Inorganica Chimica Acta, 112 (1986) 209–214

Arsenic–Boron Derivatives.
5*. A ^{1}H and ^{11}B Nuclear Magnetic Resonance Study of the Methylated Arsine Adducts of Boron Trihalides

JAAFAR M. CHEHAYBER and JOHN E. DRAKE

Department of Chemistry, University of Windsor, Windsor, Ont., N9B3P4, Canada

Received July 8, 1985

Abstract

The ^{1}H NMR chemical shifts for the adduct series $(CH_3)_nAsH_{3-n}BX_3$ and the ^{11}B NMR chemical shifts for the adduct series $(CH_3)_nAsH_{3-n}BX_3$, $(CH_3)_nAsH_{3-n}BX_2Y$ and $(CH_3)_nAsH_{3-n}BXYZ$ (where n = 1, 2, 3; $X \neq Y \neq Z$ = Cl, Br or I) have been reported. The values of the chemical shifts are examined in view of their use as indicators of acid–base strength. The ^{11}B chemical shifts were found to fit Malinowsky's criteria of pairwise additivity.

Introduction

The properties of amine adducts have been widely studied by NMR spectroscopy [1–16]. These reports discuss a variety of topics including exchange reactions, long range B–H coupling, the evaluation of relative acid and base strength and correlations between NMR parameters and the strength of the B–N bond with data extracted from ^{1}H, ^{19}F, ^{11}B and ^{13}C NMR spectra.

Investigations on phosphine adducts [5, 10, 17–23] have been centered on correlations of chemical shifts and coupling constants with bond strength and adduct stability and have included variable temperature studies. Fewer reports have appeared on the NMR spectra of the arsine adducts [24–26] and these have dealt with trimethylarsine as the Lewis base. In this study we report on the ^{1}H NMR spectra of the simple adducts and on the ^{11}B NMR spectra of the mixed adducts of methyl, dimethyl, and trimethylarsine.

Experimental

Trimethylarsine and the three boron trihalides were checked for purity as reported earlier [27]. Dimethylarsine [28] and methylarsine [29] were prepared by the reduction of sodium dimethylarsonate and sodium methylarsonate respectively by Zn dust and HCl. The ^{1}H NMR spectra were recorded at room temperature on a Varian EM-360 permanent magnet instrument operating at 60 MHz and on a Bruker WP80 spectrometer operating at 60 MHz. The ^{11}B NMR spectra were recorded on a Bruker CPX100 multinuclear pulsed Fourier transform spectrometer operating at 28.88 MHz.

All adducts were white or off-white moisture and air sensitive solids with melting points of 46, 68 and 78 °C for the chloride, bromide and iodide adducts of $MeAsH_2$; 104, 122 and 130 °C for those of Me_2AsH; and 310, 245 and 275 °C for those of Me_3As respectively.

(A) Formation of the Adducts $Me_nAsH_{3-n}BX_3$ (n = 1, 2, 3; X = Cl, Br)

The arsine Lewis base and the boron trihalide Lewis acid were condensed in an approximately 1:1 molar ratio (*ca.* 0.5 mmol) in an NMR tube (Wilmad Glass, N.J.) which was held at −196 °C. The tube was then isolated on the vacuum line and the reactants were warmed slowly to room temperature by using a series of baths (−126 °C, −95 °C, −78 °C, −12 °C and 0 °C). After 0.5 h at room temperature the tube was momentarily opened to the pump to remove any excess of reactants. Deuterated methylene chloride was then distilled in and the tube was torch-sealed.

(B) Formation of the $Me_nAsH_{3-n}BI_3$ Adducts

Boron triiodide (0.2 g; 0.5 mmol) was purified by agitation with dry benzene (0.5 ml) and a trace of elemental mercury in a nitrogen-filled glove bag. The solution was introduced into an NMR tube which was then transferred to the vacuum line, held at −196 °C and opened to the line to pump away nitrogen. A slight excess of the arsine was then distilled in. The reaction was allowed to proceed under the same conditions mentioned for the preparation of the chlorides and bromides. Benzene was removed by vacuum distillation and the last traces were removed by pumping on the product for *ca.* 30 min. Deuterated methylene chloride was then distilled in and the tube sealed.

