Dimethylboric anhydride: a convenient preparation and full characterization

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Dimethylboric anhydride, $(CH_3)_2BOB(CH_3)_2$, has been prepared by limited hydrolysis of dimethylboron chloride and complete characterization has been carried out. The Lewis acid character of boron and the donor strength of oxygen have been studied using tensimetric and nuclear magnetic resonance techniques.

Evidence for boron–oxygen π-bonding obtained from complex formation studies, using trimethylboron as a reference acid, is presented and discussed. The reduced acidity of the boron atoms, in comparison with trimethylboron, is discussed in terms of boron–oxygen π-bonding.

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Introduction

Dimethylboric anhydride, $(CH_3)_2BOB(CH_3)_2$, contains two electron-accepting atoms bridged by one electron-donating atom, and could conceivably behave as either a Lewis acid or a Lewis base. In the former case, both mono- and di-adducts might be possible. Although this interesting compound was first prepared by McKennon in 1936 (1), very few references to it are found in the literature (2–4).

In view of the interesting Lewis amphoteric character of the compound, some studies of complex formation have also been carried out using tensimetric (5) and nuclear magnetic resonance (n.m.r.) techniques.

Experimental

A. Apparatus

Preparation and purification of the compounds were carried out in a standard high vacuum apparatus to which a gas–liquid chromatography system was attached. The gas–liquid chromatography system comprised a Gow–Mac stainless steel gas-density thermistor detector Model #140, used in conjunction with a Gow–Mac power supply #9999. The sample introduction system, connected to the high vacuum apparatus by a Teflon valve, was operated by a pair of 3-way valves (Hoke, C-415K). Nitrogen carrier gas was rerouted through the introduction system by simultaneously closing a bypass 2-way valve (Hoke, C-413K) and opening both 3-way valves. Good separation characteristics were found for a 10-ft, 7-mm inner diameter column, packed with 30–60 mesh celite and containing 20% by weight of Fisher paraffin oil. Purified sample was collected in two U-traps lightly packed with glass wool, through which the effluent gases could be directed and frozen out at liquid nitrogen temperatures.

The mass spectrum was obtained using an Associated Electrical Industries (A.E.I.) MS-9 spectrometer. The infrared spectrum was obtained using a Perkin–Elmer Model 421 spectrometer in conjunction with a 5 cm gas cell with potassium bromide windows. Nuclear magnetic resonance spectra were run on a Varian A-60 spectrometer; sample tubes were flamed lightly under vacuum, and were sealed off after the components of the solution had been distilled in from the vacuum system.

B. Materials

Dimethylboron chloride was prepared by reacting equimolar quantities of boron trichloride (Matheson of Canada, Ltd., C.P. grade) with tetramethyltin (M & T Chemicals, Inc.) in a stainless steel Hoke cylinder at 140 °C for 12 h. The use of alkyltin compounds for the preparation of alkylboron halides has been described in the literature (6, 7). The reaction conditions employed in this study gave an improved yield (approximately 95% based on boron trichloride). The other major product was dimethyltin dichloride. The crude dimethylboron chloride was purified chromatographically to remove small amounts of hydrogen chloride, trimethylboron, methylboron dichloride, and boron trichloride. Dimethylboric anhydride was prepared by reacting appropriate quantities of dimethylboron chloride and water in a Pyrex vessel. Although the reaction is rapid at room temperature, repeated condensation and re-warming facilitates complete mixing of the two phases. Essentially quantitative yields of HCl and crude dimethylboric anhydride are obtained. Purification is best carried out by initial trap-to-trap distillation through a −78.5 °C trap to remove hydrogen chloride, followed by sublimation of the material from a cold trap (allowed to warm from −196 °C to room temperature by simply removing the liquid nitrogen) into a −78.5 °C trap, through which traces of more volatile materials readily pass. After purification, the yields of pure dimethylboric anhydride were approximately 85%.

Trimethylboron was prepared by the reaction of 2 moles of boron trichloride with 3 moles of tetramethyltin. Chromatography indicated yields greater than 95% in all experiments. Trimethylphosphine was prepared by the Grignard route using dibutylether solvent, and purified through its silver iodide complex (8). Both of these compounds, as well as commercially available trimethylamine, dimethylether, and dimethylsulfide, were purified chromatographically. As an indication of purity of the aforementioned compounds, the vapor pressures at specific temperatures are listed, along with the literature values: dimethylboron chloride, 635 mm at 0 °C (lit. (9), 634 mm at 0 °C); trimethylboron, 85.5 mm at −63.5 °C (lit. (10), 85.6 mm at −63.5 °C); trimethylphosphine, 158 mm at 0 °C (lit. (8), 158.5 mm at 0 °C); trimethylamine, 681 mm at 0 °C (lit. (11), 681.7 mm at 0 °C); dimethylether, 33.8 mm at −78. 5 °C (lit. (12), 34.4 mm at −78.5 °C); and dimethylsulfide, 166.8 mm at 0 °C (lit. (13), 167 mm at 0 °C).

