373. *Cyclic Organic Boron Compounds. Part V.*[1] *Infrared Spectra of Borazoles and Boroxoles.*

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The infrared spectra of eleven borazoles and twenty boroxoles, having various substituents, have been recorded and assignments have been proposed. The BN and BO ring stretching vibrations fall at ~1450 and ~1350 cm.$^{-1}$ for the two classes respectively, but these are of relatively little use for diagnosis owing to close correspondence to values of B–N and B–O stretching frequencies in appropriate acyclic compounds. However, medium-to-strong absorption near 720 cm.$^{-1}$ appears to be characteristic for both classes when substituents on the boron atoms can conjugate with the ring and this absorption is assigned to one of the out-of-plane ring vibrations. The effects of structure on group frequency shifts are considered, as is hyperconjugation in alkylboronic anhydrides.

SPECTROSCOPIC information on a number of borazoles [2-6] and boroxoles [6-9] has been reported. For borazole itself the fundamental infrared and Raman frequencies have been assigned; [2,3] these data have been extended to certain substitution derivatives (see Table 7). Interest has been either theoretical (comparison with benzenoid compounds, calculation of force constants and of distribution of potential energy among various internal co-ordinates) or analytical. The present paper is concerned with the identification and assignment of characteristic group frequencies and with the effect on these of structural factors. For this purpose we examined the spectra of many of these compounds and have brought together published information on others.

The band most frequently regarded as characteristic of the borazoles has been that at about 1450 cm.$^{-1}$ due to the ring B–N stretching frequency and recognised by its high intensity. For two compounds, $(Et{\cdot}NH{\cdot}B{\cdot}NEt)_3$ and $(Bu^nO{\cdot}B{\cdot}NEt)_3$, attention has also been drawn to a medium-intensity doublet in the 720 cm.$^{-1}$ region, assigned to the out-of-plane vibrations of the $N_3B_3N_3$ or $O_3B_3N_3$ skeletons.[4] From the disclosure [10] that borazens $[B(NR_2)_3$, $B(NHR)_3$, $B(NRAr)_3$, and $B(NHAr)_3]$ have the strongest absorption at about 1450 cm.$^{-1}$ (due to the B–N asymmetric stretching vibration), it is apparent that strong absorption in that region is not diagnostic for borazoles.

Spectra of boroxoles have received scant attention. The Raman lines of the methyl- (also infrared spectrum [8]), methoxy-, dimethylamino-, and chloro-derivatives have been recorded,[6] and for certain alkoxyboroxoles [*i.e.*, metaborates, $(RO{\cdot}BO)_3$] a medium-intensity doublet in the infrared spectra at about 720 cm.$^{-1}$ appeared to be characteristic and was tentatively assigned to the out-of-plane vibration of the B_3O_6 skeleton.[7] In some aryl derivatives [*e.g.*, boronic anhydrides, $(Ar{\cdot}BO)_3$], absorption in the same region was noticed.[9]

B-*Aminoborazoles*, $(R{\cdot}NH{\cdot}B{\cdot}NR)_3$.—In general, the spectra of these compounds show: (i) several strong absorption bands in the 1600—1100 cm.$^{-1}$ region; (ii) a sharp medium-intensity band at 3400—3450 cm.$^{-1}$, undoubtedly due to the N–H stretching vibration; and (iii) a characteristic band at 715 cm.$^{-1}$, in some cases resolved into a doublet.

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[1] Part IV, Aubrey and Lappert, *J.*, 1959, 2927.

[2] Crawford and Edsall, *J. Chem. Phys.*, 1939, **7**, 223.

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

[4] Lappert, *Proc. Chem. Soc.*, 1959, 59.

[5] (*a*) Spurr and Chang, *J. Chem. Phys.*, 1951, **19**, 518; (*b*) Becher and Frick, *Z. anorg. Chem.*, 1958, **295**, 83; (*c*) Bradley, Ryschkewitsch, and Sisler, *J. Amer. Chem. Soc.*, 1959, **81**, 2635; (*d*) Watanabe, Narisada, Nakagawa, and Kubo, *Spectrochim. Acta*, 1960, **16**, 78.

[6] Goubeau and Keller, *Z. anorg. Chem.*, 1953, **272**, 303.

[7] Lappert, *J.*, 1958, 2790.

[8] Goubeau and Hummel, *Z. phys. Chem.* (*Frankfurt*), 1957, **69**, 77.

[9] (*a*) Snyder, Konecky, and Lennarz, *J. Amer. Chem. Soc.*, 1958, **80**, 3611; (*b*) Santucci and Gilman, *J. Amer. Chem. Soc.*, 1958, **80**, 193.

