Journal of Organometallic Chemistry, 241 (1983) 289–300
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ORGANOBORON COMPOUNDS

XXIII *. CARBON-13 STUDIES OF PHENYLBORANES

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(Received August 4th, 1982)

Summary

Correlations of the *ortho, para, meta* and C(1) carbon resonances in phenylboranes are reported. The observed ^{13}C chemical shifts of the *para* carbon atoms in phenylboranes indicate shielding decreases in the order NHR ~ NR_2 > SR > OR > organyls > halogens. The reverse trend is observed for the C(1) ^{13}C chemical shifts which in addition are found to be sensitive to the steric nature of the substituents on boron.

Introduction

Over the last few years we have been involved in an evaluation of ^{13}C NMR spectroscopy as a means of obtaining information concerning the factors affecting the nature of the boron–nitrogen bond in aminophenylboranes [1–7]. This has given a considerable amount of data and in this paper we wish to report some correlations of the *ortho, para, meta* and C(1) resonances in phenylboranes.

The first report of ^{13}C NMR data on three coordinate phenylboranes was published in 1977 [8] and more recently Odom [9] reported the details of the ^{13}C NMR spectra of some 29 phenylorganoboranes and observed that the ^{13}C NMR chemical shifts of the *para* carbon atoms (δ^{13}C *para*) in phenylboranes are consistent with mesomeric interactions of the boryl group with the aromatic system. In addition a good linear relationship between δ^{13}C (*para*) for phenylboranes and δ^{13}C (*para*) for the corresponding isoelectronic and isostructural phenylcarbocations was observed.

The application of ^{13}C NMR to the study of organoboranes has been hampered due to the quadrupolar nature of the boron nucleus (^{11}B, 82% natural abundance, $I = 3/2$). Consequentially resonances for the carbon atoms directly bonded to boron (C(1)) are either severely broadened or undetectable due to ^{11}B–^{13}C couplings which

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[*] For part XXII see ref. 21.

are incompletely relaxed by the quadrupole mechanism [10]. As a result a number of papers have appeared commenting on the difficulty of observing the resonances for the carbon atoms directly bonded to boron [8,10–12]. To date the techniques which have been successful in determining $\delta^{13}C(C(1))$ values are:

(a) running the spectrum at a low temperature (below −40°C),
(b) heteronuclear triple resonance experiments (i.e. $^{13}C(^{11}B, ^{1}H)$),
(c) using compounds where the electric field gradient at boron is zero [13–16],
(d) running the spectrum in the absence of a solvent [7].

Technique c is of limited applicability and is effectively confined to tetrahedral boron anions where all four ligands are identical [e.g. $Ph_4B^- Na^+$ [13]]. Techniques a and b are both time consuming and inconvenient. It was therefore of considerable value to discover a new method (d) which was both of wide applicability and quick to perform [7].

The technique involves running a spectrum of a 30% v/v solution of the organoborane in $CDCl_3$, using TMS as reference, then running a spectrum of the neat sample in the absence of any solvent, reference or foreign material present (an internal DMSO capillary lock was used). Comparing the two spectra it is possible to see the 'emergence' of the C(1) signal in the spectrum of the neat sample where it was absent in the solution spectrum. The chemical shift of the C(1) ($\delta^{13}C(C(1))$) may then be referenced to TMS. This technique is exemplified in Fig. 1 by bromo-3-methyl-piperidinophenylborane.

We have obtained the $\delta^{13}C(C(1))$ values for over 70 phenylboranes using this technique and the only compounds where we were unable to observe C(1) resonances were those compounds which are, even when neat, still very mobile. The $\delta^{13}C(C(1))$ value for these compounds were obtained by running the spectrum at a low temperature.