Results

A. Characterization

Dimethylboric anhydride as prepared and purified above was found to have a molecular weight of 97.5 using the gas density method (calculated 97.72). The vapor pressure of the liquid was measured at several temperatures between −20.2 and +10.0 °C, with results as given in Table I. Values calculated using the least square equation $\log P_{\mathrm{liq}} = 8.459 - 1718/T$ are also given. From the equation, the heat of vaporization is calculated as 7.86 kcal, the boiling point +34.8 °C, and the Trouton constant 25.5. The melting point is −21.2 °C using the magnetic plunger of Stock (14). The vapor pressure of the solid material was determined at three temperatures as shown in Table I. These values determine the equation $\log P_{\mathrm{solid}} = 13.63 - 3028/T$, from which the heat of sublimation is calculated to be 13.86 kcal.

TABLE I

Vapor pressure data for dimethylboric anhydride

Temperature (°C)	Observed pressure (mm)	Calculated pressure (mm)
Liquid		
+10.0	244.0	247.2
+ 8.0	224.6	223.9
+ 5.5	195.9	197.2
0.0	150.0	148.3
− 7.0	102.4	101.2
−15.0	63.2	63.8
−20.2	46.3	46.6
Solid		
−22.9	33.6	34.2
−35.0	8.0	8.3
−45.3	2.3	2.2

Mass spectral data are reported in Table II. While the molecular ion is too weak for a mass determination at high resolution, the fragment at 83 *m/e* was shown in this way to be $C_3H_9B_2{}^{11}O$. The observed and calculated masses differ by less than 1 p.p.m.

Infrared data are reported in Table III, where tentative assignments have been made as discussed later.

The ambient temperature proton n.m.r. spectrum of dimethylboric anhydride in CS_2, $CHCl_3$, $CFCl_3$, and C_7D_{14} consisted of a single broad resonance (half-width: 3.5 c.p.s.) 0.43 p.p.m. downfield from tetramethylsilane (TMS). Varying the concentration between 2 and 20 mole % did not affect the chemical shift.

TABLE II

Mass spectrum of dimethylboric anhydride[a]

m/e	Ion	$I(\%)^b$	*m/e*	Ion	$I(\%)^b$
10	B^{10}	0.3	40	$C_2H_6B^{10}$	27.0
11	B^{11}	1.1	41	$C_2H_6B^{11}$	85.0
13	CH	1.3	42	$CH_4B^{10}O$	31.3
15	CH_3	5.8	43[c]	$CH_4B^{11}O$	100
25	CH_2B^{11}	1.1	44	$C^{13}H_4B^{11}O$	1.6
26	C_2H_2, $B^{10}O$	1.8	51	$CH_3B^{10}B^{10}O$	0.3
26.5[e]	$CH_3B^{11}B^{11}O$	0.1	52	$CH_3B^{10}B^{11}O$	0.5
27	$B^{10}OH$, $B^{11}O$	2.8	53	$CH_3B^{11}B^{11}O$	1.1
28	$B^{11}OH$	3.3	57	$C_2H_7B^{10}O$	0.4
29	C_2H_5	4.0	58	$C_2H_7B^{11}O$	1.6
33[e]	$C_2H_6B^{10}B^{10}O$	1.3	81	$C_3H_9B^{10}B^{10}O$	3.0
33.5[e]	$C_2H_6B^{10}B^{11}O$	4.0	82	$C_3H_9B^{10}B^{11}O$	21.3
34[e]	$C_2H_6B^{11}B^{11}O$	4.2	83[d]	$C_3H_9B^{11}B^{11}O$	42.3
34.5[e]	$C^{13}CH_6B^{11}B^{11}O$	0.1	84	$C^{13}C_2H_9B^{11}B^{11}O$	1.5
36	$C_2H_2B^{10}$	1.2	96	$C_4H_{12}B^{10}B^{10}O$	≃0
37	$C_2H_2B^{11}$	3.8	97	$C_4H_{12}B^{10}B^{11}O$	≃0
38	$CB^{10}O$	2.5	98	$C_4H_{12}B^{10}B^{11}O$	0.1
39	$CB^{11}O$	8.3			

[a] Peaks of less than 1 % of the base peak are not listed unless considered pertinent.
[b] % intensity relative to the base peak.
[c] Exact mass calculated, 43.0355; found, 43.0351.
[d] Exact mass calculated, 83.0839; found, 83.0840.
[e] Doubly charged ion.