[10] Aubrey, Lappert, and Pyszora, *J.*, 1960, 5239.

Complexity in region (i) arises from the presence of, *inter alia*, BN and CN stretching and of CH, CH_2, CH_3, and NH deformation modes. In the methyl derivative, the strong absorption due to the methyl group makes assignment of a BN stretching frequency on relative-intensity grounds difficult, but in the higher homologues a band of outstanding intensity is clearly distinguished and may be allocated to the BN stretching mode, probably being a mixed vibration of cyclic and exocyclic modes.

The NH stretching frequencies are of the same order as in corresponding borazens, $B(NHR)_3$ in which they fall at 3420 ± 20 cm.$^{-1}$ for R = alkyl or benzyl, and 3390 cm.$^{-1}$ for R = phenyl,[10] and both sets are appreciably higher in frequency and in intensity than for amines. As for borazens, the explanation must be that there is double-bond character in the BN bonds and, as the values for borazoles and borazens are so similar, there seems no indication that double bonding in borazoles is more extensive, although appreciable aromatic character would be expected to be shown by this ring. Details are in Table 1.

TABLE 1. *Infrared bands* (*cm.*$^{-1}$) *of* B-*aminoborazoles*, $(R{\cdot}NH{\cdot}B{\cdot}NR)_3$.

R	Me	Et	Pr^i	Bu^n	Bu^s	Bu^t	$Ph{\cdot}CH_2$	Ph
νN-H	3425	3436	3425	3436	3436	3425	3448	3425
νB-N	1513(?)	1493	1488	1493	1488	1493	1449	1497
Ring deformn. ω_{10} *	790	800	~781	787	775	790	796	782
Ring deformn. ω_6 and ω_7 *	713	717	709	709	709	—		757,† 738
	704	710						699, 693

* See text. † Includes aromatic vibrations.

In the 720 cm.$^{-1}$ region, in those cases where the absorption was resolved into a doublet, the higher-frequency band was a shoulder on that at lower frequency; in the other cases the absorption was broad.

The spectrum of the ethyl homologue was recorded, not only for a pure liquid sample (Table 4 and Fig. 1), but also for solutions of varying dilutions in carbon tetrachloride; no solvent effects were detected, suggesting only weak or no intermolecular association.

B-*Alkoxyborazoles*, $(RO{\cdot}B{\cdot}N{\cdot}R')_3$.—We have investigated only one member of this class, $(Bu^nO{\cdot}B{\cdot}NEt)_3$. This shows four particularly intense bands: at 1436 (νBN), 1379 (doublet) (CH_3 deformation), 1280 (νBO), and 1170 cm.$^{-1}$ (νCO). There is medium-intensity absorption at 728 cm.$^{-1}$. The value assigned to the BO stretching vibration compares with one at 1269 cm.$^{-1}$ for monoalkoxyborazens,[10] and both values are significantly lower than for trialkyl borates;[11] this has been discussed for borazens, in terms of more powerful back-donation from nitrogen to boron than to oxygen.[10]

The spectra of seven *B*-alkoxyborazoles have been recorded by Bradley, Ryschkevitsch, and Sisler,[5] and assignments for absorptions down to 1136 cm.$^{-1}$ were made. The BO stretching vibration (although referred to as a bending mode) was found at 1318—1330 cm.$^{-1}$ and the CO band at 1136—1157 cm.$^{-1}$. In the 1400—1450 cm.$^{-1}$ region, a medium-to-strong absorption band at ~1445 cm.$^{-1}$ was noted and also a very strong one at 1428 cm.$^{-1}$. The former was assigned to the BN stretching vibration and the latter to a methylene deformation. On intensity grounds, we prefer reversal of these assignments and we regard it as important that absorption at 715 cm.$^{-1}$ was also observed. A second BN mode at 1183 cm.$^{-1}$ was reported, which we do not find.

Boroxoles.—(i) *Introduction*. The compounds examined comprised eleven alkyl and phenyl metaborates, $(RO{\cdot}BO)_3$, five alkyl- and phenyl-boronic anhydrides, $(R{\cdot}BO)_3$, and two aminoboroxoles, $(Me{\cdot}NH{\cdot}B{\cdot}O)_3$ and $(Me_2N{\cdot}B{\cdot}O)_3$. With the simplest of these, methylboronic anhydride, it should be possible to assign all the fundamentals, partly because the geometry is established from an electron-diffraction study,[12] and also because the Raman spectrum is available.[6] Boronic anhydride and metaborate molecules, having D_{3h} symmetry (substituents considered as point masses), should have 14 skeletal vibrations. These

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[11] Werner and O'Brien, *Austral. J. Chem.*, 1955, **8**, 355.

