An Infrared Study of Co-ordinated BH_3 and BH_2 Groups as Proton Acceptors in Hydrogen Bonding

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Boron co-ordination compounds of the type L,BH_3 (L = Me_3N, Et_3N, Py, and Et_3P) and Me_3N,BH_2X (X = Cl, Br, and I) are shown to form hydrogen-bonded complexes with OH (MeOH, PhOH, and p-$F\cdot C_6H_4\cdot OH$) in carbon tetrachloride solution. These complexes appear to be formed *via* $OH \cdots BH_3$ and $OH \cdots BH_2$ interactions and are readily detected by the appearance of a low-frequency i.r. OH stretch. Formation of similar complexes with the more extensively halogenated amine–boranes Me_3N,BHX_2 (X = Cl, Br, and I) and Me_3N,BX_3 (X = F, Cl, and Br) could not be observed. Cyclotriborazanes $(RNH\cdot BH_2)_3$ are shown to undergo self-association in solution and this is attributed to a related $NH \cdots BH_2$ interaction.

We have reported[1] the appearance of low-frequency O–H stretching absorptions upon addition of Me_3N,BH_3 to dilute solutions of methanol and phenol in carbon tetrachloride. We suggested that these absorptions are due to the formation of hydrogen-bonded complexes in which the BH_3 group acts as a proton acceptor. In this paper we examine the interaction of hydroxylic compounds (MeOH, PhOH, and p-$F\cdot C_6H_4\cdot OH$) with Me_3N,BH_3 (and Me_3N,BD_3), Et_3N,BH_3, Py,BH_3, and Et_3P,BH_3. The effect of successive substitution of halogen (Cl, Br, and I) for H in the BH_3 group of Me_3N,BH_3 is also examined. Earlier we suggested that the temperature- and concentration-dependence of the N–H absorptions of Me_2NH,BH_3 in CCl_4 is due to a $NH \cdots BH_3$ interaction. Here we report the similar self-association of some cyclotriborazanes[2] $(RNH\cdot BH_2)_3$, which like Me_2NH,BH_3, contain N–H and B–H bonds and tetraco-ordinated N and B atoms. Quantitative study of the self-association of Me_2NH,BH_3 will be described elsewhere.

RESULTS

Interactions involving OH *Compounds.*—Data for ternary solutions of OH compound and borane derivatives in CCl_4 are in Table 1 and, for PhOH as the proton donor, some spectra are shown in Figure 1 (a). In these solutions, the concentration of OH compound at 0·05M is sufficiently low to ensure that self-association is negligible in relation to complex formation with the borane derivative. In fact, if 0·697 l. mole^{-1} is taken as the value of the equilibrium constant relating to cyclic dimerization of phenol,[3] a simple calculation shows that 94% of the molecules (at 25°) are unassociated at this concentration. We find that the amine–boranes Et_3N,BH_3 and Py,BH_3 and the phosphine–borane Et_3P,BH_3 behave like Me_3N,BH_3 and reduce the intensity of the free-OH stretch and produce a broader band at a lower frequency. With PhOH as the proton donor, the deuteriated compound Me_3N,BD_3 gives, within the limits of experimental error, identical results to Me_3N,BH_3.

The variation of the position of the associated-OH band, for a given OH compound, is not great. The hydrogen-bonded shifts, Δν, lie in the following ranges: MeOH, 84—91; PhOH, 141—157; and p-$F\cdot C_6H_4\cdot OH$, 146—161 cm.$^{-1}$. On the basis of the Δν value and the concentration of free-OH (as measured by its absorbance), hydrogen bonding with PhOH is, as might be expected, stronger than with MeOH. With the more positive hydrogen of p-$F\cdot C_6H_4\cdot OH$, the Δν values are greater than those for PhOH by about 5 cm.$^{-1}$, indicating stronger bonding in this case. The stoicheiometry of the PhOH–Me_3N,BH_3 complex has

TABLE 1

Interaction of borane complexes (0·3M) with OH compounds (0·05M) in CCl_4 at 25° (cell path length 1·00 mm.)

