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STUDIES ON TRIVALENT BORON COMPOUNDS
III. THE VIBRATIONAL SPECTRA OF THE METHOXYBORON CHLORIDES, METHYLBORONIC ACID AND METHYLBORINIC ACID

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1. INTRODUCTION

In compounds of type XBY_2 and X_2BY, the force constants, k_{BX} and k_{BY}, of the BX- and BY-bonds are a measure of the degree of π-donation of the substituents X and Y in these bonds. Spectroscopical data of tetrahedral boron compounds of type BX_4^- with sp^3 hybridization around boron, have yielded the force constant values, k_{BX}, for single σ-bonds between boron and the ligand, X^-. Any increase over this value observed in XBY_2 or X_2BY molecules can be correlated with the degree of π-bond participation in the BX-bond. A critical examination of the relative increments of force constant values for different substituents, X, should, accordingly, yield the order of their respective donor capacities.

To this purpose, the infrared and Raman spectra of the molecules Cl_2BOCH_3, $ClB(OCH_3)_2$, $(CH_3)_2BOH$ and $CH_3B(OH)_2$ have been recorded; the assignments to the fundamentals were made and the force constants calculated for the skeleton, XBY_2. For another series of compounds: F_2BOCH_3[1], $FB(OCH_3)_2$[2] and the methyl haloboranes, the spectroscopical results published earlier[3,4] were used.

The data reported in this paper, together with those on ^{11}B NMR experiments[5] and on electrical dipole moments[6], will be used to discuss the problem of internal coordinative saturation in trivalent boron compounds.

2. EXPERIMENTAL

The Raman spectra of the liquid samples were recorded with a two-prism spectrograph, type Huet II B, equipped with a photomultiplier and recording attachment of Steinheil GmbH.

The infrared spectra were observed on gaseous samples. A Perkin-Elmer model 21 B instrument with NaCl and KBr prisms was used to cover the range 4000–400 cm^{-1}. The spectrum of $CH_3B(OH)_2$, however, was obtained in the crystal phase only, over the same spectral range as for the other compounds using a Grubb-Parson spectrometer equipped with a KBr prism and a grating.

3. THE VIBRATIONAL SPECTRA

It was assumed that X_2BOY molecules have C_s symmetry, the BOY-plane being the plane of symmetry. In molecules where Y is CH_3, this involves the assumption that the hydrogen atoms are oriented in the most symmetrical configuration. The fundamental vibrations of the C_s point group are divided into two classes that are both infrared active; they are tabulated in Table 1.

TABLE 1

FUNDAMENTAL VIBRATIONS OF X_2BOY MOLECULES WITH C_s SYMMETRY

X_2BOY skeleton				*CH_3 group*		
Class	*Symbol*		*Description $Y=CH_3$, H*	*Class*	*Symbol*	*Description*
A′	ν_1	ν_{BO}	BO val.	A′	ν_{sCH_3}	symm. CH val.
	ν_2	ν_{sX_2BO}	tot. symm.		ν_{asCH}	asymm. CH val.
	ν_3	δ_{sX_2BO}	symm. X_2BO def.		δ_{sCH_3}	symm. def.
	ν_4	ν_{YO}	CO val., OH val.		δ_{asCH_3}	asymm. def.
	ν_5	γ_{X_2BO}	X_2BO def. out of plane		γ_{CH_3}	torsion
	ν_6	δ_{BOY}	BOC def., BOH def.			
				A″	ν_{asCH}	asymm. CH val.
A″	ν_7	ν_{asX_2B}	asymm. BX val.		δ_{asCH_3}	asymm. def.
	ν_8	ν_{asX_2BO}	asymm. X_2BO def.		ρ_{CH_3}	rocking
	ν_9	τ_{BOY}	BOC torsion, BOH torsion		τ_{CH_3}	torsion

Considerations on minimal potential energy for the $XB(OY)_2$-type molecules result in a structure with C_2 symmetry, the direction of the BX-bond being the two-fold symmetry axis. There are again two classes of fundamentals, both infrared active, which are shown in Table 2.

