

Molecular Structures of Gaseous (Methoxy)dimethylborane, $(\text{CH}_3)_2\text{BOCH}_3$, and Bis(methoxy)methylborane, $\text{CH}_3\text{B}(\text{OCH}_3)_2$, Studied by Electron Diffraction

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The molecular structures of the title compounds were studied with main emphasis on effects from dative π -bonding in the B–O bonds throughout the series $(\text{CH}_3)_{3-n}\text{B}(\text{OCH}_3)_n$, $n=1,2,3$. Some complementary refinements were included for $\text{B}(\text{OCH}_3)_3$ to ensure consistent treatment for the three molecules. For $\text{CH}_3\text{B}(\text{OCH}_3)_2$ a *syn,anti* periplanar conformer was found to be prevailing. The molecules were found to possess planar, or nearly coplanar, conformation and to have short B–O bonds, which have been ascribed to effects from π -electron back donation from oxygen to the formally empty $2p_z$ orbital of boron. The $r_e(\text{BO})$ values were 1.361(2), 1.375(4) and 1.368(2) Å respectively for $n=1,2$ and 3, and the corresponding averages of the overlapping B–O and O–C bonds were 1.391(2), 1.396(2) and 1.396(2) Å. Neither $r(\text{BO})$ nor the average parameter shows consistent elongations as would be expected if the decreased possibilities for π -bonding in each B–O bond throughout the series were dominating the B–O bond-length variations in these compounds.

Simplified valence force fields have been derived and used to calculate vibrational amplitudes and shrinkage corrections.

Gaseous trimethoxyborane, $\text{B}(\text{OCH}_3)_3$, has been found to possess a planar heavy atom skeleton with a B–O bond length of 1.367(4) Å.¹ The bond length compares favourably with the mean trigonal bond length of crystalline borates of 1.365 Å.² It is short compared to the mean tetrahedral bonds of 1.475 Å in the crystalline borates² and to a single bond estimate of 1.47 Å.¹ The coplanar conformation and the short B–O bond are attributed to substantial amounts of double bond character. This originates

from π -acceptor behaviour of the coordinatively unsaturated trigonal boron atom when attached to ligands with electrons available for donation into the formally empty boron $2p_z$ -orbital. Naturally, the double bond strength depends on the π -electron donor capacity of the ligand and on the number of strong π -donors attached to each boron.

The OCH_3 group is classified as a strong and CH_3 , allegedly through hyperconjugative interactions,³ as a weak π -donor.⁴ Consequently, as compared to $\text{B}(\text{OCH}_3)_3$ the possibilities for π -bonding in each B–O bond should be enhanced in $\text{CH}_3\text{B}(\text{OCH}_3)_2$ and even more so in $(\text{CH}_3)_2\text{BOCH}_3$. In fact, electron-diffraction studies of the analogous thioboranes, $(\text{CH}_3)_{3-n}\text{B}(\text{SCH}_3)_n$, $n=1,2,3$, have shown a trend for the B–S bond length variation in a direction which could be related to such variation in the π -bond order.^{5–7} This paper accounts for structural studies of the mentioned monomethoxy and bismethoxy methylboranes which together with the previous study¹ complete the corresponding oxygen series, $(\text{CH}_3)_{3-n}\text{B}(\text{OCH}_3)_n$, $n=1,2,3$, hereafter referred to as BO1, BO2 and BO3. To ensure consistent treatment for the three molecules, some refinements have been included for BO3.

Variation in the π -bond orders is of course not the only possible effect of the described substitution changes. Considering the high electronegativity of oxygen, a bond-length variation opposing that of double-bond enhancement would be predicted, as bonds to a central atom are known to become shorter when its number of electronegative ligands is increased. Unfortunately, most electronegative ligands also have electrons available for back donation to the boron $2p_z$ -orbital, and as described

Table 1. Experimental and refinement conditions.

Compounds	$(\text{CH}_3)_2\text{BOCH}_3/\text{BO1}$		$\text{CH}_3\text{B}(\text{OCH}_3)_2/\text{BO2}$	
Electron wavelength, λ (Å)	0.05849		0.05862	
Photographic plate	Replica 23		Kodak Electron Image	
Sample temperature (°C)	-45		-14 to -22	
Nozzle temperature (°C)	ca. 20		ca. 20	
Nozzle-to-plate distances (mm)	500.12	250.12	500.12	250.12
Pressure during sample run-in (10^{-5} Torr)	2	2	5-6	6
Beam current (μA)	30-35	25-30	10-15	10-15
Exposure times (min)	1-1½	2-3	1-1½	3-3½
Background, polynomial degree	7	9	7	9
No. of plates	3	4	6	4
Data interval, Δs (Å ⁻¹)	0.125	0.25	0.125	0.25
Data range, $s(\text{min})-s(\text{max})$ (Å ⁻¹)	1.75-15.00	5.00-29.00	1.75-15.00	5.00-29.00
Weighting scheme ^a				
$s1-s2$	5.00-12.00	5.00-20.0	5.00-12.00	5.00-20.00
$w1-w2$	0.15-0.03	0.15-0.015	0.15-0.03	0.15-0.015
W	1.0	1.0	1.0	1.0

^a See Ref. 14 for the meaning of $s1$, $s2$, $w1$, $w2$. W is the relative weight on data from different camera distances which are on approximately the same scale.

in connection with ¹¹B NMR-studies of trivalent boron compounds,⁸ the effects from variation in π - and σ -bonding are not easily separated. These complications are also discussed in connection with *ab initio* MO-studies of the corresponding acids, H_2BOH , $\text{HB}(\text{OH})_2$ and $\text{B}(\text{OH})_3$.⁹

EXPERIMENTAL AND DATA PROCESSING

Pure samples of BO1 and BO2 prepared by reacting methanol with appropriate aminoboranes,¹⁰ were supplied for this investigation by Professor Nöth and coworkers at the University of Munich.

Electron-diffraction photographs were made in a Balzers' Eldigraph KDG-2¹¹ with an accelerating voltage of 42 kV under experimental conditions as summarized in Table 1. The given electron wavelengths were calibrated against diagrams of gaseous benzene ($r_a(\text{CC})=1.3975$ Å).¹² The uncertainty in the s -scale is estimated to 0.1%.

The optical densities (D) of the BO1 diagrams were recorded in intervals of 0.25 mm, while oscillating the plates on an integrating densitometer constructed by A. Almenningen and P. Molin. For BO2 a Joyce-Loebl microdensitometer was used to record the plates in a rectangular coordinate system, using a data-collection and initial data-processing procedure as briefly outlined elsewhere.¹³ The data

reductions were carried out in routine manner¹⁴ using blackness calibrations^{12a} of $1.0+0.13D^2+0.17D^3$ and $1.0-0.047D+0.1D^2-0.013D^3$, respectively, for Replica 23 and Kodak Electron Image plates. An automatic background subtraction procedure analogous to that described by L. Hedberg,¹⁵ was used for each individual curve on the modified¹⁴ (by $s/|f'_B(s)||f'_C(s)|$) form. The resulting modified molecular intensities were averaged for each camera distance to give the final curves shown in Figs. 1 and 2. The corresponding experimental radial distribution (RD) curves are shown in Figs. 3 and 4. They were computed from composite intensities obtained by scaling and averaging in the overlap regions using pertinent theoretical intensity values for the unobserved or uncertain inner regions, *i.e.* for $s < s_{\text{min}}$ of Table 1, and artificial damping constants of 0.0020 Å.² The scattering amplitudes ($|f'(s)|$) and phases ($\eta(s)$)¹⁴ were calculated using the partial wave method¹⁶ based upon analytical HF-potentials¹⁷ for the B-, C- and O-atoms and the best electron density for bonded hydrogen¹⁸ for the H-atom. The inelastic scattering factors used were those of Tavard *et al.*¹⁹