It would appear that increased viscosity, obtained either by cooling or by using neat samples, facilitates the detection of a sharp resonance for the C(1) carbon. At a

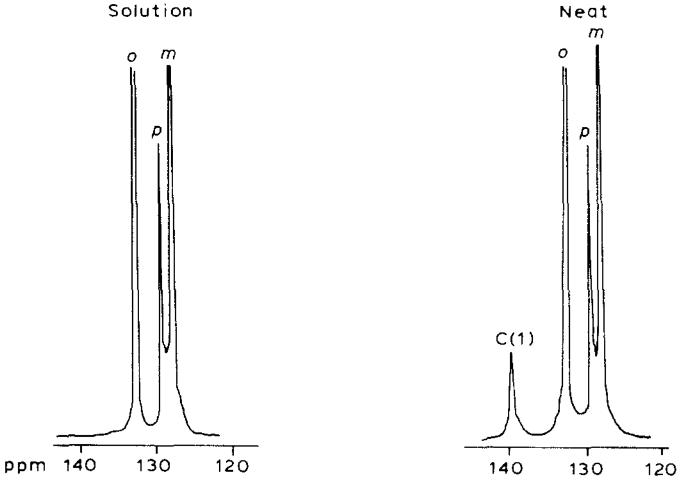
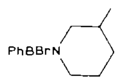


Fig. 1. ^{13}C NMR spectrum (aromatic portion) of 

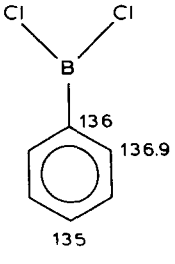
higher viscosity Brownian motion is slower and this is characterised by an increased molecular correlation time leading to ^{11}B decoupling.

The $\delta^{13}C$ (C(1)) show the largest range of all the aromatic carbons with $PhBF_2$ (124 ppm) [9] having the lowest recorded value and $PhB(Cl)N\!\left\langle\substack{Et\\ Ph}\right.$ (150 ppm) the highest. Most workers, including Odom [9] report that, for the limited number of phenylboranes they studies, there was no obvious relationship between $\delta^{13}C(C(1))$ and the electronic nature of the boron substituents. However, on studying the $\delta^{13}C(C(1))$ values of over 70 phenylboranes some general trends in $\delta^{13}C(C(1))$ have been observed and some tentative correlations are proposed.

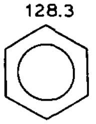
The difficulty of rationalising $\delta^{13}C(C(1))$ values arises due to the shielding of the C(1) depending on the degree of delocalisation of the phenyl π electron density onto boron and the π interactions between boron and the other substituents. In addition because the C(1) carbon atom is directly bonded to boron it is a centre for both inductive and mesomeric effects and a clear partitioning of the σ and π contribution to $\delta^{13}C(C(1))$ is difficult.

We have observed that $\delta^{13}C($*para*$)$ values indicate B–C p_π–p_π bonding decreasing in the following order for substituents attached to boron: halogens > organyls > OR > SR > NR_2 ~ NHR and these observations are in agreement with those of Odom [9].

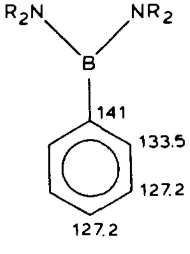
The BCl_2 group is a strong mesomeric acceptor of electrons from the phenyl group and this is reflected in the most deshielded $\delta^{13}C$ (*para*) values (135 ppm). In contrast the $B(NR_2)_2$ groups, however, are weak mesomeric donors and shield *para* carbons relative to benzene (~ 127 ppm). The $\delta^{13}C$ (C(1)) values show the opposite trend, being most shielded in $PhBCl_2$ and least shielded in bis-amino-phenylboranes. Indeed, it has been observed that, for almost all the phenylboranes studied, factors which shield the *para* carbon atoms deshield the C(1) carbon atoms and vice versa. A good illustration is a comparison of the chemical shifts of the aromatic carbons in $PhBCl_2$ and $PhB(NMe_2)_2$:



(A)



(B)



(C)

In compounds of type A, where the boryl group is a strong mesomeric acceptor, the *para* carbon atoms are strongly deshielded, but in compounds of type C, where the boryl group is a weak mesomeric donor, the *para* carbon atoms are shielded while the C(1) carbon atoms are strongly deshielded. Indeed the most shielded *para* carbon atoms and the most deshielded C(1) carbon atoms are found in compounds of type C, e.g. $PhB(NMe_2)NBu^s_2$ (C(1) 144.8 ppm, *para* 126.8 ppm).

