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STUDIES ON TRIVALENT BORON COMPOUNDS
II. DIPOLE MOMENT MEASUREMENTS

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1. INTRODUCTION

In a previous article[1] we have discussed the ^{11}B NMR data in relation to the change in internal coordination saturation around boron. In this paper we will discuss the use of dipole moment measurements in the investigation of the donor capacities of different substituents in trivalent boron compounds.

The change in bonding characteristics from covalent boron $>B-\ddot{\underset{\cdot\cdot}{X}}:$ to coordinatively saturated boron $>\overset{\delta^-}{B}\Leftarrow\overset{\delta^+}{X}:$, results in a considerable increase of the partial bond moment of the B–X bond. Usually, the partial moment of the B–X bond increases with increasing donor capacity of the X atom or group. In order to draw up a scale of donor capacities the true values of the partial bond moments themselves should be estimated. These, however, can not be evaluated, principally because the symmetrical BX_3-structures are planar so that the resulting total electrical dipole moment amounts to zero, due to internal compensation of the three BX-moments.

We will, therefore, interpret instead the trend of the sum of these unknown partial moments, *i.e.*, the molecular moment for a series of compounds with the X_2BY,XBY_2,X_2BOY and $XB(OY)_2$ skeleton. The experimental results will be compared with calculated values, based on fixed geometries for these molecules.

2. EXPERIMENTAL

2.1. *The synthesis of compounds of type* $X_2BY, XBY_2, X_2BOY, XB(OY)_2$.

This was usually carried out using previously published methods, as mentioned in part I of this series[1].

2.2. *Dipole moment measurements*

Although the technique for the determination of the electrical dipole moment in dilute solutions in a non-polar solvent is generally considerably easier than that in the gas phase, we nevertheless preferred the latter method. The preparation of solutions of extremely hygroscopic substances without some degree of hydrolysis taking place is difficult. On the other hand, these substances can be handled without fear of hydrolysis in a vacuum system with float valves. Moreover, molecular weight measurements in the gas phase (*e.g.*, on F_2BOCH_3) have shown that molecular association in the gas phase can be ruled out as a complicating factor[2]. Also, the infrared spectra of F_2BOCH_3 in the gas phase are in accordance with the monomolecular species[2].

For the calculation of the dipole moment from experimental data, the classical Debye equation was used

$$\mu^2 = \frac{9\,kT}{4\,\pi N}\cdot\frac{M}{d}\left[\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right]$$

The polarization was determined from measurements of the dielectric constant of the compounds at various known pressures and temperatures. The gas-cell and the measuring equipment for the determination of the dielectric constant in the gas phase at elevated temperatures have been described previously[3]. The gas density was calculated by means of the general gas law, using pressure and temperature data. The molecular refraction was calculated by means of the atomic refractivities cited by Partington[4].

For products the boiling points of which are above room temperature, the dielectric constant of the saturated vapour was measured. The pressure in the gas cell was then determined by the temperature of the liquid in the reservoir situated beneath the cell. The pressure of the saturated vapour in the cell can be read from the vapour pressure curve of the substance.

For products having boiling points below room temperature, the pressure was read directly from a manometer attached to the gas-cell assembly.

$FB(OCH_3)_2$ cannot be prepared in the pure form in the liquid phase, but is reported to be stable in the gas phase. The product was, therefore, synthesized *in situ* in the cell by evaporating equimolar amounts of F_2BOCH_3 and $B(OCH_3)_3$ directly into the cell. The pressures were then measured by means of an isoteniscope. A fresh preparation was made for each pressure and scale reading.

A graph of dielectric constant against pressure shows a linear relationship for all the compounds studied, indicating the absence of molecular association.