[12] Bauer and Beach, *J. Amer. Chem. Soc.*, 1941, **63**, 1394.

modes divided themselves into 5 symmetry classes: $3A_1'$; $2A_2'$; $2A_2''$; $5E'$ and $2E''$; of which vibrations belonging to A_2'' and E' should be observed in the recorded infrared spectra (E' are also Raman-active).

The two A_2'' vibrations may be approximately described as out-of-plane side-chain bending and ring bending modes, and these have been found by Goubeau and Hummel[8] for methylboronic anhydride at 570 (ω_6) and 459 cm.$^{-1}$ (ω_7); for the other boronic anhydrides investigated these vibration frequencies fall outside the range recorded.

Corresponding modes have, however, been located much higher for 1,3,5-trisubstituted benzenes and melamine,[13] and the medium-to-strong absorption band observed for metaborates[7] in the 720 cm.$^{-1}$ region undoubtedly belongs to this symmetry class. The constancy in absorption frequency in the series Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, and Bu^s, favours the assignment of this band to the out-of-plane ring bending mode, but a small separation of these two modes (in melamine 30 cm.$^{-1}$) or even an overlap of absorption bands cannot be ruled out. It is possible that the shoulder observed on the high-frequency side of the main band at ~720 cm.$^{-1}$ represents the other out-of-plane deformation mode.

The five E' vibrations consist of two ring stretching and one side-chain stretching mode, one ring bending, and one side-chain bending mode. Only the first three would be expected to fall in the 5000—650 cm.$^{-1}$ region and these have been found[8] for methylboronic anhydride at 1384 (ω_8), 1226 (ω_9), and 783 cm.$^{-1}$ (ω_{10}), respectively.

The ω_8 (ring stretching) mode is found for boronic anhydrides and metaborates in the narrow range 1387—1335 cm.$^{-1}$ as the strongest band in the spectrum and is undoubtedly a B–O ring vibration, being in the same range as the B–O asymmetric stretching vibrations of trialkyl orthoborates.[11]

The ω_9 mode, which can be described approximately as a B–C stretching mode, is found at ~1200 cm.$^{-1}$ which is ~100 cm.$^{-1}$ higher than the corresponding absorption of trialkylborons.[14] Similar increases in frequency due to side-chain stretching modes have been observed for mesitylene (C–C) and melamine (C–N).[13]

The ring vibration ω_{10}, observed[8] in methylboronic anhydride at 783 cm.$^{-1}$, appears in all spectra of anhydrides and metaborates as a weak-to-medium intensity band in the 825—760 cm.$^{-1}$ region.

However, for a complete and reliable treatment of boronic anhydride and metaborate molecules more information is required than at present available and the results to date must of necessity be interpreted on a semi-empirical basis.

TABLE 2. *Infrared bands (cm.$^{-1}$) for boronic anhydrides,* $(R{\cdot}BO)_3$.*

R	Me	Et	Bu^n	Bu^t	Ph
^{11}B–O (ω_8)	1370	1380	1387	1357	1451
^{10}B–C (ω_9)	1222	1225	1202	1147	1104 †
^{11}B–C (ω_9)	1253	1265	1236	1160	1087 †
Ring deformn. (ω_{10})	783	798	798	760	778

* The spectrum of isobutylboronic anhydride in carbon disulphide was also examined, but only in the 1250—650 cm.$^{-1}$ region. † Assignment not certain owing to complexity of aromatic absorptions in this region.

(ii) *Boronic anhydrides.* Assignments for B–O ring stretching (ω_8), B–C stretching (ω_9), and ring vibrations (ω_{10}) are listed in Table 2. The selection of a band at ~1370 cm.$^{-1}$ as arising from the B–O stretching mode is based on the observations that (*a*) in each spectrum this is the band of greatest intensity, (*b*) in many cases there is indication of ^{10}B/^{11}B isotopic splitting, and (*c*) the values are similar to those found for orthoborates.[11] On the other hand, Santucci and Gilman[9] assigned bands at 1170—1198 cm.$^{-1}$ in spectra of arylboronic anhydrides to the B–O stretching mode; we regard these as arising from aromatic CH deformation modes [see Table 5 and Fig. 2 for $(Ph{\cdot}BO)_3$]. The separation of the presumed ^{11}BC and ^{10}BC bands and also their relative intensities [see Table 6 and Fig. 3 for $(Et{\cdot}BO)_3$] are consistent with the interpretation and their location is in the same