TABLE 2

FUNDAMENTAL VIBRATIONS OF $XB(OY)_2$ MOLECULES WITH C_2 SYMMETRY

$XB(OY)_2$ skeleton				*CH_3 group*		
Class	*Symbol*		*Description $Y=CH_3$, H*	*Class*	*Symbol*	*Description*
A	ν_1	ν_{BX}	BX val.	A and B	ν_{sC-H}	CH symm. val.
	ν_2	ν_{XBO_2}	XBO_2 tot. symm.		ν_{asC-H}	CH asymm. val.
	ν_3	δ_{sXBO_2}	XBO_2 symm. def.		ν_{asC-H}	CH asymm. val.
	ν_4	ν_{sOY}	symm. val. OC, OH		δ_{sCH_3}	symm. def.
	ν_6	δ_{sBOY}	symm. def. BOC, BOH		δ_{asCH_3}	asymm. def.
	ν_{10}	τ_{sBOY}	symm. torsion BOC, BOH		δ_{asCH_3}	asymm. def.
	ν_7	ν_{asBO}	BO asymm. val.		γ_{CH_3}	wagging
	ν_8	δ_{asXBO_2}	XBO_2 as. def.		ρ_{CH_3}	rocking
	ν_9	τ_{asBOY}	asymm. torsion BOC, BOH		τ_{CH_3}	torsion
	ν_{11}	ν_{asOY}	asymm. val. OC, OH			
	ν_{12}	δ_{asBOY}	asymm. def. BOC, BOH			
	ν_5	γ_{XBO_2}	XBO_2 def. out of plane			

Cl_2BOCH_3 and $ClB(OCH_3)_2$

The infrared and Raman frequencies for both molecules are given in Tables 3 and 4. The spectra are reproduced in Figs. 1a, b and 2a, b, respectively. The Raman spectra are very weak; therefore depolarization measurements were unpracticable. Rotational fine structure is only observed in the infrared spectrum of $ClB(OCH_3)_2$

for the band at 1170 cm^{-1}. The frequency assignments were therefore done mainly by comparison with similar compounds and by taking into consideration the intensity variations.

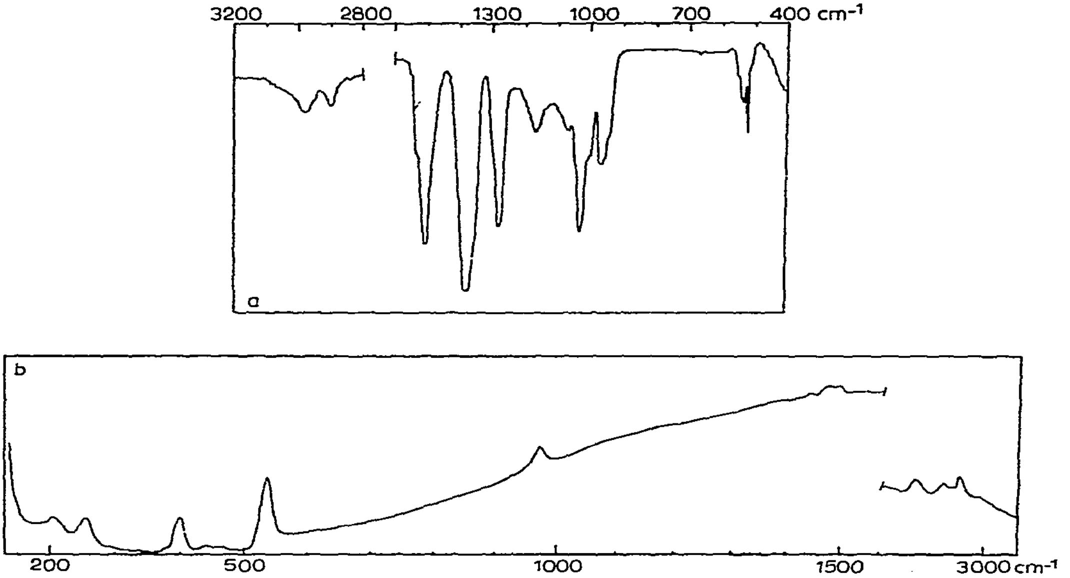


Fig. 1. The infrared (a) and Raman spectra (b) of Cl_2BOCH_3.