Borane complex	Δν [b] (cm.$^{-1}$)	Associated-OH band Absorbance	Associated-OH band $\Delta\nu_{\frac{1}{2}}$ [c] (cm.$^{-1}$)	Free-OH band absorbance [d]
Methanol [a]				
None	—	—	—	0·32
Me_3N,BH_3 ...	84	0·14	75	0·19
Et_3N,BH_3 ...	91	0·12	79	0·17
Py,BH_3	90	0·12	85	0·15
Et_3P,BH_3 ...	85	0·12	72	0·14
Me_3N,BH_2Cl	71	0·10	104	0·18
Me_3N,BH_2Br	81	0·08	100	0·18
Me_3N,BH_2I ...	87	0·11	115	0·18
Phenol [a]				
None	—	—	—	1·03
Me_3N,BH_3 ...	142	0·45	96	0·43
Et_3N,BH_3 ...	157	0·48	100	0·38
Py,BH_3	148	0·42	106	0·38
Et_3P,BH_3 ...	141	0·40	82	0·37
Me_3N,BH_2Cl	142	0·40	110	0·45
Me_3N,BH_2Br	153	0·34	117	0·45
Me_3N,BH_2I ...	149	0·25	125	0·51
Me_3N,BD_3 ...	142	0·47	95	0·41
p-Fluorophenol [a]				
None	—	—	—	1·01
Me_3N,BH_3 ...	148	0·52	97	0·34
Et_3N,BH_3 ...	161	0·51	103	0·31
Py,BH_3	152	0·50	103	0·31
Et_3P,BH_3 ...	146	0·48	87	0·28
Me_3N,BH_2Cl	150	0·41	110	0·36
Me_3N,BH_2Br	158	0·40	121	0·41
Me_3N,BH_2I ...	155	0·30	124	0·48

[a] The frequencies of the free-OH bands for 0·05M solutions are: MeOH, 3643; PhOH, 3610; p-$F\cdot C_6H_4\cdot OH$, 3612 cm.$^{-1}$. The respective values of ν_{OH} (free) for the ternary solutions differ by, at most, only 2 cm.$^{-1}$ from these values. [b] Experimental error in Δν is about ±3 cm.$^{-1}$ and is mainly due to the difficulty of locating the peak position of the associated-OH band. [c] Experimental error is about ±5 cm.$^{-1}$. [d] Absorbances will be slightly less than the true values because of the slit-width effect. They are reproducible to within ±0·02 except for MeOH for which the reproducibility is slightly less satisfactory.

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[1] M. P. Brown and R. W. Heseltine, *Chem. Comm.*, 1968, 1551.

[2] M. P. Brown, R. W. Heseltine, and L. H. Sutcliffe, *J. Chem. Soc.* (*A*), 1968, 612.

[3] D. L. Powell and R. West, *Spectrochim. Acta*, 1964, **20**, 983.

been investigated by recording spectra for different concentrations of Me_3N,BH_3. The absorbance of the free-OH stretch is taken as a measure of the free PhOH concentration (Table 2). A knowledge of this parameter together with the known initial concentrations of PhOH and Me_3N,BH_3 permits the ready calculation of equilibrium constants on the basis of assumed equilibria of various stoicheiometries. The small effect of PhOH self-association is ignored. Table 2 shows that constant values of K are obtained on the assumption of a 1 : 1 complex but not 1 : 2 or 2 : 1 complexes. These results, therefore, indicate a complex with 1 : 1 stoicheiometry.