---

*Part 4 is ref. 1a.

0020-1693/86/$3.50

(C) Formation of the Mixed Adducts $Me_nAsH_{3-n}BX_2Y$ and $Me_nAsH_{3-n}BXY_2$ (n = 1, 2, 3; X, Y = Cl, Br)

Equimolar quantities (0.5 mmol) of BX_3 and BY_3 were distilled into the evacuated NMR tube on the vacuum line. The contents were then allowed to equilibrate and after 1 h at room temperature, the reactants were held at −196 ℃ and a slight excess of the appropriate arsine was distilled into the vessel. Gradual warming, by the use of a series of slush baths as described above, resulted in the formation of a white solid. After 30 min at room temperature, the tube was momentarily opened to the vacuum line, deuterated methylene chloride distilled in and the tube torch-sealed.

(D) Formation of the Mixed Adducts $Me_nAsH_{3-n}BX_2I$ and $Me_nAsH_{3-n}BXI_2$ (n = 1, 2, 3; X = Cl, Br)

Boron triiodide was handled as in section (B). The tube was then attached to the vacuum line and nitrogen pumped away. An equimolar amount of BX_3 (X = Cl, Br) was then distilled in and the contents were left to equilibrate. After 1 h at ambient temperature, the appropriate arsine was distilled in and the reaction allowed to proceed as in (C). Benzene was then carefully removed by vacuum distillation followed by pumping for 30 min. CD_2Cl_2 was then distilled in and the tube torch-sealed.

(E) Formation of $Me_nAsH_{3-n}BClBrI$

A predetermined amount of purified BI_3 (*ca.* 0.2 g in 0.5 ml of C_5H_5) was placed in the tube in the glove bag. The tube was transferred to the vacuum line and equimolar amounts of BCl_3 (0.5 mmol) and BBr_3 (0.5 mmol) were distilled into the tube at −196 ℃. The contents were then allowed to stand for 1 h at room temperature. The arsine (*ca.* 0.15 mmol) was distilled in, the reaction allowed to proceed and the products were treated as in sections (C) and (D) above.

(F) Test for Pairwise Additivity of ^{11}B Chemical Shifts

The ^{11}B chemical shifts are related to the pairwise parameters by the formula:

$$\delta(^{11}B) = \eta_{X,X} + 2\eta_{X,Y} + \eta_{D,Y} + 2\eta_{D,X}$$

where δ is the ^{11}B chemical shift of the adduct $D \cdot BX_2Y$, η is the pairwise parameter, D is the arsine, X and Y the halogens. The parameters $\eta_{X,Y}$ were calculated [16] relative to Me_2OBF_3 so for this reason all chemical shifts were adjusted to this reference. The parameters $\eta_{D,X}$ and $\eta_{D,Y}$ were calculated from the experimental data of the unmixed adducts $D \cdot BX_3$ by the formula:

$$\delta(^{11}B) = 3\eta_{X,X} + 3\eta_{D,X}$$

The values of $\eta_{X,Y}$ and $\eta_{D,X}$ are listed in Table III.

Results and Discussion

The adducts which are the subject of this investigation are white, moisture sensitive solids as reported earlier for similar compounds [24, 25, 30–33]. They were found to be slightly soluble in polar solvents such as chloroform and methyliodide. Methylene chloride is a relatively better solvent and so this deuterated solvent was used for recording the ^1H NMR spectra because the AsH chemical shifts lie in the same region as that of CH_2Cl_2. The BI_3 compounds tended to darken on extended exposure to light, indicative of the photosensitivity often associated with iodides. The methylarsine adducts, particularly that of BCl_3, appear to dissociate much more readily than their respective dimethyl and trimethylarsine analogs. A glance at the melting points suggests the trend of stability which is established for the phosphine analogs, although melting points are of course not necessarily a direct indication of stability. $MeAsH_2BCl_3$ turns completely to a pale-white viscous liquid in a few hours. Immediately after its formation, $MeAsH_2BCl_3$ continues to exert a positive pressure which is indicative of gradual HCl elimination similar to H_2 elimination in $MeAsH_2BH_3$ [35]. A monitoring of the As–H symmetric and asymmetric stretching frequencies at *ca.* 2235 and 2254 cm^{-1} in the Raman spectrum shows a gradual loss of intensity along with broadening (Fig. 1) indicative of decomposition through As–H bond cleavage. The IR spectrum of the volatile material above the solid confirms the presence of HCl [36]. Presumably HCl elimination proceeds according to the equation