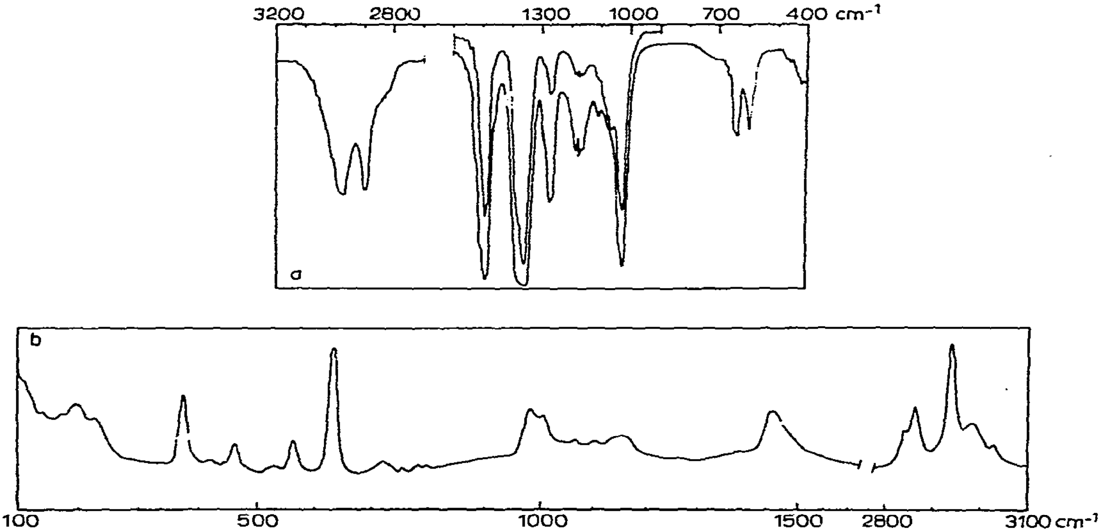


Fig. 2. The infrared (a) and Raman spectra (b) of $ClB(OCH_3)_2$.

$(CH_3)_2BOH$

The infrared data, together with those published by Ulmschneider and Goubeau[7], are given in Table 5 and the spectrum is shown in Fig. 3. Rotational fine structure facilitates the assignment. Using interatomic distances, measured on

TABLE 3

INFRARED AND RAMAN FREQUENCIES OF Cl_2BOCH_3

IR		Raman		Assignment
$\nu(cm^{-1})$	Int.	$\nu(cm^{-1})$	Int.	
2980	3	2963	5	$\nu_{CH}(A'')$
2950	5	2949	3	$\nu_{CH}(A')$
2900	4	2894	3	$\nu_{CH}(A')$
1505	8	1490	1	$\delta_{CH}(A'')$
1450	3 sh	1469	2	$\delta_{CH}(A')$
		1434	1	$\delta_{CH}(A')$
1380	10			ν_1
1280	7			$\gamma_{CH}(A')$
1165	3			ρ_{CH}
1070	2 sh			$2\ \nu_2$
1030	7			ν_4
1000	3 sh			$2\ \nu_9$
965	4	983	4	ν_7
540	5	546	10	ν_2
520	6			ν_9
		475	1	ν_5
410	2	408	6	ν_3
		262	4	ν_8
		220	3	ν_6

TABLE 4

INFRARED AND RAMAN FREQUENCIES OF $ClB(OCH_3)_2$

IR		Raman		Assignment
$\nu(cm^{-1})$	Int.	$\nu(cm^{-1})$	Int.	
3005	3 sh	3001	3	ν_{CH}
2970	5	2974	9	ν_{CH}
2895	5	2882	3	ν_{CH}
2845	2 sh	2854	2	ν_{CH}
1505	5 sh	1497	3	δ_{CH}
1490	7	1476	4	δ_{CH}
1460	3 sh	1465	4	δ_{CH}
1360	10			ν_7
1270	6			γ_{CH}
1170	4	1168	2	ν_1
1110	1			γ_{CH}
1060	3 sh	1082	1	ν_4
1025	7	1018	4	ν_{11}
		996	4	ρ_{CH}
640	4	642	9	ν_2
593	4	577	3	ν_5
		545	1	ν_9
470	2	473	3	ν_3
458	2	453	1	ν_{10}
		433	1	
		387	5	ν_8
		237	2	ν_6
		199	3	ν_{12}
		185	2	τ_{CH_3}

analogous compounds, we made an approximate calculation of the moments of inertia. Taking the C-axis perpendicular to the C_2BO-plane in the boron atom, the A-axis perpendicular to the B–O bond in the C_2BO-plane and the B-axis in the direction of the B–O bond, we find approximate values in the sequence $I_A < I_B < I_C$. We thus have an asymmetric top molecule to which the theory of Herzberg[8] can be applied.

