73. *Infrared Spectra of Ethylene and* o-*Phenylene Derivatives of Boric Acid.*

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The infrared spectra of 38 organic boron compounds have been obtained. The positions of a number of characteristic group frequencies have been noted and the structural implications are discussed, with particular reference to frequency shifts. The most significant conclusion is probably the recognition that benzo-1,3,2-dioxaboroles have aromatic character.

Aspects of the chemistry of certain ethylene[1,2] and *o*-phenylene[3] derivatives of boric acid [$(CH_2{\cdot}O)_2B{\cdot}OH$, $(HO)_2B{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}B(OH)_2$, *o*-$C_6H_4O_2B{\cdot}OH$, and $(HO)_2B{\cdot}O{\cdot}C_6H_4{\cdot}O{\cdot}B(OH)_2$] have recently been described. We now report studies of the infrared spectra, in the 650—5000 cm.$^{-1}$ region, of 38 of the compounds (formulæ I—IV).

The spectra of organic boron compounds were recently reviewed,[4] and for acyclic

[1] Blau, Gerrard, and Lappert, *J.*, 1957, 4116.

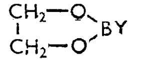
[2] Glan, Gerrard, and Lappert, *J.*, in the press.

[3] Gerrard, Lappert, and Mountfield, *J.*, 1959, 1529.

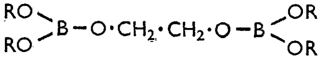
[4] Bellamy, Gerrard, Lappert, and Williams, *J.*, 1958, 2412.

substances having a tervalent boron atom the group correlations are shown in Table 1. Also relevant are the spectra of certain acyloxyboron compounds, which showed abnormally low carbonyl stretching frequencies (1690—1580 cm.$^{-1}$) ascribed to intramolecular bonding between the carbonyl-oxygen atoms of the acyloxy-group and the boron atom to which the group is attached.[5]

(I)



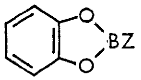
Y = OH, Cl, OR (R = Pr^n, Pr^i, Bu^i, Bu^s, or n-C_5H_{11}), SR (R = Bu^n or n-C_8H_{17}), NR_2 (R = Et or Bu^n), or O·COR (R = Me, CH_2Cl, $CHCl_2$, CCl_3, or CF_3)



$$(RO)_2B-O\cdot CH_2\cdot CH_2\cdot O-B(OR)_2$$

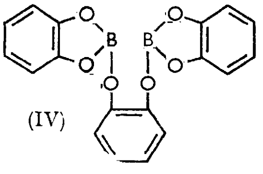
(II)

R = Bu^n, Bu^i, n-C_5H_{11}, Ph, or ·CH_2·



(III)

Z = OH, Cl, Br, Bu^t, Ph, OR (R = Me, Et, Pr^n, Bu^n, n-C_5H_{11}, n-C_8H_{17}, or Ph), SR (R = Bu^n or n-C_8H_{17}), NR_2 (R = Et or Bu^n), or O·BO_2·C_6H_4-*o*



(IV)

TABLE 1. *Assignment ranges* (*cm.*$^{-1}$).

BH [4]	2630—2350	BPh [4, a]	1440—1430	BO [4, a–c]	1350—1310
BN [d]	1510—1470	BPh_2 [4, c]	1280—1250	BS [d]	970—900
				BCl [4, a, c]	910—890

[a] Dandegaonker, Gerrard, and Lappert, *J.*, 1957, 2872. [b] Werner and O'Brien, *Austral. J. Chem.*, 1955, **8**, 355; 1956, **9**, 137. [c] Abel, Gerrard, and Lappert, *J.*, 1957, 3833. [d] Aubrey, Lappert, and Pyszora, unpublished work.

Derivatives of the Acids (I; R = OH) *and* (II; R = H).—Common structural features among these compounds are: (i) the methylene groups, (ii) B–O bonds, and (iii) C–O bonds.

