

STUDIES ON TRIVALENT BORON COMPOUNDS

I. THE BORON AND PROTON MAGNETIC RESONANCE SPECTRA OF SOME TRIVALENT BORON COMPOUNDS

J. E. DE MOOR AND G. P. VAN DER KELEN

Laboratory for General and Inorganic Chemistry (B), University of Ghent (Belgium)

(Received January 7th, 1965)

I. INTRODUCTION

A survey of the literature on the boron halides' structures reveals that the bond order increases in the series $\text{BI}_3 < \text{BBr}_3 < \text{BCl}_3 < \text{BF}_3$. This sequence is explained by an increasing bond strengthening by back-coordination [internal dative π -bonding, $(p_X \rightarrow p_B)_\pi$ bonding, donor capacity of the halogen or X atom delocalization]. This order is in contradiction with the electronegativities of the halogen atoms. The above mentioned argument is, however, consistent with many physical and chemical data such as ^{11}B magnetic resonance spectra², B-X bond distances³ and heats of reaction in complex formation⁴.

It is the purpose of this series of articles to determine the back-coordination power of other substituent atoms and groups such as O (in OH, OCH_3 and OC_2H_5), C (in CH_2). In accordance with the possible resonance structures and independent of the nature of the substituent the highest bond order to be encountered in a symmetrical planar BX_3 compound will be limited to 1.33. However, in compounds of the type X_2BY and XBY_2 with different ligands bonded to boron, higher bond orders might be found in the bonds with the atoms presenting the highest back-coordination power.

Various physicochemical measurements yield data to study this problem. The first of them, ^{11}B and ^1H magnetic resonance spectra, will be the subject of this article.

II. EXPERIMENTAL

(1) *The chemical compounds*

The products studied were synthesized and/or purified in the laboratory, along methods published by previous authors. Purity was assessed in some instances either by vapour density, mass spectrometry or infrared spectrometry.

(2) *The ^{11}B magnetic resonance spectra*

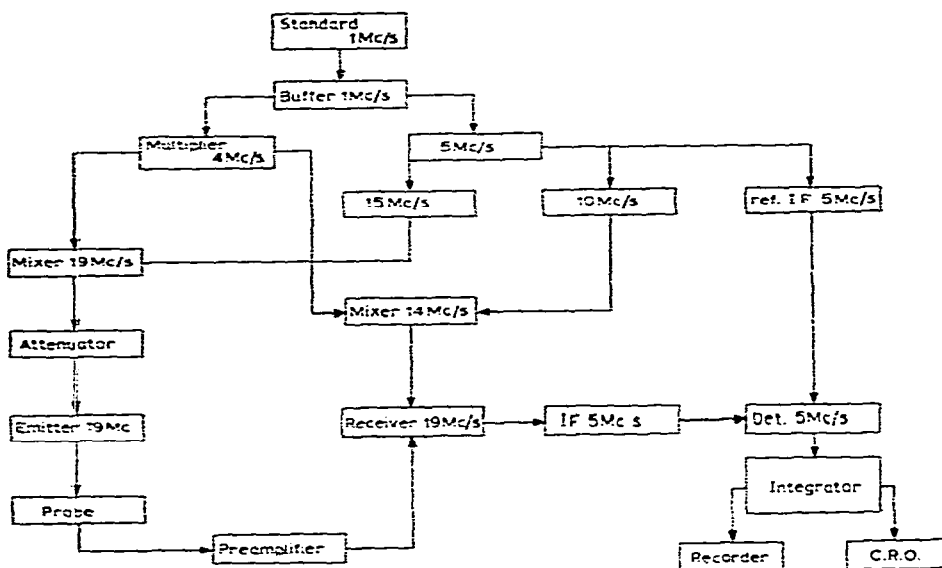
^{11}B NMR spectra were recorded at 19 Mc using an apparatus developed in this laboratory. The basic part of the instrument was the 12 inch electromagnet belonging to the Varian 4300-B dual purpose spectrometer. At 19 Mc a field of 13,909 gauss was required for ^{11}B resonance experiments. The high frequency generator for the H_1 r.f. field consisted basically of a Beckmann digital frequency counter type 7175 giving a

very stable frequency standard of 1 Mc (long term stability $3 \cdot 10^{-7}$, short term stability 10^{-8}). By appropriate multiplication and mixing techniques a 19 Mc generator of good quality was obtained. The devices for these transformations are of the plug in unit type; so a quick change to other radio frequency values of H_1 , for other nuclei (^{31}P , ^{119}Sn) can be secured. The detection was performed with a superheterodyne type receiver, operating at 5 Mc middle frequency; this allows us to use the same receiver for any frequency of the r.f. generator.

