

481. *Infrared Spectra of Boron Compounds.*

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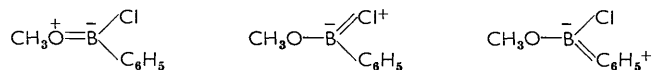
Many spectra of organoboron compounds and of some boron hydrides have been obtained. The positions of a number of characteristic group frequencies were determined and are discussed.

INFRARED spectra of organoboron compounds and boron hydrides have received little systematic study, but a few specific correlations are available, notably the assignment of a B-O stretching mode to the 1340 cm^{-1} region by Werner and O'Brien.^{1,2} This has been supported by Dandegaonker, Gerrard, and Lappert³ who also discussed the possible assignment of the B-Cl stretching frequency near 900 cm^{-1} . The spectra of some derivatives of diphenylboronous acid have also been discussed,⁴ and there have been several detailed studies of individual molecules of both organoboron compounds and boron hydrides.

During chemical studies in this field many infrared spectra have been accumulated. We have reviewed these to see how far existing correlations could be confirmed and if new ones might be added, and now give our results.

Organoboron Compounds.—*The B-O stretching frequency.* This was identified as falling at 1340 \pm 10 cm^{-1} in boronite esters¹ and mixed esters² (although the band in cyclohexyl diphenyl borate was displaced to 1363 cm^{-1}). Dandegaonker *et al.*³ found the absorption between 1350 and 1330 cm^{-1} in phenylchloroboronites and in phenylboronates, and in diphenylboronous acid and its derivatives it occurs⁴ at 1325 \pm 2 cm^{-1} .

We have examined 56 borates, boronates, and boronites. In all, a strong absorption is found in the range 1350—1310 cm^{-1} , with 51 absorbing within the narrower limits 1346—1316 cm^{-1} . The band is very intense and is thus readily identified. Its high frequency, intensity, and stability of position contrast with other absorptions of this type, such as that of the P-O link, which fall at markedly lower frequencies and tend to be influenced more by the nature of other substituents. Werner and O'Brien¹ suggested that the B-O bond has some double-bond character, and the stability in position of this absorption and its high intensity are probably associated with this. In all the compounds studied the boron valencies are linked with phenyl, chlorine, or oxygen atoms each of which can donate electrons to make up the boron octet. Resonance can therefore be expected between canonical forms, which in a compound such as methyl phenylchloroboronite can be represented as:



The occurrence of resonance of this type is independently supported by dipole-moment studies.⁵ This would be expected to lead to higher frequencies and intensities in the B-O link, as is confirmed by the strong band near 1340 cm^{-1} being absent from the spectra of these compounds when they are coupled with strong electron donors such as pyridine or other tertiary bases. In such couples resonance of this type is largely suppressed and it becomes difficult to recognise the less intense B-O absorption which occurs at lower frequencies. 2-Aminoethyl diphenylboronite behaves similarly and does not absorb near 1340 cm^{-1} , presumably owing to the lengthening of the B-O bond due to internal complex formation.⁶ This correlation is therefore only applicable to situations in which the boron octet is not fully completed.

¹ Werner and O'Brien, *Austral. J. Chem.*, 1955, **8**, 355.

² *Idem, ibid.*, 1956, **9**, 137.

³ Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 2872.

⁴ Abel, Gerrard, and Lappert, *ibid.*, p. 3833.

⁵ Curran, McCusker, and Makowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5188.

⁶ Letsinger and Skoog, *ibid.*, 1955, **77**, 2491.

B-Cl. The asymmetric and symmetric B-Cl stretching frequencies of boron trichloride have been assigned ⁷ at 955 cm.⁻¹ (*E*) and 471 cm.⁻¹ (*A*₁), and Dandegaonker *et al.*³ noted a strong band near 900 cm.⁻¹ in alkyl phenylchloroboronites which they assign to the B-Cl mode. We have confirmed this observation in thirteen compounds of this type in all of which a strong band occurs between 909 and 893 cm.⁻¹. Diphenylboron chloride absorbs strongly at 895 cm.⁻¹ and phenylboron dichloride at 885 cm.⁻¹, but in di-*n*-butyl chloroboronate the frequency falls to 858 cm.⁻¹, which may be due to the increased electron-donating powers of the oxygen atoms. In bis(diethylamino)boron chloride this process is carried a stage further and it is no longer possible to identify a B-Cl absorption from amongst a number of less intense bands at lower frequencies. Similarly the 895 cm.⁻¹ band of diphenylboron chloride is removed by complex formation with tertiary bases.

B-Aryl. Both the P-Aryl ⁹ and Si-Aryl ¹⁰ linkages have been assigned a characteristic frequency near 1430 cm.⁻¹, and the former absorbs also near 1000 and the latter near 1100 cm.⁻¹. In the 42 B-Aryl compounds studied we also find a strong sharp absorption between 1440 and 1430 cm.⁻¹. This appears to be the 1470—1438 cm.⁻¹ band of mono-substituted aromatic compounds,¹¹ and the fact that the lowest of these values relates to iodobenzene in which the electronegativity of the substituent is also low, may be significant. The origin of the second band is less clear and its position varies.