$$n MeAsH_2BCl_3 \longrightarrow [MeAsHBCl_2]_n + n HCl$$

Trimers and tetramers of this type were suggested in the polymerization of $MeAsH_2BH_3$ [35]. There was

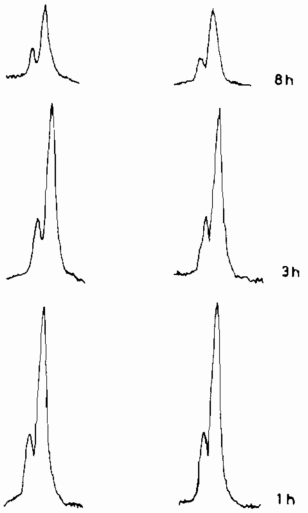

Fig. 1. The AsH stretching modes of $MeAsH_2BCl_3$ in the Raman spectrum at different times from preparation.

also some slight indication of similar decomposition with $MeAsH_2BBr_3$ but the Me_2AsHBX_3 adducts showed no signs of dissociation. Even with $MeAsH_2BCl_3$ the decomposition was hardly detectable in the first hour and all spectra were recorded as quickly as possible after formation of the adducts. The ^1H NMR spectra were obtained within five minutes and the ^{11}B NMR spectra, which took longer, were recorded at –20 °C. Thus we have confidence in the data which were entirely reproducible.

^1H NMR Spectra

The ^1H NMR spectra of the Me_3AsBX_3 species appear as broad singlets which at higher resolutions are seen to be distorted quartets [25]. The splitting results from the 1:1:1:1 quartet arising from long-range coupling with the ^{11}B nucleus ($I = 3/2$; 81.2%) overlapping with the septet arising from coupling with the ^{10}B nucleus ($I = 3$; 18.8%) [25].

In Me_2AsHBX_3, the methyl protons again appear as broad singlets centered around 1.6 to 1.8 ppm (Fig. 2). However, in addition to the coupling with the boron nuclei, there is no further spin–spin coupling with the proton on arsenic so that the peaks are not resolved. The proton on arsenic is seen as a typical broad hump, arising from the quadrupole ($I = 3/2$; 100%) on arsenic, in the region 4.6–5.1 ppm with relative intensity one-sixth that of the methyl resonance. In Fig. 2 the ^1H impurity in CD_2Cl_2 can be seen at 5.18 ppm indicating the problem of lack of solubility as well as providing an additional internal standard. The ^1H NMR spectra of $MeAsH_2BCl_3$ and $MeAsH_2BBr_3$ (see Fig. 3 for $MeAsH_2BBr_3$) surprisingly show relatively sharp triplets, centred around 1.6–2.3 ppm, for the methyl protons as expected for spin–spin coupling with the two protons on arsenic (J_{HH} being 6.1 and 5.5 Hz for the chloride and bromide respectively), comparable to 7.5 Hz in free $MeAsH_2$. Thus there is essentially no evidence of coupling with the boron nucleus. The absence of coupling may be a result of an increase in the quadrupole around boron, which would decrease the likelihood of observing the effect of small splittings. While this may not be the answer to a complex situation, it is at least consistent with the weakest As–B bond leading to the greatest distortion from a pseudotetrahedral environment around boron. The iodide adduct gives a broad singlet similar to that found for the Me_2AsHBX_3 species. The two AsH protons appear as expected as humps in the spectra similar to those observed in Me_2AsHBX_3.