The sweep unit used was an instrument comparable to the Varian VK-3507 unit but allowing a sweep over 130 ppm at a higher sweep rate to limit the time for recording a spectrum and covering the whole chemical spectrum for ^{11}B . A Varian V 4230 B-probe, nominal range 8–16 Mc, was provided with an appropriate trimming capacitance to allow operation at 19 Mc.

The sensitivity of the receiver allowed measurements on samples contained in 15 mm o.d. tubes as well as on samples in the standard 5 mm tubes. Spinning the sample did not influence the resolution as the band width seems mainly to be determined by the quadrupole moment of the ^{11}B nucleus.

The whole instrument, represented by the block diagram of Fig. 1, formed a good-working, high-resolution equipment for ^{11}B resonance measurements.



All the measurements were done at room temperature on liquid samples. Only for gaseous compounds whose boiling points were below -40° concentrated solutions in chloroform were used. The samples were always sealed off on the Stock-type vacuum line. Trimethyl borate served as an external reference. The substitution method was used, and audio side bands were generated for calibrations. The accuracy of the chemical shift values is within 2%.

(3) The proton magnetic resonance spectra

The spectra were recorded with a Varian V 4300-B spectrometer, operating at 56.44 Mc/s. Compounds, the boiling point of which was higher than 0° , were studied

as the neat liquids. An exception was made for $\text{CH}_3\text{B}(\text{OH})_2$ which was dissolved in D_2O . For low boiling products (b.p. $< -20^\circ$) chloroform solutions were made. All the compounds were vacuum-distilled in a Stock apparatus into 5 mm o.d. pyrex sample tubes. TMS served as the external reference and the substitution method was used.

III. ^{11}B NMR DATA AND DISCUSSION

The ^{11}B chemical shift data for the compounds studied are listed in Table I, together with some literature data which are relevant for the discussion. Coupling between the ^{11}B and ^{19}F nuclei could only be observed for the methylfluoroboranes. The $J(^{11}\text{B}-^{19}\text{F})$ values cited from other sources were measured on ^{19}F NMR spectra.

TABLE I
 ^{11}B NMR DATA OF SOME BORON COMPOUNDS
 ^{11}B chemical shift in ppm.

| Product | δ (ppm) | δ (lit.) | Ref. |
|---|----------------|-----------------|------|
| NaBH_4 | | +61.0 | 2 |
| BI_3 | | +23.7 | 2 |
| NaBF_4 | | +20.4 | 8 |
| $\text{H}_2\text{N}:\text{BF}_3$ | | +20.2 | 2 |
| $(\text{F}_2\text{BOC}_2\text{H}_5)_3$ | +19.1 | | |
| $(\text{F}_2\text{BOCH}_3)_3$ | +18.9 | | |
| BF_3 (gas) ^a | | +6.6 | 2 |
| $\text{FB}(\text{OC}_2\text{H}_5)_2$ | +3.3 | | |
| $\text{FB}(\text{OCH}_3)_2$ | +2.5 | | |
| $\text{B}(\text{OC}_2\text{H}_5)_3$ | +0.9 | +0.6 | 8 |
| $\text{B}(\text{OCH}_3)_3$ | 0 | 0 | |
| $\text{B}(\text{OH})_3$ | | -0.7 | 8 |
| $\text{ClB}(\text{OCH}_3)_2$ | -6.2 | | |
| $\text{HB}(\text{OCH}_3)_2$ | | -8.0 | 8 |
| CH_3BF_2 (CHCl_3) ^b | -10.0 | | |
| $\text{B}_2\text{N}(\text{C}_2\text{H}_5)_2$ | | -12.9 | 2, 9 |
| $\text{CH}_3\text{B}(\text{OH})_2$ (H_2O) | -13.8 | | |
| $\text{C}_2\text{H}_5\text{B}(\text{OH})_2$ | | -14.3 | 2 |
| $\text{Cl}_2\text{BOC}_2\text{H}_5$ | | -14.4 | 8 |
| Cl_2BOCH_3 | -14.8 | | |
| $(\text{CH}_3\text{BO})_3$ | -15.1 | | |
| $\text{C}_6\text{H}_5\text{B}(\text{OH})_2$ | | -15.2 | 2 |
| BBr_3 | | -22.2 | 2 |
| BCl_3 | -29.2 | -29.2 | 2 |
| $(\text{CH}_3)_2\text{BOH}$ | -36.5 | | |
| $(\text{CH}_3)_2\text{BF}$ (CHCl_3) ^c | -42.0 | | |
| CH_3BCl_2 | -43.3 | | |
| $(\text{CH}_3)_2\text{BCl}$ | -57.4 | | |
| $(\text{CH}_3)_3\text{B}$ | -68.7 | -68.2 | 2 |