STRUCTURE ANALYSES

Refinements of geometrical and vibrational parameters were carried out by the least-squares method based on averaged modified molecular

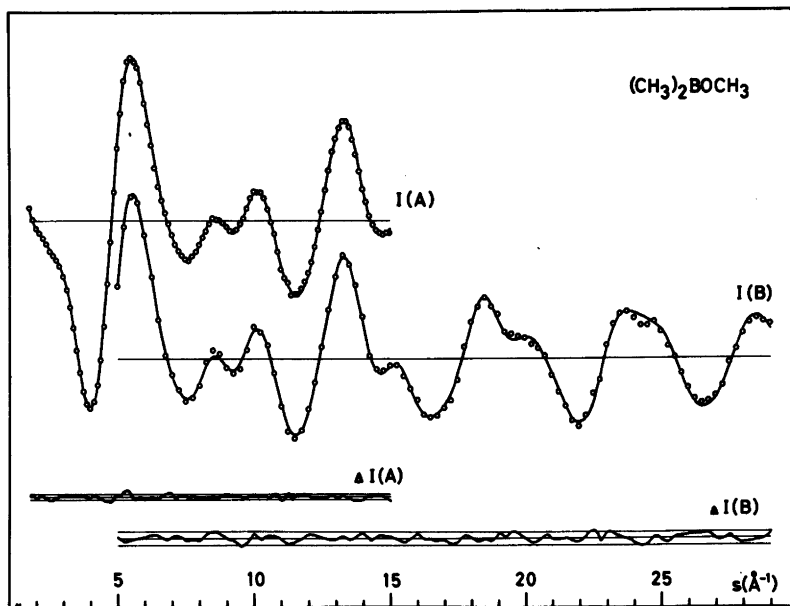


Fig. 1. Experimental modified molecular intensities (o) for $(\text{CH}_3)_2\text{BOCH}_3$ and the theoretical counterparts (full line) calculated according to the parameter values of Table 4, $I(\text{A})$ and $I(\text{B})$, respectively, for the 50 and 25 cm camera distances. The $\Delta I(\text{A})$ and $\Delta I(\text{B})$ curves are the differences between experimental and theoretical intensities and the included horizontal lines given are the estimated average uncertainties of the experimental points (three standard deviations).

intensities for each camera distance using the data ranges and weighting matrices given in Table 1.¹⁴ All structural parameters quoted are obtained in such refinements neglecting effects from data correlation. The standard deviations obtained in this manner (σ_{LS}) were, however, augmented by a factor f to account for such correlations. Some comparative least-squares refinements using diagonal ($p_{ij}=0, i \neq j$) weight matrices and non-diagonal ones with standard values for the off-diagonal elements,²⁰ gave f -estimates of 1.5 for torsional angles and 2.0 for the remaining parameters.

Hilderbrandts normal coordinate program²¹ was used to derive approximate simplified valence force fields (SGVFF) for the molecules, and subsequently to compute the vibrational amplitude quantities (l and K -values)²² and centrifugal correction terms (δr_{cent})²³ for the interatomic distances. The results were used to convert the electron-diffraction distance parameter, r_a , to the corresponding r_x -values.²⁴ The calculated r_a to r_x conversions for nonbonded distances involving

hydrogens were judged to be quite uncertain due to not well known torsional behaviour of the methyl groups. Shrinkage correction (d)²⁴ necessitated by introduction of geometrical models, were therefore carried out for the skeletal nonbonded distances only, rather than using complete r_x -models for the molecules. The asymmetry constants for the bonds (κ_{ij})¹⁴ were estimated from the expression $\kappa_{ij} = al^4/6$, using the calculated l -values and $a=2 \text{ \AA}^{-1}$.²⁴ The a estimate of 2 \AA^{-1} for bond distances was also used in calculations of the r_a to r_x corrections, which were computed for comparison purposes with results from *ab initio* MO-studies of analogous compounds.

Geometrical models

The interpretations of the experimental RD -curves for BO1 and BO2 as indicated by the assignments of the main features of the curves in Figs. 3 and 4, show that nearly planar heavy atom skeletons of conformations given by the inserted

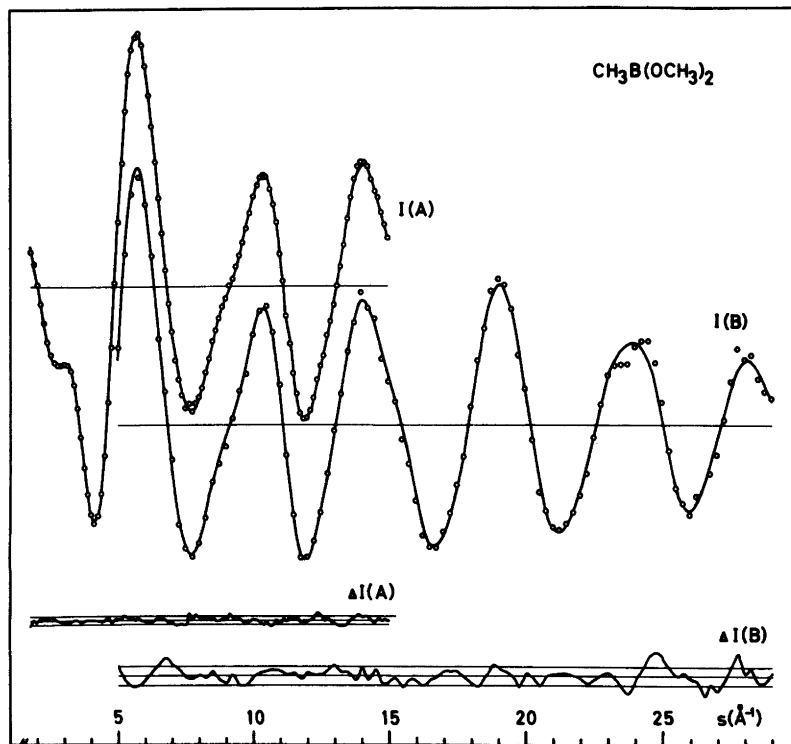


Fig. 2. Experimental modified molecular intensities (O) for $\text{CH}_3\text{B}(\text{OCH}_3)_2$ the theoretical counterparts (full line) and the differences (ΔI), presented as in Fig. 1.

ORTEP plots of the molecules, are consistent with the data.

