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THE INTERCONVERSION OF AQUEOUS BORON SPECIES AND THE INTERACTION OF BORATE WITH DIOLS: A ^{11}B N.M.R. STUDY

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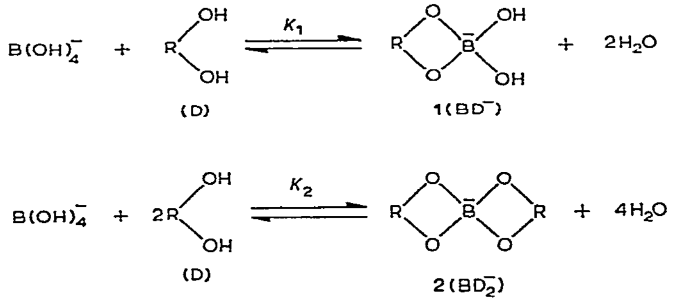
ABSTRACT

^{11}B n.m.r. spectroscopic studies have shown that the interconversion of boric acid and tetrahydroxyborate (borate) anions in aqueous solution is pH dependent. Evidence has also been obtained for the condensation of monomeric species in the pH range 5–11 to give polyborates. The interaction of 1,2-diols with borate anions at pH 12 to form 1:1 and 2:1 anionic complexes has been demonstrated by the existence of discrete ^{11}B resonances for these three anions in the equilibrating systems. The effect of substituents of 1,2-diols on complex formation has been investigated. The difference in chemical shift between borate complexes of 1,2- and 1,3-diols can be used to distinguish 5- and 6-membered ring complexes. Evidence for a 7-membered ring complex in aqueous solution is reported.

INTRODUCTION

The formation of complexes between borate and hydroxy compounds has been examined by detecting the changes in conductivity[1] and pH[2-4] which occur on adding hydroxy compounds to boric acid or borax solutions, and by measuring the

$$\underset{\text{(BH)}}{B(OH)_3} + OH^- \underset{}{\overset{K_a}{\rightleftharpoons}} \underset{(B^-)}{B(OH)_4^-} \qquad 1$$



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electrophoretic mobility[5,6] of hydroxy compounds in borax solutions. Evidence from these studies concerning the structure of the complexes and the concentration of the complexes in solution is largely indirect. Spectroscopic methods offer physical means of examining chemical equilibria and measuring directly the concentration of species in solution. Raman spectroscopy has been used to study borate complex formation[7]. We now report the use of ^{11}B n.m.r. spectroscopy to investigate boron species in aqueous solutions of borate in the presence and absence of simple diols.

The interconversion of boric acid and borate anions, and the interaction of borate with diols may be represented by the equilibria *1–3*.

These equilibria in aqueous solution are rapidly established and reversible[8], and the positions of the equilibria depend upon the pH of the solution and the stereochemistry of the diol.