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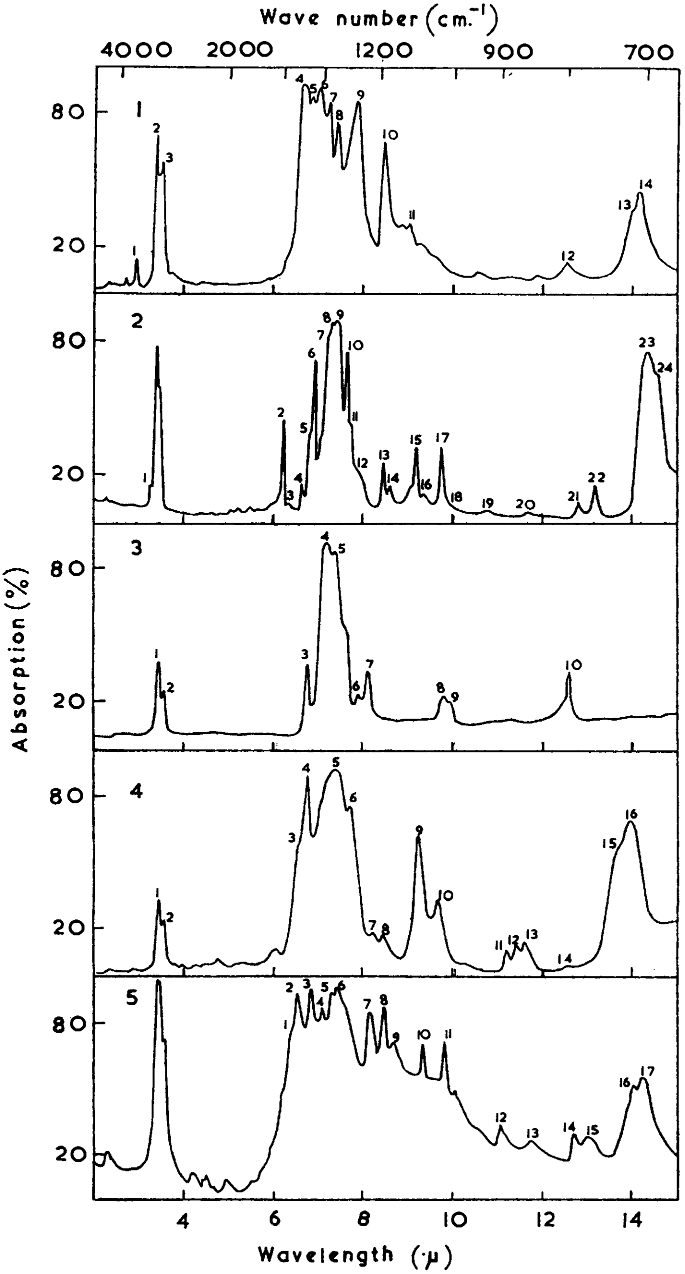
[13] Jones and Orville-Thomas, *Trans. Faraday Soc.*, 1959, **55**, 203.

Infrared spectra of (1) *tris*-B-*ethylaminoborazole* (*see Table* 4), (2) *tri*-B-*phenylboroxole* (*phenylboronic anhydride*) (*see Table* 5), (3) *tri*-B-*ethylboroxole* (*ethylboronic anhydride*) (*see Table* 6), (4) *tri*-B-*methoxyboroxole* (*methyl metaborate*) (*see Table* 6), *and* (5) *tris*-B-*dimethylaminoboroxole* (*see Table* 4).



region as the ^{11}BC asymmetric stretching frequency for trimethylboron (1150 cm.$^{-1}$).[14] In the phenylboronic anhydride spectrum, unequivocal assignment for the BC stretching frequency is not easily made, because of the predominance of aromatic vibrations in the relevant (1000—1300 cm.$^{-1}$) region; however, for a series of arylboronic anhydrides an

[14] Lehmann, Wilson, and Shapiro, *J. Chem. Phys.*, 1958, **28**, 777.

absorption band in the range 1080—1110 cm.$^{-1}$ has been put forward as characterising the BC stretching mode (Santucci *et al.*[9]).

Snyder, Konecky, and Lennarz[9] regarded a band at ~700 cm.$^{-1}$ in the spectra of arylboronic acids as characteristic of these compounds (for phenylboronic anhydride, a shoulder at 690 cm.$^{-1}$); however, for the aliphatic compounds we notice no absorption in this region, although we confirm the observation with phenylboronic anhydride (see Table 5 and Fig. 2).