3. CALCULATIONS OF MOMENTS, AND RESULTS

3.1. *General considerations*

The analysis of the vibrational spectra of the X_2BOY-type products studied (which will be discussed in a subsequent report) and of the spectral data for F_2BOCH_3[2], show that these compounds have C_s symmetry. The structure of the $XB(OY)_2$-type products, however, cannot be derived unequivocally from the vibrational spectra. Either C_{2v} symmetry (planar configuration) or C_2 symmetry (spatial configuration) can be correlated with the spectral data, and the theoretical dipole moments will therefore be calculated for both structures. The bond angles in the planar configurations, $X\text{–}\widehat{B}\text{–}Y$, $X\text{–}\widehat{B}\text{–}O$ and $O\text{–}\widehat{B}\text{–}O$, are taken as equal to 120°, whereas for the $B\text{–}\widehat{O}\text{–}Y$ angle a value of 113° is assumed, in agreement with electron diffraction data for analogous molecules[5]. The direction of the partial bond moments is derived from electronegativity considerations. As the electronegativities of F, Cl, and CH_3 are higher than that of B, the B–X moment for $X = F$, Cl or CH_3 is accordingly taken in the sense $\overrightarrow{B\text{–}X}$. Similarly, a purely covalent B–O bond should yield a partial moment $\overrightarrow{B\text{–}O}$, directed from boron to oxygen. By analogy with the comparable $\overrightarrow{\mathrm{C{-}O}}$ moment, a value of about 1.0 D could be estimated for such a moment. A purely dative $\mathrm{B}\leftarrow\mathrm{O}$ bond, however, would invert the direction of the moment, *i.e.*, $\overrightarrow{\mathrm{OB}}$, and would yield a value of 3.6 D, as calculated by Phillips[6]. This means that when a $\mathrm{B}\overset{\leftarrow}{=}\mathrm{O}$ bond with 33% coordinative contribution (π-donation) is considered, as for instance in the case of $B(OCH_3)_3$, there still results a moment of about 0.2 D in the sense $\overrightarrow{\mathrm{OB}}$. As a real contribution of back-coordination is to be expected for the compounds under study, we will assume in our calculations the partial moment in the sense $\overrightarrow{\mathrm{OB}}$.

TABLE 1

EXPERIMENTAL DATA FOR THE DIPOLE MOMENTS OF TRIVALENT BORON COMPOUNDS

	Compound	*t* (°C)	ε'_{200} *mm Hg*	μ(*D*)
1	$FB(OCH_3)_2$	84.2	1.0022076	1.91
2	$ClB(OCH_3)_2$	82.6	1.0019917	1.71
3	$CH_3B(OH)_2$	119.0	1.0008394	1.16
4	F_2BOCH_3	84.4	1.0035520	2.62
5	Cl_2BOCH_3	56.0	1.0036452	2.35
6	$(CH_3)_2BOH$	82.6	1.0015341	1.53
7	CH_3BF_2	25.8	1.0021111	1.60
8	CH_3BCl_2	24.9	1.0020397	1.45
9	$(CH_3)_2BF$	25.4	1.0017124	1.34
10	$(CH_3)_2BCl$	22.0	1.0011502	0.86

When the electronegativities of H, C and O are taken into account, the direction of the OY-moment is rather unequivocal: $\overrightarrow{\mathrm{Y{-}O}}$, for $Y = CH_3$ or H. We therefore take for these well known parameters the values reported by Smyth[7,8]:

$$\overrightarrow{\mathrm{CH_3O}} = \overrightarrow{\mathrm{H_3C}} + \overrightarrow{\mathrm{CO}} = \overrightarrow{\mathrm{HC}} + \overrightarrow{\mathrm{CO}} = 1.18\ \mathrm{D}.$$

$$\overrightarrow{\mathrm{HO}} = 1.51\ \mathrm{D}.$$

3.2. *Calculation of the molecular moment for type X_2BOY structures*

Since both the BX-moments enclose an angle of 120°, their resultant has the value of a single $\overrightarrow{\mathrm{BX}}$-moment and falls along the bisector of $\widehat{\mathrm{XBX}}$, together with the produced part of the OB-moment (Fig. 1). For the OBX_2 skeleton moment we thus obtain:

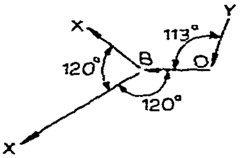


Fig. 1. Configurational parameters for X_2BOY molecules.

$$\overrightarrow{\mathrm{OBX_2}} = \overrightarrow{\mathrm{BX}} + \overrightarrow{\mathrm{OB}}.$$

Combining this moment with the $\overrightarrow{\mathrm{YO}}$-moment yields the molecular moment, $\overrightarrow{\mathrm{M}}$:

$$\overrightarrow{\mathrm{M}}^2 = \overrightarrow{\mathrm{OBX_2}}^2 + \overrightarrow{\mathrm{YO}}^2 + 2\,\overrightarrow{\mathrm{OBX_2}}\cdot\overrightarrow{\mathrm{YO}}\cdot\cos 67° \qquad \text{(a)}$$