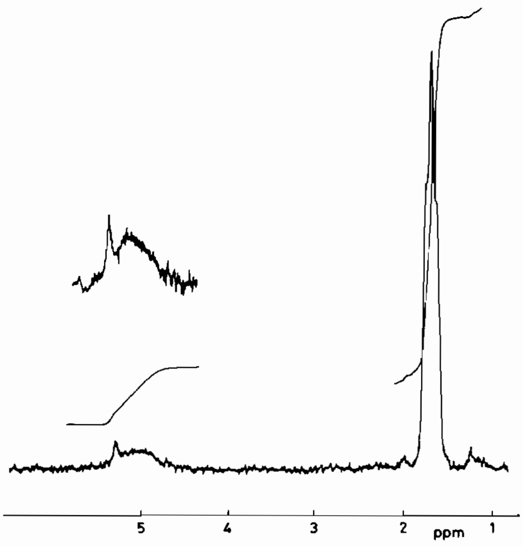

Fig. 2. ^1H NMR spectrum of Me_2AsHBI_3.

Fig. 3. ^1H NMR spectrum of $MeAsH_2BBr_3$.

Previous reports on the chemical shifts of trimethylarsine boron trihalide adducts have produced conflicting results [25, 26]. However, we obtained essentially the same values for the Me_3AsBX_3 species as reported previously [25] and it can be seen from Table I that the trends in the chemical shifts are consistent for the three series of methylarsines. Thus all three series show a down-field shift of the methyl protons upon adduct formation, with the BI_3 adduct being furthest downfield as expected for the established order of Lewis acidity $BI_3 > BBr_3 > BCl_3$. The unusual chemical shifts in the other report [26] have been explained in terms of anisotropic solvent effects. The arsenic protons show the same trends as noted for the methyl protons. It was noticed in comparing the corresponding $Me_nPH_{3-n}BX_3$ series that the complexation shift for the phosphorus protons was least for the dimethylphosphine and greatest for phosphine despite the fact that the latter is claimed to be the weaker Lewis base. The same trend is evident in these

TABLE I. ^{1}H NMR Chemical Shifts for $Me_nAsH_{3-n}BX_3$ (n = 1, 2, 3; X = Cl, Br, I)$^{a, b, c}$

Compound	δMe	δAsH
Me_3As	0.95	
Me_3AsBCl_3	1.50 (0.55)	
Me_3AsBBr_3	1.60 (0.65)	
Me_3AsBI_3	1.69 (0.74)	
Me_2AsH	0.97	2.39
$Me_2AsHBCl_3$	1.63 (0.66)	4.61 (2.22) [2.08]
$Me_2AsHBBr_3$	1.76 (0.79)	5.00 (2.61) [2.28]
Me_2AsHBI_3	1.83 (0.86)	5.10 (2.71) [2.33]
$MeAsH_2$	0.975	1.46
$MeAsH_2BCl_3$	1.65 (0.67)	6.13 (4.67) [2.66]
$MeAsH_2BBr_3$	2.30 (1.32)	6.83 (5.37) [2.96]
$MeAsH_2BI_3$	2.38 (1.40)	6.90 (5.44) [3.56]

[a] All spectra recorded in CD_2Cl_2 solutions. Chemical shifts (ppm) are downfield from external TMS. [b] Complexation chemical shifts, where Δδ = δ (adduct) – δ (free base), are given in curved brackets ( ). [c] Δδ values for Me_2PH and $MePH_2$ adducts taken from ref. 18 are shown in square brackets [ ].

arsine series. There is probably no simple explanation although it could be related to the fact that the bond angle changes around P or As are probably greatest for the weaker Lewis bases as they have to undergo the largest rearrangement on complexation. Nevertheless it is a matter of fact that the average complexation shifts for δH_P or δH_{As} for the DBX_3 series follows the inverse order of that expected for their relative Lewis basicity $MeAsH_2(5.16) < PH_3(4.57) < MePH_2(3.06) < Me_2AsH(2.51) < Me_2PH(2.23)$. For the methyl protons the order is the same $MeAsH_2(1.13) < Me_2AsH(0.77) < Me_3As(0.69)$.