TABLE 3. *Infrared bands (cm.$^{-1}$) of metaborates,* (RO•BO)$_3$.

R	Me	Et	Pr^n	Pr^i	Bu^n	Bu^i	Bu^s	Bu^t	Ph	Cl•CH$_2$•CH$_2$	CH$_2$Bu^t	C$_6$H$_{13}$•CHMe
νB–O	1351	1341	1355	1335	1345	1353	1337	1370	1378	1350	1342	1342
δCH(O•B<)	1427	1433	1427	1406	1427	1429	1409	—	—	1441	1425	1416
νC–O	1085	1080	1083	1119	1088	1083	1129	1182	1225	1092	1087	1082
Ring deformn. (ω_{10})	799	804	870(?)	789	810	823	822	—	789	812	?	820
Ring deformn. (ω_6)	718	722	722	723	723	724	724	—	700	715	733	735
(ω_7)	736	736	734	733	734	736	735		715	709	722	725

TABLE 4. *Frequencies and assignments of absorption bands (cm.$^{-1}$) in* (A) (Et•NH•B•NEt)$_3$ *and* (B) (Me$_2$N•BO)$_3$.

Frequency[a] A		Frequency[a] B		Assignment
3436	(1)			N–H stretch
2932	(2)			C–H stretch
2857	(3)			
		1575	(1)	B–N stretch (CH$_3$ bending)[b]
		1534	(2)	
1493	(4)			Ring stretch (ω_8)
		1456	(3)	CH$_3$ deformation (B–N stretch)[b]
1452	(5)			CH$_3$ and CH$_2$ deformation
1417	(6)	1412	(4)	
1376	(7)	1384	(5)	
		1342	(6)	Ring stretch (ω_8)
1342	(8)			?
1269	(9)	1224	(7)	CH$_3$ wagging
1180	(10)			CH$_3$ wagging
		1180	(8)	NC$_2$ stretch
		1149	(9)	CH$_3$ wagging
1104	(11)			C–N stretch
		1074	(10)	
		1017	(11)	
		903	(12)	
		847	(13)	
800	(12)	787	(14)	Ring deformn. (ω_{10})
		767	(15)	
717	(13)	714	(16)	Ring out-of-plane deformn. (ω_6) and (ω_7)
710	(14)	703	(17)	

[a] Numbers in parentheses refer to (A) Fig. 1 and (B) Fig. 5. [b] In the text alternative assignments are discussed.

TABLE 5. *Frequencies (cm.$^{-1}$) and assignments of absorption bands in phenylboronic anhydride.*

Frequency[a]		Assignment[b]
3031	(1)	C–H stretch (A_1)
1605	(2)	C–C stretch (A_1)
1575	(3)	C–C stretch (B_1)
1490	(4)	C–C stretch (A_1)
1458	(5)	C–H deformn.[c]
1447	(6)	C–C stretch (B_1)
1387	(7)	?
1370	(8)	Ring vibration (boroxole) (ω_8)
1351	(9)	
1312	(10)	C–C stretch (B_1)
1295	(11)	C–H deformn. (B_1)
1264	(12)	?
1182	(13)	C–H deformn. (A_1)
1163	(14)	C–H deformn. (B_1)
1104 1087	(15)	B–C stretch (ω_9)?
1064	(16)	C–H deformn. (B_1)
1026	(17)	C–H deformn. (A_1)
1000	(18)	Ring deformn. (A_1)
927	(19)	C–H deformn. (B_2)
855	(20)	C–H deformn. (A_2)
778	(21)	Ring deformn. (boroxole) (ω_{10})
761	(22)	C–H deformn. (B_2)
698	(23)	Ring deformn. (B_2)
670	(24)	Ring out-of-plane deformn. (boroxole)

[a] Numbers in parentheses refer to Fig. 2. [b] Aromatic vibrations are designated A_1, A_2, B_1, or B_2, as appropriate (cf. Whiffen, *J.*, 1956, 1350). [c] Absorption due wholly, or in part, to liquid paraffin.