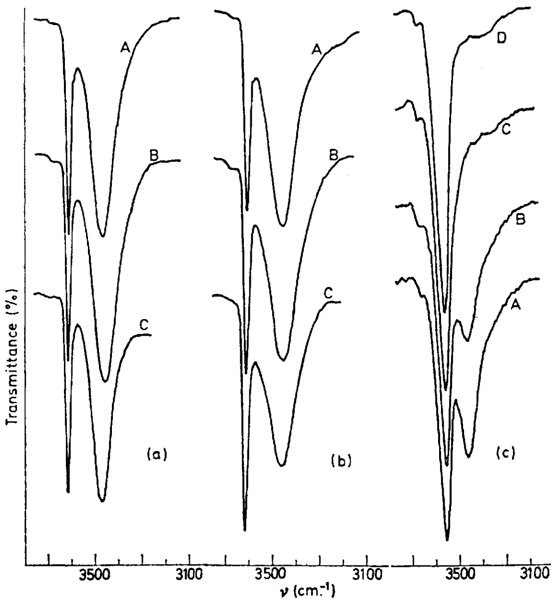

FIGURE 1 (a) OH Bands: Interaction of PhOH (0·05M) with some borane complexes (0·3M) in CCl_4: A, Me_3N,BH_3; B, Et_3N,BH_3; C, Et_3P,BH_3. (b) OH bands: Interaction of p-$F{\cdot}C_6H_4{\cdot}OH$ (0·05M) with compounds Me_3N,BH_2X (0·3M) in CCl_4: A, X = Cl; B, X = Br; C, X = I. (c) OH bands: Interaction of p-$F{\cdot}C_6H_4{\cdot}OH$ (0·05M) with A, Me_3N,BH_3; B, Me_3N,BH_2Cl; and C, $Me_3N,BHCl_2$ in benzene; D, p-$F{\cdot}C_6H_4{\cdot}OH$ (0·05M) in the absence of amine–borane

TABLE 2

Interaction of PhOH (0·03M) with Me_3N,BH_3 in CCl_4 (25°)

$[Me_3N,BH_3]$ (M)	Free-OH absorbance [a]	Equilibrium constant 1 : 1 Complex [b] (l. mole⁻¹)	1 : 2 Complex [b] (l.² mole⁻²)	2 : 1 Complex [b] (l.² mole⁻²)
0	0·624	—	—	—
0·1	0·428	5·1	69	117
0·2	0·328	4·8	31	148
0·3	0·256	5·1	21	200
0·4	0·212	5·1	15	245
0·5	0·183	5·0	12	281
0·6	0·161	5·0	9	317

[a] Cell path length 1·00 mm. [b] Phenol : amine–borane.

The compounds Me_3N,BH_2X (X = Cl, Br, and I) interact similarly with the OH compounds (Table 1). The corresponding spectra are shown in Figure 1 (b) for complexes with p-$F{\cdot}C_6H_4{\cdot}OH$. For a given OH compound, the intensity of the associated-OH band mainly decreases in the order $Me_3N,BH_3 > Me_3N,BH_2Cl > Me_3N,BH_2Br > Me_3N,BH_2I$ although the half-band widths, $\Delta\nu_{\frac{1}{2}}$, mainly decrease in the reverse order. The values of $\Delta\nu$ for the bromide are greater than those for the chloride but the position of the iodide relative to the others is less certain.

The more extensively halogenated compounds Me_3N,BHX_2 and Me_3N,BX_3 cannot be examined in carbon tetrachloride solution because of their low solubilities in this solvent. Benzene is a suitable alternative solvent although it has the disadvantage that it complexes weakly with OH compounds, causing a reduction in the frequency of the 'free-OH' stretch. Nevertheless, complexing of the BH_3 and BH_2X adducts with the OH compounds also takes place in this solvent (Table 3 and Figure 1 (c)). The intensities of both OH bands indicate that complexing is less extensive in this solvent. The smaller values of $\Delta\nu$ are largely explained by changes in position of the free-OH bands rather than associated-OH bands.

TABLE 3

Interaction [a] of borane complexes (0·3M) with PhOH and p-$F{\cdot}C_6H_4{\cdot}OH$ (0·05M) in benzene at 25°

	PhOH [b] $\Delta\nu$ (cm.⁻¹)	p-$F{\cdot}C_6H_4{\cdot}OH$ [b] $\Delta\nu$ (cm.⁻¹)
Me_3N,BH_3	93	96
Me_3N,BH_2Cl	91	95
Me_3N,BH_2Br	97	98
Me_3N,BH_2I	89	98

[a] Data are not given for MeOH solutions because the weaker associated-OH band maximum is difficult to locate precisely. [b] Free-OH frequencies (0·05M in C_6H_6) are: PhOH, 3557; p-$F{\cdot}C_6H_4{\cdot}OH$, 3557 cm.⁻¹. In the ternary solution these frequencies are at about 3555—3556 cm.⁻¹. The estimated experimental error in $\Delta\nu$ is about ±4 cm.⁻¹.

