731. *The Infrared Spectra and Structures of Some Acyloxy-derivatives of Boron.*

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The infrared spectra of a number of acyloxy-derivatives of boron are discussed. Some abnormally low carbonyl stretching frequencies are ascribed to intramolecular bonding between the carbonyl-oxygen atoms of the acyloxy-group and the boron atom to which the group is attached. The tendency for this co-ordination decreases as the electron-donor and -acceptor properties of the carbonyl group and the boron atom respectively decrease. Spectra also reveal disproportionation of certain of the acyloxy-boron compounds into carboxylic and boron acid anhydrides, apparently increasing with the capacity for co-ordination.

During investigations of the infrared spectra of certain acetoxy-derivatives of boron (*i.e.*, containing the grouping Me·CO·O·B<) some abnormally low stretching frequencies of ester-type carbonyl groups have been observed, and these have structural implications. The CO stretching frequencies of ester groups are known [1,2] to be lowered from the value of about 1740 cm.$^{-1}$ found in simple aliphatic esters by conjugation at the α-carbon atom [3]

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[1] Jones and Sandorfy, " Chemical Application of Spectroscopy," Interscience Publ., Inc., New York, 1956, Chapter 4.

[2] Bellamy, " Infrared Spectra of Complex Molecules," Methuen, London, 1954, Chapter 11.

[3] Thompson and Torkington, *J.*, 1945, 640.

or hydrogen bonding,[4] and to be raised by electronegative α-substituents [5] or conjugation of the lone-pair electrons on the ether-type oxygen atom.[5]

Compound	State	Carbonyl frequencies (cm.$^{-1}$) and assignments		
		Carboxylic anhydride	Acyloxy-boron group	
			free	bonded
$Bu^n{}_2B\cdot OAc$	liquid	1825, 1757	—	1603
,,	*cyclo*hexane soln.	1709 *	—	1608
$[(AcO)_2B]_2O$	solid	—	1718	1605
$Bu^n{}_2B\cdot O\cdot CO\cdot CF_3$	liquid	—	1786	1672
$[(CF_3\cdot CO\cdot O)_2B]_2O$	solid	—	1770	1655
$PhB(OAc)_2$	solid	1815, 1745	1700	1610
$PhB(O\cdot CO\cdot CF_3)_2$	liquid	—	1761	—
$Ph_2B\cdot O\cdot CO\cdot CF_3$	liquid	—	1770	—
$(AcO\cdot BCl)_2O$	solid	1789 †	—	1587
$(CF_3\cdot CO\cdot O\cdot BBu^n)_2O$	solid	—	—	1689
$(CF_3\cdot CO\cdot O)_3B$	solid	—	1775, shoulder at ~1800	1661
$Bu^n{}_2B\cdot O\cdot CHMe\cdot CO_2Et$	liquid	—	1742	—
$Bu^n{}_2B\cdot O\cdot CMe{=}CH\cdot CO_2Et$	liquid	—	—	1598 ‡
$Bu^n{}_2B\cdot O\cdot CMe{=}CH\cdot CO_2Et$	CCl_4 soln.	—	—	1595 ‡
$Ph_2B\cdot O\cdot CMe{=}CH\cdot CO_2Et$	solid	—	—	1574 §

* Weak band due to trace of acetic acid. † Weak band due to trace of acetyl chloride. ‡ Also a strong band at 1528 cm.$^{-1}$, assigned to conjugated C=C. § Also strong band at 1531 cm.$^{-1}$ assigned to conjugated C=C.