^{11}B NMR Spectra

All observed and calculated ^{11}B chemical shifts and the mean complexation shifts $\Delta\delta^{11}$B along with reported shifts for the free boron trihalides [37–40] are listed in Table II. Figure 4 displays the changes in the ^{11}B chemical shifts across the series BCl_3, BBr_3 and BI_3. Typical ^{11}B NMR spectra for the $MeAsH_2/BCl_3/BBr_3$, $Me_2AsH/BBr_3/BI_3$, $Me_3As/BCl_3/BI_3$, and $Me_3As/BCl_3/BBr_3/BI_3$ systems are shown in Figs. 5, 6, 7 and 8 respectively.

The only ^{11}B chemical shift data available in the literature for arsine adducts [29] are those of Me_3AsBBr_3 and Me_3AsBI_3 at –16.4 and –88.1 ppm respectively from external Et_2OBF_3. Our results agree with that for Me_3AsBBr_3 but not with Me_3AsBI_3. It

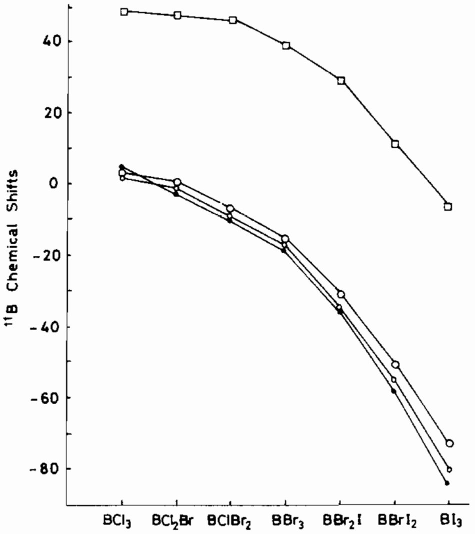

Fig. 4. Changes in ^{11}B chemical shifts across the series BCl_nBr_{3-n} and BBr_nI_{3-n} (n = 1, 2, 3) for the $MeAsH_2$, Me_2AsH, and Me_3As adducts and free boron halides.

TABLE II. ^{11}B Chemical Shifts of Unmixed and Mixed Boron Trihalide Adducts of Me_nAsH_{3-n} (n = 1, 2, 3)^{a}

	Free boron trihalide	$MeAsH_2$^{b}	Me_2AsH	Me_3As	$\overline{\Delta\delta}\,^{11}B^{c}$
BCl_3	47.61 (47.66)	4.62	4.03	4.51	43.22
BCl_2Br	46.36 (46.04)	–1.80 [–1.12]	–1.62 [–1.17]	–1.09 [–0.21]	47.86
$BClBr_2$	43.74 (43.58)	–9.12 [–8.53]	–8.52 [–8.03]	–7.46 [–6.59]	52.10
BCl_2I	37.49 (37.00)	–15.49 [–16.43]	–15.60 [–15.18]	–13.76 [–13.18]	52.44
BBr_3	39.99 (39.90)	–17.63	–16.56	–14.66	56.23
BClBrI	33.26 (32.80)	–25.31 [–25.52]	–24.17 [–23.72]	–22.10 [–21.24]	57.08
BBr_2I	28.00 (27.70)	–36.09 [–36.28]	–33.82 [–33.93]	–31.33 [–30.97]	61.74
$BClI_2$	19.57 (19.00)	–44.78 [–45.91]	–42.30 [–42.81]	–39.84 [–39.29]	61.87
$BBrI_2$	12.79 (12.50)	–57.82 [–58.35]	–54.54 [–54.70]	–51.03 [–50.70]	67.25
BI_3	–6.74 (–6.20)	–83.83	–78.87	–73.83	72.11

[a] Spectra recorded in CD_2Cl_2 relative to external Et_2OBF_3 and reported relative to Me_2OBF_3 by adding 0.70 ppm, positive shifts refer to low field. (#) contain literature values from references 37–40. [#] contain calculated ^{11}B chemical shifts from pairwise parameters of Table III. [b] Recorded at –20 °C to minimize decomposition. [c] Mean complexation chemical shift $\overline{\Delta\delta}\,^{11}B = \left[\frac{\Sigma\delta\,^{11}B(\text{adduct}) - \delta\,^{11}B\,(\text{free acid})}{3}\right]$.