In contrast to the compounds Me_3N,BH_2X, those of formulae Me_3N,BHX_2 (X = Cl, Br, in 0·6 and 0·3M-solutions; X = I in 0·3M-solution) and Me_3N,BX_3 (X = F, Cl, and Br, in 0·15M-solutions) are not observed to interact with any of the three OH compounds (0·05M). No associated-OH bands are observed. In Figure 1 (c) the spectrum of a p-$F{\cdot}C_6H_4{\cdot}OH$–$Me_3N,BHCl_2$ solution is compared with spectra of similar solutions of Me_3N,BH_3 and Me_3N,BH_2Cl and with that for a binary p-$F{\cdot}C_6H_4{\cdot}OH$ solution. For the dibromide and di-iodide, as for $Me_3N,BHCl_2$, there was slight broadening of the free-OH band but there was no indication of a separate associated-OH band. Unfortunately the use of a more inert solvent than benzene seems ruled out by solubility problems.

N–H *Stretching Absorptions of Cyclotriborazanes* [2] $(RNH{\cdot}BH_2)_3$.—The frequencies for these compounds are given in Table 4 and the concentration and temperature-dependent bands for *cis*-$(BuNH{\cdot}BH_2)_3$ are shown in Figure 2. Similar spectra are observed for *cis*-$(PrNH{\cdot}BH_2)_3$. These spectra resemble those [1] of Me_2NH,BH_3 in CCl_4 except that the N–H absorption of the unassociated

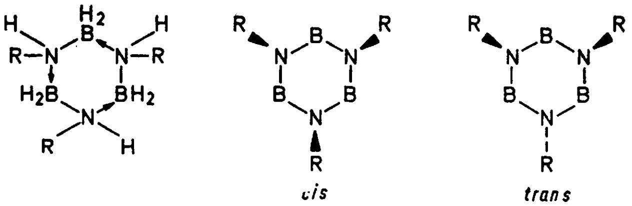

TABLE 4

N–H Stretching frequencies (cm.$^{-1}$) of cyclotriborazanes $(RNH{\cdot}BH_2)_3$

	cis-Isomer			*trans*-Isomer		
	Solid [a]	CCl_4 solution		Solid [a]	CCl_4 solution	
R		Free-NH	Associated-NH		Free-NH	Associated-NH
Et [b]	3220	3295 3260	—	3267 3236	3297 3278	—
Pr	3220	3295 3263	3226	3263 3230	3298 3277	3258
Bu	3218	3295 3263	3225	3250 [c]	3298 3278	3257

[a] As KBr discs and Nujol mulls. [b] Associated-NH bands are not clearly observed for the Et derivatives because of their low solubilities. [c] Sample liquefied in the i.r. beam.

TABLE 5

Molecular weight data for $(BuNH{\cdot}BH_2)_3$ in CCl_4

cis-Isomer		*trans*-Isomer	
Concn. (M)	M.W. (Found) / M.W. (Calc.)	Concn. (M)	M.W. (Found) / M.W. (Calc.)
0·08	1·70	0·08	1·03
0·04	1·27	0·06	1·04
0·02	1·10	0·03	1·00
0·01	0·98		

$(RNH{\cdot}BH_2)_3$ molecules consists of a doublet. The molecular weights (Table 5) obtained by vapour pressure osmometry substantiate the i.r. evidence for association. The *trans*-isomers appear to associate much less extensively than the *cis*-; there is very little sign of the characteristic low-frequency band at concentrations of about 0·1M and only at about 1·0M is this band of comparable intensity with the free-NH doublet. It is noteworthy that the similarity of N–H absorptions of *cis*- and *trans*-isomers is only revealed by study of dilute solutions. At moderate concentrations, the spectra differ markedly because of more extensive self-association of the former and in the crystalline phase the absorptions also differ. The lesser tendency of the *trans*-isomers to associate, also revealed by molecular weight studies (Table 5), is probably explained by their lower symmetry.[2]