The carbonyl stretching frequencies of various acetoxy- and trifluoroacetoxy-boron compounds are listed in the Table. These compounds are mixed anhydrides of boron acids and carboxylic acids and in some cases the results show that disproportionation occurs, giving an equilibrium between the mixed anhydride and the individual carboxylic and boron acid anhydrides. However, in these cases the situation is quite clear and the carbonyl bands of the carboxylic anhydrides and the acetoxy-boron compounds can easily be differentiated and assigned. For example, in the spectrum of acetyl di-*n*-butylboronite $Bu^n{}_2B\cdot OAc$, bands at 1825 and 1757 cm.$^{-1}$ are due to some acetic anhydride present and the third band at 1603 cm.$^{-1}$ must be due to the boronite. The material is therefore more correctly formulated as the equilibrium mixture, $2Bu^n{}_2B\cdot OAc \rightleftharpoons Bu^n{}_2B\cdot O\cdot BBu^n{}_2 + Ac_2O$. The relative band intensities indicate that at room temperature much less than 50% of the boronite is disproportionated. The carbonyl stretching frequency of the mixed anhydride (1603 cm.$^{-1}$) is exceptionally low and there are only two ways in which the electron-deficient boron atom can influence this frequency so markedly. First, double-bond formation between the boron atom and the attached ether-type oxygen atom, by sharing of a lone pair from the oxygen, could complete the boron octet (*i.e.*, $>\overset{\curvearrowleft}{B{-}O}\cdot Ac$). This would, however, be expected to raise the carbonyl frequency, as does the similar electron displacement in vinyl or phenyl esters [5] (*i.e.*, $\overset{\curvearrowleft}{C{=}C}\overset{\curvearrowleft}{{-}O}\cdot Ac$). Secondly, the boron atom can relieve its electron-deficiency by sharing a lone pair or π-electrons from the carbonyl group (*i.e.*, $>B{\leftarrow}O{=}C{<}$). Electron-withdrawal from the ester group in this manner has an obvious analogy with hydrogen-bonding of the carbonyl group and would result in a lower frequency, as observed.

This interpretation of the low carbonyl frequency is confirmed by measurements on other acetoxyboron compounds. For example, tetra-acetyl diborate $(AcO)_2\cdot B\cdot O\cdot B(OAc)_2$ has two carbonyl stretching bands, at 1718 and 1605 cm.$^{-1}$, of approximately equal intensities. Only two of the four acetoxy-groups can co-ordinate to the two boron atoms and these are responsible for the 1605 cm.$^{-1}$ band; the remaining two acetoxy-groups absorb fairly normally at 1718 cm.$^{-1}$.

Trifluoroacetoxyboron compounds show similar effects to the acetoxyboron compounds but the carbonyl frequencies are raised 50—70 cm.$^{-1}$ by the electronegative trifluoromethyl

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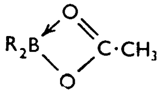
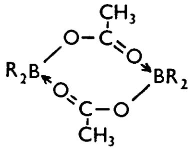
[4] Rasmussen and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1073.

[5] Hartwell, Richards, and Thompson, *J.*, 1948, 1436.

group. There is, however, less tendency for the carbonyl-oxygen of the trifluoroacetoxy-group to co-ordinate with boron than for the carbonyl-oxygen of the acetoxy-group itself, as is shown by the spectrum of $Bu^n{}_2B{\cdot}O{\cdot}CO{\cdot}CF_3$ which, in the liquid state, at room temperature has a band at 1786 cm.$^{-1}$ due to non-co-ordinated carbonyl groups as well as a weaker band at 1672 cm.$^{-1}$ due to co-ordinated carbonyl groups. This is consistent with competition of the electronegative trifluoromethyl group with boron for electrons from the carbonyl bond (*i.e.*, $\geqslant B \leftarrow O{=}C \rightarrow CF_3$). In the trifluoroacetoxy-derivatives of boron there also seems to be a smaller tendency for disproportionation to the carboxylic anhydride than in the acetoxy-derivatives.

(I)





(II)

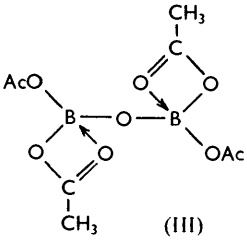
In the spectrum of liquid diacetyl phenylboronate there are, in addition to weak bands due to acetic anhydride, two carbonyl bands at 1610 (co-ordinated $>B{\cdot}OAc$) and at 1700 cm.$^{-1}$ (non-co-ordinated $>B{\cdot}OAc$). In $PhB(O{\cdot}CO{\cdot}CF_3)_2$ and $Ph_2B{\cdot}O{\cdot}CO{\cdot}CF_3$, co-ordination $C{=}O \rightarrow B\leqslant$ does not occur to a significant extent. Both these compounds have single high-frequency carbonyl bands (1761 and 1770 cm.$^{-1}$ respectively), and the only other bands in the double-bond region are relatively weak ones near 1600 cm.$^{-1}$ due to the aromatic rings. It must be concluded that electron-withdrawal by the CF_3 groups and electron-release by the phenyl groups is sufficient, in combination, to prevent chelation.