TABLE 2

CALCULATED MOLECULAR MOMENT OF TRIVALENT BORON COMPOUNDS

	Molecule	Spatial (C_2)	Planar (C_{2v})
1	$FB(OCH_3)_2$	$\overrightarrow{BF}+\overrightarrow{OB}=1.45$	$\overrightarrow{BF}+\overrightarrow{OB}=3.33$
2	$ClB(OCH_3)_2$	$\overrightarrow{BCl}+\overrightarrow{OB}=1.25$	$\overrightarrow{BCl}+\overrightarrow{OB}=3.13$
3	$CH_3B(OH)_2$	$\overrightarrow{BC}+\overrightarrow{OB}=1.00$	$\overrightarrow{BC}+\overrightarrow{OB}=3.39$
4	F_2BOCH_3	$\overrightarrow{BF}+\overrightarrow{OB}=1.96$	
5	Cl_2BOCH_3	$\overrightarrow{BCl}+\overrightarrow{OB}=1.52$	
6	$(CH_3)_2BOH$	$\overrightarrow{BC}+\overrightarrow{OB}=0.49$	
7	CH_3BF_2		$-\overrightarrow{BC}+\overrightarrow{BF}=1.18$
8	CH_3BCl_2		$-\overrightarrow{BC}+\overrightarrow{BCl}=1.03$
9	$(CH_3)_2BF$		$-\overrightarrow{BC}+\overrightarrow{BF}=0.92$
10	$(CH_3)_2BCl$		$-\overrightarrow{BC}+\overrightarrow{BCl}=0.44$

By combining the experimental moment value, $\vec{M}$, with the known $\overrightarrow{YO}$-vector in eqn. (a), the sum of $\overrightarrow{BX}+\overrightarrow{OB}$ can be calculated. These values are shown in Table 2, column 2.

3.3. *Calculation of the $XB(OY)_2$-moment*

3.3.1. *Planar structure* (*Fig.* 2). The resultant, $\vec{r}$, of both $\overrightarrow{YO}$-moments is given by

$$\vec{r}^2=\overrightarrow{YO}^2+\overrightarrow{YO}^2+2\,YO\cdot\cos 106^\circ$$

or

$$\vec{r}=1.206\cdot\overrightarrow{YO}.$$

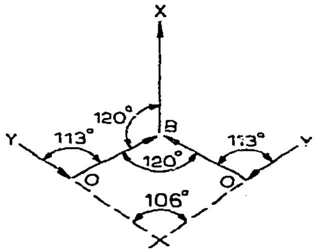


Fig. 2. Planar configuration of $XB(OY)_2$ molecules.

The resultant of the XBO_2 skeleton again equals the sum of the partial moments, $\overrightarrow{BX}+\overrightarrow{OB}$. Thus the molecular moment, $\vec{M}$, is given by

$$\vec{M}=\overrightarrow{BX}+\overrightarrow{OB}-1.206\,\overrightarrow{YO}.$$

3.3.2. *Spatial configuration* (*Fig.* 3). The resultant moment of the XBO_2 skeleton is again equal to the sum of the partial moments, $\overrightarrow{BX}+\overrightarrow{OB}$. The $\overrightarrow{YO}$-vectors, however, are to be resolved along the three cartesian coordinates. It is evident that the contributions of both $(\overrightarrow{YO})_z$- and $(\overrightarrow{YO})_y$-moments are mutually equal and opposed so that their resultant becomes zero. Only the $\overrightarrow{(YO)}_x$-component gives a real contribution to the molecular moment, $\overrightarrow{M}$. The equation for the molecular moment then becomes

$$\overrightarrow{M} = \overrightarrow{BX} + \overrightarrow{OB} + 2\,\overrightarrow{(YO)}_x,$$

with $\overrightarrow{(YO)}_x = \overrightarrow{YO} \cdot \cos 67° \cdot \cos 60° = 0.196\,\overrightarrow{YO}$. By introducing the appropriate values

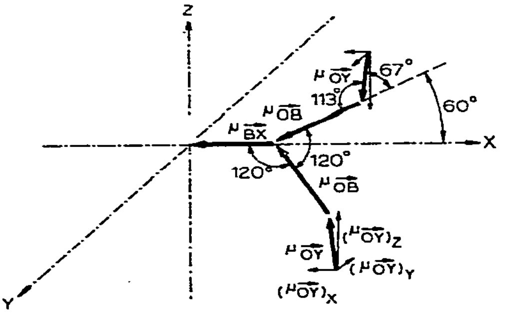


Fig. 3. Spatial configuration of $XB(OY)_2$ molecules.

for the $\overrightarrow{YO}$-moment into the equations of section 3.3.1 and 3.3.2. and combining with the experimental moment value, $\overrightarrow{M}$, we obtain the values for the sum $\overrightarrow{BX} + \overrightarrow{OB}$, given in columns 2 and 3, of Table 2.