TABLE 5

INFRARED FREQUENCIES OF $(CH_3)_2BOH$

This work			*Ulmschneider*[7]		
ν (cm⁻¹)	*Int.*	*Assignment*	*ν (cm⁻¹)*	*Int.*	*Assignment*
3630	6	ν_4	3675	st	ν_{OH}
2980	7 br	ν_{CH}	2960	st	ν_{CH_3}s+as
2040	1		2045	s	
1665	1	$\nu_2 \cdot \delta_{OH}$	1667	s	
1430	5	δ_{CH_3}	1525	s	
1325	10 br	δ_{CH_3} ?	1445	mst	δ_{CH_3}
1275	7 sh	ν_1 ?	1336	sst	δ_{CH_3}
1205	9	ν_7	1276	s	ν_1
1150	6	2 ν_9	1204		
			1212	sst	ν_7
			1221		
965	8 sh	ρ_{CH_3}	1164	s	2 γ_{OH}
950	9	δ_{OH}	995,969	sst	$\delta_{OH} \cdot \rho_{CH_3}$
715	5	ν_2	718,738	mst	ν_2
			586	st	γ_{OH}
			392,410	mst	ν_8, ν_5
			353	s	ν_3

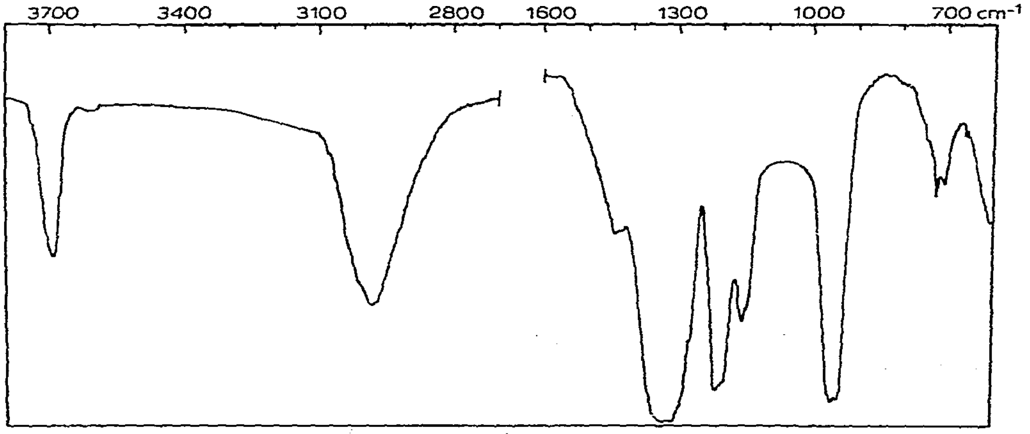


Fig. 3. The infrared spectrum of $(CH_3)_2BOH$.

$CH_3B(OH)_2$

Methylboronic acid is a solid (m.p. 92°, vapor pressure about 2.5 mm Hg at 25°). Therefore, only the infrared spectrum of the solid, in a KBr-disc pellet, could be recorded. As a result no fine structure could be observed and the assignments are based on comparisons and intensity relations. The recorded spectrum is shown in Fig. 4 and the frequency data are tabulated in Table 6.

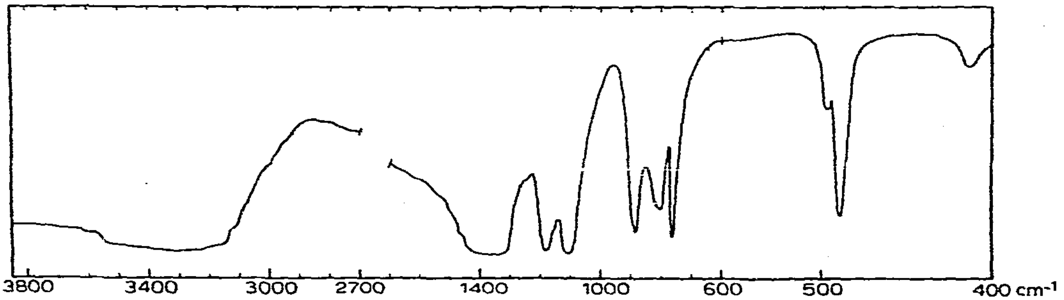


Fig. 4. The infrared spectrum of $CH_3B(OH)_2$.