TABLE III

Vibrational frequencies and suggested assignments for dimethylboric anhydride[a]

Frequencies (cm^{-1})	Suggested assignments
2990 m *ca* 2920 sh	C—H sym. and asym.
1405 vsb[b]	CH_3 def. asym. B—O asym. B—O sym.
1320 vs	CH_3 def. sym.
1165 sh	CH_3 rock
1135 s	B—C asym.
940 m	CH_3 rock
730 w	B—C sym.

[a]Abbreviations: w = weak, m = medium, s = strong, v = very, b = broad, sh = shoulder; sym. = symmetric, asym. = asymmetric.
Spectra taken in the gas phase at 4 mm and 16 mm pressure in a 5 cm cell.
[b]Approximate half-width at 16 mm is 200 cm^{-1}.

B. Complex Formation

Trimethylamine – Dimethylboric Anhydride

The saturation pressures obtained from a 4.5 cc[1] sample of dimethylboric anhydride treated with a carefully matched volume of trimethylamine are recorded in Table IV. Values are substantially less than calculated for an ideal solution, presumably the result of complex formation by the equilibrium

$$(CH_3)_2BOB(CH_3)_2\cdot N(CH_3)_3 \rightleftarrows (CH_3)_2BOB(CH_3)_2 + N(CH_3)_3$$

The saturation pressures in Table IV correspond to the equation $\log P_{mm} = 10.43 - 2816/T$, implying a "boiling point" of 99.5 °C and a Trouton constant of 34.6.

TABLE IV

Saturation pressures of trimethylamine – dimethylboric anhydride

Temperature (°C)	Observed pressure (mm)	Calculated pressure[a] (mm)
24.6	9.6	9.5
28.3	12.4	12.5
34.6	19.2	19.4
36.3	21.4	21.7
42.5	32.0	32.8
44.8	37.7	38.0
54.3	69.3	68.9
58.3	87.4	87.4

[a]Calculated from $\log P_{mm} = 10.43 - 28.6/T$.

The 1:1 adduct (4.5 cc) was treated with an additional 4.5 cc of trimethylamine. After standing for 15 h at −78.5 °C, 4.5 cc of trimethylamine were recovered by pumping through a −196 °C trap, while the sample remained at −78.5 °C, indicating that a 2:1 complex, if it does exist at this temperature, is very weak.

The above equilibrium was studied in the gas phase using a sample prepared by treating 2.7 cc of dimethylboric anhydride with a matched volume of trimethylamine. In the temperature range 47.0 to 72.0 °C, dissociation ranged from 72 to 85%. The variation of pressure with temperature and other data are recorded in Table V. A check of the dissociation pressures as the sample was cooled showed that no decomposition had taken place. Variation of the equilibrium constant with temperature is represented by the equation $\log K_p(\text{atm}) = 5.007 - 2073/T$. Therefore, for the above reaction, the enthalpy and entropy of dissociation are: $\Delta H^0 = 9.5$ kcal and $\Delta S^0 = +22.9$ e.u.

Trimethylphosphine – Dimethylboric Anhydride

The addition compound was formed in the tensimeter by bringing together 18.8 cc of dimethylboric anhydride and a matched volume of trimethylphosphine. In the gas phase at room temperature, the complex was found to be 98% dissociated. The saturation pressures of the liquid reported in Table VI determine the equation $\log P_{mm} = 9.077 - 2019/T$, from which one calculates a "boiling point" of 52.6 °C and the Trouton constant as 28.4.

Dimethylether – Dimethylboric Anhydride

Dimethylether was treated with a matched volume of dimethylboric anhydride. The volumes in the gas phase at room temperature were found to be additive. Furthermore when the mixture was cooled to −78.5 °C the pressure above the liquid was slightly greater (6%) than that calculated using Raoult's law. It may be concluded that an adduct does not form down to −78.5 °C.

