595. *Chemical and Spectroscopic Evidence for the Occurrence of π-Character in Carbon–Boron Bonds.*

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Many organoboron compounds possess properties which suggest the presence in these compounds of carbon–boron π-bonding. This is discussed, and additional spectroscopic evidence is presented.

π-BONDING between carbon and boron has frequently been postulated to explain the properties of certain organoboron compounds. αβ-Unsaturated boronic esters and acids, for example, possess chemical and spectral properties strongly suggesting such bonding, a hypothesis in this instance supported by simple molecular orbital calculations.[1] We now supply additional experimental evidence for carbon–boron π-bonding, and discuss some earlier postulates of this bonding.

Evidence from Chemical Behaviour.—Carbon tetrachloride adds to dibutyl vinylboronate to form dibutyl 1,3,3,3-tetrachloropropylboronate; the low value for the first transfer constant ($3{\cdot}3 \pm 0{\cdot}7 \times 10^{-3}$) [1] is as expected if the intermediate radical is stabilized by electron delocalization involving the carbon–boron π-bonding, *viz.*,

$$\mathrm{CCl_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}B(OBu)_2 \longleftrightarrow CCl_3{\cdot}CH_2{\cdot}\overset{+}{C}H{\cdot}\overset{-}{\dot{B}}(OBu)_2}$$

The relative stability towards disproportionation of vinyl- and propenyl-alkylboron compounds provides further chemical evidence for carbon–boron π-bonding.[2] Unless steric effects are a determining factor, as in large and branched-chain alkyl groups, unsymmetrical triorganoboron compounds (*e.g.*, BMe_2Et) are believed to have only a transient existence at ambient temperatures, disproportionating into the symmetrical triorganoboron compounds. These disproportionations undoubtedly proceed *via* a four-centre mechanism involving the p_π-orbital of boron. Clearly, if this p_π-orbital is involved in internal dative bonding, as is believed to occur in alkoxy- and amino-boranes and might occur in alkenylalkylboron compounds,[2] the tendency of the boron compound to disproportionate will be greatly reduced. Ritter and his co-workers [2] found that dimethylvinylborane decomposes only to the extent of about 33% after storage at room temperature for about 5 days. Similarly, methyldivinylborane can be heated to 100° for short periods without significant decomposition. The stability of these unsymmetrical boron compounds contrasts with the transient existence of such species as $BMeEt_2$, supporting the suggestion that mesomerism in alkenylboron derivatives restricts the boron atoms to a planar configuration and therefore inhibits disproportionation.

The stability of the perfluorovinylboron compounds is also interesting.[3] These are the first covalent organoboron compounds to contain a fully fluorinated organic group bonded to boron. Organoboron compounds having halogen atoms in the organic groups tend to decompose to form boron trihalides. Thus fluoromethylboron difluoride readily yields boron trifluoride,[4] and although 2-chloroethylboron compounds have not yet been obtained pure there is clear evidence that they are unstable.[5] It has long been held that a boron compound in which a highly fluorinated organic group is attached to boron would tend to decompose with formation of substances having boron–fluorine bonds. Thus, reaction between bispentafluoroethylmercury and boron trichloride affords boron trifluoride, and no compound containing a perfluoroalkyl–boron group is obtained by this

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[1] Matteson, *J. Amer. Chem. Soc.*, 1960, **82**, 4228.

[2] Parsons and Ritter, *J. Amer. Chem. Soc.*, 1954, **76**, 1710; Parsons, Silverman, and Ritter, *ibid.*, 1957, **79**, 5091.

[3] Stafford and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6238.

[4] Goubeau and Rohwedder, *Annalen*, 1957, **604**, 168.

[5] Hawthorne and Dupont, *J. Amer. Chem. Soc.*, 1958, **80**, 5830.

method.[6,7] The behaviour of the perfluorovinylboron compounds is, however, significant. The dichloride is stable for short periods at 100° and at room temperature for several days before boron trifluoride is detected. Similarly, gaseous triperfluorovinylboron is stable for several days at room temperatures. The perfluorovinylboron compounds may owe their relatively high stability, compared with that of halogenoalkylboron compounds, to a contribution of the π-electrons of the perfluorovinyl group to the p_π-orbital of the boron atom, thereby inhibiting fluorine shift from the side chain to boron.