Microwave and *ab initio* MO-studies of the parent molecules H_2BOH and $\text{BH}(\text{OH})_2$ ^{9,25-27}, have revealed differences in the B–H bond lengths *syn* and *anti* to the O–H bond in H_2BOH (Δ : 0.005 Å) and in the B–O (Δ : 0.01 Å) as well as the O–H (Δ = –0.01 Å) bonds of the *syn* and *anti* moieties in $\text{HB}(\text{OH})_2$. Corresponding differences would be possible also for the methyl derivatives, but they were ignored in the geometrical models. Symmetrically different B–O, B–C and O–C distances were thus assumed to be equal. Local C_{3v} -symmetries were introduced for the methyl groups which were distinguished only by their attachments, *i.e.* boron or to oxygen. Additionally, the C–H bond lengths had to be constrained by $r(\text{C}_\text{B}-\text{H})=r(\text{C}_\text{O}-\text{H})$. The B–O bond distances, of main interest in this study, are close to the O–C bond lengths. This makes their determinations highly inter-dependent and also strongly correlated with the associated

amplitudes of vibration. Therefore, the average (\bar{r}) of these distances, which could be determined with high accuracy, and their difference (Δ) were introduced as variables rather than the actual bond distances. The geometrical models thus introduced for the three molecules were described by 13, 15 and 7 variables for BO1, BO2 and BO3, respectively. The definitions are given subsequently together with the structural results (Tables 4–6).

Force field calculations

The vibrational spectral data for BO1 and BO2²⁸ do not give complete sets of fundamental vibrational frequencies. It was therefore decided to design initial SGVFF's from force fields of $\text{B}(\text{CH}_3)_3$ (referred to as BR3) and of BO3 for which the reported spectral data appear to be complete.²⁹⁻³¹ The experimental data used are comprised in Table 2 for all four molecules. The table also contains

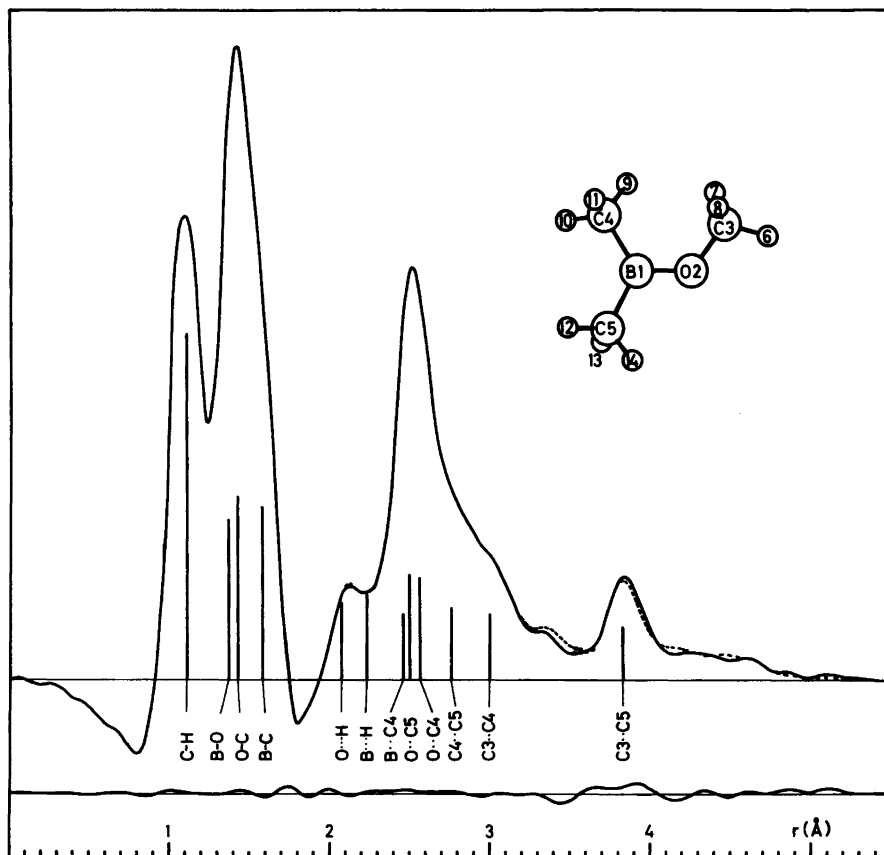


Fig. 3. Experimental radial distribution curve (full line) for $(\text{CH}_3)_2\text{BOCH}_3$ compared to the theoretical counterpart (broken line). The corresponding difference curve is also shown.

approximate assignments and frequencies calculated from the final force fields given in Table 3.

For BR3 the bond distances and valence angles were taken from an electron-diffraction study of the molecule,³² which consistent with the interpretation of the spectroscopic data,^{29,30} suggested freely rotating methyl groups. Our calculations were, however, based on a model with localized hydrogens of C_{3h} -symmetry using a small and rather arbitrarily chosen force constant for the methyl torsion. An initial force field with only one interaction constant (see Table 3) yielded methyl deformations ($\delta(\text{BCH}_3)$) in disagreement with the reported assignment²⁹ which lists 1422 and 1470 cm^{-1} as the E'' and A'' modes, respectively. The relative magnitude of in-plane and out-of-plane methyl deformations were reversed by introducing

interactions between the $\text{H}-\text{C}-\text{H}$ and $\text{B}-\text{C}-\text{H}$ internal coordinates. However, this did not alter the computed l - and K -values significantly. Therefore, the simpler force field originally developed in connection with normal coordinate analyses of aminoboranes,³³ appeared adequate for our purpose.

Normal coordinate calculations have recently been reported for BO_3 in connection with vibrational spectroscopic³¹ and electron-diffraction¹ investigations. In this work the force field of the latter study¹ has been modified for use in Hilderbrandts MSAV-program²¹ which required redefinitions of out-of-plane bending and torsion. Also, non-bonded interaction constants, which made comparison of force fields³¹ difficult, were omitted. The new force field is presented in Table 3.

Table 2. Observed fundamental vibrational frequencies (cm^{-1}) for the series $(\text{CH}_3)_3\text{B}$ to $\text{B}(\text{OCH}_3)_3$ compared to values calculated from the force fields of Table 3.

Approximate assignments ^a	BR3		BO1		BO2		BO3	
	Obs. (Ref. 29)	Calc.	Obs. (Ref. 28)	Calc.	Obs. (Ref. 28)	Calc.	Obs. (Ref. 31)	Calc.
Skeletal								
$\nu(\text{BC})$	680	680	(715) ^b	682	—	—	—	—
'	1155	1152E	1185 ^c	1205	700	693	—	—
$\nu(\text{BO})$	—	—	—	—	1282	1297	729	727
'	—	—	1285	1280	1347	1362	1364	1384E
$\nu(\text{OC})$	—	—	1058	1054	1042	1037	1041	1043
'	—	—	—	—	1074	1074	1125	1112E
$\delta(\text{CBC})$	321	322E	?	314	—	—	—	—
$\delta(\text{OBC})$	—	—	?	216	?	248 ^c	—	—
$\delta(\text{OBO})$	—	—	—	—	?	188 ^c	521	509E ^c
$\delta(\text{BOC})$	—	—	?	470	?	512 ^c	187	188 ^c
'	—	—	—	—	?	409 ^c	317	319
$\gamma(\text{B})$	336	339	?	444	?	499	667	659
$\tau(\text{XBOC})$	—	—	?	140	?	142	165	144
"	—	—	—	—	?	133	102	130
Methyl								
$\nu(\text{C}_\text{B}\text{H})$	2880	2885		2881	—	—	—	—
'	2926	2882E		2881		—	—	—
'	2980	2982		2993		2879	—	—
'	2984	2982E		2994		2995	—	—
"	2974	2982E		2992	2880	2994	—	—
"	2984	2983	2867	2993		—	—	—
$\nu(\text{C}_\text{O}\text{H})$	—	—	2963	—	2975	2851	2867	2858
'	—	—		—		2851	2882	2859E
'	—	—		2858		2969	2942	2969
'	—	—		2966		2969	2953	2969E
"	—	—		2964		2968	2964	2969
"	—	—		—		2968	2974	2969E
$\delta(\text{BCH}_3)$	1297	1298		1328		—	—	—
'	1306	1306E		1340		—	—	—
'	1420	1422		1419		1319	—	—
'	1470 ^c	1443E	1332	1436 ^c		1435 ^c	—	—
"	1422	1298		1332		1332	—	—
"	1470	1309E		1337	1488	—	—	—
$\delta(\text{OCH}_3)$	—	—		—		1454	1450	1467
'	—	—		—		1456	1468	1469E
'	—	—		—		1485	1470	1522
'	—	—	1470	1450		1485	1510	1522E
"	—	—		1514		1451	1485	1465E
"	—	—		1446		1451	1489	1466
$\rho(\text{BCH}_3)$	858	861E	855	871		—	—	—
'	900	918	900	919	848	901	—	—
"	900	919E	953	939	907	989	—	—
"	967	1064		1023		—	—	—
$\rho(\text{OCH}_3)$	—	—		—		1149	1183	1187
'	—	—	1135 ^c	1122	1190	1171	1204	1166E
"	—	—		1133	1215	1145	1115	1151
"	—	—		—		1146	1165	1149E