Hennion, McCusker, Ashby, and Rutkowski[15] observed that reaction of t-butylmagnesium chloride with boron halides affords, instead of tri-t-butylboron, substantial amounts of isobutyl derivatives. It was of interest to see whether reaction with a trialkyl

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[15] Hennion, McCusker, Ashby, and Rutkowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5190; Hennion, McCusker, and Rutkowski, *ibid.*, 1958, **80**, 617.

borate [where only one alkoxy-group is replaced to give $Bu{\cdot}B(OH)_2$, and from this the anhydride $(Bu{\cdot}BO)_3$] led to rearrangement or not. The infrared spectrum of the product showed that it was t-butyl- and not isobutyl-boronic anhydride. The evidence is principally that the product showed no absorption between 850 and 760 cm.$^{-1}$, whereas isobutylboronic anhydride had a strong band at 830 cm.$^{-1}$. The ν_4 skeletal vibration of the t-butyl group falls at 415 cm.$^{-1}$ and that of the isopropyl group at 840—793 cm.$^{-1}$ for hydrocarbons.[16] A further notable difference between the two compounds was the presence of medium-intensity bands at 1101 and 1058 cm.$^{-1}$ in the spectrum of isobutylboronic anhydride. Two other absorptions might appear to offer scope for distinguishing the isomers: the ν_2 and ν_3 skeletal vibrations at 1140—1250 cm.$^{-1}$ and the CH deformations at 1350—1400 cm.$^{-1}$ (these values having been observed in hydrocarbons).[16] However, as these fall in regions of other strong bands, the evidence would be less decisive. The infrared spectroscopic technique, therefore, offers a method, alternative to that of nuclear magnetic resonance,[17] for distinguishing compounds having iso- from those having t-butyl groups attached to a boron atom.

(iii) *Metaborates.* In the spectrum of methyl metaborate (Table 6 and Fig. 4), the strongest bands appear at 1351vs, 1486 (shoulder at ~1520), 1427 (shoulders), 1085, and 718 cm.$^{-1}$ (shoulder at ~736 cm.$^{-1}$). On intensity grounds, and because of the close correspondence to the B–O stretching frequency in orthoborates,[11] that at 1351 cm.$^{-1}$ must be assigned to the B–O stretching frequency; it does not seem possible to distinguish cyclic and exocyclic B–O bond stretching vibrations. Bands at ~1486 and 1427 cm.$^{-1}$ (the latter with a shoulder at slightly higher frequency) are present for all other metaborates investigated, except the t-butyl and phenyl compounds (for the latter there is a medium-intensity band associated with νC⁚C). It is probable, therefore, that these are characteristic of CH or CH_2 deformation modes, with lower values than usual for such groups,[16] because they are adjacent to an oxygen atom attached to the highly electronegative boron atom. This view is supported by observations on orthoborates, where similar absorptions have been recorded.[11] Relevant data are summarised in Table 3.

TABLE 6. *Frequencies (cm.$^{-1}$) and assignments of absorption bands in* (A) $(MeO{\cdot}BO)_3$ *and* (B) $(Et{\cdot}BO)_3$.

Frequency [a] A		Frequency [a] B [b]		Assignment
2907	(1)	2941	(1)	C–H stretch
2841	(2)	2870	(2)	
1520	(3)	1471	(3)	C–H deformn.
1486	(4)	1404	(4)	
1351	(5)	1380	(5)	Ring stretch (ω_8)
1304	(6)			
		1265	(6)	B–C stretch (ω_9)
		1225	(7)	
1221	(7)			
1186	(8)			CH_3 wagging
1085	(9)			C–O stretch
1037	(10)	1037	(8)	CH_3 wagging (?)
		1003	(9)	C–C stretch (?)
898	(11)			
879	(12)			
863	(13)			
799	(14)	798	(10)	Ring deformn. (ω_{10})
736	(15)			Ring out-of-plane deformn. (ω_6) and (ω_7)
718	(16)			

[a] Numbers in parentheses refer to (B) Fig. 3 and (A) Fig. 4. [b] Gas-phase spectrum.

The narrow range (43 cm.$^{-1}$) over which the B–O stretching frequency falls and the wider spread (150 cm.$^{-1}$) of the C–O bands is closely paralleled in the orthoborates.[11] The infrared spectrum of tri-t-butyl borate, $B(OBu^t)_3$, has not previously been described; strong bands at 1349 and 1185 cm.$^{-1}$ can confidently be assigned to the asymmetric B–O and C–O stretching vibrations, respectively. Consequently, as for the orthoborates so for the metaborates, the values of both of these frequencies are higher for the phenyl and t-butyl compounds than for any others of those studied. This is consistent with there being a higher degree of double-bond character in the B–O bonds when there is the

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[16] Sheppard and Simpson, *Quart. Rev.*, 1953, **7**, 19.