^a $J(^{11}\text{B}-^{19}\text{F})$ 15 cps. ^b $J(^{11}\text{B}-^{19}\text{F})$ 78 cps; lit. 77 cps. ^c $J(^{11}\text{B}-^{19}\text{F})$ 128 cps.

The ordering of the ^{11}B chemical shift values for the ternary boranes does not show the expected correlation of decreasing chemical shift with increasing electronegativity of the substituents. Another effect, π -donation, yielding an increment in

shielding arising from delocalization, is to be considered to explain the sequences. The total ^{11}B chemical shifts thus can be written

$$\delta = (1/x_X) + A_\pi$$

where $1/x_X$ stands for the electronegativity term and A_π for the π -electron induced increment.

Applying this equation qualitatively to the data of Table 1 for certain groups of compounds allows one to derive sequences for π -electron delocalizations for the substituents, e.g.

$$A_\pi(\text{F}) > A_\pi(\text{Cl}) \quad \text{and} \quad A_\pi(\text{F}) > A_\pi(\text{Br})$$

or even within atom groups such as

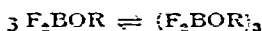
$$A_\pi(\text{ClBO}_2) > A_\pi(\text{Cl}_2\text{BO})$$

wherein the substituents on boron have nearly equal electronegativity. This method of accounting for the ^{11}B chemical shifts does, however, not hold for the comparison in systems with many electron atoms (BI_3 , BBr_3). Here neighbour anisotropy effects start to play an important role.

The trend observed in the $J(^{11}\text{B}-^{19}\text{F})$ coupling constants for BF_3 and the methylfluoroboranes shows that the electron density in the B-F bonds increases in going from BF_3 to $(\text{CH}_3)_2\text{BF}$.

Methyl and ethyl difluoroborate trimer (F_2BOR)₃

From Raman and infrared spectral data (which will be published soonly) we have gained certainty as to the trimeric constitution of the molecular species present in liquid alkyl difluoroborate ($\text{R} = \text{CH}_3$ and C_2H_5). Trimers were also proposed by McCusker and Kilzer⁵ and by Kirshenbaum⁶ as a result of molecular weight measurements. If the equilibrium for the trimerization reaction



is completely shifted to the right, the ^{11}B NMR spectra should show only one single peak and the chemical shift value should fall in the region for sp^3 hybridized boron atoms.

The spectra of these compounds either measured on the pure liquids or on their solutions in benzene always yielded a single peak at about 19 ppm, which is well within the sp^3 region for ^{11}B chemical shifts. The results are shown in Table 2.

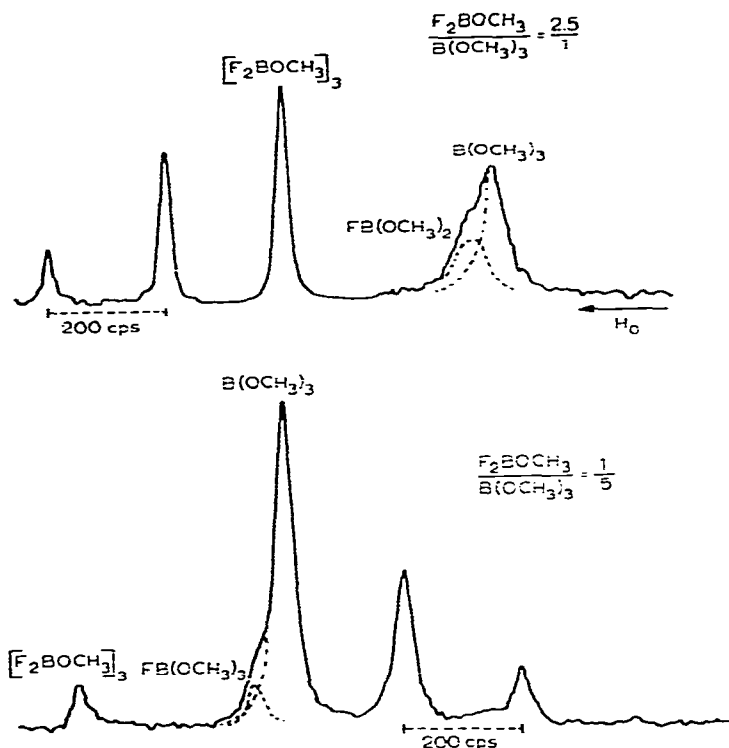
TABLE 2
 ^{11}B CHEMICALS SHIFT OF DIFLUOROBORATES

