fock estimates of dipole moments are claimed to be usually too large by about 0.2 D.[31] The experiments do not give direct information about the directions of the dipole moments. Based on comparisons of experimental results for HBF_2 [0.971(10) D] and F_2BNH_2 [2.595(30) D] with that given above for H_2BNH_2, it has been argued[7] that the direction of the dipole of H_2BNH_2 should be opposite the result of molecular orbital calculations.[17] The statements made[7,17] are in contradiction, but both studies fail to state clearly the employed definition of the dipole moment. The convention used in our calculations, $\mu = \Sigma q\bar{r}$, defines the dipole in the direction of the line joining the negative to the positive charge ($q^- \xrightarrow{r} q^+$), and the obtained directions are indicated by the arrows included in Fig. 1. According to the described argumentation[7] and a definition given in a later study by the same authors,[61] the opposite definition was used, and the results of our MO-calculations for H_2BNH_2 are in complete agreement with the forwarded arguments.[7] Similar considerations have deduced[61] that the direction of the moment for the BOH-group makes an angle of 16.4° with the OH-bond, which appear to be in qualitative agreement with the calculated directions for H_2BOH and $HB(OH)_2$. Focussing on the obtained nature of the polar $B^+ - X^-$ bond, the resultant dipole seems to be in contradiction to the population analyses for H_2BNH_2 and in accordance with the expectations for $HB(NH_2)_2$, $(H_2B)_2NH$ and $(H_2B)_2O$ molecules. However, the importance of the other bond moments, as already demonstrated by the dipole moments of H_2BOH and $HB(OH)_2$, should be remembered. In fact, this was clearly seen by vectorial addition of moments to each atom from a chosen reference point based on the atomic charges obtained in the Mulliken population analyses. This crude and dubious estimation of the resultant dipole moments was consistent with the reults of the proper calculation with respect to the directions of the dipoles. The relative magnitudes were of course not reproduced, but nevertheless the importance of even small charges far from central location in the molecule was remarkable.

It has been reported that the B–X overlap population decreased by a small amount for H_2BOH[19] and even increased for H_2BNH_2[17] upon rotation about the B–X bonds. Our results (Table 4) show an insignificant increase in both these cases. It appears that changes in the n(B,X) values are accompanied by changes in $n(B,H_B)$, whereas $n(B,H_O)$ and $n(B,H_N)$ are unaffected. By rotation the population of the boron $2p_z$ orbital, $N[B(p_z)]$, has decreased by 0.26 a.u., and the gross charge transfer from borane group, ΔQ, has increased by 0.09 a.u. for H_2BNH_2. The corresponding values for H_2BOH are 0.10 and 0.03 a.u., respectively. These results are consistent with a substantial drop in the backdonation from nitrogen and a lesser reduction from oxygen upon rotation. It should also be noted that p_z-populations of the boron in planar moieties of the perpendicular ($\phi_1 = 0$, $\phi_2 = 90°$) forms of $HB(NH_2)_2$ and $(H_2B)_2NH$ approach the

Table 5. Comparisons of rigid, and in parentheses partially optimized, rotational barriers (ΔE, in kcal mol^{-1}) and B–X bond distances (r(BX), in Å) and overlap populations (n^{π}(B,X) and n^{σ}(B,X) in a.u.) of the minimum energy geometries (Fig. 1).

Molecule	ΔE	r(BX)	n^{π}(B,X)	n^{σ}(B,X)
H_2BOH	15.1(14.1)	1.364	0.22	0.55
$HB(OH)_2$	10.4	1.377	0.17	0.56
	10.6	1.366	0.18	0.58
$(H_2B)_2O$	3.7(2.9)	1.383	0.17	0.52
H_2BNH_2	38.4(35.5)	1.398	0.30	0.52
$HB(NH_2)_2$	19.1(17.5)	1.424	0.21	0.58
$(H_2B)_2NH$	21.7(20.2)	1.435	0.21	0.50

N^{π}(B)-value of planar H_2BNH_2. The N(B)-values of the planar ($\phi_1 = 0$) and perpendicular ($\phi_2 = 90°$) moieties of the $(H_2B)_2NH$ are close to the corresponding values of planar and orthogonal H_2BNH_2. A similar trend is obtained for $(H_2B)_2O$, but the differences for the planar and perpendicular moieties are marginal. These results are consistent with the previously described rotational dependencies of the various B–X bond lengths. The n(B,O), N(B) and N(O) values for H_2BOBH_2 found to be 0.70, 4.45 and 8.75 a.u. both for D_{2d}- and C_2 ($\angle$BOB = 150°, $\phi = 45°$)-models, were found to be invariant also in other non-planar conformations, but did not provide a basis for further speculations on the nature of the B–O bond.

CONCLUDING REMARKS

Our calculations have been shown to reproduce well experimental structural parameters of $HB(OH)_2$[9] and $HB(NH_2)_2$,[6] rotational barrier for $HB(NH_2)_2$[6b] and dipole moments for $HB(OH)_2$,[8] $HB(NH_2)_2$[6] and H_2BNH_2.[7] The obtained structural results for the six molecules also compare favourably with experimental values for their methyl derivatives[3–5] with an apparent exception for $(H_2B)_2O$ and $[(CH_3)_2B]_2O$ which, however, has been satisfactorily explained by the large conformational differences of these two molecules.