[17] Davies, Hare, and White, *J.*, 1960, 1040.

possibility of inductive or conjugative electron release. The large increases in the C–O stretching frequencies on proceeding from primary (1082 ± 3 cm.$^{-1}$) to secondary (1124 ± 5 cm.$^{-1}$) and tertiary (1182 cm.$^{-1}$) alkyl derivatives correspond to observations on the effect of branching on similar vibrations in alcohols.[18]

In the 720 cm.$^{-1}$ region, the band at higher frequency was a shoulder of the other; there is thus close resemblance to the situation with *B*-aminoborazoles.

(iv) B-*Aminoboroxoles.* The spectra of the compounds [$(Me_2N{\cdot}BO)_3$ and $(MeNH{\cdot}BO)_3$] showed strong absorption bands in the range 1540—1000 cm.$^{-1}$ and also at 702 ± 3 cm.$^{-1}$. In order to make assignments in the higher-frequency region, the spectra were compared with those of corresponding borazens[10] [$B(NHMe)_3$ and $B(NMe_2)_3$]. For the latter, bands at 1509, 1413, and 1384 cm.$^{-1}$ were assigned to deformation modes of the methyl groups, leaving others at 1449 (^{11}B) and 1471 cm.$^{-1}$ (^{10}B, weaker) as asymmetric B–N stretching vibrations. By analogy, we allocate bands in trisdimethylaminoboroxole (see Table 4 and Fig. 5) at 1456 (BN) and 1342 cm.$^{-1}$ (BO), leaving others at 1534, 1412, and 1384 cm.$^{-1}$ as CH_3 deformations. Similarly, in the spectrum of trismethylaminoboroxole, bands at 1468 and 1351 cm.$^{-1}$ are assigned to BN and BO stretching frequencies, respectively. However, assignment of a band as the B–N stretching frequency must be speculative and it is possible that for the former compound it is the 1534 cm.$^{-1}$ band.

Hyperconjugation in Alkylboronic Anhydrides.—It has been suggested[19] that trimethylboron, unlike the other Group IIIB alkyls, is monomeric because of hyperconjugative stabilisation, *i.e.*, because of contributing canonical structures of the type $Me_2\bar{B}{=}CH_2\ H^+$. Although there has recently been some doubt (see, *e.g.*, ref. 20) regarding the validity of the theory of hyperconjugation, we thought that examination of B–C stretching frequencies in the α-methyl series (*i.e.*, Me, Et, Pr^i, and Bu^t) of alkylboronic anhydrides might throw some light on the problem. The boronic anhydrides, rather than the trialkylborons, were chosen because among the latter isomerisation of the more highly branched homologues takes place,[15] presumably owing to steric strain. Hyperconjugation would imply decreased bond-shortening in the series Me > Et > Pr^i > Bu^t and this should be reflected in the B–C stretching frequencies. Although we have no information on isopropylboronic anhydride, the results in Table 2 appear to support hyperconjugation. However, the shift from the methyl to the t-butyl compound is so large that it may alternatively or additionally be due to lengthening of the Bu^t–B bond, due to steric strain.

A further observation, although not providing an unambiguous answer, is that t-butylboronic anhydride is much more readily oxidised than the n-butyl isomer. It has been assumed[21] that oxidation of trialkylborons proceeds by co-ordination of molecular oxygen with the boron atom and a subsequent 1,3-shift of alkyl from boron to oxygen to form an alkylperoxyboron compound. If attack by oxygen is rate-determining, then, if hyperconjugative effects are excluded, the n-butyl derivative should be the more labile, both on steric grounds and from considerations of inductive effects (Bu^t > Bu^n). The alternative explanation, however, is that the alkyl migration is rate-determining.

Characteristic Ring Vibrations.—In Table 7 are collected data on ring stretching [and ring out-of-plane deformation modes (in parentheses)] vibrations of borazoles and boroxoles: where no parenthetical observation is made, published results are incomplete. Frequencies are quoted in cm.$^{-1}$ and mean values are shown, unless there are wide discrepancies between different publications.

It seems that the presence of the out-of-plane ring vibrations near 720 cm.$^{-1}$ is characteristic for those borazoles and boroxoles, where the substituents on the boron atoms (RO, ArO, R_2N, RNH, Cl, Ar) can conjugate with the ring; the exceptions are t-butoxy- and t-butylamino-groups and the anomaly may be due to a steric effect.

[18] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.
[19] Mulliken, *Chem. Rev.*, 1947, **41**, 207.
[20] Dewar and Schmeising, *Tetrahedron*, 1959, **5**, 160.
[21] Abraham and Davies, *Chem. and Ind.*, 1957, 1622; *J.*, 1959 ,429.