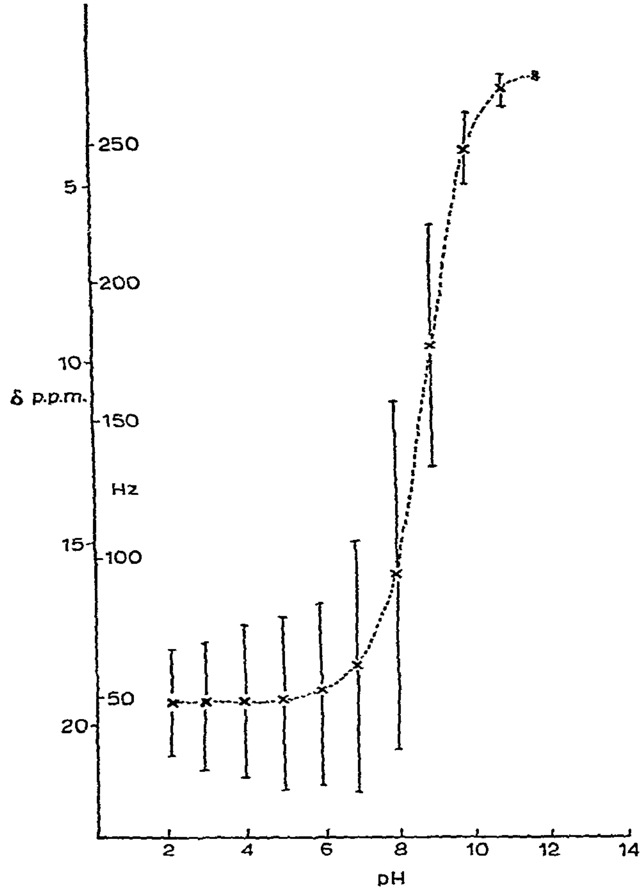

Fig. 1. ^{11}B n.m.r. data at 12.83 MHz of solutions of borax, boric acid, and sodium metaborate (0.8M in borate) at different pH values. The mean chemical shift of the three borates at a given pH is shown by ×, and the line width at half height ($W_{0.5}$) is shown by a vertical bar. Methyl ether–boron trifluoride was used as external reference at δ 0.0.

The equilibrium constants for the reactions can be represented by the following equations:

$$K_a = [B^-]/[HB][OH^-] \quad (4)$$

$$K_1 = [BD^-]/[B^-][D] \quad (5)$$

$$K_2 = [BD_2^-]/[B^-][D]^2$$

The concentration of the boron species can be measured directly from the ^{11}B n.m.r. spectra, and the equilibrium constants can thus be calculated.

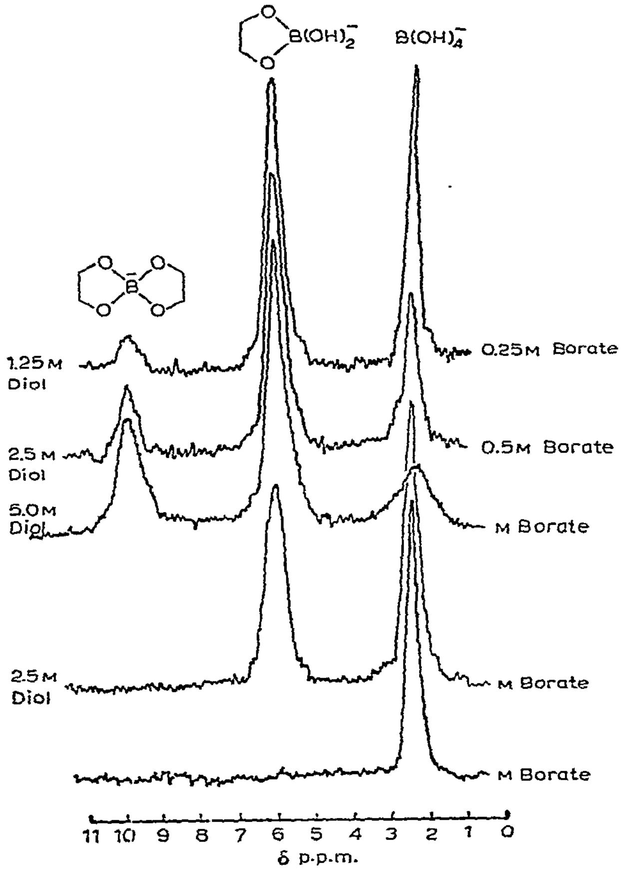

Fig. 2. ^{11}B n.m.r. spectra at 12.83 MHz of ethane-1,2-diol–borax solutions at pH 12, at different diol and borate concentrations, showing the variation of the extent of complex formation with diol and borate concentration. The reference signal of the methyl ether–boron trifluoride complex at δ 0.0 is not shown.