Table 2. *Continued.*

$\tau(\text{BCH}_3)$	"	?	126	?	124	-	-	-	-
"	"	?	130E	?	130	?	124	-	-
$\tau(\text{OCH}_3)$	"	-	-	?	209	?	202	?	207
"	"	-	-	-	-	?	213	230	218

^a Vibrations symmetric and asymmetric with respect to the skeleton (C_3 -symmetry) are identified by ' and ", respectively. The degenerate modes for $\text{B}(\text{CH}_3)_3$ and $\text{B}(\text{OCH}_3)_3$ (C_{3h} -symmetry) are identified by E after the calculated value. ^b Taken from $(\text{CH}_3)_2\text{BOH}$ ³⁴ for which the $\nu(\text{BC})_{\text{as}}$ is 1205 cm^{-1} . ^c See text for comments on reassignments, mixed modes and uncertain assignments.

The geometrical parameters used were consistent with the final results (Table 6) with the exception that C_{3h} -symmetry (*i.e.* $\theta(\text{BOCH})=0$) was assumed. The assignments of the normal vibrations (Table 2) as based on calculated potential energy distributions (PED) showed that the two degenerate

$\delta(\text{OBO})$ and $\delta(\text{BOC})$ vibrations at 509 and 188 cm^{-1} are intermixed and that the former contains large contributions of B—O stretch. Similar features appeared also in the previous calculations.^{1,31} The various force fields and calculation procedure yielded vibrational amplitude quantities in quite

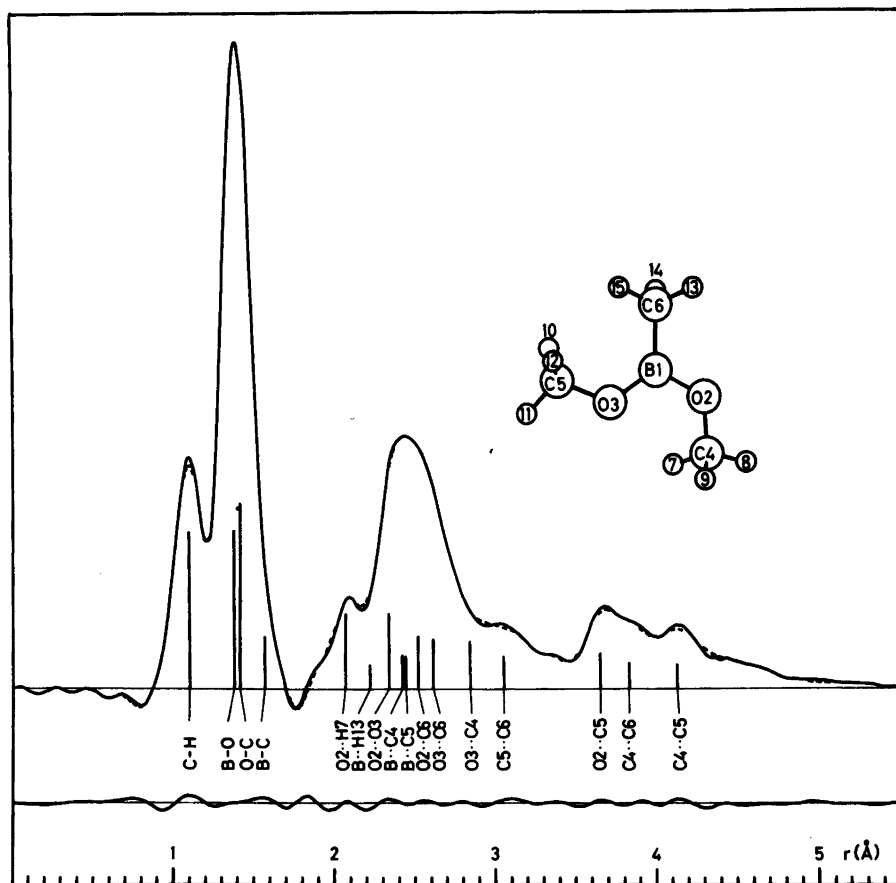


Fig. 4. Experimental radial distribution curve (full line) for $\text{CH}_3\text{B}(\text{OCH}_3)_2$ compared to the theoretical counterpart (broken line). The corresponding difference curve is also shown.

Table 3. Simplified valence force field for the series $B(CH_3)_3$, $(CH_3)_2BOCH_3$, $CH_3B(OCH_3)_2$ and $B(OCH_3)_3$.

Definition ^a	BR3	BO1	BO2	BO3
k_r (aJ Å ⁻²)				
B-C	3.60	3.60	3.60	—
B-O	—	4.50	4.50	4.40
O-C	—	5.05	5.05	5.09
C(B)-H	4.75	4.77	4.77	—
C(O)-H	—	4.68	4.68	4.69
k_θ (aJ rad ⁻²)				
CBC	0.62	0.60	—	—
OBC	—	0.70	0.70	—
OBO	—	—	1.12	1.12
BOC	—	1.07	1.07	1.07
BCH	0.62	0.62	0.62	—
HC(B)H	0.45	0.45	0.45	—
OCH	—	0.88	0.88	0.88
HC(O)H	—	0.52	0.52	0.52
k_τ (aJ rad ⁻²)				
BO	—	0.17	0.17	0.17
CB	0.03	0.03	0.03	—
CO	—	0.08	0.08	0.08
k_γ (aJ rad ⁻²)				
B	0.24	0.30	0.30	0.43
$k_{r,r}$ (aJ Å ⁻²)				
BC/BC	0.40	0.40	—	—
BC/BO	—	0.40	0.40	—
BO/BO	—	—	0.40	0.71
$k_{r\theta}$ (aJ Å ⁻¹ rad ⁻¹)				
OC/OCH	—	0.42	0.42	0.42

^aThe meaning of the k subscripts are: r , stretch; θ , bend; τ , torsion; and γ , out-of-plane bend of a central atom in a planar four atom group. See molecular models Figs. 2-4. 1 aJ = 10^{-18} J = 1 mdyn Å.

good correspondence. For the important amplitudes associated with the closely spaced B-O and O-C bonds the new values are intermediate to those previously reported.^{1,31}

The merging of force constants from BR3 and BO3 to produce force fields for BO1 and BO2, was carried out using 0.40 aJ Å⁻² for all skeletal stretch, stretch interactions. (See Table 3). The bond distance and valence angle parameters used were consistent with the final results (Tables 4 and 5). However, overall C_s-symmetries were assumed, with the dihedral angles equal to 0° or 180° as preferred according to preliminary structural refinements.