These diametrically opposed trends in $\delta^{13}C$ (*para*) and $\delta^{13}C(C(1))$ could be tentatively rationalised in the following way. The C(1) carbon atoms being directly attached to electron deficient boron, is normally the most deshielded carbon, but in compounds of type A, where the boryl group is a strong mesomeric acceptor, the C(1) carbon atom is at its 'least deshielded' while the *para* carbon atom is at its most deshielded. In compounds of this type B–C p_π–p_π bonding is strong and there is a large delocalisation of phenyl π electron density onto boron. This clearly deshields the *para* carbon atoms, but results in the C(1) carbon atoms being deshielded to a lesser extent than in compounds of type C, where the boryl group is a weak mesomeric donor. In compounds of type C the *para* carbon atoms are weakly shielded mesomerically and there is therefore very little delocalisation of phenyl π electron density onto boron to offset the deshielding of the C(1) carbon atom. Thus compounds of type A, where the boryl group is a mesomeric acceptor the deshielding of the C(1) carbon atom is partially offset by the delocalisation of phenyl π electron density onto boron. This rationalisation appears to hold for all the compounds studied, but may not be of general applicability because δ^{13}C(C(1)) is affected by other factors such as the anisotropy of neighbouring groups and bond angle. Indeed all chemical shifts represent the net effect of many factors which may well work in opposition to one another. However, it seems that for phenylboranes of the type PhBXY(X, Y = NR_2, OR, SR, hal, Ph), δ^{13}C(C(1)) might provide a quantitative measure of the extent of delocalisation of phenyl π electron density onto boron and hence of the degree of B–C p_π–p_π bonding, when the effects of the other substituents on boton are taken into account.

General trends

Compounds of the type $PhBR_2$

For this class of compound it is observed that the C(1) carbon atoms become less deshielded when the boron substituents are changed in the sequence NHR, NR_2, SR, OR. The *para* carbon atoms show the reverse trend. Suitable examples are given in Table 1.

Compounds of the type $PhB(NR_2)X$ (X = Cl, Br, Ph, OR, SR, NR_2, NHR)

Because of the large number and diversity of compounds studied the regions in which the aromatic carbon atoms resonate are given in Fig. 2. Reference to Fig. 2 indicates that the X = Cl, Br, OR and SR the variation in δ^{13}C(C(1)) between homologous series (where NR_2 is held constant and X is varied) is small compared to the variation δ^{13}C(C(1)) within a homologous series (where NR_2, is varied and X is held constant). It is observed that the shielding of the C(1) carbon is more affected

TABLE 1

δ^{13}C (C(1)) AND *para* VALUES FOR SOME PHENYLORGANOBORANES

Compound	δ^{13}C(C(1)) (ppm)	δ^{13}C(*para*) (ppm)
$PhB(OMe)_2$	131.7	129.7
$PhB(SMe)_2$	138	129
$PhB(NMe)_2$	141	127.2
$PhB(NHBu^s)_2$	141.3	127.4