Further chemical evidence for carbon–boron π-bonding comes from the reduced electrophilic character of boron in certain compounds. In alkylboron halides there is a marked increase in pyrophoric character with branching of the alkyl groups. Steric and inductive factors suggest that reaction with oxygen would be faster for straight-chain than for branched-chain alkyl compounds. It has been suggested[8] that in the straight-chain compounds the boron atom's electrophilic character is reduced by contributions of resonance forms of the type $R\overset{+}{C}H_2{:}\overset{-}{B}Cl_2$. Delocalization of the vinyl groups' electrons into the boron p_π-orbital has been suggested to explain the absence of reaction between trivinylboron and oxygen at room temperature whereas under similar conditions triethylboron is rapidly consumed.[2] Carbon–boron π-bonding may also determine the properties of trimethylboron. Application of molecular-orbital theory to the electronic structure of trimethylboron leads to the conclusion[9] that exceptionally strong trigonal hyperconjugation stabilizes this molecule, and is responsible for trimethylboron's existing as a monomer rather than as the dimer, analogous to hexamethyldialuminium. There is an important distinction between the "hyperconjugation" postulated[9] for trimethylboron and that of organic chemistry. The σ-bonds in trimethylboron would have a charge separation $^{-}C{-}B^{+}$ of a magnitude not usually encountered in C–C bonds. Drift of electron density toward the boron p_π-orbital from the *pseudo*-p_π-orbitals which can be formed from the hydrogen atoms[10] of trimethylboron would lower the energy of the molecule not only by delocalization, but also by partial neutralization of the charge separations in the σ-bonds.

Exceptionally strong hyperconjugation in trimethylboron would tend to reduce the ability of the molecule to function as a Lewis acid, as is found experimentally: towards trimethylamine as reference base, Lewis acidity decreases in the sequence $Me_3Al > Me_3Ga > Me_3In > Me_3B > Me_3Tl$.[11] This sequence, except for the position of boron, perhaps reflects to some degree a decreasing tendency on the part of metals to accept partial negative charge with increasing electropositive character. Undoubtedly the position of boron in the order of acceptor power is due in part to steric factors.[12] Steric interference between groups on the donor and those on the acceptor in addition compounds $Me_3N{\cdot}M^{III}Me_3$ would be at a maximum when M^{III} is the smallest element of the group, the $N{-}M^{III}$ bond length then a minimum. Even if steric effects were negligible, however, it is doubtful[12] if trimethylboron would be a stronger acid than trimethylgallium. In the light of the molecular-orbital treatment of the bonding in trimethylboron[9] it seems reasonable to assume that part of the weakness of trimethylboron as an acid lies in the relatively large reorganizational energy[12] required in passing from the free acid, trimethylboron, to an adduct such as Me_3N,BMe_3. In trimethyl-aluminium and -gallium, as monomers, stabilization by π-bonding would be low, if current views on the inability of heavy atoms to form π-bonds by using p_π-orbitals are correct, so that relatively less adjustment energy is required in rehybridization of the acceptor atoms from sp^2 in the acids to the near sp^3-configuration in the adducts.

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[6] Kaesz, Phillips, and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6228.
[7] Lagowski and Thompson, *Proc. Chem. Soc.*, 1959, 301.
[8] McCusker, Ashby, and Makowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5182.
[9] Mulliken, *Chem. Rev.*, 1947, **41**, 207.
[10] Coulson, *Quart. Rev.*, 1947, **1**, 144.
[11] Coates and Whitcombe, *J.*, 1956, 3351.
[12] Stone, *Chem. Rev.*, 1958, **58**, 101.