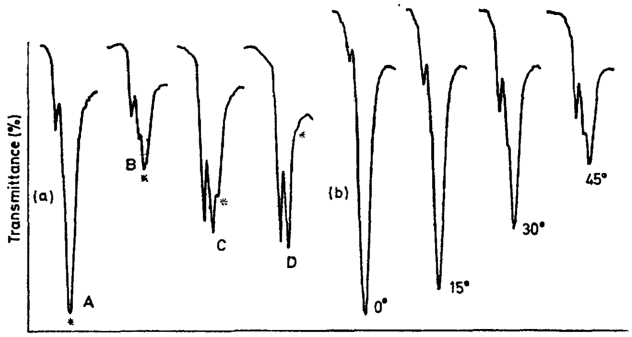

FIGURE 2 N–H bands of *cis*-$(BuNH{\cdot}BH_2)_3$ in CCl_4
(a) Concentration dependence; A, 0·08M, 1·0 mm. cell; B, 0·04M, 1·0 mm. cell; C, 0·02M, 5·0 mm. cell; D, 0·01M, 10·0 mm. cell; * denotes associated-NH band (3225 cm.$^{-1}$); (b) temperature-dependence of a 0·08M solution, 1·0 mm. cell

B–H *Stretching Absorptions.*—The effect of p-$F{\cdot}C_6H_4{\cdot}OH$ (0·2M) on the BH_3 absorptions of Me_3N,BH_3 (0·1M) is to lower the intensity (Figure 3 (a)). The strongest component, the antisymmetric stretch,[4] of the absorptions appears to be affected most. There is no observable change in frequency of the peak maxima (2273m, 2319m, and 2370s cm.$^{-1}$). The reason for using a solution of a different composition from those used for examination of OH bands is that the requirement here is a high degree of complexing of Me_3N,BH_3 molecules rather than of p-$F{\cdot}C_6H_4{\cdot}OH$. Although at 0·2M there is significant p-$F{\cdot}C_6H_4{\cdot}OH$ self-association, this does not interfere in the B–H stretching region of the spectrum.

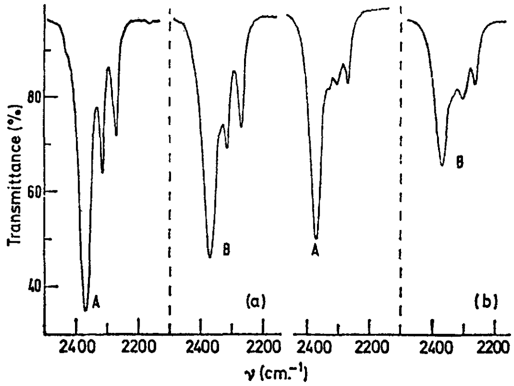

FIGURE 3 B–H Absorptions: (a) Me_3N,BH_3 (0·1M) in CCl_4, (A) without and (B) with p-$F{\cdot}C_6H_4{\cdot}OH$ (0·2M), 0·1 mm. cell; (b) Me_2NH,BH_3 in CCl_4 at comparable effective path lengths, (A) 0·002M, 2·5 mm. cell and (B) 0·09M, 0·056 mm. cell

Perturbations of the BH_3 absorption of Me_2NH,BH_3 when it undergoes self-association in CCl_4 are seen from Figure 3 (b) to be very similar. According to observation of the N–H stretches, the degree of association at 0·002M is low, the free-NH band having an absorbance of about twice as large as that of the associated-NH band, whereas at 0·09M it is very much higher, the free-NH band having only a negligible intensity compared to that of the associated-NH band. The BH_3 absorptions of Me_3N,BH_3, which has no protonic hydrogen atom for self-association, are independent of concentration, in contrast to those of Me_2NH,BH_3.

In recording these spectra, the weak CCl_4 band at about 2300 cm.$^{-1}$ has been carefully balanced by the use of a suitable reference cell and CO_2 absorption has been overcome by flushing the spectrometer with dry nitrogen.