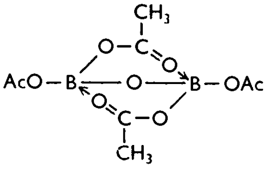
It seems clear from the above that, when conditions are suitable, the boron atoms in acetoxyboron compounds achieve a tetrahedral (sp^3) configuration by completing their octets by the formation of co-ordinate bonds with the carbonyl-oxygen atoms. This could in theory involve either intra- (*e.g.*, I) or inter-molecular (*e.g.*, II) electron-displacement. To decide between these two possibilities the spectra of dilute solutions of $Bu^n{}_2B{\cdot}OAc$ in *cyclo*hexane were measured. Invariably a strong band was observed at 1608 cm.$^{-1}$ together with weak bands at 1709 and near 1745 cm.$^{-1}$. The last two bands are due to a small amount of acetic acid, presumably arising from hydrolysis by traces of moisture picked up during manipulation of solvent and sample. The use of solvents which are more difficult to dry rigorously led to the production of larger amounts of acetic acid, as shown by increased absorption at 1709 cm.$^{-1}$. Over the concentration range studied (0·0244—0·0133M) the extinction of the 1608 cm.$^{-1}$ band is constant within about 5% and this small variation can be accounted for by variation in the amount of material hydrolysed. We therefore conclude that the structure of the acetyl di-*n*-butylboronite is best represented by (I). Molecular models show that the carbonyl-oxygen atom and the boron atom can approach sufficiently close for chelation. In the case of trifluoracetyl di-*n*-butylboronite the situation is not so clear because, in the liquid itself, both co-ordinated and non-co-ordinated molecules occur. By analogy with the corresponding acetoxy-compound we would expect co-ordination to be intramolecular (*i.e.*, chelation) but, because the co-ordinate bond is weaker in the trifluoroacetyl compound, rotational isomerism occurs in the liquid state to give a high proportion of molecules with non-chelated conformations. Cooling the material to −180° intensifies the low-frequency band at the expense of the high-frequency band. This could be due, however, to either an increase in dimerisation or a change in the proportion of rotational isomers.

Compounds based upon the B–O–B skeleton may undergo chelation to give either four-membered (III) or six-membered (IV) rings but we have at the moment no results which distinguish between them.

Electronic effects of various groups attached to the boron atom upon its acceptor properties are shown by the following carbonyl-frequency sequences of the chelated acyloxy-groups: (*a*) $(CF_3{\cdot}CO{\cdot}O{\cdot}BBu^n)_2O$ > (*b*) $Bu^n{}_2B{\cdot}O{\cdot}CO{\cdot}CF_3$ > (*c*) $[(CF_3{\cdot}CO{\cdot}O)_2B]_2O$;

and (*d*) $AcO{\cdot}BBu^n_2 \approx$ (*e*) $[(AcO)_2B]_2O >$ (*f*) $(AcO{\cdot}BCl)_2O$. Thus the central oxygen atom in (*a*) can back-co-ordinate electrons to the boron atoms $(\overset{\frown}{B{-}O})$, thereby causing weaker co-ordination of the trifluoroacetoxy-groups in (*a*) than in (*b*). This is demonstrated by the change in carbonyl frequency from 1689 cm.$^{-1}$ for (*a*) to 1677 cm.$^{-1}$ for (*b*). The effect of the central oxygen atom in (*c*) is offset by electron-withdrawal by the second trifluoroacetoxy-group attached to each boron atom. This brings the carbonyl frequency of the chelated trifluoroacetoxy-group in (*c*) down to 1655 cm.$^{-1}$. The carbonyl frequencies of the chelated acetoxy-groups in (*d*) and (*e*) are approximately the same, showing that a second acetyl group attached to boron in (*e*) does not offset the effect of the central oxygen atom as does the trifluoroacetoxy-group in (*c*). A further frequency lowering to 1587 cm.$^{-1}$ occurs in the spectrum of (*f*), owing to attachment of electronegative chlorine atoms to the boron atoms.