Further experimental support for π-bonding in trimethylboron comes from the fact that the equilibrium constant for the reaction $(CD_3)_3B_{(g)} + Me_3N_{(g)} = Me_3N,B(CD_3)_{3(g)}$ is greater than for the analogous reaction involving Me_3B.[13] Ready formation of the heavy addition compound $Me_3N,B(CD_3)_3$ is in agreement with the expectation that replacement of hydrogen atoms in trimethylboron by deuterium would lead to reduction of hyperconjugation with resultant increase in Lewis acidity.

Carbon–boron π-bonding also appears to influence the Lewis acidity of vinylboron difluoride. The gas-phase enthalpies of dissociation of the two addition compounds $Me_3N,BEtF_2$ and $Me_3N,BF_2{\cdot}CH{:}CH_2$ are not detectably different.[14] σ^* values for organic groups bonded to boron indicate that the difference in electron-attracting power between a vinyl and an ethyl group in a compound RBF_2 should be sufficient to cause a measurable difference in Lewis acidity—the vinyl compound being the stronger electron-pair acceptor.[15] The observed equal acidity of the two organoboron fluorides strongly suggests that in vinylboron difluoride the expected inductive effect of the vinyl group is offset by some other factor, the most plausible being delocalization of π-electrons of the vinyl group into the boron p_π-orbital. This idea is supported by fluorine-19 nuclear magnetic resonance studies described below.

Evidence from Spectroscopic Studies.—The presence of conjugation in αβ-unsaturated organoboron compounds is suggested by both the position and the relative intensity of the C=C stretching band in the infrared spectra. Absorption frequencies for the C=C stretching band in unsaturated boron compounds are recorded in Table 1. Typical behaviour of a non-conjugated carbon–carbon double bond is illustrated by allylboron difluoride, in which the C=C stretching band occurs at 1650 cm.$^{-1}$, since the intermediate methylene group prevents conjugation. The corresponding band in αβ-unsaturated organoboron compounds, with the exception of the perfluorovinyl compounds, lies in the region 1630—1605 cm.$^{-1}$. This shift, considered together with the greater intensity of the band in these compounds compared to that in allylboron difluoride, provides strong evidence that these double bonds are conjugated with a group which removes electrons by π-delocalization.[16]

Additional evidence for conjugation in the vinylboron halides comes from consideration of the positions and intensities of the C=C stretching band in the spectra of the compounds $CH_2{:}CH{\cdot}BCl_2$ and $Me_3N,BCl_2{\cdot}CH{:}CH_2$. In the addition compound, boron does not possess a vacant orbital to accept π-electrons from the vinyl group, and therefore C=C stretching in this compound should show a weaker absorption at higher frequency than the corresponding peak in vinylboron dichloride, if delocalization occurs in the latter. Comparison of solutions in dichloromethane, at the same concentration, shows a shift of the double-bond absorption from 1599 cm.$^{-1}$ in the halide to 1613 cm.$^{-1}$ in the adduct and a decrease in intensity from 80% to 35% absorption.

In perfluorovinylboron compounds, the C=C stretching band occurs at higher frequencies than in the ordinary αβ-unsaturated boron compounds. This is as expected since the C=C stretching frequency increases when fluorine atoms are attached to carbon atoms forming the double bond.[17] For example, the C=C absorption changes from 1647 cm.$^{-1}$ in propene to 1767—1792 cm.$^{-1}$ in the fluoroethylenes. However, the C=C stretching band in perfluorovinylborons occurs at a significantly lower frequency than in normal fluoroalkenes, as would be expected if delocalization of the double-bond π-electrons into the boron p_π-orbital occurs. In this case again, formation of a trimethylamine adduct causes a shift to higher frequency of the C=C absorption (Table 1) as the possibility of overlap is destroyed.

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[13] Love, Taft, and Wartik, *Tetrahedron*, 1959, **5**, 116.

[14] Coyle and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6223.

[15] Kaesz and Stone. Amer. Chem. Soc. Monograph, " Organometallic Chemistry " (Ed. Zeiss), Reinhold, 1960, (Ch. 3).