The fact that the minimum energy geometries for the six compounds under investigation are all found to be coplanar, may be taken as evidence for considerable π-character in the B–O and B–N bonds. This conclusion is substantiated by the relatively high rotational barriers, except perhaps for the somewhat atypical one for $(H_2B)_2O$. The obtained barriers (Tables 1 and 2) are summarized in Table 5 and compared with the r(BO) and r(BN) bond distances (Fig. 1) and the corresponding π- and σ-overlap populations (Table 4) obtained for the minimum energy geometries. The bond distances, which compare favourably with experimental values, are shorter than the estimates for the single bond lengths. This may be considered as corroborating evidence for partial double bonding as are also the substantial π-overlap populations encountered. The ΔE, r(BX) and n^{π}(BX) values indicate that the degree of π-bonding is larger in the boron-nitrogen compounds than in their isoelectronic oxygen counterparts, and in the monoderivatives (H_2BXH, X = O,NH) as compared to both $HB(XH)_2$ and $(H_2B)_2X$, with less pronounced changes for the oxygen series. Further interpretation of these quantities in terms of varying π-bonding among the six molecules is not obvious. However, taking the σ-bond populations into account, it is seen that the shorter bonds in X–B–X bonding as compared to those in B–X–B bonding may be due to differences in the σ-bond strength. This allows for a further conclusion that the dative π-bonding is of comparable importance in the $HB(XH)_2$ and $(H_2B)_2X$ molecules, as is indicated by the obtained n^{π}(B,X)-values and which is approximately consistent with the ΔE-values for the nitrogen compounds. However, the rather low ΔE-value for $(H_2B)_2O$ as compared to the other rotational barriers and the trends in the variations of r(B,X) and n(B,X) throughout the series of molecules (Table 5) appears to be inconsistent with the above conclusion. In comparison with the molecular

structures of methyl derivatives of the six studied parent molecules, $(H_2B)_2O$ was again atypical. The modest changes in the B–O bond length, the p_z-orbital population and the gross charge transfer encountered upon rotation about the B–O bonds as compared to the corresponding boron–nitrogen results, suggest support of the interpretation of ^{11}B NMR-data[34] which implies that the boron has comfortable electron acceptor behaviour even in non-planar forms in boron-oxygen compounds, due to the presence of a second lone electron pair in oxygen. Together with the previously discussed bonding conditions of non-planar conformations of $(H_2B)_2O$ and for the permethylated derivative, this could consolidate the low rotational barrier in $(H_2B)_2O$ and an n^{π}(B,O)-value as large as that of $HB(OH)_2$. Conformational differences of $(H_2B)_2O$ and $[(CH_3)_2B]_2O$ may then account satisfactorily for the discrepancy in r(BO) for the two molecules.

It has been pointed out in a previous section that any acceptor behaviour of the boron $2p_z$ orbital in non-planar conformations would tend to obscure the relationship between the rotational barriers and the π-bond order in the planar form. The claimed larger π-bond character of the B–N than of the B–O bonds is based on substantial barrier differences and supported by our interpretations of the population analyses. However, for H_2BSH a slightly higher rotational barrier as compared to that of H_2BOH (19.5 and 16.4 kcal mol^{-1}, respectively) has been, with claimed support in the population analyses, taken as evidence for a greater importance of π-bonding in the planar mercaptoborane than in hydroxyborane.[19] The change in some of the discussed quantities for H_2BOH and H_2BNH_2 upon rotation to the orthogonal form may also be noteworthy for H_2BSH:[19,62] elongation for r(BS) by 0.09 Å, to 1.88 Å; decrease in ∠BSH by 5°, to 94°; and decrease in the $2p_z$ population by 0.16 a.u., to 0.05 a.u. As compared to the small changes in the corresponding quantities for H_2BOH, these results suggest substantial drop in backdonation from sulfur upon rotation to the perpendicular form, approximately consistent with the situation for H_2BNH_2. Therefore, the magnitudes of the ΔE(BS) and ΔE(BO) values, being relatively close, cannot be used to judge the relative importance of π-bonding in the planar forms. The reductions of the barriers to rigid rotation of about 11 kcal mol^{-1} for both molecules obtained when the boron $2p_z$ is excluded from the calculations clearly demonstrate the importance of this orbital for the bonding conditions,[19,62] but significant differences for H_2BOH and H_2BSH are not obvious. The reported overlap populations n^{π}(B,S) and n^{π}(B,O) of 0.23 and 0.26 a.u., respectively, suggest slightly higher π-bond character in the B–O bond than in the B–S bond, in agreement with the results for the permethylated species, $(CH_3)_2BOCH_3$ and $(CH_3)_2BSCH_3$.[2] However, all evidence considered suggests that the degree of π-bonding for these B–O and B–S bonds cannot be ranged unambiguously.

The charge distributions in the molecules, as obtained from the Mulliken population analyses (Table 4), show that there are gross charge transfers from the borane groups in all six molecules. The general conclusion from the population analysis is, therefore, that boron is a π-acceptor but a stronger σ-donor, so as to make the bonds polar in the B^+-X^- sense. Fig. 1 shows the calculated directions of the dipoles, not directly obtainable from experiments. For H_2BNH_2 the result appears to be in contradiction to the B^+-N^- polarity concept. It is, however, entirely consistent with arguments forwarded[7] on the basis of experimental magnitudes of the dipole moments for F_2BH, H_2BNH_2 and F_2BNH_2. Also, the obtained directions for H_2BOH and $HB(OH)_2$ are in qualitative agreement with that proposed for the BOH-group[61] and the importance of the O–H bond vectors is obvious (Fig. 1). In general, the importance of the moments involving the periferically located hydrogens for the resultant dipole should be stressed.

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