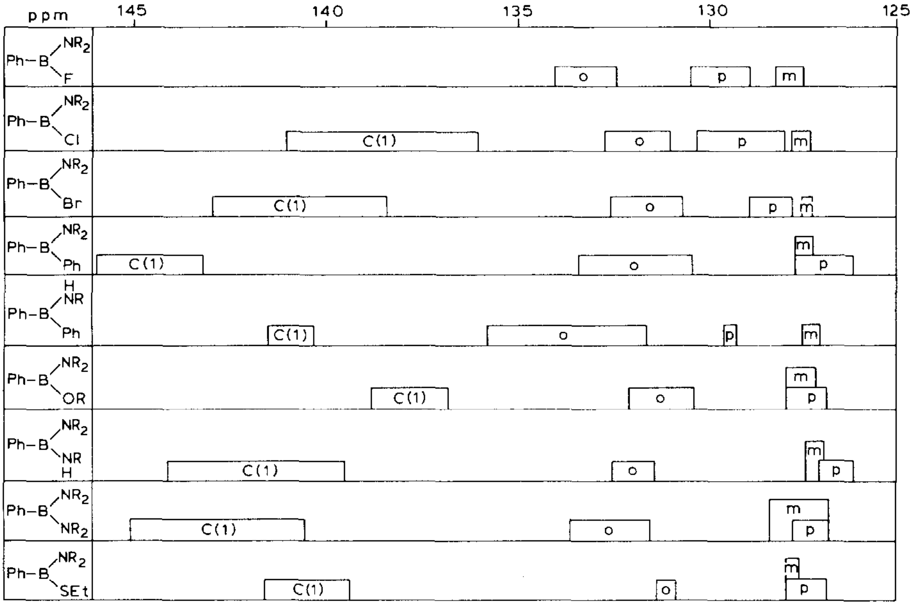
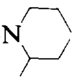


Fig. 2. Regions in which the aromatic carbon atoms resonate.

by the steric nature of the amino group than by the nature of the group X. When X is an amino group the C(1) carbon atoms are markedly deshielded and this deshielding increases progressively for more bulky amino groups.

Correlations for δ^{13}C(C(1))

δ^{13}C(C(1)) and the number of carbon atoms in the amino group

We observed that the C(1) carbon atom becomes progressively more deshielded as the amino groups become more bulky. Suitable examples are given in Table 2. For bis-amino-phenylboranes the δ^{13}C(C(1)) values range from 139.4 in PhB(NMe$_2$)NHBu^n to 145 ppm in PhB(NPr$^i_2$)N . However increasing the chain length of the amino group has little effect or δ^{13}C(C(1)). It is the branching on the carbon atom closest to boron which leads to a marked deshielding of the C(1) carbon atom and a slight shielding of the *para* carbon atoms. In contrast the δ^{13}C(*para*) varies from 127.7 in the least hindered systems to 126.3 ppm in the most hindered systems.

The result of increasing the steric hindrance about the $>$B–NR$_2$ bond using bulky R groups, will be to weaken the B–N p_π–p_π bonding since the bond must be coplanar for effective overlap of the filled nitrogen *p* orbital with the empty *p* orbital on boron. In addition there is very little delocalisation of the phenyl π electron density onto boron via B–C p_π–p_π bonding in these systems and this is evidenced by δ^{13}C(*para*) values which are slightly shielded relative to benzene. It is therefore possible that, because back donation from the two amino groups is sterically reduced and that there is little B–C π bonding, the increased electron deficiency of boron is

TABLE 2

$\delta^{13}C$ (C(1)) VALUES FOR SOME PHENYLORGANOBORANES

Compound	$\delta^{13}C(C(1))$	Compound	$\delta^{13}C(C(1))$
$PhB(NMe_2)Cl$	137.2	$PhB(SEt)NMe_2$	139.2
$PhB(NPr_2{}^n)Cl$	138.3	$PhB(SEt)NPr_2^i$	141.4
$PhB(NPr_2^i)Cl$	141.0		
$PhB(NBu_2{}^n)Cl$	138.6	$PhB(NMe_2)Br$	138.3
$PhB(NBu_2{}^s)Cl$	140.8	$PhB(NPr_2^i)Br$	142.5
$PhB(NHBu^n)_2$	141.3	$PhB(NMe_2)NHBu^2$	139.4
		$PhB(NMe_2)NHBu^t$	142.0
$PhB(OMe)NMe_2$	136.7		
$PhB(OMe)NPr_2^i$	138.8		

relieved by inductive withdrawal from the C(1) carbon atom. The C(1) carbon atoms are therefore deshielded and this is not offset by B–C π bonding.