| Conditions | | F_2BOCH_3 | $\text{F}_2\text{BOC}_2\text{H}_5$ |
|------------|-----|---------------------------|------------------------------------|
| neat, | 70° | + 18.6 ppm | + 19.3 ppm |
| | 25° | + 18.9 ppm | + 19.1 ppm |
| solution, | 50° | + 18.4 ppm | |
| | 25° | + 18.6 ppm | + 19.5 ppm |

These data clearly indicate that there is no measurable dissociation below 70° into monomeric items, thus invalidating the early conclusions of Goubeau and Lücke⁷ about the dimerization equilibrium in the liquid state.

The disproportionation of dimethyl fluoroborate, FB(OR)₂

In several experiments we have tried to separate the dialkylfluoroborate (CH₃ or C₂H₅) from the reaction mixture of trialkylborate and alkyldifluoroborate trimer according to the method proposed by Goubeau and Lücke⁷; in none of these the product could be obtained. The ¹¹B NMR spectrum of such mixtures showed prominent peaks for (F₂BOR)₃ and B(OR)₃, with a small shoulder on the high field side of the latter (Fig. 2). By a graphical analysis of these overlapping peaks we found that the small peak had a chemical shift value of +2.5 resp. +3.2 ppm, for the methyl, resp. the ethyl ester. These values agree rather closely with the expectations for monomeric FB(OR)₂.



The relative changes in the intensity of both collapsed peaks, could be derived with only moderate accuracy. Qualitatively this empirical analysis of the multi-component peak shows that the highest concentration of FB(OR)₂ is obtained for a molar ratio F₂BOR/B(OR)₃ equal to 5. The data of Table 3 show that the chemical shift for FB(OR)₂ is independent of the molar ratio F₂BOR/B(OR)₃.

These data provide evidence for the conclusion that the dialkylfluoroborates are in chemical equilibrium with the above-mentioned compounds and the equilibrium concentration of the monofluoroborate is rather low.

TABLE 3

¹¹B-NMR DATA ON THE FORMATION OF DIALKYLFLUOROBORATES

| Temp. | Molar ratio B(OR) ₃ /BF ₂ OR | FB(OCH ₃) ₂ | FB(OC ₂ H ₅) ₂ |
|-------|---|------------------------------------|--|
| 25° | 5:1 | +2.52 ppm | |
| | 2.5:1 | +2.26 | |
| | 1:1 | +2.24 | |
| | 1:2.5 | +2.42 | |
| | 1:5 | +2.55 | +2.42 ppm |
| 50° | 1:5 | +2.56 | |

IV. PMR DATA AND DISCUSSION

The proton magnetic resonance data are shown in Table 4. We did not observe coupling between protons and fluorine. In the spectra of the methylfluoroboranes proton-carbon-13 coupling escaped observation, probably because of the broadening of these signals.

TABLE 4

PMR DATA OF TRIVALENT BORON COMPOUNDS

| Product | $\tau(\alpha\text{-protons})$ | $J(^{13}\text{C}-\text{H})$ | $\tau(\text{OH})$ | $\tau(\beta\text{-protons})$ |
|--|-------------------------------|--|-------------------|------------------------------|
| (CH ₃) ₂ BOH | 9.97 | 117 | 6.65 | |
| (CH ₃ BO) ₃ | 9.73 | 117 | | |
| CH ₃ B(OH) ₂ (D ₂ O) | 9.54 | 116 | 5.02 | |
| (CH ₃) ₂ BCl | 9.34 | 117 | | |
| CH ₃ BF ₂ (CHCl ₃) | 9.29 | | | |
| (CH ₃) ₂ BF (CHCl ₃) | 9.20 | | | |
| (CH ₃) ₃ B (CHCl ₃) | 8.92 | 115 | | |
| CH ₃ BCl ₂ | 8.88 | 117 | | |
| B(OCH ₃) ₃ | 6.91 | 145 | | |
| ClB(OCH ₃) ₂ | 6.56 | 147 | | |
| (F ₂ BOCH ₃) ₃ | 6.23 | 154 | | |
| Cl ₂ BOCH ₃ | 6.10 | 149 | | |
| B(OCH ₂ CH ₃) ₃ | 6.04 | 126 (CH ₃) 144 (CH ₂) | | 8.74 |
| (F ₂ BOCH ₂ CH ₃) ₃ | 5.53 | 129 (CH ₃) 154 (CH ₂) | | 8.51 |
| B(OH) ₃ | | | 4.54 | |