DISCUSSION

Amine–boranes, R_3N,BH_3 and some of the related boron compounds described above do not contain lone pairs of electrons, or even π electrons, requirements normally considered necessary for formation of hydrogen bonds. These compounds, stable in the air but moderately reactive by most standards, do however contain Lewis bases, which if released from the complex would participate as proton acceptors. In view of this it is necessary to establish that the compounds are chemically

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[4] J. N. G. Faulks, N. N. Greenwood, and J. H. Morris, *J. Inorg. Nuclear Chem.*, 1967, **29**, 329; R. C. Taylor, 'Boron–Nitrogen Chemistry,' Advances in Chemistry Series, No. 42, American Chemical Society, Washington D.C., 1964, p. 59.

unchanged in the solutions under observation. One possibility which must be excluded is reaction with the solvent or impurity. Strong evidence against such reaction is the use of two solvents, CCl_4 and C_6H_6, with different chemical properties. Water is the only probable common impurity. Addition of trace amounts has no effect on the spectra and larger amounts would be readily detected spectroscopically. A more serious possibility is a disproportionation or similar reversible reaction of the boron compound. The fact that from many of the actual solutions studied we have successfully recovered the compounds in high yield (Me_2NH,BH_3 from CCl_4, Me_3N,BH_3 from CCl_4–PhOH, and other examples) does not necessarily rule out this type of reaction. The most convincing evidence is spectroscopic. For example, the C–H stretching frequencies, when not obscured by those of other components in the solutions, are completely unchanged. This is a sensitive criterion, as C–H stretching bands of Me_3N,BH_3, for example, are readily distinguishable from those of, say, Me_3N. The B–H stretching bands, too, provide convincing evidence. The changes here are inconsistent with any major chemical rearrangement. Stability of *cis*- and *trans*-isomers of the cyclotriborazanes in CCl_4 is also good evidence against a reversible disproportionation which would lead to isomerization.

We consider then, that our i.r. observations are evidence of weak complex formation between amine–borane and OH compound, in the ternary solutions, and related self-association of Me_2NH,BH_3 and $(RNH{\cdot}BH_2)_3$, in the binary solutions. The molecular interactions clearly involve on the one hand an electropositive hydrogen atom attached either to oxygen or nitrogen, and on the other, a proton-accepting group. The perturbations of the BH_3 frequencies of Me_3N,BH_3 (ternary solutions) and Me_2NH,BH_3 suggest that the BH_3 groups are the proton acceptors in these cases although the spectroscopic evidence is not conclusive. Nevertheless, Burg [5] also came to a similar conclusion and suggested weak $NH \cdots BH_3$ forces in solid and liquid Me_2NH,BH_3 on the basis of a spectroscopic study. He observed perturbation of the BH_3 frequencies of Me_2NH,BH_3 in the liquid phase compared with CCl_4 solution. He also observed some changes in the NH frequencies, although he incorrectly assigned the free-NH band at 3303 cm.$^{-1}$ (his value) and did not therefore observe the characteristic concentration- and temperature-dependence of the solution spectra.

Other evidence for the proton acceptor being the Lewis acid function of the molecule and not the Lewis base comes from comparing a series of Me_3N adducts such as the BH_3, BH_2Cl, $BHCl_2$, and BCl_3 adducts. All have Me_3N in common but only the BH_3 and BH_2Cl adducts appear to form complexes. However, steric effects *per se* rather than the successive decrease in the number of B–H bonds could be responsible. A stronger piece of evidence is the very similar behaviour of Et_3N,BH_3 and Et_3P,BH_3. Direct involvement of Et_3N and Et_3P would lead to the expectation of a much weaker interaction for the phosphorus compound since Et_3P is a much weaker base than Et_3N.

A high dipole moment for the boron compound is likely to be an important factor leading to complex formation but is clearly not the only requirement. This is shown by comparing the dipole moments [6] of Me_2NH,BH_3 and Me_3N,BH_3 (5·0 and 4·7 D respectively) with those [7,8] of Me_3N,BF_3, Me_3N,BCl_3, and Me_3N,BBr_3 (5·8, 6·3, and 6·6 D respectively). A considerable contribution to hydrogen bond energies derives from electrostatic forces.[9] For this reason the charge distribution is important. That implied by a simple formula of the type $R_3N^{+}-^{-}BH_3$ is an oversimplification, as considerable delocalization of negative charge occurs over the three hydrogen atoms.[10] In view of this we suggest that two possible explanations of complex formation should be considered: (i) the formation of weak $B \cdots H–O$ bonds, and (ii) the formation of weak $H^{\delta-} \cdots H–O$ bonds between the hydridic H atoms attached to boron and the protonic H atom of OH group. Another possibility is of course one in which both the boron atom and the hydrogen atoms attached to it take part in hydrogen bond formation, *i.e.*, the interaction is a property of the BH_3 (or BH_2) group as a whole. The experimental evidence is not very helpful in deciding between these possibilities. The explanation for the limiting case of an observed interaction being with Me_3N,BH_2X and not Me_3N,BHX_2 may be steric, close approach of $H^{\delta+}$ to B being prevented in BHX_2 adducts, or simply that two $H^{\delta-}$ atoms are necessary because of a chelating effect. The absence of frequency changes in ν_{B-H} on addition of OH compound might be more plausibly explained by $B \cdots H–O$ rather than $H \cdots H–O$ interactions but it does not appear to constitute a strong criterion for or against involvement of the hydridic H atoms. More helpful evidence may come from an *X*-ray study [11] of solid Me_2NH,BH_3, preliminary results of which indicate a comparable $BH_3 \cdots H–N$ interaction and an analysis of the relevant interatomic distances should be interesting and perhaps decisive.