Specifying the dihedral angles only by the central atom-pairs (*cf.* Tables 4 and 5), the sets of values were for BO1: $\theta(B-O)=0$, $\theta(C3-O)=180$, $\theta(C4-B)=0$ and $\theta(C5-B)=180$ °; and for BO2: $\theta(O2-B)=180$, $\theta(O3-B)=0$, $\theta(C4-O2)=0$, $\theta(C5-O3)=180$, and $\theta(C6-B)=0$ °.

The frequency at 1205 cm⁻¹ for BO1 was according to the PED rather uncharacterized (Table 2), but it could be assigned to a B-C stretching vibration, as compared to the observed counterpart of 1135 cm⁻¹. However, it appears that the assignments of 1135 and 1185 cm⁻¹ could be exchanged, which would also give better fit for the

Table 4. Results for $(\text{CH}_3)_2\text{BOCH}_3$ distance (r , d) and amplitude (l) quantities in Å and angles (\angle , θ) in degrees. The numbering of the atoms is given in Fig. 3.

	Force field ^a		Electron diffraction ($R_w = 4.42\%$) ^b			
	Δr	l_{calc}	l_{obs}	r_a	Angles	
$\text{C}_B - \text{H}$	(0.0707)	0.0787	} 0.077(1)	1.103(2)	$\angle \text{BCH}$	111.7(5)
$\text{C}_O - \text{H}$	(0.0375)	0.0787			} 0.0535 ^c	1.575(2)
$\text{B} - \text{C}$	(0.0033)	0.0535	}	1.391(2)		
$\bar{r}(\text{OC}, \text{BO})$	—	—			}	0.060(3)
$\Delta(\text{OC}, \text{BO})$	—	—	}	1.361(2)		
$\text{B} - \text{O}$	(0.0024)	0.0487			0.0487 ^c	1.421(2)
$\text{O} - \text{C}$	(0.0110)	0.0476	0.0476 ^c	2.232(7)	$\angle \text{OBC4}$	121.3(8)
$\text{B} \cdots \text{H9}$	—	0.113	0.113 ^c	2.072(6)	$\angle \text{OBC5}$	116.4(6)
$\text{O} \cdots \text{H6}$	—	0.101	0.101 ^c	2.454(6)	$\theta(\text{C3OBC4})$	14.1(38)
$\text{B} \cdots \text{C3}$	0.0067	0.069	0.074	} (3) 2.558(10)		
$\text{O} \cdots \text{C4}$	0.0038	0.071	0.076			
$\text{O} \cdots \text{C5}$	0.0037	0.074	0.077			
$\text{C4} \cdots \text{C5}$	0.0035	0.076	0.080			
$\text{C3} \cdots \text{C4}$	0.0060	0.125	0.114(7)	2.996(9)		
$\text{C3} \cdots \text{C5}$	0.0144	0.077	0.075(6)	3.829(7)		

^a The Δr values are, in parentheses the calculated $r_a - r_o$ corrections for the bonds, and for the nonbonded distances the calculated shrinkages(d). ^b The distance and angle parameters within braces correspond to the independent geometrical parameters described in the text. ^c Parameters fixed during the refinement. See text.

Table 5. Results for $\text{CH}_3\text{B}(\text{OCH}_3)_2$, distance (r , d) and amplitude (l) quantities in Å and angles (\angle , θ) in degrees. The numbering of the atoms is given in Fig. 4.

	Force field ^a		Electron diffraction ($R_w = 5.36\%$) ^b			
	Δr	l_{calc}	r_a	Angles		
$\text{C}_B - \text{H}$	(0.0711)	} 0.0787	1.106(2)	$\angle \text{BCH}$	110.4(24)	
$\text{C}_O - \text{H}$	(0.0380)			} 0.0535	1.571(6)	$\angle \text{OCH}$
$\text{B} - \text{C}$	(0.0043)	}	1.396(2)			$\theta(\text{H7C4O2B})$
$\bar{r}(\text{OC}, \text{BO})$	—			}	0.042(6)	$\theta(\text{H11C5O3B})$
$\Delta(\text{OC}, \text{BO})$	—	}	1.375(4)			$\theta(\text{H13C6BO2})$
$\text{B} - \text{O}$	(0.0030)			0.0489	1.417(3)	$\angle \text{O2BC6}$
$\text{O} - \text{C}$	(0.0120)	0.0477	2.215(31)	$\angle \text{O3BC6}$	125.0(6)	
$\text{B} \cdots \text{H13}$	—	0.113	2.074(8)	$\angle \text{BO2C4}$	121.2(8)	
$\text{O} \cdots \text{H7}$	—	0.102	2.343(6)	$\angle \text{BO3C5}$	122.9(6)	
$\text{O2} \cdots \text{O3}$	0.0030	0.063	2.424(10)	$\theta(\text{C4O2BC6})$	191.9	
$\text{B} \cdots \text{C4}$	0.0075	0.071	2.444(8)	$\theta(\text{C5O3BC6})$	-11.9	
$\text{B} \cdots \text{C5}$	0.0078	0.071	2.523(7)	} (76)		
$\text{O2} \cdots \text{C6}$	0.0028	0.071	2.611(8)			
$\text{O3} \cdots \text{C6}$	0.0036	0.069	2.739(16)			
$\text{O2} \cdots \text{C5}$	0.0142	0.070	3.651(14)			
$\text{O3} \cdots \text{C4}$	0.0059	0.113	4.134(14)			
$\text{C4} \cdots \text{C5}$	0.0204	0.120	3.828(18)			
$\text{C4} \cdots \text{C6}$	0.0154	0.075	3.050(21)			
$\text{C5} \cdots \text{C6}$	0.0074	0.123				

^{a-c} See footnotes to Table 4. All amplitudes in the electron-diffraction study were maintained at the l_{calc} values.

Table 6. Results for $B(OCH_3)_3$, distance (r , d) and amplitude (l) quantities in Å and angles (\angle , θ) in degrees.

	Force field ^a		Electron diffraction ($R_w = 4.42\%$) ^b			
	Δr	l_{calc}	l_{obs}	r_a	Angles	
C—H	(0.0374)	0.0787	0.076(3)	1.106(3)	\angle OCH θ (BOCH) \angle BOC	109.0(5) 31.6(20) 121.0(2) ^b
$\bar{\nu}$ (OC, BO)	—	—	—	1.396(2)		
Δ (OC, BO)	—	—	—	0.056(3)		
B—O	(0.0034)	0.0490	0.0490 ^c	1.368(2)	θ (OBOC)	0. ^c
O—C	(0.0124)	0.0475	0.0475 ^c	1.424(2)		
O...H	—	0.102	0.098(5)	2.068(4)		
O...O	0.0018	0.061	0.062	2.368(3)		
B...C	0.0087	0.071	0.072			
O...C	0.0073	0.109	0.099(4)	2.422(3)		
O...C	0.0146	0.070	0.075(5)	2.779(5)		
C...C	0.0220	0.115	0.115(9)	3.666(4)		
				4.188(6)		

^{a-c} See footnotes to Table 4. The elements of the correlation matrix $|\rho_{ij}| \leq 50\%$. See also Ref. 1.