Dimethylsulfide – Dimethylboric Anhydride

Dimethylsulfide was treated with a matched volume of dimethylboric anhydride. The volumes in the gas phase at room temperature were found to be additive. At temperatures below −45.2 °C, the pressures observed were only 10% below those expected for pure dimethylsulfide. This presumably indicates some degree of insolubility of dimethylboric anhydride in dimethylsulfide at

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[1] The abbreviation cc in this paper refers to gas volumes at standard temperature and pressure. Pressures were measured using a cathetometer reading to 0.01 mm and errors in the calculated volumes are considered to be about 1%.

TABLE V

Gas phase dissociation trimethylamine – dimethylboric anhydride

Temperature (°C)	Observed P_{mm}	Calculated $P_{mm}{}^{a}$	α	$K_p{}^{b}$ (atm)	Calculated $K_p{}^{c}$ (atm)
47.0	25.10	14.62	0.717	0.0330	0.0341
50.0	25.57	14.75	0.733	0.0390	0.0392
53.0	26.08	14.89	0.751	0.0444	0.0449
55.0	26.38	14.98	0.761	0.0478	0.0491
57.0	26.84	15.07	0.781	0.0551	0.0536
60.0	27.22	15.21	0.789	0.0592	0.0611
63.0	27.67	15.35	0.803	0.0659	0.0693
65.0	28.08	15.44	0.819	0.0750	0.0755
67.0	28.47	15.53	0.833	0.0849	0.0820
70.0	28.88	15.67	0.843	0.0934	0.0927
72.0	29.17	15.76	0.851	0.101	0.100

[a] Calculated pressure for no dissociation.
[b] Calculated from observed data.
[c] Calculated from $\log K_p = 5.007 - 2073/T$.

TABLE VI

Saturation pressures of trimethylphosphine–dimethylboric anhydride

Temperature (°C)	Observed P_{mm}	Calculated $P_{mm}{}^{a}$
−15.0	18.1	18.1
−10.0	25.7	25.5
− 6.0	33.2	33.2
− 4.0	36.4	37.8
0.0	48.6	48.6
4.0	61.1	62.2
5.0	65.8	66.0
7.4	75.4	76.1
10.0	89.6	88.7
15.0	119.9	118.9
20.0	156.5	155.2

[a] Calculated from $\log P_{mm} = 9.077 - 2019/T$.

these temperatures and it may be concluded that a complex is not formed.

Trimethylboron – Dimethylboric Anhydride

A 49.6 cc sample of trimethylboron was treated with an equivalent amount of dimethylboric anhydride in the tensimeter. Below −78.5 °C, the observed pressures were within 5% of those expected for pure trimethylboron. These data would suggest that dimethylboric anhydride is quite insoluble in trimethylboron at these temperatures and it may be concluded that a complex is not formed.

Dimethylboron Chloride – Dimethylboric Anhydride

A 24.1 cc sample of dimethylboron chloride was treated with a matching volume of dimethylboric anhydride in the tensimeter. After standing 6 h at −78.5 °C, the observed pressure was 7.7 mm, essentially the same as that of pure dimethylboron chloride at −78.5 °C. We conclude that no complex is formed and that dimethylboric anhydride is insoluble in dimethylboron chloride in this temperature region.

Nuclear Magnetic Resonance Studies of Complexes

Room temperature n.m.r. data are listed in Table VII. Chemical shifts of the protons on dimethylboric anhydride show shifts to high field when complexed to a Lewis base, while the Lewis base protons are shifted to lower field. Comparing this data to the tensimetric data shows the magnitude of the chemical shift increases as the strength of the complex increases,

TABLE VII

60 Mc n.m.r. chemical shifts of some acid–base systems

	Proton chemical shifts[a]	
System	Me_4B_2O	Other
Me_4B_2O	0.43	
Me_3N		2.23
$Me_4B_2O{:}NMe_3$	0.03	2.45
Me_3P		1.02[b]
$Me_4B_2O{:}Me_3P$	0.38	1.13[c]
Me_2O		3.30
$Me_4B_2O{:}Me_2O$	0.43	3.30
Me_2S		2.12
$Me_4B_2O{:}Me_2S$	0.43	2.12
Me_3B		0.77
$Me_4B_2O{:}Me_3B$	0.43	0.77
Me_2BCl		0.97
$Me_4B_2O{:}Me_2BCl$	0.62[d]	0.62[d]

[a] In p.p.m. relative to TMS. All samples 10% in chloroform.
[b] Doublet $J_{P-C-H} = 8.0$ c.p.s.
[c] Doublet $J_{P-C-H} = 6.7$ c.p.s.
[d] Single peak indicating rapid exchange.

in agreement with work done by other workers (15–17). The single resonance observed for the dimethylboron chloride – dimethylboric anhydride system will be discussed in the next section.