RESULTS AND DISCUSSION

Examination of aqueous borate solutions by ^{11}B n.m.r. spectroscopy

Preliminary investigations showed[9] that the ^{11}B chemical shift of solutions of borax (50 mg/ml, ~0.5M*) was pH dependent due to the rapid equilibration of boric acid with borate ions. There is evidence[10], however, that, in the pH range 5–11, polyborates as well as monomeric boron species exist in solutions of concentrations greater than 0.1M. Two ^{11}B resonances observed for 0.5–2.0M borate solutions of pentaborate salts were attributed to monomeric boron species and a pentaborate species[11,12]. In order to establish the effect of polyborate formation on the n.m.r. spectra of borate solutions, the previous work[9] has been repeated, using a concentration of 0.8M, and extended to cover solutions of sodium metaborate and boric acid.

At a given pH-value, the n.m.r. parameters of solutions of sodium metaborate, borax, and boric acid were the same (Fig. 1). Only one signal was observed for each of these solutions over the pH range 2–12, and the change in chemical shift over this pH range may be ascribed to the variation in relative concentrations of boric acid and borate anions in a rapidly interconverting system[9] (equilibrium *1*). The variation of line-width ($W_{0.5}$, width at half height) with pH for this system, however, indicates the existence of other species.

The n.m.r. signals at δ 2.4 ($W_{0.5}$ 5 Hz) and at δ 19.5 ($W_{0.5}$ 55 Hz) are assigned to the monomeric borate anion and boric acid molecule, respectively. If the reaction occurred exclusively between these two monomeric species, the line-widths of the signals for the solutions in the pH range 4–11 would be expected to have values intermediate between those of the monomeric species because the boric acid–borate ion interconversion is extremely fast[8]. The line-widths of up to ~150 Hz for solutions of intermediate pH-values suggest that rapid interconversion occurs not only between boric acid and borate ions but also between these monomeric species and polyborate ions. The work of Ingri[10], Edwards[13], Dale[14], and more recently of Mesmer[15] has established the structures of the polyborate ions and the dependence of their formation on pH and concentration.

Although the types of polyborate present cannot be directly inferred from the ^{11}B n.m.r. data, there is a definite indication that these species do exist in 0.8M solutions in the pH range 5–11.

^{11}B n.m.r. spectroscopic examination of borate complexing of ethane-1,2-diol and propane-1,3-diol

The diol–borax systems were examined at pH 12 because complex formation is favoured at this pH and the reaction rates proved to be sufficiently low for separate resonances to be observed. In the spectra of ethane-1,2-diol–borax solutions at different molar ratios (Fig. 2), the chemical shift values of the high-field signal corresponds exactly to that of the borate ion in the absence of diol and, on the basis of their

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*Throughout this text, concentrations are expressed as the molarity of monomeric boron species.

increasing intensity with diol stoichiometry, the low-field signals at δ 6.1 and 10.0 are assigned to the 1:1 (**3**) and 2:1 (**4**) anionic complexes, respectively. These results provide direct evidence of the existence of the two types of anionic complexes in solution and, since the relative concentration of each anion can be measured directly, the calculation of equilibrium constants does not involve any approximations (*cf.* Refs. 2–4). Full n.m.r. data are given in Table I, and equilibrium constants calculated from these data are compared with literature values in Table II.