Methylene groups are responsible for strong absorption in the 1471—1389 cm.$^{-1}$ region. The CH deformation mode in the methylene group generally appears at 1465 ± 20 cm.$^{-1}$, but the frequency can be influenced by the following factors:[6] (i) changes of phase (leading to shifts of up to 10 cm.$^{-1}$); (ii) introduction of electronegative groups in the immediate vicinity (shifts of up to 100 cm.$^{-1}$); and (iii) ring strain. The only relevant factor is (ii) and would arise because of the existence of canonical forms of type $-CH_2-\overset{+}{O}=\overset{-}{B}<$. Evidence for this is that the compounds absorb at about 1410 cm.$^{-1}$; slightly larger shifts have been observed with vinylic ethers.[7]

All the compounds (I) and (II), with the exception of most of the carboxylates (I; Y = O·COR where R = Me, CH_2Cl, $CHCl_2$, or CCl_3), had a band at 1340 ± 80 cm.$^{-1}$ as the strongest in the spectrum and this arises from the B–O stretching mode. The absence of such absorption in carboxylates (except I; Y = O·CO·CF_3) supports the view (see below) that they are chelated (VIII) and hence contain quadrivalent boron. It has already been noted that the B–O correlation rule applies only to situations in which the boron octet is not completed.[4] In ethylene dialkylaminoboronates (I; Y = NR_2) the B–O absorption band has apparently fallen to 1299 cm.$^{-1}$, which indicates a lowering of bond order in the B–O links; this would be expected owing to strong nitrogen to boron back-co-ordination (cf. V).

All the compounds (I) and (II) absorbed strongly at ~1100 cm.$^{-1}$, undoubtedly owing to the C–O stretching. In aliphatic ethers the strong C–O absorption band is at 1150—1060 cm.$^{-1}$ and its position is influenced by structural factors. Extreme cases are (I; Y = SR)

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[5] Duncanson, Gerrard, Lappert, Pyszora, and Shafferman, *J.*, 1958, 3652.

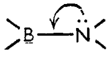
[6] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, p. 20.

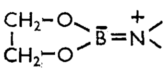
[7] Mikawa, *Bull. Chem. Soc. Japan*, 1956, **29**, 110.

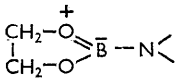
at 1102 ± 3 cm.$^{-1}$, (II; R = Bu^{i}) at 1036 cm.$^{-1}$, and (II; R = Ph) at 1070 cm.$^{-1}$. Some of the compounds have a doublet in this region and this may arise because of the presence in these substances of two types of C–O bonds [*e.g.*, in (I; Y = OR)].

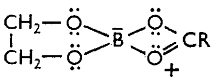
Among the other absorptions which can readily be assigned are: (i) the 905 cm.$^{-1}$ (B–Cl) band in ethylene chloroboronate (I; Y = Cl) and the triplets at 971—893 cm.$^{-1}$ (B–S) in the thioesters.

For the amino-compounds (I; Y = NR_2), the region 1538—1250 cm.$^{-1}$ shows nine absorption bands, of which four are very strong. Although it is difficult to make unequivocal assignments for the B–O and B–N stretching modes from the relative intensities, we tentatively suggest that the 1527 and 1299 cm.$^{-1}$ bands are those due to B–N and B–O respectively. This implies a B–N bond order higher than normal and a B–O bond order lower than normal, *i.e.*, that structure (VI) is relatively more important than structures of type (VII). This view is supported by a thermochemical and theoretical treatment,[8] which showed that nitrogen is more effective than oxygen in back-co-ordination to boron.


(V)


(VI)


(VII)


(VIII)

The carbonyl stretching frequencies of the carboxylates (I; Y = O·COR) are listed in Table 2, and by analogy with an earlier treatment,[5] the abnormally low values are assigned to a co-ordinated $({>}C{=}O{:} \longrightarrow B{\leqslant})$ group. As general conclusions it is apparent that: (i) chelation of type (VIII) occurs in all compounds except the trifluoroacetate; (ii) that the compounds that do chelate have also a higher-frequency band (free C=O) of at least equal intensity [see Fig. 1 for R = Me, where *a* denotes $\nu_{CO(free)}$ and *a′* denotes $\nu_{CO(bonded)}$]; and (iii) that the positions of the bands depend on R and are highest when R is most electronegative (*i.e.*, $CF_3 > CCl_3 > CHCl_2 > CH_2Cl >$ Me). That the trifluoroacetate is not chelated (Fig. 2, where *a* denotes ν_{CO}) is interpreted as being due to the relatively low basic strength of the carbonyl-oxygen atom in that compound because of the powerful electron-attraction of the trifluoromethyl group. Chelation in the other carboxylates is evidently not very strong (because of the presence also of absorption due to a free carbonyl group), and this is to be expected in view of the low acceptor capacity of the boron atom when surrounded by oxygen atoms capable of back-co-ordination. The presence of the two carbonyl stretching frequencies is interpreted as implying an equilibrium between (VIII) and a non-co-ordinated form. In an attempt to test this hypothesis, the spectrum of a solution of the acetate (I; Y = OAc) in methylene dichloride at −70° was examined. It was thought that cooling might disturb an equilibrium; however, no significant difference was noted from that measured at 20°, nor was the spectrum significantly changed when measured on the solid as a mull in liquid paraffin.