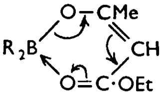

(III)

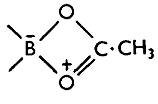

(IV)

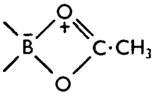
Similar effects are shown by the spectra of 1-ethoxycarbonylethyl dibutylboronite and 2-ethoxycarbonyl-1-methylvinyl dibutylboronite (*i.e.*, $Bu^n_2B{\cdot}O{\cdot}CHMe{\cdot}CO_2Et$ and $Bu^n_2B{\cdot}O{\cdot}CMe{:}CH{\cdot}CO_2Et$). The former substance has a carbonyl frequency (1742 cm.$^{-1}$) which is normal for an alkyl ester, showing that the carbonyl group is not involved in bonding to boron. On the other hand the latter has two strong bands at much lower frequencies (1598 and 1528 cm.$^{-1}$) than occur in the spectrum of enolised ethyl acetoacetate itself[4] in which chelation to a proton (*i.e.*, hydrogen-bonding) occurs. These bands, which are assigned to modes involving C=O and C=C stretching, have the same frequencies in the spectrum of a dilute carbon tetrachloride solution of the dibutylboronite and it follows that the substituted vinyloxy-group is chelated as in (V).

The diphenylboronite (V; R = Ph) has similar bands at 1574 and 1531 cm.$^{-1}$, showing that the electron release from the phenyl groups is not sufficient to restrict chelation in this case.

From molecular models it is clear that there is no steric hindrance to chelation in 1-ethoxycarbonylethyl dibutylboronite, and therefore its inability to chelate must be due to electronic effects. Thus the oxygen atom attached to boron in this compound must share its lone-pair electrons with the boron atom to an extent which decreases the Lewis acid strength of the boron atom below the level at which an ester-carbonyl group can co-ordinate. It appears that in oxyboron compounds co-ordination of an ester-carbonyl group is inhibited unless the lone-pair electrons of the oxygen atoms directly attached to boron are conjugate to another unsaturated system. For example, in the vinyl dibutylboronite, the electron-displacements indicated in (V) favour chelation by increasing both the electron-acceptor properties of the boron atom and the electron-donor properties of the carbonyl-oxygen atom. Similarly in acetoxyboron compounds, resonance stabilisation of the chelate ring can arise owing to contributions of structures (VIa and b) to the states of the molecules.


(V)

(VIa)



(VIb)

EXPERIMENTAL

Except for the compound $(AcO{\cdot}BCl)_2O$ [6] the preparation and physical constants of the boron compounds are described by Gerrard, Lappert, and Shafferman.[7]

*cyclo*Hexane, used as solvent, was dried and stored over sodium. Carbon tetrachloride was dried and distilled from phosphoric oxide. The spectra were measured with a Grubb–Parsons double-beam S3A spectrometer fitted with a sodium chloride prism, and the frequencies quoted are correct to ±4 cm.$^{-1}$. The spectra of solid samples were determined from paraffin oil mulls and liquid samples were measured as capillary films. The spectra of solutions of $Bu^n_2B{\cdot}OAc$ in *cyclo*hexane were obtained by using a cell of fixed thickness (0·02 cm.) and the extinction data for the 1608 and the 1709 cm.$^{-1}$ band are given below.

Molar concentration		0·0244	0·0146	0·0133
Transmission (%)	1608 cm.$^{-1}$	35	54·5	63
Optical density/concn.		18·7	18·0	17·8
Transmission (%)	1709 cm.$^{-1}$	83·2	85·7	88
Optical density/concn.		3·3	4·6	4·9

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[6] Gerrard and Wheelans, *J.*, 1956, 4296.

[7] Gerrard, Lappert, and Shafferman, preceding paper.