TABLE I

^{11}B N.M.R. SPECTROSCOPIC DATA FOR 1,2-DIOL–BORAX SOLUTIONS AT pH 12

Diol	*Diol–boron ratio*[a]	δ_3[b]	δ_2[b]	δ_1[b]	A_3[c]	A_2[c]	A_1[c]
Ethane-1,2-diol	0.25:1	—	6.0 (11)	2.3 (7)	—	11	89
	1.25:1	9.8	6.1 (14)	2.4 (8)	4	39	57
	2.50:1	10.1 (15)	6.2 (14)	2.5 (14)	13	54	33
	2.50:1*	—	6.1 (12)	2.4 (7)	—	50	50
	5.00:1	10.0 (18)	6.1 (16)	2.4 (15)	24	62	14
	5.00:1*	9.9 (14)	6.0 (14)	2.3 (10)	15	57	28
	5.00:1**	9.8	6.1 (12)	2.3 (8)	7	51	42
	12.5:1	9.9 (28)	6.1 (21)	—	—	—	—
Propane-1,2-diol	0.25:1	—	6.0 (12)	2.3 (5)	—	12	88
	1.25:1	9.5	6.0 (11)	2.3 (6)	16	42	42
	2.50:1	9.8 (21)	6.1 (12)	2.4 (8)	25	52	23
	5.00:1	9.8 (30)	6.0 (14)	2.3	63	35	2
Pinacol	0.25:1	8.0	5.2 (11)	2.4 (6)	7	14	79
	1.25:1	8.2	5.3 (10)	2.3 (6)	30	33	37
	1.88:1	8.1	5.2 (13)	2.4 (7)	44	40	16
	2.50:1	8.0 (45)	5.2 (21)	2.4	80	17	3
Cyclohexane-*cis*-1,2-diol	0.25:1	—	5.8 (12)	2.4 (6)	—	12	88
	0.50:1	—	5.8 (8)	2.5 (6)	—	18	81

[a] The total concentration of borate is M, except in cases marked with * and ** which are 0.5M and 0.25M, respectively. The observing frequency was 12.83 MHz unless otherwise indicated. [b] δ_n, Chemical shift in p.p.m. downfield of $Me_2O{\cdot}BF_3$, and width at half-height ($W_{0.5}$) in Hz shown in brackets in cases where the values were determined. [c] A_n, Relative area of signal at δ_n as % of the total area of the signals.

For solutions of propane-1,3-diol and borax (Fig. 3, Table III) examined at 12.8 MHz, only one additional peak was observed to high field and slightly overlapping with the borate-ion resonance. However, at higher observing frequencies (28.87 MHz), where the chemical shift difference between the resonances is larger relative to the line-widths (Fig. 3), signals which can be assigned to the complexes **5** and **6** were clearly resolved at δ 1.6 and 1.2, respectively. These assignments are consistent with the variations of signal intensities with diol stoichiometry as seen with 1,2-diols. Calculation of K_1 and K_2 (Table II) from these spectra shows that the

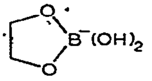
TABLE II

COMPARISON OF PREVIOUSLY PUBLISHED EQUILIBRIUM CONSTANTS (K_1 AND K_2) AND THEIR METHOD OF DETERMINATION WITH VALUES OBTAINED FROM THIS ^{11}B N.M.R. STUDY FOR VARIOUS DIOLS

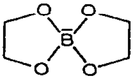
Diol	*Method*	*Temperature (degrees)*	K_1	K_2
Ethane-1,2-diol	pH-Change^4	25	2.15	1.15
	pH-Change^4	35	1.87	0.89
	pH-Change^3	25	1.85	0.1
	^{11}B-n.m.r.	33	1.00	0.1
Propane-1,2-diol	pH-Change^4	25	4.05	3.85
	pH-Change^4	35	3.40	2.36
	pH-Change^3	25	3.10	1.6
	^{11}B-n.m.r.	33	1.8	1.5
Pinacol	pH-Change^4	25	11	216
	pH-Change^4	35	5	88
	^{11}B-n.m.r.	33	3.5	8.5
Cyclohexane-*cis*-1,2-diol	pH-Change^4	35	1	0.3
	^{11}B-n.m.r.	33	1.9	—
Propane-1,3-diol	pH-Change^{16}	25	1.15	—
	^{11}B-n.m.r.	33	1.2	0.05

complexing ability of propane-1,3-diol is comparable to that of ethane-1,2-diol (*cf.* Refs. 3 and 4).

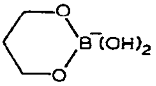
The difference in chemical shift of a boron nucleus in a six-membered ring complex (5 and 6) is 4–9 p.p.m. to high field of that of a nucleus in a five-membered ring complex (3 and 4). This difference was exploited to examine situations in which a five- and/or a six-membered ring complex may be formed, as for example with mixtures of ethane-1,2-diol and propane-1,3-diol in the presence of borate.