TABLE 6

INFRARED FREQUENCIES OF $CH_3B(OH)_2$

ν (cm^{-1})	*Int.*	*Assignment*
3560/3000	6 br	ν_4, ν_{11}
2995	1 sh	ν_{CH}
2940	1 sh	
1492	4 sh	δ_{CH}
1377	8 br	ν_7
1257	2 sh	ν_1
1190	7	δ_{OH}
1117	7	δ_{OH}
901	6	γ_{CH_3}
836	5 sh	γ_{CH_3}
820	5	ν_2
778	6	τ_{BOH}
515	2 sh	$\nu_5(^{10}B)$
494	4	ν_8
484	7	$\nu_5(^{11}B)$
405	3 br	ν_3

4. FORCE CONSTANTS FOR X_2BOY AND $XB(OY)_2$ MOLECULES. THEORETICAL CALCULATIONS OF FREQUENCIES

Starting from reasonable force constants for the molecules of type BX_3 and $B(OY)_3$, derived from literature data, the force constants for the molecules of type X_2BOY and $XB(OY)_2$ have been calculated using the method reported earlier[1]. The results are shown in Table 7. Using these data in the Lechner equations we calculated the fundamental frequencies. As can be seen from Table 8, the agreement with the experimental frequencies is quite good.

TABLE 7

FORCE CONSTANTS FOR TRIVALENT BORON COMPOUNDS IN DYNE 10^{-5} cm^{-1}

	F_2BOCH_3[a]	Cl_2BOCH_3	$(CH_3)_2BOH$
k_{BX}	5.20	2.85	3.77
k_{BO}	6.65	6.12	4.85
k_{XBX}	0.60	0.43	0.29
k_{XBO}	0.45	0.18	0.28
	$FB(OCH_3)_2$	$ClB(OCH_3)_2$	$CH_3B(OH)_2$
k_{BX}	5.00	—	4.05
k_{BO}	4.82	4.87	4.76
k_{XBO}	0.54	0.40	0.54
k_{OBO}	0.59	—	0.35

[a] See ref. 1.

TABLE 8

CALCULATED AND EXPERIMENTAL FUNDAMENTAL FREQUENCIES OF SOME TRIVALENT BORON COMPOUNDS IN cm^{-1}

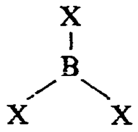
	F_2BOCH_3[a]		Cl_2BOCH_3		$(CH_3)_2BOH$	
	Calcd.	*Expt.*	*Calcd.*	*Expt.*	*Calcd.*	*Expt.*
ν_1	1440	1420	1382	1380	1292	1276
ν_2	800	813	496	546	678	718
ν_3	476	480	287	408	369	353
ν_7	1390	1385	967	965	1204	1204
ν_8	456	460	259	262	405	405
	$FB(OCH_3)_2$[b]		$ClB(OCH_3)_2$		$CH_3B(OH)_2$	
	Calcd.	*Expt.*	*Calcd.*	*Expt.*	*Calcd.*	*Expt.*
ν_1	1382	1368	—	1170	1257	1292
ν_2	739	767	—	642	820	745
ν_3	471	458	—	473	405	432
ν_7	1396	1393	1360	1360	1379	1380
ν_8	479	485	387	387	494	492

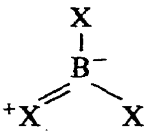
[a] See ref. 1; [b] see ref. 2.

