Co-ordinated BH_3 as a Proton Acceptor Group in Hydrogen Bonding

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WE report infrared evidence for a moderately strong and specific interaction between the co-ordinated BH_3 group in amine-boranes and a protonic H atom. Firstly, we find (Figure 1) that the spectra of Me_2NH,BH_3 in CCl_4 solutions are both concentration- and temperature-dependent in a manner characteristic of compounds undergoing intermolecular hydrogen bonding. The broader, lower frequency N–H stretching absorption observed at 3210 cm.$^{-1}$, which is favoured at lower temperatures and higher concentrations, clearly indicates the presence of associated species in these solutions. At lower concentrations than shown here, this absorption becomes insignificant. The only N–H stretch then observed is the sharper one at 3300 cm.$^{-1}$ which we assign to the unassociated Me_2NH,BH_3 molecule. Although a weak peak at about this position was previously noted by Burg[1] for both CCl_4 and CS_2 solutions of Me_2NH,BH_3, its concentration- and temperature-dependence was apparently not observed and consequently its significance was not appreciated.

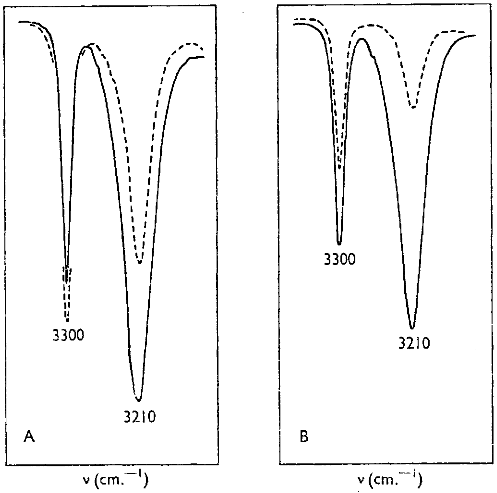

FIGURE 1. *The* N–H *stretching absorptions of* Me_2NH,BH_3 *in* CCl_4. *A* 0·0041 M *solution at* 0° (———) *and at* 43° (– – –) [*cell path length* (*l* = 0·98 *cm.*)]. *B;* 0·0021 M *solution* (– – –) (*l*=0·98) *and* 0·0093 M *solution* (———) (*l*=0·51 *cm.*) *at* 22°.

Secondly, spectra of ternary solutions of Me_3N,BH_3 and either MeOH (Figure 2) or PhOH (Figure 3) in CCl_4, show a strong, new and broader O–H stretching absorption at 3550 cm.$^{-1}$ (MeOH) or 3465 cm.$^{-1}$ (PhOH). In these solutions, the

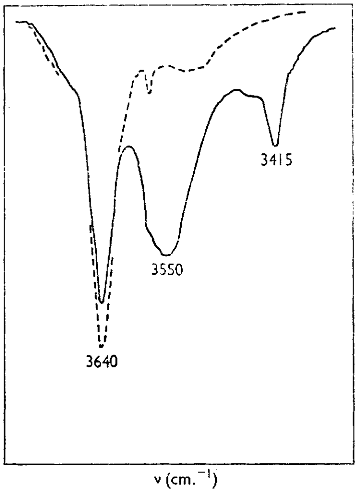

FIGURE 2. *The* O–H *stretching absorptions* (*l* = 0·25 *cm.*) *at* 27° *of a* MeOH *solution* (0·05M) in CCl_4 *before* (– – –) *and after* (———) *addition, of* Me_3N,BH_3 (0·30M). (*The absorption at* 3415 *cm.*$^{-1}$ *is an overtone or combination band of* Me_3NBH_3).

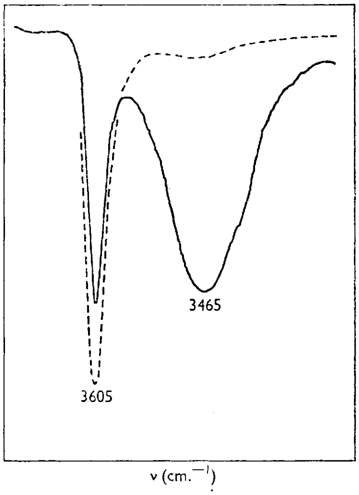

FIGURE 3. *The* O–H *stretching absorptions* (*l* = 0·10 cm.) *at* 27° *of a* PhOH *solution* (0·05M) *in* CCl_4 *before* (– – –) *and after* (———) *addition of* Me_3N,BH_3 (0·30M).

concentration of MeOH or PhOH is kept low to minimise self-association of these compounds.

The frequency shifts we thus observe are 90 cm.$^{-1}$ (Figures 1 and 2) and 140 cm.$^{-1}$ (Figure 3). Although they are smaller than the frequency shifts for strong O–H · · · O bonds, for example, which usually exceed 200 cm.$^{-1}$ and are often very much greater,[2,3] these shifts are nevertheless comparable in magnitude to those for many known hydrogen bonding systems, *e.g.* *N*-methylurethane[3] in CCl_4 ($\Delta\nu = 102$ cm.$^{-1}$). For comparison, some examples of other frequency shifts[4] are: $PhOH/C_6H_6$, 56 cm.$^{-1}$; $PhOH/MeCO_2Me$, 132 cm.$^{-1}$; and $PhOH/Et_2O$, 270 cm.$^{-1}$. A feature of Me_2NH,BH_3 solutions in CCl_4 is that association should be so evident at concentrations as low as 0·002- and 0·004-M. A spectrum of a 0·05M solution confirms that association is very much more extensive at this concentration. In contrast, both MeOH and PhOH at 0·05M concentration in CCl_4 (see Figures 2 and 3) are virtually unassociated. This indicates that the free energy changes involved in the association of Me_2NH,BH_3 are relatively large.

The appearance of a strong, broad, lower frequency stretching absorption in the infrared spectrum is generally considered to be the best and least ambiguous criterion for hydrogen bonding.[2,3] If we apply this criterion then we are led to the conclusion that the BH_3 group (or part of it) in amine-boranes can participate in hydrogen bonding.† This is of interest since neither the BH_3 group nor the amine-borane molecule possesses a lone pair of electrons or a π-electron system. The only previously reported example known to us of a proton acceptor group not in either of the above categories is that of the cyclopropane ring,[5] and here the interaction appears much weaker.

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† Additional evidence in support of this is now available. In a personal communication (11th September, 1968) Dr. N. A. Bailey, Sheffield University, informed us that preliminary results of an *X*-ray crystallographic examination of solid Me_2NH,BH_3 shows some molecular association in that there is a short intermolecular B---H–N contact and apparent distortion of the BH_3 group.

[1] A. B. Burg, *Inorg. Chem.*, 1964, **3**, 1325.
[2] G. C. Pimental and A. L. McClellan, "The Hydrogen Bond," Freeman, San Francisco, 1960.
[3] H. E. Hallam, in "Infrared Spectroscopy and Molecular Structure," ed. Mansel Davies, Elsevier, Amsterdam, 1963, ch. 12, p. 405.
[4] Ref. 2, p. 86.
[5] L. Joris, P. von R. Schleyer, and R. Gleiter, *J. Amer. Chem. Soc.*, 1968, **90**, 327.