[16] Bellamy, " The Infra-red Spectra of Complex Molecules," Wiley, New York, 2nd end., 1958.

[17] Torkington and Thompson, *Trans. Faraday Soc.*, 1945, **41**, 236.

The C=C stretching band in perfluorovinylboron difluoride occurs at a higher frequency than in any other perfluorovinylboron compound and a similar relation holds for the C=C stretching band of vinylboron difluoride, compared to that of the other vinylboron halides. If the argument based on correlation of position of the C=C band with electron delocalization is correct, this suggests that carbon–boron π-bonding in perfluorovinyl- and vinyl-boron difluoride is less significant than in other vinylboron and perfluorovinylboron compounds listed in Table 1. As discussed below, fluorine-19 and boron-11 nuclear magnetic resonance studies also indicate that there is less carbon–boron π-bonding in organoboron fluorides. Presumably the boron p_π-orbital in the two difluorides is partially filled by p_π-electrons from the fluorine atoms of the BF_2 group, so that contribution of π-electron density from the unsaturated group to boron is less necessary to relieve electronic unsaturation at the boron atom. Nuclear magnetic resonance studies [18] can also be interpreted as indicating that fluorine atoms are more effective than chlorine atoms in π-bonding to boron, again implying that the relative contribution by the vinyl group of π-electron density to the vacant boron orbital would be less in the vinylboron fluorides than in the chlorides.

TABLE 1. C=C *Stretching bands in some unsaturated organoboron compounds.*

Compound	C=C stretch (cm.$^{-1}$)	Compound	C=C stretch (cm.$^{-1}$)	Compound	C=C stretch (cm.$^{-1}$)
$CH_2{:}CH{\cdot}CH_2{\cdot}BF_2$ [a]	1650 [b]			$CF_2{:}CFBF_2$ [h]	1725 [b]
				$CF_2{:}CFBCl_2$ [h]	1695 [b]
$CH_2{:}CH{\cdot}B(OH)_2$ [c]	1605 [d]	$CH_2{:}CH{\cdot}B(OBu)_2$ [c]	1610 [e]	$Me_3N,BCl_2{\cdot}CF{:}CF_2$	1736
$CH_2{:}CMe{\cdot}B(OH)_2$ [c]	1615 [d]	$CH_2{:}CMe{\cdot}B(OBu)_2$ [c]	1625 [e]		
$CH_2{:}CHBF_2$ [a]	1629 [b]	$(CH_2{:}CH)_2BF$ [a]	1625 [b]	$(CF_2{:}CF)_2BCl$ [h]	1677 [b]
$CH_2{:}CHBCl_2$ [a]	1610,[b] 1599	$(CH_2{:}CH)_2BCl$ [a]	1612 [b]	$(CF_2{:}CF)_3B$ [h]	1678 [b]
$Me_3N,BCl_2{\cdot}CH{:}CH_2$	1613 [f, g]	$(CH_2{:}CH)_3B$ [a]	1610 [b]		

[a] Ref. 19. [b] Gas phase. [c] Ref. 1. [d] Chloroform solution. [e] Neat liquid. This work, methylene chloride solution. [g] Band is much weaker in complex. [h] Ref. 3.

The ultraviolet spectral properties of $\alpha\beta$-unsaturated organoboron compounds have also suggested resonance interaction between π-electrons of the carbon–carbon double bond and the p_π-orbital of an adjacent boron atom, *e.g.*, the observation by Letsinger and Skoog [20] of an absorption maximum at 223 mμ (ε 1000) in the spectrum of 2-methylprop-1-enylboronic acid. Neither alkenes nor alkylboronic acids absorb in this region.