OCH_3 rocking modes. As also noted for BR3 and BO2, B—C stretch contributed substantially to a $\delta(BCH_3)$ deformation about 1435 cm^{-1} . The frequency at 314 cm^{-1} was clearly of $\delta(BC_2)$ scissor character, whereas the two remaining in-plane skeletal bending modes $\delta(OBC)$ and $\delta(BOC)$, at 216 and 470 cm^{-1} were heavily intermixed, the latter also containing a large contribution from the B—O stretching mode.

Problems arose concerning the assignment of the two B—O and one B—C stretching modes for BO2. Whereas the frequency at 1362 cm^{-1} was clearly of B—O stretch character, the lower frequency at 693 cm^{-1} contained approximately equal contributions from B—C and B—O stretch. According to the PED there are no other candidates for B—C stretch assignments. Contributions of about 20% from B—O stretch were found for two vibrations around 1300 cm^{-1} , one of which was clearly a $\rho(BCH_3)$ mode, whereas the second at 1297 cm^{-1} was otherwise rather uncharacterized. We have, therefore, apparently in contradiction to previous assignments of $CH_3B(OCH_3)_2$ ²⁸ and for the analogous $ClB(OCH_3)_2$, $CH_3B(OH)_2$ and $FB(OCH_3)_2$,³⁴ assigned the two B—O stretching vibrations to 1347 and 1297 cm^{-1} . Such high assignments of the symmetric BO_2 stretching vibrations have been suggested for several $XB(OR)_2$ molecules, i.e. $X=H, D, Cl$ ³⁵ and $X=NCO$ and NCS .³⁶ It has been pointed out, however, that exceptions (e.g. $FB(OCH_3)_2$ at 768 cm^{-1}) rule out the existence of a characteristic BO_2 symmetric stretching frequency.^{35b} The skeletal in-plane

bending modes are intermixed in two pairs: $\delta(BOC)$ and $\delta(OBC)$ characters at 218 and 409 cm^{-1} ; and $\delta(BOC)$ and $\delta(BO_2)$ characters at 188 and 512 cm^{-1} , the latter of which also containing contributions from B—O stretch.

The composed force fields of BO1 and BO2 reproduce the available experimental spectral data fairly well and give values for the skeletal deformations in reasonable ranges as compared to experimental counterparts in similar molecules.³⁴ Further adjustments of the force fields were not found worthwhile. It should be noted that no adjustment of $k(BO)$ was necessary to obtain satisfactory fit between calculated and observed $\nu(BO)$ values, and thus the vibrational spectral data do not suggest pronounced variations in the B—O bond strength throughout the BO1 to BO3 series.

Structural refinements

The final structural refinements were carried out essentially for two models: firstly imposing planar skeletons and secondly relaxing the constraints on the $\theta(BO)$ parameters. Using BO1 as a test case it was shown that the calculated l and d -values were not affected to a degree important for the analyses by changing $\theta(BO)$ to 15° , and values computed for the planar models were used throughout the analyses for all three molecules. Amplitudes, shrinkage corrections and r_a to r_c conversions calculated from the force fields in Table 3, are given for the important distances in Tables 4–6. The

Table 7. Standard deviations (σ_{LS} , r and l in Å; \angle and θ in degrees) and the elements of the correlation matrices, $|\rho_{ij}| \geq 50\%$, for the structural results in Tables 4 and 5. The $K1$ and $K2$ values are scale constants.

BO1	σ_{LS}	i	j, ρ_{ij}	BO2	σ_{LS}	i	j, ρ_{ij}
$\bar{r}(\text{CH})$	0.0005	1		$\bar{r}(\text{CH})$	0.0011	1	
$r(\text{BC})$	0.0007	2		\bar{r}	0.0004	2	
\bar{r}	0.0004	3	1, +50	Δ	0.0032	3	
Δ	0.0015	4		$r(\text{BC})$	0.0029	4	3, +66
$\angle \text{O}-\text{C}-\text{H}$	0.25	5		$\angle \text{B}-\text{C}-\text{H}$	1.21	5	
$\angle \text{B}-\text{C}-\text{H}$	0.27	6		$\angle \text{O}-\text{C}-\text{H}$	0.37	6	3, -61
$\angle \text{B}-\text{O}-\text{C}3$	0.25	7		$\angle \text{O}2-\text{B}-\text{C}6$	0.24	7	
$\angle \text{O}-\text{B}-\text{C}4$	0.34	8		$\angle \text{O}3-\text{B}-\text{C}6$	0.28	8	7, -72
$\angle \text{O}-\text{B}-\text{C}5$	0.32	9	8, -89	$\angle \text{B}-\text{O}2-\text{C}4$	0.39	9	8, +61
$\theta(\text{BO})$	2.50	10	8, -80; 9, +81	$\angle \text{B}-\text{O}3-\text{C}5$	0.31	10	
$l(\text{CH})$	0.0006	11		$\theta(\text{BO})$	5.09	11	8, +53; 9, +64
$l(\text{B}\cdots\text{C}3)$	0.0020	12	7, +58; 9, +66; 10, +59	$K1=40.2$	0.31	12	3, +66; 4, +67
$l(\text{C}3\cdots\text{C}4)$	0.0037	13		$K2=41.4$	0.44	13	3, +77; 4, +62; 12, +57
$l(\text{C}3\cdots\text{C}5)$	0.0020	14					
$K1=36.2$	0.19	15	2, +51				
$K2=37.0$	0.31	16	4, +52; 11, +52				

calculated l -values were used in grouped refinements of the amplitudes by maintaining the calculated differences within each group or by constraining the amplitude parameters to the calculated values.

Generally the amplitudes associated with distances involving hydrogens not shown in Tables 4–6, were fixed at the calculated values. It proved impossible to refine the conformational orientations of the various methyl groups for BO1 and BO2. A preferred set of torsional angles for each molecule was found (Table 4 and 5) as a result of several refinements where these angles were systematically fixed at different values. In each case the l -values were calculated using geometrical models with appropriate torsional angles. Although the various refinements pointed fairly consistently to the chosen sets, it should be stressed that the preferences are not unquestionable and that the other geometrical parameters in some cases were affected by changes in these angles.

Both the planar and nonplanar models were refined with all amplitudes fixed at the calculated values and by also refining as many amplitudes or groups of amplitudes as possible. The parameter values for each molecule chosen to represent our final results for each molecule are given in Tables 4–6. The corresponding molecular intensities and radial distribution curves are compared with their experimental counterparts for BO1 (Figs. 1 and 3) and for BO2 (Figs. 2 and 4). Also the computed

agreement factors $^{14} (R_w = \Sigma w(s)\Delta^2(s)/\Sigma w(s)I_{\text{obs}}^2(s))$, in Tables 4–6) reflect the goodness of the least-squares fit. The parenthesized standard deviations include effects from correlation among the data and for distance parameters uncertainty in the s -scale. The standard deviations obtained in the least-squares refinement (σ_{LS}) and elements of the correlation matrices for BO1 and BO2 are comprised in Table 7.