5. DISCUSSION

5.1. *The chemical bond in BX_3 molecules*

It has been recognized for some time that the chemical properties of BX_3 molecules cannot be explained simply by a covalent structure of type A, with some degree of ionic character in the BX-bond. Various degrees of resonance contribution of structures such as B, dependent on the donor capacity of the substituents X, must be assumed. Contribution of type B structures strengthen the bond, the maximum


(A)


(B)

B–X bond order being apparently 1.33. The increased bond order is revealed, for instance, by shortened bond distances[9] and by enhanced valence force constants. In Table 9 a summary of known force constants for BX_3- and BX_3Y-type molecules is

TABLE 9

FORCE CONSTANTS FOR BORON COMPOUNDS WITH sp^2 AND sp^3 HYBRIDIZATION IN DYNE 10^{-5} cm^{-1}

	Compound	sp^2	sp^3	*Compound*
k_{B-F}	BF_3	6.86[18]	5.27[18]	BF_4^-
k_{B-Cl}	BCl_3	3.21[4]		
k_{BO}	$B(OCH_3)_3$	4.55[19]	3.80[a]	$F_3B:O(CH_3)_2$
k_{BC}	$B(CH_3)_3$	3.69[20]	3.53[20]	$(CH_3)_3B:NH_3$
k_{BN}	$B[N(CH_3)_2]_3$	5.50[21]	3.65[20]	$(CH_3)_3B:NH_3$

[a] Calcd. using the spectrum of Begun *et al.*[22]

given, corresponding to sp^2 and sp^3 hybridization of boron, respectively. The f.c.-values for sp^2 hybridization are systematically higher than those for sp^3 hybridization and it is generally accepted that the ratio of these values reflects the respective bond-order ratios. On the assumption that k(B–F) in sp^3 configuration is the B–F single-bond value, a resonance contribution of 30% of type B structure in BF_3 is calculated. The k(B–O)- and k(B–N)-values in trivalent compounds were calculated using a different force field from that used in the case of the corresponding tetravalent compounds. For this reason, only a qualitative interpretation of force constant data is possible in this case.

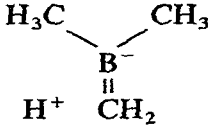
There is however complete parallelism with the changes observed in going from BF_3 to BF_4^-. Nitrogen, and to a lesser degree oxygen, appear to form $(p–p)$-π bonds towards boron. The data of ^{11}B NMR measurements[1] and the spectroscopical arguments developed above clearly indicate that there is a comparable degree of double-bond character in the molecules BF_3, $B(OCH_3)_3$ and $B[N(CH_3)_2]_3$, corresponding to a bond order of about 1.30 for each of these molecules. This means that F, O and N in BX_3 compounds are equally capable of the formation of $(p–p)$-π bonds. In order to discover whether F and O can attain higher B–X bond orders than 1.33, we will discuss mixed compounds in section 5.2.

On the other hand, for molecules BCl_3, BBr_3 and $B(CH_3)_3$ the spectroscopical argument[9] reveals double-bond character of the BX-bond decreasing in the order: $B–Cl > B–Br > B–I > B–CH_3$.

These conclusions are in good agreement with the chemical properties of these compounds. The tendency towards complex formation will increase the more the BX_3 molecule is internally unsaturated. Consequently, increasing tendency for complex formation can be expected in the sense $BF_3 < BCl_3 < BBr_3$; this was confirmed by the experiments of Brown[10].

Furthermore, Cotton and Leto[11] calculated the reorganisation energy for the transformation of BX_3 (sp^2) into BX_3Y (sp^3); this parallels the sequence cited above.

Boron trimethyl, $B(CH_3)_3$, is, however, an exception that does not fit into this theoretical frame. Physicochemical measurements do not indicate any reasonable double-bond character in the B–C bond. Nevertheless, the molecule is very stable towards hydrolysis and complex formation, suggesting a high value of the reorganisation energy. Mulliken[12] therefore suggested that this molecule should be stabilized by trigonal hyperconjugation (structure C):



(C)

This would, however, also imply double-bond character in the B–C bond. Moreover, the proton chemical shift should be much lower than in other metalalkyls. As can be seen from Table 10 the τ-value is slightly lower than could be expected from the electronegativity effect only, but this value is by no means as low as one would expect on the assumption of a considerable double-bond character. Also, the coupling constant $J(^{13}C\text{–}H)$ observed in the PMR spectra of methylboron derivatives[5] is surprisingly low and in no relation to double-bond character in the B–C bond.