The relation between $\Delta\nu$ and the strength of hydrogen bonds is not simple,[12] but $\Delta\nu$ very roughly increases with the strength of the bond. Values of $\Delta\nu$ in Table 1 are comparable with those observed for moderately strong

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[5] A. B. Burg, *Inorg. Chem.*, 1964, **3**, 1325.

[6] J. R. Weaver and R. W. Parry, *Inorg. Chem.*, 1966, **5**, 713.

[7] C. M. Bax, A. R. Katritzky, and L. E. Sutton, *J. Chem. Soc.*, 1958, 1258.

[8] G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J. Chem. Soc.*, 1945, 146.

[9] S. Bratoz, ' Advances in Quantum Chemistry,' vol. 3 ed. Per-olov Löwdin, Academic Press, London, 1967, 209.

[10] R. Hoffmann, ' Boron–Nitrogen Chemistry,' Advances in Chemistry Series, No. 42, American Chemical Society, Washington D.C., 1964, p. 78; D. R. Armstrong and P. G. Perkins, *J. Chem. Soc.* (*A*), 1969, 1044.

[11] N. Bailey, personal communication (Sheffield University).

[12] (*a*) G. C. Pimental and A. L. McClellan, ' The Hydrogen Bond,' Freeman, San Francisco, 1960; (*b*) L. J. Bellamy, Advances in Infrared Group Frequencies,' Methuen, London, 1968, ch. 8.

hydrogen bonds, *e.g.*, for many O · · · H–O bonds such as those [13] in complexes of PhOH with esters ($MeCO_2Me$, 170 cm.$^{-1}$), ketones (Me·CO·Et, 200 cm.$^{-1}$) and aldehydes (EtCHO, 170 cm.$^{-1}$) *etc.*, and also similar complexes with organic cyanides [14] (PhCN, 144 cm.$^{-1}$). Further, the value of K (5·0 l. mole^{-1}) which we find for formation of the Me_3N,BH_3–PhOH complex is of the same order as values [13,14] for most of these systems. A more interesting comparison would be of ΔH values and with this aim in mind we are studying the spectra as a function of temperature.

Finally, whether or not these $BH_3 \cdots H$ and $BH_2 \cdots H$ interactions can be properly termed hydrogen bonds depends on how these are defined. If the definition is based on experimental criteria, as followed by Pimentel and McClennan,[15] rather than on specific electronic requirements (such as a lone pair) of the proton acceptor, then clearly there is no doubt that the term hydrogen-bonding may be properly used to describe these intermolecular forces.

EXPERIMENTAL

Spectra were recorded on a Perkin-Elmer 257 spectrometer and wavenumbers were measured by linear interpolation from reference peaks of separate MeOH (3643 cm.$^{-1}$) and $PhCONH_2$ (3423 cm.$^{-1}$) solutions in CCl_4 and were generally accurate to ±2 cm.$^{-1}$. Several were checked by recording them on a Perkin-Elmer 125 spectrometer. The instruments were flushed with dry air or nitrogen. The cells were maintained at 25° by water circulating through a hollow brass block around the cell.