In a series of sixteen compounds containing the residue Ph₂B a strong absorption is found between 1280 and 1250 cm.⁻¹ which can reasonably be assigned to the Ph-B group, particularly as it is strongly marked in diphenylboron chloride and in the corresponding bromide. In alkyl phenylchloroboronites the band shifts towards lower frequencies and is now found (11 compounds) as a strong absorption between 1220 and 1198 cm.⁻¹. In dialkyl phenylboronates no strong bands are found in either of these regions but a new strong one in the range 1175—1125 cm.⁻¹ (13 compounds).

One other interesting feature of these spectra is the splitting of the out-of-plane CH aromatic deformation absorptions which occurs when more than one aromatic ring is directly attached to the boron atom. This has previously been reported by Abel *et al.*⁴ who reported a separation of 20 cm.⁻¹ in the "doublet" produced. This finding has been confirmed in all cases studied here and applies also to the spectrum of sodium tetraphenylboron.

B-CH₃ and B-N frequencies. The asymmetric and symmetric deformations of a methyl group attached to an element X are usually constant in position and depend in part upon the electronegativity of X.^{12,13} The symmetric one is particularly characteristic and useful correlations arise from this fact. For boron, considerations of electronegativity ¹² suggest that the symmetric frequency should fall in the 1350—1300 cm.⁻¹ range. Trimethylboron ¹⁴ absorbs at 1460 cm.⁻¹ and 1305 cm.⁻¹ and these bands can reasonably be assigned to the asymmetric and symmetric methyl deformation modes. In addition, nine compounds containing the CH₃-B group were studied by Becher *et al.*^{8,14,15} in either the Raman or the infrared region. All show comparable bands which fall in the ranges 1460—1405 cm.⁻¹ and 1320—1280 cm.⁻¹ and can be similarly assigned. Although less specific than most other CH₃-X frequencies these may well be useful in particular cases.

The compounds studied by Becher *et al.*¹⁵ include instances in which the boron is directly attached to nitrogen. In Me₂B·NH·C₆H₅, for example, the B-N absorption is

⁷ Lindeman and Wilson, *J. Chem. Phys.*, 1956, **24**, 242.

⁸ Becher, *Z. anorg. Chem.*, 1953, **271**, 243.

⁹ Daasch and Smith, *Analyt. Chem.*, 1951, **23**, 853.

¹⁰ Young, Servais, Currie, and Hunter, *J. Amer. Chem. Soc.*, 1948, **70**, 3758.

¹¹ Josien and Lebas, *Bull. Soc. chim. France*, 1956, **53**, 57.

¹² Sheppard, *Trans. Faraday Soc.*, 1955, **51**, 1465.

¹³ Bellamy and Williams, *J.*, 1956, 2753.

¹⁴ Goubeau and Becher, *Z. anorg. Chem.*, 1952, **268**, 1.

¹⁵ Becher, *ibid.*, 1957, **289**, 262; Becher and Goubeau, *ibid.*, 1952, **268**, 133.

assigned at 1332 cm^{-1} , and 1343 cm^{-1} is quoted for the corresponding pyrrole derivative. The B-N link is likely to possess double-bond character in the same way as the B-O link, and the assignment is therefore reasonable, particularly as four other compounds they studied appear to show strong bands in the 1378—1332 cm^{-1} region, and the complex of trimethylboron with ammonia (in which the B-N link has no double-bond character) shows no comparable band⁸ and the B-N stretching frequency is then assigned at 1105 cm^{-1} . We have observed bands near 1350 cm^{-1} for $(\text{Bu}^n_2\text{N})_3\text{B}$ and $(\text{Et}_2\text{N})_3\text{B}$, but not for complexes of boron trichloride with secondary bases. Whilst this correlation must be regarded as tentative it should be realised that both the B-O and B-N stretching absorptions are liable to occur at similar frequencies.

Boron Hydrides.—The spectra of many boron hydrides are available in the literature. Diborane has been studied,^{16,18} and detailed assignments have been given for pentaborane,¹⁹ dimethylaminodiborane,²⁰ and dimethylaminoborane.²¹ The spectra of tetraborane, pentaborane, and dihydropentaborane have also been described,²² but no detailed assignments were given. We re-examined some of these materials and added the spectra of decaborane and its monoethyl, diethyl, and monoiodo-derivatives. Four different types of boron-hydrogen link have been described in the various hydrides and these differences should be reflected in the infrared spectra. In addition to the well-known bridged-ring hydrogen atoms, normal BH_2 and BH groups occur in most cases. The latter are, however, divisible into two classes as nuclear resonance studies have shown²³ that the B-H links at apical positions in compounds such as pentaborane are characteristically different from those at other positions.