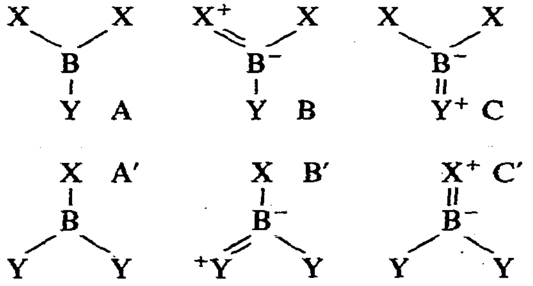
TABLE 10

PROTON MAGNETIC RESONANCE PARAMETERS OF METAL ALKYLS, $M(CH_3)_n$

Compound	τ	x_M	*Ref.*
$Ge(CH_3)_4$	10.14	1.8	23
$Si(CH_3)_4$	10.00	1.8	
$Sn(CH_3)_4$	9.93	1.8	23
$As(CH_3)_3$	9.26	2.0	24
$B(CH_3)_3$	8.92	2.0	

5.2. *The chemical bond in X_2BY and XBY_2 molecules*

The relevant physicochemical data needed for the discussion of the bond order in these molecules are found in Tables 7 and 9 of this work and in Parts I and II of this series of reports. The possible resonance structures for these molecules are presented by the canonical formulae A, B and C and A′, B′ and C′, respectively. In structures of type A and A′, the p_z-orbital of boron yields no contribution to the bonding hybrid orbitals.



5.2.1. *Fluoroboric acid methylesters.* The high value of k_{BO} in F_2BOCH_3 suggests a considerable contribution of resonance structure C, whereas the value of k_{BF} implies that there is practically no contribution of type B structure. The bond order for the B–F bond is thus about equal to unity and the coordination saturation of boron is carried almost completely by the BO double-bond character.

In $FB(OCH_3)_2$, the k_{BF} is even smaller than in the difluoro compounds; the k_{BO}-value is also decreased but is still higher than for $B(OCH_3)_3$. It is evident that in the monofluoro derivative also the main part of coordinative saturation stems from both oxygen atoms (structure C′).

Because the k_{BF}-value in these esters is nearly constant, the observed changes in the sum of the partial moments, $\overrightarrow{BF}+\overrightarrow{OB}$, as reported in Table 2 of the previous report may be ascribed to changes of the $\overrightarrow{OB}$-moment. The data of Table 7 then show that the coordinative contributions of the oxygen atom in F_2BOCH_3 is larger than the contribution of each of the oxygen atoms in $FB(OCH_3)_2$.

In these compounds $(p–p)$-π bonds are apparently stronger with O than with F.

5.2.2. *Chloroboric acid methylesters.* Similar trends in the values of k_{BO} and of the partial moments, $\overrightarrow{BCl}+\overrightarrow{OB}$, as for the fluoro derivatives suggest that these values may be similarly interpreted.

The k_{BCl}-value for Cl_2BOCH_3 is considerably smaller than for BCl_3, where the bond order should be 1.22, according to Pauling[9]. This decrease can be explained by the less important double-bond character of the BCl-bond in Cl_2BOCH_3 compared with that in BCl_3.

From the ^{11}B resonance data we concluded that the π-electron contribution to the chemical shift is smaller in Cl_2BOCH_3 than in $ClB(OCH_3)_2$ $[A_\pi(Cl_2BO) < A_\pi(ClBO_2)]$, in accordance with our previous statements[5].

The obvious conclusion is that oxygen is a better donor than chlorine towards boron.

5.2.3. *Aminoboranes.* The B–N bond in $Cl_2BN(CH_3)_2$ and in $(CH_3)_2BNH_2$ has a bond order of 2.0; this is based on force constant data of Goubeau *et al.*[13,14]. Nitrogen thus seems to be a better donor towards boron than either chlorine or methyl. In analogous oxygen derivatives the maximum observed bond order is 1.5[1], suggesting that N should be a better donor than O. This conclusion has already been drawn by Skinner[15] as a result of thermochemical measurements.