TABLE 2. *Carbonyl frequencies* (*cm.*$^{-1}$) *for compounds* (I; Y = O·COR).

R	Co-ordinated	Free	R	Co-ordinated	Free
Me	1605	1731	CCl_3	1637	1761
CH_2Cl	1613	1742	CF_3	—	1783
$CHCl_2$	1634	1754			

o-*Phenylene Derivatives* (III) *and* (IV).—All the compounds, except *o*-phenylene phenylboronate (III; Z = Ph), have, among the strongest bands, those at 1245 ± 20 and 1447 ± 40 cm.$^{-1}$. These collectively may be regarded as characteristic of, and diagnostic for, the boron-containing ring. The 1245 ± 20 cm.$^{-1}$ band is undoubtedly the ring-C–O stretching mode; this is supported by noting (ref. 6, p. 115) that the C–O stretching

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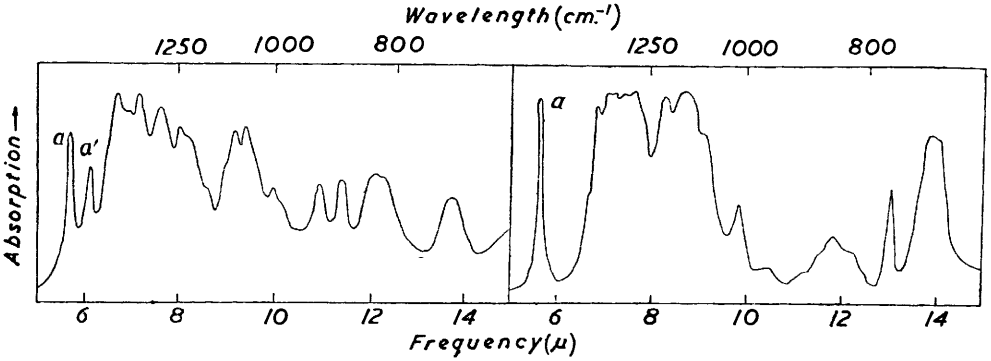
[8] Skinner and Smith, *J.*, 1954, 3930.

frequency in aromatic ethers falls at 1270—1230 cm.$^{-1}$. It is very probable, therefore, that the 1447 ± 40 cm.$^{-1}$ band is due to the ring B–O stretching vibration. This value, however, is substantially higher than that (1350—1310 cm.$^{-1}$) usually found in tervalent boron–oxygen compounds. The implication is that the B–O bond order in compounds (III) and (IV) is higher than, for example, in trialkyl borates. This would be consistent with such *o*-phenylenedioxyboron compounds' having contributing canonical forms to type (IX), with the boron atom in an aromatic-type ring, displaying 6π-electron resonance. The same proposal has already been made (but without any compelling evidence) to account for the stability of *o*-phenylenedioxyboron compounds [2] and ultraviolet spectra of certain compounds of type (III).[9]

A doublet at 1352 ± 10 and 1337 ± 7 cm.$^{-1}$ occurred in all compounds [except (IV) (only at 1337 cm.$^{-1}$), *o*-phenylene phenylboronate (III; Z = Ph) (only at 1330 cm.$^{-1}$), and *o*-phenylene di-*n*-butylaminoboronate (III; $Z = NBu^n{}_2$) (only at 1355 cm.$^{-1}$)], but was not readily discernible in the alkyl *o*-phenylene borates (III; Z = OR) owing to predominance of the very strong alkyl-BO absorption.

Fig. 1. Fig. 2.



Infrared absorption spectra for (*Fig.* 1) *acetyl ethylene borate and* (*Fig.* 2) *ethylene trifluoracetyl borate* (*liquid films*).

o-Phenylene chloroboronate (III; Z = Cl) and the thioborates (III; Z = SR) showed no absorption band normally associated with B–Cl and B–S bond, respectively. This could be due to there being a lower B–Cl and B–S bond order in these compounds [owing to contributing structures (IX)] than in those previously examined. The dialkylaminoboronates (III; $Z = NR_2$) had a distinct band at 1354 cm.$^{-1}$, which may tentatively be assigned to the B–N stretching frequency; that the value is significantly lower than that (1527 cm.$^{-1}$) proposed for the corresponding mode in derivatives of ethylene hydrogen borate is again consistent.