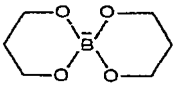
3 (δ 6.0)



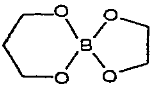
4 (δ 10.0)



5 (δ 1.6)



6 (δ 1.2)



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Spectra of these mixtures (Table IV) show that the existence of five- and six-membered ring complexes can be distinguished by ^{11}B n.m.r. spectroscopy. Under these conditions, the formation of the mixed spirocyclic anion (7) must also be considered.

TABLE III

THE ^{11}B N.M.R. DATA[d] OF 1,3- AND 1,4-DIOLS IN BORAX SOLUTION AT pH 12

Diol	*Diol–boron ratio*^{a}	δ_3^b	δ_2^b	δ_1^b	A_3^c	A_2^c	A_1^c
Propane-1,3-diol	0.25:1	2.4 (6)	—	—	100		
	1.25:1	2.4 (7)	1.75 (9)	—	64	36	—
	2.50:1§	2.4	1.65	1.10	30	64	6
	2.50:1	2.4 (8)	1.80 (10)	—	31	69	
	2.50:1*	2.4 (6)	1.75 (8)	—	43	57	
	5.00:1§	2.4	1.65	1.12	14	75	11
	5.00:1	—	1.85 (10)	—		100	
	5.00:1*	2.4	1.70 (8)	—	24	76	
	5.00:1**	2.3 (7)	1.65 (9)	—	38	62	
	12.50:1	—	1.70 (10)	—		100	
Butane-1,3-diol	1.25:1	2.4 (6)	1.90 (8)	—	42	58	
	2.50:1	2.3 (6)	1.80 (8)	—	24	76	
	5.00:1	—	1.90 (9)	—		100	
8	2.50:1	2.2 (8)	—	—	100		
	5.00:1	2.1 (12)	—	—	100		
	0.50:1†	2.2 (8)	9.8	—	50	50	
	1.25:1†	2.2 (12)	—	—	100		
	2.50:1†	2.2 (11)	—	—	100		
	2.50:1††	2.2 (18)	—	—	100		
Butane-1,4-diol	2.50:1	2.5 (6)	—	—	100		
9	0.25:1	2.3 (6)	3.4	—	75	25	
	1.25:1	2.5 (6)	3.6 (13)	—	48	52	
	5.00:1	2.5	3.5	—	10	90	

[d] The key is the same as in Table I; † and †† indicate that the pH of the solutions was 10.5 and 9.0, respectively; § indicates an observing frequency of 28.87 MHz.

TABLE IV

THE ^{11}B N.M.R. DATA[d] OF MIXTURES OF ETHANE-1,2-DIOL (D_{12}), PROPANE-1,3-DIOL (D_{13}), AND BORATE (B)

Concentration of			δ_4^b	δ_3^b	δ_2^b	δ_1^b	A_4^c	A_3^c	A_2^c	A_1^c
D_{12}	D_{13}	B								
1.25	1.25	1.00	—	6.1 (12)	2.3 (8)	1.8 (10)	—	34	39	27
2.50	2.50	1.00	9.9 (17)	6.0 (17)	2.3	1.7	7	45	10	38
3.75	1.25	1.00	10.2 (16)	6.1 (15)	2.3	1.7	12	62	9	17
1.25	3.75	1.00	—	6.0 (19)	—	1.8 (12)	—	27	—	73
6.25	6.25	1.00	9.8	6.0 (33)	—	1.7 (17)	36	41	—	23

[d] At pH 12 in M borate solution. The key is the same as in Table I.