B-H Stretching frequencies. The hydrogen atoms which form bridge rings between two boron atoms perform breathing motions which cause a series of absorptions in the range 2220—1600 cm^{-1} . These have been defined in diborane and pentaborane and similar bands are found in all the other compounds studied which contain this structure. Their number and position vary considerably, however, and although there is usually at least one band in the 1900—1800 cm^{-1} range there is no other regularity. The normal BH and BH_2 stretching modes always fall in the range 2630—2350 cm^{-1} . There appears to be no basic frequency difference but the BH_2 group can be identified by the doubling due to asymmetric and symmetric modes. Similarly no difference could be detected at the resolution available between the stretching frequencies of the normal and apical BH groups in compounds such as decaborane and pentaborane.

B-H Deformation frequencies. The BH_2 "scissoring" mode in diborane absorbs at 1180 cm^{-1} and a corresponding band, which is sometimes a closely separated doublet, can be identified in the range 1205—1140 cm^{-1} in all compounds containing this group. The 973 cm^{-1} BH_2 wagging mode of diborane can similarly be identified in other materials in the range 975—945 cm^{-1} . Neither of these bands appears in compounds such as decaborane which contain only BH links. The identification of the deformation frequencies of the latter must necessarily be more tentative. A band occurs very near 900 cm^{-1} for decaborane, pentaborane, tetraborane, and dihydropentaborane (all of which contain apical BH links) which is not present for the few compounds studied which lack this structure. Further, the band is much weaker for monoethyldecaborane. This suggests a possible correlation which should be studied further. The deformation frequency of normal BH links appears to occur elsewhere but is less easy to identify. Hrostowski and Pimentel¹⁹ assign absorptions in the 1620—1440 cm^{-1} region to this

¹⁶ Price, *J. Chem. Phys.*, 1948, **16**, 894.

¹⁷ Lord and Nielsen, *ibid.*, 1951, **19**, 1.

¹⁸ Anderson and Barker, *ibid.*, 1950, **18**, 698.

¹⁹ Hrostowski and Pimentel, *J. Amer. Chem. Soc.*, 1954, **76**, 998.

²⁰ Mann, *J. Chem. Phys.*, 1954, **22**, 70.

²¹ Price, Fraser, Robinson, and Longuet-Higgins, *Discuss. Faraday Soc.*, 1950, **9**, 131.

²² McCarty, Smith, and McDonald, *Analyt. Chem.*, 1954, **26**, 1027.

²³ Schaeffer, Shooley, and Jones, *J. Amer. Chem. Soc.*, 1957, **79**, 4606.

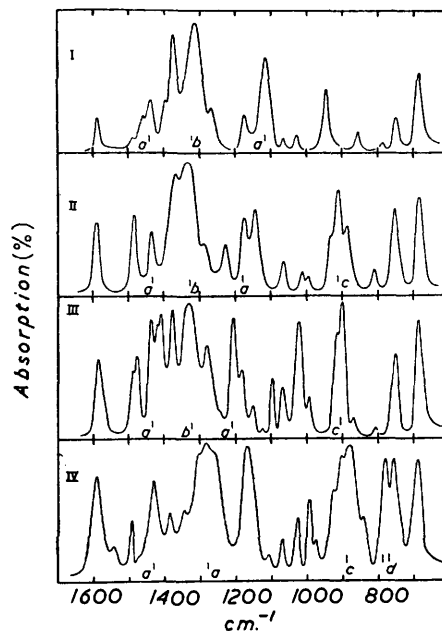
vibration in pentaborane and bands in this region are found in the other appropriate compounds. The frequency appears abnormally high however in relation to those discussed above, and as all these materials also contain bridged-ring structures it is possible that these absorptions arise from these. An alternative, and in some ways more attractive, assignment would be the region $1075\text{--}1010\text{ cm.}^{-1}$ in which a common band is again found in the series of compounds containing B-H links at non-apical positions. The present data are however insufficient to enable these possibilities to be differentiated.

Experimental.—Spectra were measured either in a G.S.2 Grubb-Parsons double-beam grating spectrometer fitted with a 2400 line/inch N.P.L. replica grating, or in a Grubb-Parsons S.3A double-beam model with a sodium chloride prism. Samples were studied as liquid films, as solid mulls in paraffin oil, or as vapours as appropriate.

Results.—As the spectra have been submitted for reproduction in the D.M.S. punched-card system, only relevant portions are discussed. However, to present an overall picture of the results, four typical spectra (I, di-*n*-propyl phenylboronate; II phenyl phenylchloroboronite; III, ethyl phenylchloroboronite; IV, diphenylboron chloride) are shown in the Figure. Specific assignments are indicated: *a*, B-Ph; *b*, B-O; *c*, B-Cl; *d*, splitting of C-H band in the phenyl rings.

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