Discussion

The original synthesis of dimethylboric anhydride involved dehydration of dimethylboric acid using phosphorus pentoxide (1):

$$2(CH_3)_2BOH + P_2O_5 \rightarrow 2HPO_3 + (CH_3)_2BOB(CH_3)_2$$

In our hands, this method proved unsatisfactory. The products obtained were highly variable, and a pure compound exhibiting the reported vapor pressure of 118 mm at 0 °C (1) could not be isolated. We were thus led to seek an alternative route, and report here a convenient, reproducible method involving partial hydrolysis of dimethylboron chloride, which gives rise to easily separable products:

$$2(CH_3)_2BCl + H_2O \rightarrow (CH_3)_2BOB(CH_3)_2 + 2HCl$$

A similar reaction has been used to prepare diphenylboric anhydride (18) and di-*n*-butylboron anhydride (19).

Although an elemental analysis of dimethylboric anhydride was not carried out, the preparative method, the gas density molecular weight, and the accumulated spectroscopic data establish the identity of the compound beyond all doubt.

Mass Spectrum

It is evident from the spectrum that rearrangements are taking place. For example, the base peak at 43 *m*/*e* was shown by its exact mass to be $CH_4B^{11}O$. Only one metastable peak at 20.3 *m*/*e* was observed, corresponding to

$$(CH_3)_2B^{11}OB^{11}(CH_3)^+ \rightarrow (CH_3)_2B^{11+} + (CH_3)B^{11}O$$

Suggested assignments of other peaks are listed in Table II. The presence of only one observable metastable peak, coupled with occurrence of rearrangement, allows little interpretation of the fragmentation pattern. The isotopes of boron simplify identification of boron-containing ions.

The region of 33, 33.5, and 34 *m*/*e* is of some interest. The peak at 33.5 must be due to a doubly charged ion, and $(CH_3)B^{10}OB^{11}(CH_3)^{2+}$ is our assignment. The peak at 34 has a C^{13} isotope peak at 34.5, indicating it is also a doubly charged ion, assigned to be $(CH_3)B^{11}OB^{11}(CH_3)^{2+}$. Any C^{13} isotope peak of the peak at 33 is masked by the 33.5 peak mentioned. The removal of two electrons from a molecule is facilitated by the presence of π-electron density (20). The presence of these peaks, and also a small peak at 26.5 attributed to $CH_3B^{11}B^{11}O^{2+}$, support the evidence for B–O π interaction recently reported for this compound (21).

Infrared Spectrum

The C—H stretching frequencies require no comment. In accord with Lehmann *et al.* (22), who place all B—C asymmetric stretching frequencies in the range from 1116 to 1138 cm^{-1}, we assign the 1135 cm^{-1} absorption to the B—C asymmetric stretch. The B—C symmetric stretch is assigned to the weak absorption at 730 cm^{-1}, following Ulmschneider and Goubeau (23), who have similarly assigned absorptions at 718 and 738 cm^{-1} in dimethylboric acid. From the work of Lehmann *et al.* on trimethylboron (22) and tetramethyldiborane (24), it is clear that the absorptions at 1165 and 940 cm^{-1} may be assigned to CH_3 rocking modes.

There is general agreement that in methylboron compounds the asymmetric methyl deformation occurs in the region of 1450 cm^{-1}, while the symmetric mode occurs in the region 1350–1300 cm^{-1} (25). On this basis, we assign the absorption at 1320 cm^{-1} to the symmetrical methyl deformation, while the band due to asymmetric methyl deformation presumably lies within the very broad absorption centered at 1405 cm^{-1}.

The B—O stretching frequencies are somewhat difficult to assign. Ulmschneider and Goubeau (23) assign a weak shoulder at 1276 cm^{-1} in the spectrum of dimethylboric acid to the B—O stretch. No equivalent exists in the spectrum of the anhydride. Abel *et al.* (26) report two B—O stretching frequencies[2] for diphenylboric anhydride at 1262 and 1378 cm^{-1}. It is conceivable that both symmetric and asymmetric modes of the B—O—B group, as well as the symmetric CH_3 deformation mentioned previously, are contained in the broad band at 1405 cm^{-1}.