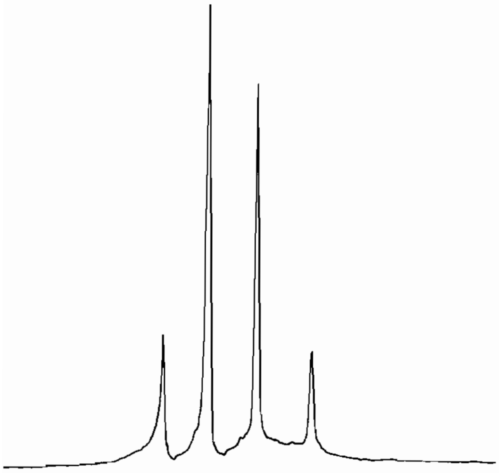

Fig. 5. The ^{11}B NMR spectrum of $MeAsH_2/BCl_3/BBr_3$ system.

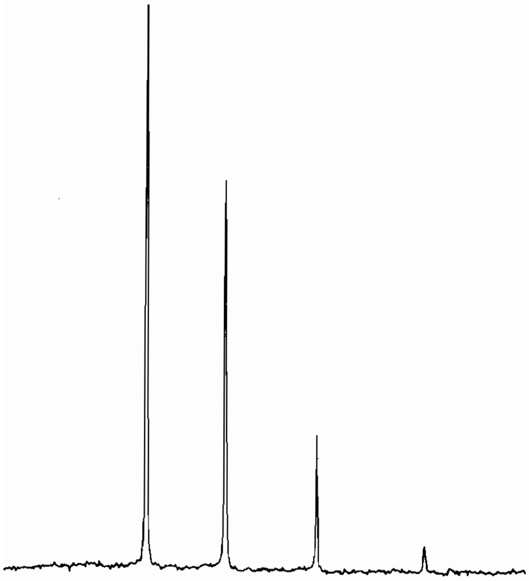

Fig. 6. The ^{11}B NMR spectrum of Me_2AsH/BBr_3BI_3 system.

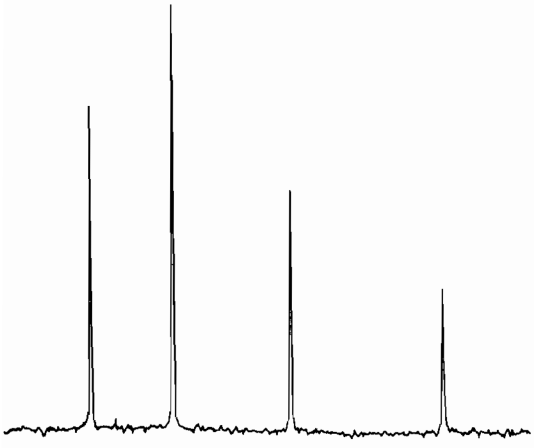

Fig. 7. The ^{11}B NMR spectrum of $Me_3As/BCl_3/BI_3$ system.

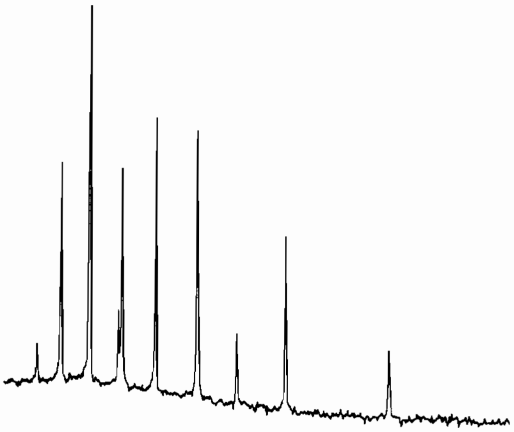

Fig. 8. The ^{11}B NMR spectrum of $Me_3As/BCl_3/BBr_3/BI_3$ system.