The results presented in Tables 4–6 were obtained from refinements where the amplitudes associated with the skeletal bond distances were fixed at the calculated values. It was believed that this would represent the more consistent procedure for the three molecules. It should be noted that when this group was included in the refinements, the average parameter, \bar{r} , remained unaffected, whereas the difference parameter (Δ) and consequently the individual B–O and O–C bond lengths were affected. Δ was 0.054(4), 0.047(11) and 0.058(3) Å, respectively, for BO1, BO2 and BO3, while the corresponding l -value groups, represented here by $l(\text{BO})$, refined to 0.054(2), 0.047(3) and 0.047(2) Å. This demonstrates that the variation in the B–O bond length throughout the series of molecules should be evaluated by conferring also to the average parameter.

For BO2 refinements of the amplitudes were altogether problematic, and results judged to be unacceptable were obtained. For example, the amplitudes associated with the one-angle skeletal

distances became smaller than the bond distance amplitudes. For BO1 and BO3 amplitudes were included in the final refinements, but this did not affect the geometrical parameters significantly.

For BO2 also the possibility of conformational mixtures had to be considered, although the *syn,anti* conformer alone appeared to represent the electron diffraction data rather well (Figs. 2 and 4). The predominance of the *syn,anti* conformer is consistent with the results for the sulphur analogue, $\text{CH}_3\text{B}(\text{SCH}_3)_2$.⁶ The prevailing conformer of the parent molecule, $\text{HB}(\text{OH})_2$, is also the *syn,anti* form according to *ab initio* MO-calculations^{9,27} and to interpretations of microwave spectral data.²⁵ The latter actually identified the *syn,syn* form as a coexisting second conformer²⁵ whereas the calculations indicated that the *syn,anti* form was preferred by about 10 kJ mol^{-1} . For BO2 it was shown that the R -factor ratios as compared to 100% *syn,anti* were 1.02 and 1.04, respectively, for mixtures with 5 and 10% of *syn,syn*. However, these results cannot be taken as conclusive evidence against small amounts of a second conformer, also considering the many assumptions introduced in the analysis.

Of the different nonplanar forms of the *syn,anti* periplanar form of BO2, the one where both methoxy groups were rotated in opposite directions about the B–O bonds appeared to be favoured. A model with $\theta(\text{O2–B}) = 180 - \theta(\text{O3–B})$ gave a deviation from planarity of $12(8)^\circ$ (Table 5) and a least squares agreement factor of 5.36% as compared to 5.58% for the planar model. For BO1 the planar model gave $R_w = 4.44\%$ as compared to 4.42% obtained for $\theta(\text{BO}) = 14(4)^\circ$ (Table 4). It is possible that the nonzero $\theta(\text{BO})$ values indicate the presence of large amplitude motions which are not properly accounted for by the shrinkage corrections. A dynamic model was therefore tested for BO1. It was described by the root-mean-square amplitude (δ) for the torsional vibration³⁷ assumed to be harmonic about $\theta(\text{BO}) = 0^\circ$, and framework l - and K -values were employed. For fixed l -values a minimum was obtained at $\delta = 11(4)^\circ$ as compared to $\delta = 9^\circ$ calculated from the torsional force constant³⁷ given in Table 3. The agreement factor was 4.73% as compared to 4.77 and 4.76% for the planar and nonplanar models with fixed amplitudes of vibration. In conclusion, the torsional angles obtained for BO2 and BO1 are hardly significantly different from zero, and it appears that the data may equally well be represented by dynamic models with equilibrium at $\theta(\text{BO}) = 0^\circ$. Although torsional angles

of $10 - 15^\circ$ cannot be ruled out, we conclude that BO1 and BO2 possess planar or nearly planar heavy atom skeletons. As before¹ refinements of the skeletal torsional angle for BO3 resulted in oscillations ($\theta(\text{BO}) = \pm 1(4)^\circ$) about zero. An R_w -factor of 5.66% was obtained for $\theta(\text{BO}) = 10^\circ$ as compared to 5.05% for $\theta(\text{BO}) = 0^\circ$ for fixed l -values. The final refinements (Table 6) were therefore carried out for $\theta(\text{BO}) = 0^\circ$. Comparisons of the new results for BO3 with the previous ones show that the structural parameters concerning the methyl groups have been affected, whereas the skeletal ones, of main interest in this study, are in good agreement.

DISCUSSION

The structural results for the methoxy boranes are compared with those of the analogous thio-boranes⁵⁻⁷ in Fig. 5. As for the sulfur compounds, the obtained planar or nearly planar heavy atom skeletons may be related to dative π -bonding. The B–C bond length in $\text{B}(\text{CH}_3)_3$ ³² has been used to derive an alternative covalent radius for boron of 0.85 \AA ,³⁸ as compared to 0.81 \AA given by Pauling.³⁹ Thus, the B–S bonds (Fig. 5) as well as the B–Se bond in $\text{B}(\text{SeCH}_3)_3$, were found to be short by approximately 0.05 \AA ,³⁸ as compared to Schomaker-Stevenson single bond estimates.³⁹ This was taken as corroborating evidence for partial double bond characters of the B–Se and B–S bonds. The B–O bonds are found to be short by about 0.11 \AA as compared to a corresponding single bond estimate. This is suggestive of a higher degree of π -character in the B–O bond than in the bonds between boron and the next two elements of Group VI. In the thio-boranes (Fig. 5) both the B–S bond and the average of B–S and S–C vary in a manner consistent with the fact that several π -donors competing for one $2p_z$ -orbital would decrease the possibility for π -bonding in each bond.⁶ Comparison of the corresponding parameters for BO1, BO2 and BO3, reveal that $r(\text{BO})$ probably is shorter in BO1 than in BO2 and BO3. However, the results for the two latter are not different with respect to the \bar{r} parameter, and a B–O bond in BO3 intermediate to those in BO1 and BO2 is suggested although the significance of this may be questioned. Thus, a consistent lengthening of the B–O bond in the BO1 to BO3 series is not observed, and this would necessitate introduction of an opposing effect on the bond length in order to retain the previous conclusion of greater π -character in the B–O bonds than in corresponding

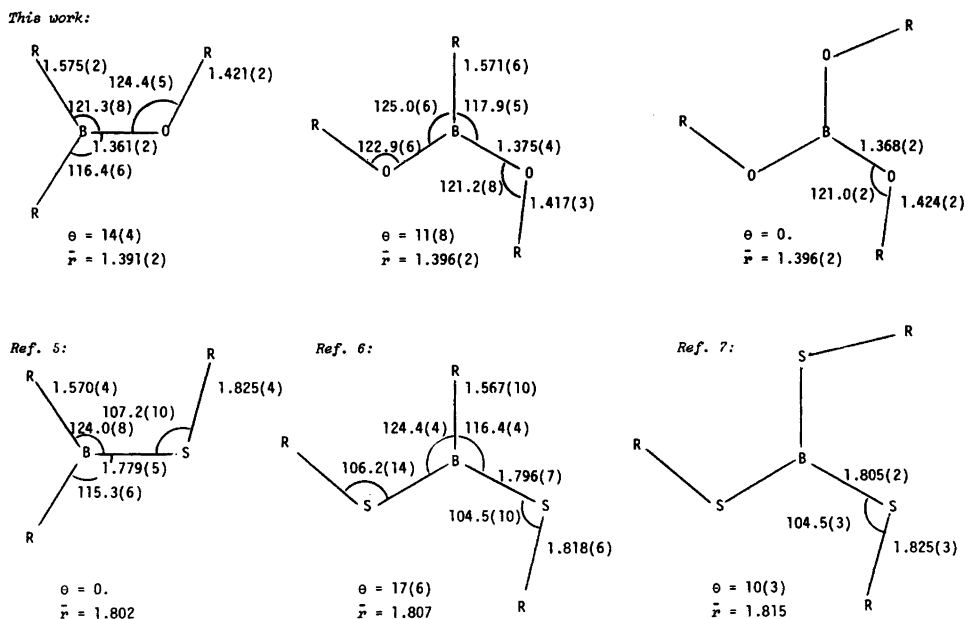


Fig. 5. The nonhydrogen structural results (cf. Tables 4–6) for $(\text{CH}_3)_2\text{BOCH}_3$, $\text{CH}_3\text{B}(\text{OCH}_3)_2$ and $\text{B}(\text{OCH}_3)_3$, compared with the corresponding results of the thio analogues.^{5–7} $\text{R} = \text{CH}_3$ and distances are given in Å and angles in degrees.