Complex Formation

The results of the tensimetric studies provide interesting information about the donor strength

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[2] Diphenylboric anhydride, as synthesized in this laboratory, exhibited a strong absorption at 1262 cm^{-1}, although there was no appreciable absorption at 1378 cm^{-1}.

of the oxygen atom towards acceptor molecules, and the acceptor strength of the boron atoms toward strong Lewis bases, such as trimethylamine. This information, when examined with reference to other acceptor–donor systems, provides some insight into the B—O bond, and the effects of π-bonding in this bond (21).

Examining first the data on oxygen base strength, it is evident that dimethylboric anhydride does not behave as a Lewis base towards trimethylboron. This is not unexpected, since no complex is formed between dimethylether and trimethylboron under equivalent conditions (27). Unfortunately, the boron trihalides, which are stronger Lewis acids, cannot be used since the following cleavage reaction occurs (2):

$$3(CH_3)_2BOB(CH_3)_2 + 2BX_3 \rightarrow 6(CH_3)_2BX + B_2O_3$$

However, if a dimethylboron halide were used, the products would be identical with the reactants:

$$(CH_3)_2BOB(CH_3)_2 + (CH_3)_2B^*Cl \rightleftarrows (CH_3)_2B^*OB(CH_3)_2 + (CH_3)_2BCl$$

In fact, the single resonance observed in the room temperature spectrum of this system (Table VII) is consistent with a rapidly exchanging system of this nature. Dimethylboron chloride, a stronger acceptor than trimethylboron, shows no indication of complex formation, and it may be concluded that the basicity of oxygen in dimethylboric anhydride is rather low.

The results of the study of the Lewis acid characteristics of dimethylboric anhydride show that it is considerably weaker than trimethylboron. The enthalpies of dissociation of $(CH_3)_2BOB(CH_3)_2 \cdot N(CH_3)_3$ and $(CH_3)_3B \cdot N(CH_3)_3$ are 9.5 and 17.62 kcal (28), respectively. The trimethylphosphine adduct of dimethylboric anhydride is completely dissociated in the gas phase, while $(CH_3)_3B \cdot P(CH_3)_3$ is not (29). Finally dimethylsulfide forms a recognizable adduct at −78.5 °C with trimethylboron (27) but not with dimethylboric anhydride.

Nuclear Magnetic Resonance Data

The n.m.r. data support the tensimetric results fully. Tensimetric studies show that only trimethylamine, of the bases studied, was strong enough to form a measurable complex in the gas phase. The large upfield shift of the B–methyl resonance in the 1:1 $Me_4B_2O \cdot NMe_3$ sample, as compared to the B–methyl resonance in the free Me_4B_2O, is consistent with the formation of a strong complex (15). The large downfield shift of the N–methyl resonance in the 1:1 $Me_4B_2O \cdot NMe_3$, as compared to the N–methyl resonance of free NMe_3 is also to be expected (16, 17). The lack of any change of chemical shift for all resonances in the samples involving dimethylether, dimethylsulfide, and trimethylboron indicate little or no complex formation, in accord with the results of the tensimetric studies. In the case of trimethylphosphine the small shifts of the P-methyl and B-methyl resonance are in accord with the weak complexing found in tensimetric work.

It is feasible to discuss these results in terms of the boron–oxygen bond, presuming that two competitive effects are involved. Purely inductive effects would be expected to increase the acceptor strength of the boron atoms relative to trimethylboron, oxygen being more electronegative than CH_3; this effect would also increase the donor strength of the oxygen atom relative to dimethylether, since $B(CH_3)_2$ is more electropositive than CH_3. On the other hand the effect of π-bonding involving oxygen lone pairs and the vacant boron 2p orbitals would be to weaken both the Lewis acidity of boron and the Lewis basicity of oxygen.

Nuclear magnetic resonance studies of hindered rotation in dimethylmethoxyboron and dimethylboric anhydride indicate a significant amount of π-bonding in these compounds (21). It is, therefore, reasonable to attribute the lower Lewis acidity of dimethylboric anhydride to this effect. The lack of evidence for a 2:1 complex between trimethylamine and dimethylboric anhydride is not inconsistent with this interpretation. When one of the two boron atoms is "electronically saturated" due to complexing with trimethylamine, the vacant p orbital is no longer available to an oxygen lone pair. Therefore, the decreased delocalization of oxygen lone-pair electrons should increase the double bond character between oxygen and the remaining uncomplexed boron atom, thereby lowering the Lewis acidity towards excess trimethylamine.

Further studies involving variable temperature n.m.r. techniques which support the above interpretations are in progress and will shortly be completed.

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