TABLE III. Pairwise Additivity Parameters for ^{11}B Chemical Shifts[a]

	η
Cl–Cl	1.16
Br–Br	−4.07
I–I	−21.41
Cl–Br	−0.62
Cl–I	−5.91
Br–I	−11.04
$MeAsH_2$–Cl	0.38
$MeAsH_2$–Br	−1.8
$MeAsH_2$–I	−6.53
Me_2AsH–Cl	0.18
Me_2AsH–Br	−1.45
Me_2AsH–I	−4.88
Me_3As–Cl	0.34
Me_3As–Br	−0.81
Me_3As–I	−3.2

[a] Relative to Me_2OBF_3, halogen–halogen parameters from ref. 16, donor–halogen parameters were calculated as explained in the 'Experimental', section (F).

should be noted that the Me_3AsBI_3 compound was found to decompose in chloroform [24] depositing a red–brown precipitate believed to be a mixture of $[Me_2AsI_2]^+I^-$ and $[Me_3AsI]^+I_3^-$ [41, 42]. All ^{11}B NMR spectra were recorded in CD_2Cl_2 solutions from which good quality Me_3AsBX_3 crystals were grown thus indicating the reliability of results obtained in this investigation.

As expected, the increased shielding of the boron atom in the adducts is characterized by an upfield trend in the chemical shift. The mean shift difference $\Delta\delta^{11}B$ increases in the same accepted order of Lewis acidity: $BI_3 > BBr_3 > BCl_3$. The $\Delta\delta^{11}B$ values of 72.11, 56.27 and 43.22 agree with those obtained for methylated phosphine adducts [18] which are 73.9, 56.9 and 44.3 for the BI_3, BBr_3 and BCl_3

adducts respectively. The compounds are listed in Table II so that the order reflects increasing Lewis acidity down the table from BCl_3 to BI_3. The order is essentially that reported for $MePH_2BXY_2$ species [18].

In Fig. 4 the trends are similar to those observed for Me_2S and Me_3N adducts [43]. The divergence at $MeAsH_2BCl_3$ may not be significant because this is the adduct which is most likely to have partially decomposed. However, it is notable that a similar divergence was also observed for the weakest adducts (Me_2SBF_3 and Me_3NBF_3) in the related systems. As with the proton shifts and as noted for other systems [17, 18, 43, 44] the total shift is greatest for the weakest Lewis base.

The chemical shifts of nuclei other than protons have been found to undergo pairwise additivity with respect to the substituent groups [45]. Miller and Hartman [13, 16] have shown this to be true for ^{11}B, ^{15}N and ^{19}F chemical shifts for several boron trihalide adducts where the donor atom was oxygen, nitrogen, sulfur or phosphorus. It can be seen from Table II that these arsine adducts behave in a similar manner in terms of their ^{11}B chemical shifts. There is very good agreement between observed and calculated chemical shifts. The poorest fit is obtained when two chlorine atoms are involved, an observation which was also noted for the Me_3N adducts when two of the halogens were either fluorine or chlorine [16].

Acknowledgement

We wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support.

References

1 (a) J. M. Chehayber and J. E. Drake, *Spectrochim. Acta, Part A:, 41,* 1205 (1985); (b) A. G. Murray and A. J. Park, *J. Organomet. Chem., 5,* 218 (1966).

2 A. Derek, H. Clague and A. Danti, *Spectrochim. Acta, Part A:, 23,* 2359 (1967).

3 J. R. Blackborow, *J. Chem. Soc., Dalton Trans.,* 2139 (1973).

4 G. E. Ryschkewitsch and W. J. Rademaker, *J. Magn. Reson., 1,* 584 (1969).

5 G. E. Ryschkewitsch and R. C. Cowley, *J. Am. Chem. Soc., 92,* 745 (1970).

6 P. H. Clippard and R. C. Taylor, *Inorg. Chem., 8,* 2802 (1969).

7 J. Fogelman and J. M. Miller, *Can. J. Chem., 50,* 1262 (1972).

8 J. M. Miller and M. Onyszchuk, *Can. J. Chem., 42,* 1518 (1964).

9 J. M. Miller and M. Onyszchuk, *Can. J. Chem., 44,* 899 (1966).

10 C. W. Heitsch, *Inorg. Chem., 4,* 1019 (1965).

11 J. S. Hartman and J. M. Miller, *Inorg. Nucl. Chem. Lett., 5,* 831 (1969).

12 B. Benton-Jones, M. E. A. Davidson, J. S. Hartman, J. J. Klassen and J. M. Miller, *J. Chem. Soc., Dalton Trans.,* 2603 (1972).