5.2.4. *Methylboronic and methylborinic acid.* The values of the force constants show without doubt that O as well as the CH_3 group acts as a donor towards boron. In fact, the BC-bond in $CH_3B(OH)_2$ seems to have more double-bond character than either of the BC-bonds in $(CH_3)_2BOH$. The same trend is found for the BO-bonds in $(CH_3)_2BOH$ compared to those in $CH_3B(OH)_2$. The sum of the partial bond moments corroborates this conclusion provided that we assume that the sign of the $\overrightarrow{BC}$-moment has changed, as is required by the resonance structures, B and B′. The anisotropy contributions due to π-bonding towards boron observed in the ^{11}B chemical shift data (A_π), is also greater for $CH_3B(OH)_2$ than for $(CH_3)_2BOH$, indicating a higher total degree of coordinative saturation for the former compound. On the other hand, the constancy of the $J(^{13}C–H)$ value in these compounds proves that the hybridization around carbon is not modified to any reasonable extent. These considerations lead to the conclusion that CH_3 and O are nearly equally capable of saturating boron coordinatively.

5.2.5. *Methylfluoroboranes and methylchloroboranes.* The force constants for these molecules have been calculated by Becher[3,4]; they are shown in Table 11. Other physicochemical data are to be found in Parts I and II of this series.

TABLE 11

FORCE CONSTANT DATA FOR METHYLHALOBORANES IN DYNE $cm^{-1} \cdot 10^{-5}$

	k_{B-C}	k_{B-F}	k_{B-Cl}
CH_3BF_2	3.6	6.3	
$(CH_3)_2BF$	3.6	6.4	
CH_3BCl_2	3.1		3.42
$(CH_3)_2BCl$	3.64		2.50

The k_{B-F}-value in the methylfluoroboranes is slightly smaller than in BF_3. The relative importance of structures B and B′ will accordingly be smaller, suggesting that part of the coordinative saturation has been taken over by the methyl group. Also, the fact that the sum of the partial bond moments in CH_3BF_2 is larger than in $(CH_3)_2BF$ can be explained by a relative lower donation from fluorine. In these molecules the methyl group seems to form $(p–p)$-π bonds with boron more easily than fluorine. This conclusion is also confirmed by the stability constants, determined by Brown[10], for BF_3, CH_3BF_2, $(CH_3)_2BF$ and $(CH_3)_3B$, respectively.

The τ-values from the PMR spectra of the methylhaloboranes also agree with the hypothesis that π-donation stems principally from the methyl group. Accordingly, the trend in the sum of the partial moments can be explained by ascribing the variations mainly to changes of the $\overrightarrow{BC}$-moment only. It is interesting to note that the observed variations are larger for chloro- than for fluoroderivatives, suggesting that F is a better donor than Cl. A similar conclusion was drawn by Coyle and Stone[16] from the coupling constant data $J(^{11}B–^{19}F)$ in mixed boron halides. It follows from these observations that CH_3 is also a better donor than chlorine.

All these results imply that resonance contributions of type C and C′ structure are predominant in methylhaloboranes.

That this picture cannot be clearly read from the force constant data is partially due to the relatively high degree of uncertainty inherent in these values[6].

6. CONCLUSION

A general, although not quantitative, classification of substituents according to their donor capacities in the B–X bond, can be derived. The following series is found: $N > O > CH_3 > F > Cl > Br > I$, which shows no parallel with the electronegativity sequence. Presumably the interatomic distance in a bond is another important factor in determining the donor properties of a substituent. Indeed, in order to form a stable $(p–p)$-π bonding orbital a filled p-orbital of the substituent should effectively overlap with the vacant p_z-orbital of boron.

According to Mulliken[17], the value of the overlap integral is inversely proportional to the interatomic distance in a bond. The electronegativity of the substituent and the interatomic distance, therefore, will determine simultaneously the donation towards boron in trivalent boron compounds.

SUMMARY

The infrared and Raman spectra of Cl_2BOCH_3, $ClB(OCH_3)_2$, $(CH_3)_2BOH$, $CH_3B(OH)_2$ have been studied. Force constants have been derived for the fundamental vibrations. These data and the data on the ^{11}B NMR shifts and on the electrical dipole moments of a series of molecules of type X_2BOY and $XB(OY)_2$ ($X = F$, Cl, CH_3 and $Y = CH_3$, H) are discussed. The internal coordinative saturation of boron proceeds through π-bonding from the ligands into the empty p_z-orbital of the planar sp^2 hybridized boron atom.

The following series in increasing order of donor capacity is found:

$N > O > CH_3 > F > Cl > Br > I$.

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