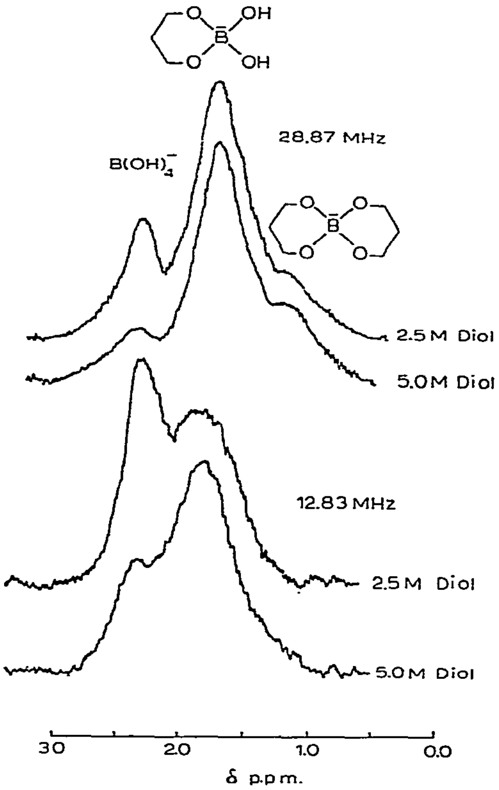


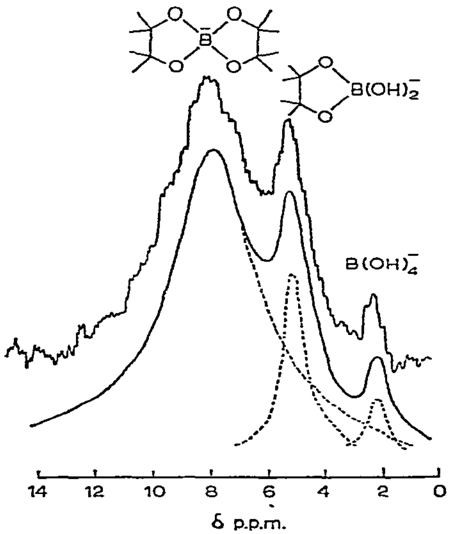
Fig. 3. ^{11}B n.m.r. spectra of two propane-1,3-diol–borax solutions at 12.83 and 28.87 MHz, showing the improved resolution at the higher observing frequency. The borate concentration of all solutions is M and the pH is 12. The reference signal of the methyl ether–boron trifluoride complex at δ 0.0 is not shown.

Because a regular increase in substituents on the boron nucleus has a regular effect on the chemical shift, *i.e.* $\delta_{BD_2^-} - \delta_{BD^-} \approx \delta_{BD^-} - \delta_{B^-}$, the chemical shift of 7 might be expected to be ~3 p.p.m. to low field of that for the uncomplexed borate ion. It will thus overlap with the signal of 3. The spectra of the solutions containing both ethane-1,2-diol and propane-1,3-diol (Table IV) show that the peak at δ 6.0 is of much greater area than expected by summing the peak areas of the spectra of the separate diol solutions. The value of K_1 (2.2) for ethane-1,2-diol calculated from these spectra, assuming that the signal at δ 6.0 is due only to 3, is higher than that calculated in the absence of propane-1,3-diol, *i.e.* 1.0, whereas K_2 is "normal" (0.15). This abnormally high value of K_1 is attributed to the formation of 7 which has a chemical shift near to δ 6.0.

Complexing ability of diols

A. Substituted 1,2-diols. ^{11}B n.m.r. spectra of borax solutions at pH 12 in the presence of propane-1,2-diol and 2,3-dimethylbutane-2,3-diol (pinacol) (Table I) and the equilibrium constants calculated from these data (Table II) support previous rationalisations[16] that increased substitution in 1,2-diols enhances complexing ability. The extent of enhancement, however, is shown to be less than indicated by earlier data[2–4]. Cyclohexane-*cis*-1,2-diol is also a slightly better chelating agent than ethane-1,2-diol. Since the relative order of magnitude of the equilibrium constants calculated from the ^{11}B n.m.r. data for different 1,2-diols shows general agreement with the previously determined values, the earlier rationalisations[16] of factors governing the complexing ability of 1,2-diols remain unaltered. There are two general points in this study which require further comment.