The alkyl *o*-phenylene borates (III; Z = OR) have a strong band at 1342 ± 10 cm.$^{-1}$ which is attributed to the stretching mode of the alkylboron–oxygen bond. In the phenyl ester (III; Z = OPh), the 1245 cm.$^{-1}$ C–O stretching mode of the ring system is of only medium intensity and a strong band at 1220 cm.$^{-1}$ is ascribed to the acyclic C–O vibration. The corresponding mode in the alkyl esters is disclosed by a band, diminishing in intensity through the series methyl to n-octyl, at 1056 cm.$^{-1}$ (Z = OMe) to 1070 cm.$^{-1}$ ($Z = O{\cdot}C_8H_{17}$-n).

The two strongest bands in the spectrum of *o*-phenylene phenylboronate (III; Z = Ph) (apart from the one at 740 cm.$^{-1}$) appear at 1330 and 1236 cm.$^{-1}$. The region 1440 ± 40 cm.$^{-1}$ is relatively free from absorption [and in this is exceptional among the compounds (III) and (IV)] with a weak band at 1475 cm.$^{-1}$ probably due to a monosubstituted aromatic

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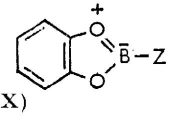
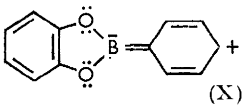
[9] Dewar, Kubba, and Pettit, *J.*, 1958, 3076.

nucleus. The shift of the B–O vibration to lower frequency in this compound suggests that structures of type (IX) are relatively unimportant and that there is overlap into the vacant boron p_z-orbitals of the π-electrons of the phenyl nucleus attached to boron [see, *e.g.*, structure (X)].


(IX)


(X)

The thioesters (III; Z = SR) show apparently characteristic splitting of the strong band at ~1245 cm.$^{-1}$ into a doublet at 1251 ± 2 and 1234 ± 2 cm.$^{-1}$.

The spectrum of *o*-phenylene hydrogen borate (III; Z = OH) was examined in some detail, because it was thought that this formulation might be supported by spectroscopic observations. Several alternative formulations (some as mixtures) are possible, but some are excluded by hydroxyl stretching frequencies at 3413 and 3300 cm.$^{-1}$; these are also shown by catechol although, in contrast to the catechol spectrum, there was a slight shoulder at 3155 cm.$^{-1}$; all the other bands in the catechol spectrum are also found for compound (III; Z = OH).

Experimental.—Spectra were measured in a Grubb–Parsons S.3A double-beam spectrometer, kindly made available by the National College of Rubber Technology (Northern Polytechnic); it was fitted with a sodium chloride prism. Samples were studied as liquid films, or as solid mulls in paraffin oil, as appropriate.

As the spectra have been submitted for reproduction in the D.M.S. punched-card system, only relevant portions have been discussed. The important assignments are summarised in Table 3, but spectra of two carboxylates [(I) with Y = O·COR where R = Me (Fig. 1) and CF_3 (Fig. 2)] are reproduced.

TABLE 3. *Assignments* (*cm.*$^{-1}$).

	C=O (free)	C=O (bonded)	B–N	$CH_2(\delta)$	B–O	C–O	B–S	B–Cl
$(CH_2{\cdot}O)_2BY'$	1783			~1410	1340 ± 80	1102—1036	971—893 *	905
$(CH_2O)_2B{\cdot}O{\cdot}COR'$	1761— 1731	1637— 1605		~1410	†	1102—1036		
$(CH_2O)_2B{\cdot}NR^2_2$ ...			1527	~1410	1299	1102—1036		
Alk_2O				1465 ± 20		1150—1060		
$ArOR^3$						1270—1230		
o-$C_6H_4O_2BZ'$ or (IV)			1354		1447 ± 40 ‡	1245 ± 20 ‡	†	†
o-$C_6H_4O_2BPh$					1330	1236		

R′ = Me, CH_2Cl, $CHCl_2$, or CCl_3. Y′ = OH, Cl, OR, SR′, or $O{\cdot}CO{\cdot}CF_3$. Z′ = Z (except for Z = Ph.

* Triplet. † Not definitely identified, but shifted to lower frequency. ‡ Ring characteristics.

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