We have examined the ultraviolet spectra of the vapours of the halides $Et{\cdot}BCl_2$, $CH_2{:}CH{\cdot}BCl_2$, $(CH_2{:}CH)_2BCl$, and $CH_2{:}CH{\cdot}BF_2$. Ethylboron dichloride and vinylboron difluoride exhibit only a weak " end absorption " down to 200 mμ, the spectra being rather similar to that of vinyl chloride. However, in vinylboron dichloride and divinylboron chloride there are maxima, at 207 mμ (ε ~7000) and 210 mμ (ε ~8000), respectively. The absence of a maximum in the spectrum of vinylboron difluoride suggests that the carbon–boron π-interaction is less significant than in the chloride: this agrees with the infrared and nuclear magnetic resonance results.

Studies of boron-11 chemical shifts [21,22] suggest that the magnitudes of the shifts are related, at least in part, to the degree to which the vacant p-orbital of the trigonal boron atom is occupied, being greatest in the extreme case of tetrahedrally-substituted boron. Values of some boron-11 chemical shifts we have obtained are given in Table 2.

The results show that in the dichlorides and the difluorides the boron atom is more shielded in the vinyl compound than in the ethyl derivative, as would be expected if π-bonding is the cause. In addition, the higher shifts for the fluorides, coupled with the

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[18] Coyle and Stone, *J. Chem. Phys.*, 1960, **32**, 1892.
[19] Brinckman and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6218.
[20] Letsinger and Skoog, *J. Org. Chem.*, 1953, **18**, 895.
[21] Onak, Landesman, Williams, and Shapiro, *J. Phys. Chem.*, 1959, **63**, 1533.
[22] Phillips, Miller, and Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 4496.

TABLE 2. *Boron*-11 *chemical shifts.*

Compound	Shift (p.p.m.)[a]	Compound	Shift (p.p.m.)[a]	Compound	Shift (p.p.m.)[a]	Compound	Shift (p.p.m.)[a]
$Et\cdot BCl_2$	−16·0	$CH_2{:}CH\cdot BCl_2$	−6·2	$EtBClF$	1·7	$CH_2{:}CH\cdot BF_2$	24·2
$Ph\cdot BCl_2$	−6·7[b]	BCl_3	0	$EtBF_2$	18·9		

[a] BCl_3 as external reference. [b] Ref. 22.

smaller effect of substituting vinyl for ethyl in the fluorides, compared with the chlorides, also suggests that carbon–boron π-bonding is less significant in the fluorides. It is of interest that the chemical shift of phenylboron dichloride, for which dipole-moment measurements indicate strong resonance involving carbon–boron π-bonded structures,[23] is very close to that of vinylboron dichloride. However, the boron-11 chemical shifts of butyl- and phenyl-boronic acids differ by only 0·9 p.p.m.[22] Clearly, if carbon–boron π-bonding is a significant factor in these chemical shifts, its importance must vary considerably as the other substituents on the boron atom are varied.

The possibility of partial donation of lone-pair electrons from fluorine orbitals of suitable symmetry into the vacant *p*-orbital of boron in boron trifluoride has long been recognized [24] and is invoked to explain the observed weakness of boron trifluoride as a Lewis acid compared with boron trichloride and boron tribromide.[25] Such interactions would occur equally well in organoboron fluorides with the character of the B–F bonds differing in RBF_2 and $R'BF_2$ if R and R′ differ in π-bonding ability. It is assumed that fluorine-19 chemical shifts can be correlated with electron density at the fluorine atom, a hypothesis supported by theoretical work [26] and experimental data, and since organic groups in general should be poorer π-donors than fluorine, a withdrawal of electron density from the remaining fluorines would be expected when one fluorine atom in boron trifluoride is replaced by an organic group, even though the latter is usually considered to be less " electronegative." Fluorine-19 chemical shifts, summarized in Table 3, show that relative to boron trifluoride

TABLE 3. *Fluorine*-19 *chemical shifts*

Compound	Shift (p.p.m.)[a]	Compound	Shift (p.p.m.)[a]	Compound	Shift (p.p.m.)[a]
BF_3[b]	0	$CH_2{:}CH\cdot CH_2\cdot BF_2$[c]	−52	Me_3N,BF_3[e]	+37
$Ph\cdot BF_2$[c]	−35	Pr^nBF_2[b]	−54	$Me_3N,BEtF_2$[e]	+38
$CH_2{:}CH\cdot BF_2$[b]	−38	$Bu\cdot BF_2$[c]	−54	$Me_3N,BF_2\cdot CH{:}CH_2$	+39
$CF_2{:}CF\cdot BF_2$[f]	−40	$EtBClF$[d]	−99		
$EtBF_2$[b]	−52	Me_2BF[c]	−107		