3.4. *Calculation of the CH_3BX_2- and $(CH_3)_2BX$-moments*

The structure of these compounds with X = F or Cl is sufficiently known from the vibrational spectra[9,10] and from electron diffraction data[11,12]. They are planar molecules and the bond angles are 120°. Owing to the tetrahedral angles, the three $\overrightarrow{HC}$-moments of the methyl-group compose to one $\overrightarrow{HC}$ resultant moment. The equations for the molecular moments of both types of molecules thus become:

$$\overrightarrow{M} = \overrightarrow{BX} - \overrightarrow{BC} + \overrightarrow{HC}$$

and appear to be equal. As the reported maximum deviation on the angle parameters is 3°, the maximum deviation in the theoretical moment values can be calculated to be 0.07 D. Differences between the experimental moment values that are smaller than 0.07 D must therefore be considered to be structurally meaningless. The results of these calculations are also given in Table 2.

3.5. *Results*

The experimental values in Debye units of the molecular electrical dipole moments are tabulated in Table 1, together with the dielectric and temperature data that were relevant for their evaluation. The accuracy of the experimental method gives an absolute deviation for these results of ±0.04 D.

5. DISCUSSION

5.1. *Structure of the $XB(OY)_2$-type molecules*

A comparison of the data of columns 2 and 3 of Table 2 shows that for the sum of the bond moments, $\overrightarrow{BX}+\overrightarrow{OB}$, very high values are obtained on the assumption of a planar configuration. Even if 50% double-bond character is assumed in the B–O bond, yielding a partial bond moment of 0.8 D, the $\overrightarrow{B\text{–}X}$ moment should have an abnormally high value *i.e.*, about twice the value for the very similar $\overrightarrow{C\text{–}X}$ moment. For the spatial configuration, however, no such extraneous assumptions should be made. The dipole moment measurements thus yield a direct proof for the spatial configuration of these molecules.

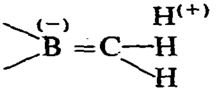
5.2. *Variation of bond moments*

The data of Table 2 show that the sum of equivalent bond moments is by no means constant. The variations of bond moments are, however, directly related to the donor capacity of the X substituent. As has been explained in the introduction, a direct comparison with the situation in the BX_3 molecules is impossible. We will therefore use here results of spectroscopical investigations, which are the subject of a subsequent report.

It is shown that in going from X_2BOY to $XB(OY)_2$, the bonds with the highest polar character (BF, BCl), have nearly constant valence force constants. This means that the $\overrightarrow{B\text{–}X}$ bond moment must also remain almost unchanged, so that variations in the sum, $\overrightarrow{BX}+\overrightarrow{OB}$, are due mainly to changes in the $\overrightarrow{OB}$ part. The data of column 2, Table 2, for compounds 1,2,4 and 5 thus show that the coordinative contribution of the oxygen atom in X_2BOY is larger than that of each oxygen atom in $XB(OY)_2$. Oxygen atoms are therefore stronger π-bonders towards boron than either F or Cl.

For the methylboronic acids (compounds 3 and 6) however, the variation of the bond moments is the reverse of that for F- and Cl-substituted products. Taken in conjunction with spectroscopical data, this observation can be explained by the assumption that O and CH_3 have almost the same facility for forming (p–p) π-bonds with boron.

The NMR spectra of the methylboron halides[1] have shown that π-donation towards boron occurs principally through the methyl group. The variation of the sum of bond moments points in the same direction; the main changes are again ascribed to the CB-moment. Resonance contributions of structures such as



are thus to be considered, meaning that CH_3-groups are better donors than either F or Cl. Moreover, it is worthy of note that the differences for the chlorides are much larger than for the fluorides. This would mean that Cl is far less likely than F to form π-bonds with boron. An analogous conclusion was drawn by Coyle and Stone[13] from their ^{19}F magnetic resonance studies of mixed boron halides. A mutual evaluation of the donor capacities of the various substituents will be discussed using vibrational spectral data.

SUMMARY

The electrical dipole moments of a series of molecules of type X_2BOY and $XB(OY)_2$ ($X = F, Cl, CH_3$; $Y = H, CH_3$) and of the methyl-chloro and -fluoro

boranes have been measured in the gas phase. These moments were also calculated theoretically. For the $XB(OY)_2$ molecules, a spatial and a planar molecular configuration can be considered. The spatial configuration is shown to represent the actual structure, in accordance with spectroscopical data. The variations in bond moments are discussed in relation to the ability of the substituent for π-donation towards boron.

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