TABLE 7. *Ring vibrations (cm.$^{-1}$) for borazoles and boroxoles.**

X in $(X{\cdot}B{\cdot}NR)_3$	X in $(X{\cdot}BO)_3$	X in $(X{\cdot}B{\cdot}NH)_3$
Ph, 1405 [5b]	RO, 1345 (735, 722) [7, a]	H, 1465 (<650) [2, 3, 5a]
Cl, 1392,[5b, 5d, a] 1440 [5d]	Bu^{t}O, 1370 (below 650) [a]	Cl, 1445 [5b, 5d] (671,680) [a]
R′O, 1442 [5c, 4] (728 [4, a])	PhO, 1378 (715, 700) [7 a]	Ph, 1472 [5b]
† R′NH, 1490 [4, 5c, a] (710 [4, a])	R, 1375 (below 650) [8, a]	$ClCH_2$, 1485 [f]
Bu^t·NH, 1493 (<650) [a]	Ar, 1351 (~700) [9a, a]	RNH and R_2N, 1493 [b]
R'_2N, 1493 [b]	R_2N, 1342 (702) [a]	
PhO, 1412 [5c]	RNH, 1351 (702) [a]	X in $(X{\cdot}B{\cdot}NPh)_3$
R′, 1410 [5d, c]	R_3SiO, 1380 (735, 720) [e]	Cl, 1375 [5b, 5d]
R'_3Si, 1441 [d]		Ph, 1368 [5d]
$Ar_3'Si$, 1429 [d]		R, 1380 [5b, 5d]
		PhNH, 1497 [a]
X in $(HB{\cdot}NX)_3$		
Ph, 1401 [5b]		
Me, 1425 (<650) [3]		

* R and R′ = alkyl (but not Bu^t for †).

[a] Present work. [b] Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1959, **81**, 3561. [c] Ryschkewitsch, Harris, and Sisler, *ibid.*, 1958, **80**, 4515. [d] Cowley, Sisler, and Ryschkewitsch, *ibid.*, 1960, **81**, 501. [e] Abel and Singh, *J.*, 1959, 690. [f] Turner, *Chem. and Ind.*, 1958, 1405.

Superior numerals relate to literature references.

EXPERIMENTAL

Preparations.—The borazoles, except for $(Cl{\cdot}B{\cdot}NMe)_3$,[22] were prepared by methods described in Parts III and IV.[1, 4] The alkylboronic anhydrides,[23] except for the methyl homologue, phenylboronic anhydride,[24] metaborates (Part I [7]), except for $(Bu^tO{\cdot}BO)_3$, and aminoboroxoles (Part IV [1]) were obtained by published methods.

Methylboronic anhydride. Methylmagnesium iodide (1 mol.) in ether was added to tri-n-butyl borate (1 mol.) in ether at −78°. The bulk of the ether was removed at 20°/20 mm. and the residue was extracted with pentane. The pentane extract afforded dibutyl methylborinate, $(Bu^nO)_2B{\cdot}Me$, b. p. 80°/20 mm., which was treated with octan-1-ol to afford *dioctyl methylboronate*, b. p. 108°/0·01 mm., n_D^{20} 1·4310 (Found: B, 3·8. $C_{17}H_{37}O_2B$ requires B, 3·8%). To the octyl ester (2 mol.) was added boron trichloride (1 mol.) $[2(RO)_2B{\cdot}Me + BCl_3 \longrightarrow 2RO(Cl)B{\cdot}Me + (RO)_2B{\cdot}Cl]$, and the products were decomposed [25] by addition of ferric chloride $[RO(Cl)B{\cdot}Me \longrightarrow \frac{1}{3}(MeBO)_3 + RCl;\ (RO)_2B{\cdot}Cl \longrightarrow RCl + \frac{1}{3}(RO{\cdot}BO)_3]$; the volatile methylboronic anhydride was condensed into a trap in the vacuum-line.

Infrared Spectra.—These were obtained on a Grubb-Parsons S.3A double-beam spectrometer, fitted with a sodium chloride prism. Samples were studied as liquid films, solutions, or mulls in paraffin oil.

The spectra are being submitted to the D.M.S. collection. Data are in the Tables.

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[22] Aubrey and Lappert, unpublished work.
[23] McCusker, Ashby, and Makowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5179.
[24] Bean and Johnson, *J. Amer. Chem. Soc.*, 1932, **54**, 4415.
[25] Lappert, *J.*, 1956, 1768; Brindley, Gerrard, and Lappert, *ibid.*, p. 1540.