13 J. S. Hartman and J. M. Miller, *Inorg. Chem., 13,* 1467 (1974).

14 J. M. Miller and T. R. B. Jones, *Inorg. Chem., 15,* 284 (1976).

15 B. W. Benton and J. M. Miller, *Can. J. Chem., 52,* 2866 (1974).

16 J. M. Miller, *Inorg. Chem., 22,* 2384 (1983).

17 J. E. Drake and B. Rapp, *J. Chem. Soc., Dalton Trans.,* 2341 (1972).

18 B. Rapp and J. E. Drake, *Inorg. Chem., 12,* 2868 (1973).

19 J. E. Drake and B. Rapp, *J. Inorg. Nucl. Chem., 36,* 2613 (1974).

20 A. H. Cowley and M. C. Damasco, *J. Am. Chem. Soc., 93,* 6815 (1971).

21 R. W. Rudolph and C. W. Shultz, *J. Am. Chem. Soc., 93,* 6821 (1971).

22 A. H. Cowley and J. L. Mills, *J. Am. Chem. Soc., 91,* 2911 (1969).

23 J. M. Van Paasschen and R. A. Geanangel, *Inorg. Chem., 17,* 3302 (1978).

24 M. L. Denniston and D. R. Martin, *J. Inorg. Nucl. Chem., 36,* 2175 (1974).

25 J. E. Drake, L. N. Khasrou and Abdul Majid, *Can. J. Chem., 59,* 2417 (1981).

26 D. C. Mente and J. L. Mills, *Inorg. Chem., 14,* 1862 (1975).

27 J. E. Drake, J. L. Hencher and B. Rapp, *J. Chem. Soc., Dalton Trans.,* 595 (1974).

28 W. H. Dehn, *Am. Chem. J., 40,* 88 (1908); *Chem. Abstr.,* 2: 2793 (1908).

29 R. C. Cookson and F. G. Mann, *J. Chem. Soc.,* 67 (1949).

30 F. Hewitt and A. K. Holliday, *J. Chem. Soc.,* 530 (1953).

31 G. M. Phillips, J. S. Hunter and L. E. Sutton, *J. Chem. Soc.,* 146 (1945).

32 Y. Gushikem and F. Watari, *J. Chem. Soc., Dalton Trans.,* 2016 (1980).

33 M. L. Denniston and D. R. Martin, *J. Inorg. Nucl. Chem., 36,* 1461 (1974).

34 L. N. Khasrou, *Ph.D. Thesis,* University of Windsor, 1980.

35 F. G. A. Stone and A. B. Burg, *J. Am. Chem. Soc., 76,* 386 (1954).

36 G. Herzberg, 'Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules', Van Nostrand, Princeton, N. J., 1967, p. 62.

37 P. N. Gates, E. F. Mooney and D. C. Smith, *J. Chem. Soc.,* 3511 (1964).

38 M. F. Lappert, M. R. Litzow, J. B. Pedley, T. R. Spalding and H. Noth, *J. Chem. Soc. A:,* 383 (1971).

39 M. F. Lappert, M. R. Litzow, J. B. Pedley and A. Tweedale, *J. Chem. Soc. A:,* 2426 (1971).

40 E. Muylle, G. P. Van der Kelen and E. G. Claeys, *Spectrochim. Acta, Part A:, 32,* 1149 (1976).

41 G. S. Harris, *Proc. Chem. Soc.,* 65 (1961).

42 R. A. Zngaro and E. A. Myers, *Inorg. Chem., 1,* 771 (1962).

43 M. J. Bula and J. S. Hartman, *J. Chem. Soc., Dalton Trans.,* 1047 (1973).

44 B. Rapp, *Ph.D. Thesis,* University of Windsor, 1973.

45 T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys., 46,* 1830 (1967).