[a] Chemical shifts were measured, unless otherwise stated, in dilute solution in CCl_3F, $\delta(BF_3) =$ 127 p.p.m. relative to internal CCl_3F. Since minor variations can be expected with changes in solution conditions, etc., values are expressed to the nearest p.p.m. [b] Ref. 14. [c] J. P. Grivet, unpublished observations. [d] From shift relative to $EtBF_2$ in mixture of composition EtBClF, $\delta(EtBF_2)$ being taken as −52 p.p.m. [e] Measured in dilute CH_2Cl_2 solution, for which $\delta(BF_3)$ is taken as 127 p.p.m., relative to external CCl_3F. [f] BF_2 fluorine atoms.

there is indeed less magnetic shielding of the fluorine nuclei with displacement of the resonance to lower applied field in organoboron fluorides. The fluorine-19 chemical shifts of the alkylboron fluorides appear at somewhat lower applied field than those of vinylboron fluorides, perfluorovinylboron difluoride, or phenylboron difluoride, while in the trimethylamine adducts of ethyl- and vinyl-boron difluoride the chemical shifts are almost identical. This agrees with the concept of carbon–boron π-bonding when the carbon atom bonded to trigonal boron has a filled p_π-orbital, leading to the appearance of the fluorine-19 resonances at higher field than in alkylboron fluorides.

Fluorine-19 nuclear magnetic resonance studies of the perfluorovinyl derivatives of boron may also reveal π-interactions The chemical shifts of the fluorine atoms of the

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[23] Curran, McCusker, and Makowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5188.
[24] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 3rd Ed., 1959, p. 318.
[25] Brown and Holmes, *J. Amer. Chem. Soc.*, 1956, **78**, 2173.
[26] Saika and Schlichter, *J. Chem. Phys.*, 1954, **22**, 26.

difluoromethylene group in the boron halides $CF_2{:}CF{\cdot}BF_2$, $CF_2{:}CF{\cdot}BCl_2$, and $(CF_2{:}CF)_3B$ are substantially lower (73—76 p p.m. and 88—100 p.p.m., respectively, for *trans-* and *cis*-fluorine atoms) than the corresponding shifts for perfluorovinyl derivatives of silicon, tin, arsenic, or mercury (83—90 and 112—125 p.p.m.).[27] Moreover, some F–F spin-coupling constants in perfluorovinyl groups bonded to boron depart markedly from the values obtained for other perfluorovinylmetals[27] or for fluoro-olefins in general.[28] It seems reasonable to infer that a rather unusual perturbation of the electron system of the perfluorovinyl group is characteristic of the boron derivatives.

EXPERIMENTAL

Infrared spectra were recorded as gases in a 4-cm. cell, or as solutions in a 0·4 mm. liquid cell, fitted with sodium chloride plates, a Perkin–Elmer Model 21 double-beam spectrometer being used with sodium chloride optics. Spectra were calibrated immediately against known peaks of a polystyrene film.

Ultraviolet spectra were obtained as gases in a 4-cm. cell fitted with quartz windows, a Cary model 11M recording spectrometer being used.

Nuclear magnetic resonance spectra were recorded at room temperature on a Varian V-4300B nuclear magnetic resonance spectrometer operating at 40 Mc./sec. for fluorine-19 and 15·1 Mc./sec. for boron-11.

The compounds studied were prepared as described in the references mentioned.

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[27] Coyle, Stafford, and Stone, *Spectrochim. Acta*, in the press.

[28] McConnell, Reilly, and McClean, *J. Chem. Phys.*, 1956, **24**, 479.