For the chemical shifts of the alkoxy protons the expected correlation with the electronegativity of the other substituents bonded on boron is found. For the methylaloboranes and for the methylboronic acids this trend is not followed and data gained from other physical measurements (which will be published soon) indicate that some degree of hyperconjugation of the methyl group might be responsible for this situation.

The absence of satellite peaks in these spectra due to ¹¹B-proton couplings over two bonds [$J(^{11}\text{B}-\text{C}-^1\text{H})$] is probably due to the high quadrupole moment of the boron atom. Such couplings have only been observed in quaternary boron compounds such as LiB(CH₃)₄¹⁰.

The carbon-13-proton coupling constants in the alkoxy and in the alkyl haloboranes are only slightly influenced by halogen substitution; this shows that the carbon atom orbitals towards hydrogen are only slightly modified on such substitutions.

ACKNOWLEDGEMENTS

The authors thank Prof. dr. Ir. Z. EECKHAUT for his interest in this work and for fruitful discussion of the paper. They also acknowledge the valuable cooperation of Mr. E. H. A. BEERNAERTS, technical engineer, who developed the intricate electronics for these experiments.

SUMMARY

The ^{11}B and ^1H magnetic resonance spectra of some trivalent boron compounds have been studied: X_2BOR , $\text{XB}(\text{OR})_2$ ($\text{R} = \text{CH}_3$, C_2H_5 ; $\text{X} = \text{F}$, Cl), $\text{B}(\text{OR})_3$, $\text{CH}_3\text{B}(\text{OH})_2$, $(\text{CH}_3)_2\text{BOH}$, $(\text{CH}_3\text{BO})_3$, BCl_3 , CH_3BCl_2 , $(\text{CH}_3)_2\text{BCl}$, CH_3BF_2 , $(\text{CH}_3)_2\text{BF}$, $(\text{CH}_3)_3\text{B}$. Evidence is found for considerable π -bonding in compounds of the type XBY_2 or X_2BY in the bonds with the most electronegative atoms or groups. This study also provides another argument for the trimeric nature of alkyl difluoroborates in the liquid state. Dialkyl fluoroborates are shown to undergo disproportionation into $\text{B}(\text{OR})_3$ and F_2BOR .

REFERENCES

- 1 L. PAULING, *The Nature of the Chemical Bond*, Cornell Univ., 1960, p. 317.
- 2 W. D. PHILLIPS, H. C. MILLER AND E. L. MUETTERTIES, *J. Am. Chem. Soc.*, 81 (1959) 4498.
- 3 N. V. SIDGWICK, *The Chemical Elements and their Compounds*, Vol. I, Oxford Univ. Press, London, 1950, p. 392.
- 4 H. BROWN AND C. HOLMES, *J. Am. Chem. Soc.*, 78 (1956) 2173.
- 5 P. A. MCCUSKER AND S. N. L. KILZER, *J. Am. Chem. Soc.*, 82 (1960) 372.
- 6 J. KIRSHENBAUM, N. SABI AND P. W. SCHUTZ, *S.A.M. Report A*, (1944) 2120.
- 7 J. GOUBEAU AND K. E. LÜCKE, *Ann. Chem.*, 575 (1951) 37.
- 8 T. ONAK, H. LANDESMAN, R. WILLIAMS AND I. SHAPIRO, *J. Chem. Phys.*, 63 (1959) 1533.
- 9 H. TURNER AND R. WARNE, *Proc. Chem. Soc.*, (1962) 69.
- 10 A. MASSEY, E. RANDALL AND D. SHAW, *Spectrochim. Acta*, 21 (1965) 263.

J. Organometal. Chem., 6 (1966) 235-241