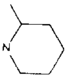
We have obtained a correlation between $\delta^{13}C(C(1))$ and the degree of steric hindrance about the B–N bond (Fig. 3) provided the bisaminophenylboranes with a progressive increase in branching on the α carbon atoms, of the amino group, are used. Hence a plot of $\delta^{13}C(C(1))$ against the number of carbon atoms in the two amino groups gives a good straight line. However, the correlation does not hold if the amino groups have long, unbranched, linear and therefore unhindered alkyl groups. The compounds used in this correlation are given in Table 3.

A good straight line correlation indicating a deshielding of the C(1) carbon by 1 ppm, for the addition of two carbon atoms in the amino group is apparent. However, this correlation only holds for hindered aminoboranes, where additional carbon atoms are added in order to maximise the steric hindrance.

The $\delta^{13}C$ (C(1)) value for $PhB(NHBu^n)_2$ would be predicted to be 143 ppm because there are eight carbon atoms in the amino groups. However $\delta^{13}C$ (C(1)) is observed at 140.8 ppm which is close to the value expected for a 4 carbon system such as $PhB(NMe_2)_2$. This is due to the steric hindrance provided by two n-butyl groups is small compared to other eight carbon systems such as $PhB(NEt_2)NHBu^t$.

TABLE 3

DETAILS OF COMPOUNDS USED IN FIG. 3

Compound	$\delta^{13}C(C(1))$ (ppm)	$\delta^{13}C$(*para*) (ppm)	Number of carbon atoms
$PhB(NPr_2^i)$ 	145.0	126.7	12
$PhB(NBu_2{}^s)NEt_2$	145.0	126.6	12
$PhB(NPr_2^i)NHBu^t$	144.0	126.3	10
$PhB(NEt_2)NHBu^t$	143.2	126.1	8
$PhB(NMe_2)NHBu^t$	142.0	126.5	6
$PhB(NMe_2)_2$	141.0	127.2	4

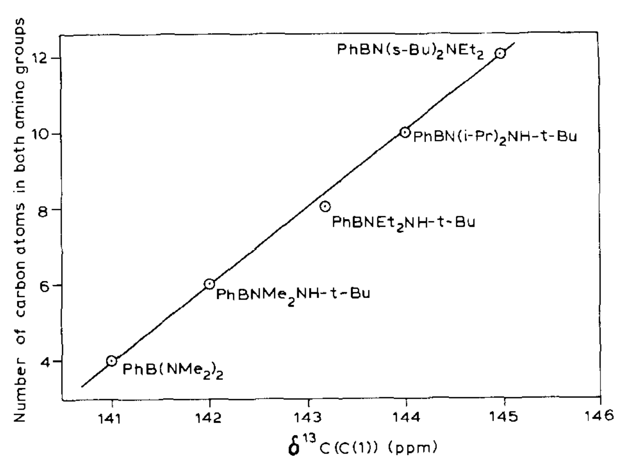


Fig. 3. Correlation of $\delta^{13}C(C(1))$ with the number of carbon atoms in the amino groups of bis-amino-phenylboranes.

$\delta^{13}C(C(1))$ and $\Delta G^\star$ for rotation about B–N in chloro(dialkyalmino)phenylboranes

Similar trends of $\delta^{13}C(C(1))$ are observed in this class of compound also. The C(1) carbon atom becomes progressively deshielded as the amino group becomes more bulky.

When the B–NR_2 bond is hindered p_π–p_π back donation from nitrogen is reduced, since the bond must be planar for effective overlap of the *p* orbitals . Thus boron becomes more electron deficient and can only relieve this by inductive withdrawal from the C(1) carbon atom since the BNR_2Cl group is a poor mesomeric acceptor and there is little delocalisation of phenyl π electron density onto boron. Hence the C(1) carbon atom becomes deshielded to a greater extent by boron and this deshielding is not offset by delocalisation of phenyl π electron density onto boron.