TABLE 6

Halogenated amine–boranes

	Sublimation [a] temp.	Found (%)					Calc. (%)				
		C	H	B	N	X [b]	C	H	B	N	X [b]
Me_3N,BH_2Cl	30—35°	33·6	10·4	10·2	13·0	32·7	33·6	10·3	10·1	13·0	33·0
Me_3N,BH_2Br	40—45	23·7	7·6	7·2	9·4	52·8	23·7	7·3	7·1	9·2	52·6
Me_3N,BH_2I	75—80	18·3	5·5	—	6·9	63·4	18·1	5·6	—	7·0	63·8
$Me_3N,BHCl_2$	65—70	25·0	7·1	7·5	9·8	49·5	25·4	7·1	7·6	9·9	50·0
$Me_3N,BHBr_2$	70—75	15·7	4·4	4·6	6·0	68·9	15·6	4·4	4·7	6·1	69·2
Me_3N,BHI_2	110—115	11·2	3·1	—	4·1	79·0	11·1	3·1	—	4·3	78·1

[a] Under high vacuum. [b] Halogen.

Solvents.—Carbon tetrachloride was dried and distilled from P_2O_5 and, in a 10 mm. cell, had negligible OH and CH absorptions. AnalaR benzene was used.

Hydroxy-compounds.—Methanol (AnalaR) and *p*-fluorophenol (m.p. 48°) were used without further purification. Phenol was resublimed and had m.p. 41°.

Boron Compounds.—Trimethylamine–borane, m.p. 94°, was recrystallized. Triethylamine–borane, n_D^{21} 1·4422 (lit.,[16] 1·4427) and pyridine–borane, n_D^{20} 1·5300 (lit.,[7] 1·5310), were purified by high-vacuum distillation. Triethylphosphine–borane, m.p. 47—48°, (lit.,[17] 48°) was prepared from Me_3N,BH_3 and Et_3P (65° for 2 hr.) and purified by vacuum sublimation. This preparation and those described below were carried out under nitrogen. Analyses are in Table 6.

Monohalogenated Compounds.—The chloride Me_3N,BH_2Cl was prepared in high yield (93%) from HCl and Me_3N,BH_3 in Et_2O at 35—40° and, after high-vacuum sublimation, had m.p. 85° (lit.,[18] 85°). The bromide, Me_3N,BH_2Br, was prepared (yield 75%) and purified similarly and had m.p. 69—70° (lit.,[18] 68°).

The iodide, Me_3N,BH_2I, was prepared [18] by adding iodine (8·8 g., 35 mmoles) in benzene (100 ml.) to Me_3N,BH_3 (5·1 g., 70 mmoles) in benzene (150 ml.) during 45 min. The pale yellow solution was refluxed for 30 min. after which time it became colourless. After evaporation of some solvent and addition of light petroleum (50 ml.), the product, m.p. 73° (lit.,[18] 73°), was crystallized and sublimed *in vacuo*.

Dihalogenated Compounds.—The *chloride* $Me_3N,BHCl_2$ was prepared, in 64% yield, by redistribution (1) between Me_3N,BH_3 (0·183 g., 2·5 mmoles) and Me_3N,BCl_3 (0·883 g., 5·0 mmoles) in a sealed tube at 180° for 10 hr. The

$$Me_3N,BH_3 + 2Me_3N,BCl_3 \rightleftharpoons 3Me_3N,BHCl_2 \quad (1)$$

product, m.p. 156—158°, was purified by fractional sublimation under high vacuum.

The bromide $Me_3N,BHBr_2$ was prepared [18] in 61% yield from Me_3N,BH_3 and BBr_3 in benzene and after crystallization and sublimation had m.p. 127—128° (lit.,[18] 127—128°).

The *iodide* Me_3N,BHI_2 was prepared from iodine and Me_3N,BH_3, at first only with considerable difficulty in low yield, but then readily provided the following procedure was closely followed. Iodine (8·7 g., 34 mmoles) was added rapidly with shaking to Me_3N,BH_3 (2·5 g., 34 mmoles) in CCl_4 (100 ml.). Immediately after addition of the iodine, the pale yellow solution began to darken rapidly and the solvent was quickly removed *in vacuo*. The brown residue after exposure to air for 48 hr. became lighter in colour. Fractional sublimation gave Me_3N,BHI_2, m.p. 112—114°, in 53% yield.

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