B–S bonds. Such considerations are, of course, rather speculative. However, oxygen being more electronegative than sulphur would act as the stronger σ -acceptor. Possible effects from σ -bond polarizations, as seen by the tendency for bonds to a

central atom to become shorter as more electronegative ligands are joined to it, would therefore presumably be more important in the oxygen series. *Ab initio* MO-calculations,^{40,41} appear to give contradictory results with respect to the

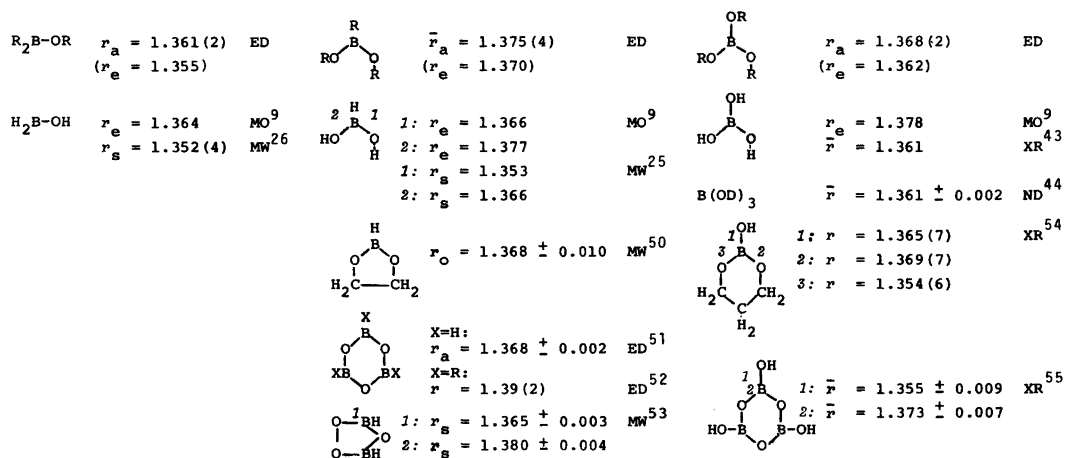


Fig. 6. B–O bond distances obtained in the present study and $r(\text{BO})$ -values in some related compounds, as obtained in molecular orbital calculations (MO), by microwave (MW) and electron-diffraction (ED) studies of gases and by X-ray-(XR) and neutron-diffraction (ND) studies of crystals. $\text{R} = \text{CH}_3$.

relative magnitudes of π -bonding in the B—O and B—S bonds as discussed elsewhere.⁹ In any case, *ab initio*- as well as PE- and NMR-results^{4,8,41,42} are consistent with weakened π -bonding in the BO1 to BO3 series. According to *ab initio* calculations⁹ this conclusion may be extended to the corresponding acids. However, neither the calculated B—O bond lengths nor those observed by microwave spectroscopy for H₂BOH²⁶ and HB(OH)₂²⁵ and by diffraction methods for crystalline B(OH)₃⁴³ and B(OD)₃⁴⁴ suggest pronounced bond length variations as seen from Fig. 6. Although the electron-diffraction r_a values may be corrected²⁴ to r_x (Tables 4–6) and to r_e (Fig. 6), caution should be exercised when results obtained by different methods are compared: The XR distance parameter, claimed to be compatible with the r_x -quantity is generally longer than expected;⁴⁵ the MW parameter r_s , although usually closer to r_e than the r_o -value, cannot theoretically be identified with the equilibrium value;²⁴ and finally, the absolute values of the r_e -parameters obtained in MO calculations are not reliable although the bond length variations within a group of related molecules may be reproduced, provided that consistent calculation procedures are employed.^{9,27} It should also be noted that even in crystals without hydrogen bonding, the trigonal B—O bonds are found in a relatively wide range of values. For example, in 8,8-dimethyl-3,5-diphenyl-2,4,6-trioxo-1-azonia-3-bora-5-boranabicyclo [3.3.0] octane the two trigonal B—O bonds of 1.337(2) and 1.404(2) Å are significantly different,⁴⁶ and reported means of other Ph—B(O—)₂-systems are 1.371(6),⁴⁷ 1.394(3)⁴⁸ and 1.367 Å.⁴⁹ Additional data on the trigonal B—O bond length are given in Fig. 6, for BO2^{50–53} and BO3^{54,55} type bonding and no variation of obvious relation to changes in the π -bond order can be established. However, for H₂BOH and HB(OH)₂ the MW-results suggest small trends which are reproduced by the MO-calculations. Within the obtained standard deviations such variations are not inconsistent with the electron-diffraction results for the methyl derivatives.

It has been noted⁵ that $r(\text{BC})$ in (CH₃)₂BSCH₃ (Fig. 5) is smaller than the $r_a(\text{BC})$ value of 1.578(1) Å in B(CH₃)₃³² by twice the standard deviation. Other electron-diffraction results for thiomethylboranes⁶ indicate a common trend to slightly shorter B—C bonds in this type of boranes than in B(CH₃)₃. This trend appears to be paralleled by the situation for

boron—oxygen compounds as judged from the present results (Fig. 5) and of other such results.^{52,56} The O—C bonds of about 1.420 Å for the present series of compounds (Fig. 5) compare favourably with other O—C(sp³) bonds as summarized previously.¹

The oxygen valence angles in the BO1 to BO3 series of molecules are larger by approximately 10° as compared to the BOH angles in H₂BOH,^{9,26} and B(OH)₃.^{9,43} Considering the B··C one-angle distances of 2.42 to 2.45 Å (Tables 4–6), importance of nonbonded repulsions would be predicted.⁵⁷ Alternative values have been proposed for the boron one-angle radii⁹ and the corresponding estimates of the preferred B··C distance is in the 2.45 to 2.61 Å range. By the same considerations such interactions would be judged negligible for the thio-analogues which exhibit B··C distances in the 2.85–2.90 Å range.^{5–7} Nevertheless, the sulfur valence angle in (CH₃)₂BSCH₃ (Fig. 5) is larger than the calculated $\angle \text{BSH}$ of 99° in H₂BSH.⁵⁸

Significant distortions from ideal trigonal arrangements around boron are obtained for BO1 and BO2, and similar distortions are observed for the thio counterparts (Fig. 5). This could be ascribed to steric problems in the *syn* C—B—O—C and C—B—S—C arrangements, the methyl carbons being separated by only 3.0 and 3.2 Å, respectively. However, such distortions are both by MW- and MO-studies shown to be present also in H₂BOH and HB(OH)₂ where H··H repulsions are considered to be of lesser importance.

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