For pinacol–borax solutions and cyclohexane-*cis*-1,2-diol–borax solutions at molar ratios greater than 2.5:1 and 0.5:1 diol–borate, respectively, white crystalline solids were formed at pH 12. The spectrum of pinacol–borax (Fig. 4) shows that, at a ratio of 2.5:1 for diol–borate, most (80%) of the boron exists as the spirocyclic complex. Of the diols examined by Dale[14], only pinacol precipitated as the spirocyclic complex from alkaline solution, and this is considered to be further evidence that the resonance at lowest field arises from the spirocyclic complex. Similarly, Dale[14] found that a precipitate of cyclohexane-*cis*-1,2-diol–borate (1:1) complex was formed, and the ^{11}B n.m.r. spectrum showed that there is only a peak corresponding to the monocyclic complex at a 0.5:1 ratio of diol–borate (Table I).



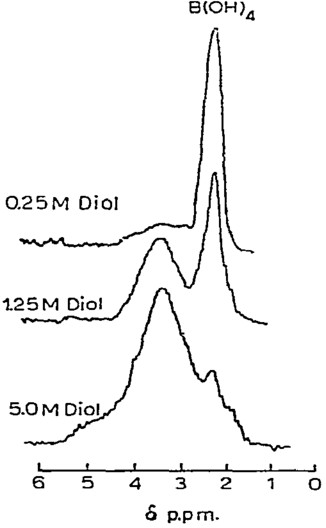


Fig. 4. ^{11}B n.m.r. spectrum at 12.83 MHz of pinacol–borate (2.5:1 molar ratio) at pH 12, showing the broad signal of BD_2^-. The lower trace is the synthesised signal and its components obtained on the Dupont curve-resolver. The reference signal of the methyl ether–boron trifluoride complex at δ 0.0 is not shown.

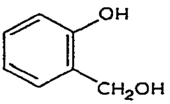
Fig. 5. ^{11}B n.m.r. spectra at 12.83 MHz of 1,2-di(hydroxymethyl)benzene (9)–borate solutions at different diol–borate ratios. The borate concentration of the solutions is M and the pH is 12. The reference signal of the methyl ether–boron trifluoride complex at δ 0.0 is not shown.

The line-widths of the resonances of many of the complexes, **1** and **2**, are generally quite narrow (10-20 Hz). However, the line-width of the resonance of the 2:1 pinacol–borate complex was large (~45 Hz) (Fig. 4). This broadening appears to increase with the number of substituents and may be caused by two factors. Firstly, the two diol molecules bound to the boron could distort the tetrahedral symmetry about the boron atom, which would increase relaxation *via* the nuclear quadrupole and broaden the absorptions. Alternatively, or in addition, the larger size of anion **2**, relative to that of the borate anion, will increase the correlation time and consequently reduce spin–lattice relaxation time, thus broadening the resonance.

B. Substituted 1,3-diols. Most examinations of diols which complex with borate have shown that 1,2-hydroxyl groups complex better than 1,3-hydroxyl groups[3,4]. The greater complexing ability of ethane-1,2-diol, compared with that of propane-1,3-diol, was attributed to the greater loss of rotational freedom in the latter diol. The present results, however, support other published data[16] and indicate that there is little difference in the complexing ability of these two diols.

The butane-1,3-diol–borax system was examined only at 12.83 MHz, and at this frequency the resonances for **1** and **2** are not resolved. Although equilibrium constants have not been calculated for complexes of butane-1,3-diol, comparison of the peak areas of free and complexed boron resonances with those of propane-1,3-diol show a slightly better complexing ability for the butane-1,3-diol.

2-(Hydroxymethyl)phenol (**8**) has been shown to form strong complexes by Böeseken[1], and the ^{11}B n.m.r. spectra of **8** in borax solutions (Table III) at pH 12 show only one resonance at δ 2.2. At lower pH values and at a very low diol–borate ratio, the resonance at δ 2.2 is still observed. Since resonances for uncomplexed boron species occur at low field at the lower pH values, the signal at δ 2.2 is attributable to a complexed form of **8**, and it is thus shown to be a good chelating diol even under conditions of low pH and low diol–borate ratios.



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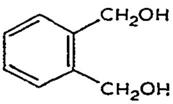

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C. 1,4-Diols. Butane-1,4-diol, even at high diol–borate ratios, does not give rise to a boron resonance attributable to a complex (Table III). This is consistent with previous reports[1,5,6] and has been rationalised in terms of the unfavourable entropy factor in forming a seven-membered ring complex. The internal rotational freedom of 1,2-di(hydroxymethyl)benzene (**9**) is smaller than that of butane-1,4-diol, and the ^{11}B n.m.r. spectra of **9** in borax solutions at pH 12 (Fig. 5) show a signal at δ 3.5 for complexed boron, which increases in intensity at the higher diol–borate ratios. Comparison of the area of the complexed and uncomplexed signals for **9** and ethane-1,2-diol (Table V) indicates that these two diols have similar complexing ability. The type of internal rotational freedom of the hydroxyl groups in **9** is similar to that in ethane-1,2-diol. This is the first case in which the condensation of a 1,4-diol with borate to form a seven-membered ring borate complex has been observed.

TABLE V

COMPARISON OF COMPLEXING ABILITY[a] OF ETHANE-1,2-DIOL AND 1,2-DI(HYDROXYMETHYL)BENZENE (9)

Diol	*Diol–boron ratio*	*Complexed boron (%)*
Ethane-1,2-diol	1.25:1	42
9	1.25:1	52
Ethane-1,2-diol	5.00:1	86
9	5.00:1	90

[a] In M borate at pH 12, as determined by ^{11}B n.m.r. spectroscopy.

In this ^{11}B n.m.r. study of complex formation, much of the earlier work has been repeated in order to establish the applicability of this spectroscopic technique. As a result of examining the model diol systems, the technique has been usefully extended to examine carbohydrates[17] and polyols[18] in order to provide direct information concerning the size of the borate ring complex and a direct indication of complexing ability.

EXPERIMENTAL

Preparation of borate solutions for ^{11}B n.m.r. studies. — (*a*) *Without diol.* Weighed quantities of borax, sodium metaborate tetrahydrate, or boric acid were dissolved in distilled water (<2.0 ml). The solutions were allowed to equilibrate at 33°, the same temperature as the n.m.r. spectrometer probe, and the pH was adjusted to the required value at this temperature. The volume was then adjusted to 2.0 ml to give a concentration of 0.8M in monomeric boron species, *i.e.* expressed as either boric acid or borate anion concentration. The borates were examined at a concentration of 0.8M, which is the saturation level for boric acid at low pH.

(*b*) *In the presence of diol.* Weighed quantities of borax and diol were dissolved in distilled water (<2.0 ml). After equilibration at 33°, the pH and volume were adjusted to the required values. The concentration of borate anion was M.

^{11}B n.m.r. measurements. — Studies at 12.83 MHz were performed with a Perkin–Elmer R10 spectrometer operating at 33°, in conjunction with a computer of average transients (CAT; Northern Scientific Ltd.) in order to increase the signal-to-noise ratio. The sweep rates of the CAT and the spectrometer were synchronised. Methyl ether–boron trifluoride was used as external reference.

The n.m.r. spectra at 28.87 MHz were measured on a Bruker electromagnet spectrometer operating at room temperature.

In favourable circumstances, when signals were well resolved, it was possible to integrate the signals accumulated on the CAT by using the integrating facilities of the spectrometer. A Dupont 310 curve-resolver was used to obtain the relative areas of the signals for situations in which they overlapped.

Calculation of equilibrium constants. — The values of $[B^-]$, $[BD^-]$, and $[BD_2^-]$ can all be calculated directly from peak areas, as

$$[B]_0 = [B^-]+[BD^-]+[BD_2^-],$$

where $[B]_0$ is the initial concentration of the monomeric borate. To calculate K_1 or K_2, only [D] is unknown and this is given by

$$[D]_0 = [D]+[BD^-]+2[BD_2^-],$$

where $[D]_0$ is the initial concentration of diol.

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