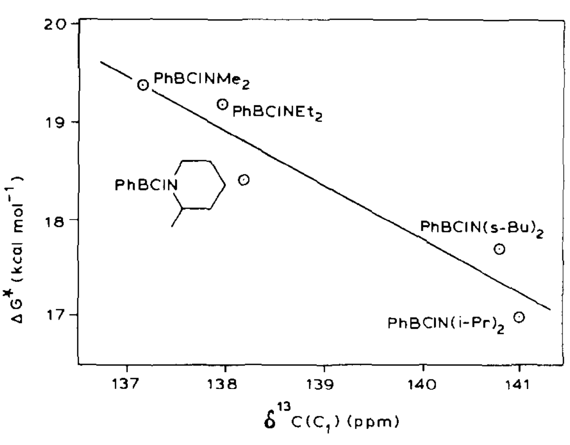


Fig. 4. Correlation of $\delta^{13}C(C(1))$ with $\Delta G^\star$ for B–N rotation in $PhBNR_2Cl$ systems.

Since the deshielding of the C(1) carbon atom correlates with the reduced p_π–p_π back donation from nitrogen, and hence reduced double bond character in the B–N bond, it should also correlate with $\Delta G^\star$, the free energy of activation for rotation about B–N. Provided the compounds considered show marked changes in steric hindrance about the B–N bond, a good straight line plot of $\Delta G^\star$ against δ^{13}C (C(1)) is obtained (Fig. 4), for a series of chloro(dialkylamino)phenylboranes.

Conclusions about δ^{13}C(C(1)) in phenylboranes

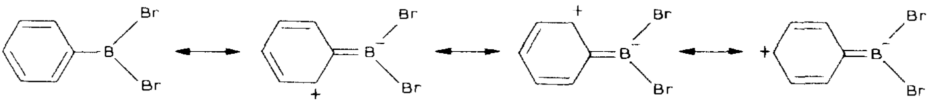
Rationalisations of chemical shifts are always difficult because an observed chemical shift is often determined by the net effect of many variables which may well work in opposition to one another. However, in the systems reported here there seem to be two main factors governing the shielding of C(1) carbon atom.

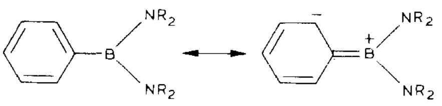
(a) The electronic and steric nature of the substituents on boron.

(b) The extent of phenyl π electron delocalisation on to boron. Because boron is electron deficient the C(1) carbon is generally deshielded relative to benzene. However, in acylic compounds, it is at its least deshielded when there is a large delocalisation of phenyl π electron density on to boron. In this way δ^{13}C(C(1)) could be taken as a measure of the degree of B–C p_π–p_π bonding since it becomes shielded when δ^{13}C (*para*) becomes deshielded. Generally, strong π back donation from all 3 boron substituents results in an offsetting of the inherent deshielding of the (C(1)) carbon, but δ^{13}C(C(1)) is most sensitive to the extent of back donation from the phenyl group.

δ^{13}C (para) values of phenylboranes PhBXY (XY = Ph, NR_2, OR, SR, NHR, hal)

For this class of compound the chemical shifts cover a range from 126–135 ppm. The ^{13}C NMR chemical shift of benzene is 128.3 ppm. The most deshielded *para* carbon atoms were observed in dibromophenylborane (135.2 ppm) and the most shielded *para* carbon atoms were found in bisdialkylaminophenylboranes and a value of about 127 ppm was obtained for most compounds of this type. The lowest recorded value of 126.3 ppm was observed for t-butylaminodi-i-propylaminophenylborane. Our results support the observations of Odom [9] that the BBr_2 group and almost all the other boryl groups act as mesomeric acceptors of phenyl π electron density while the $B(NR_2)_2$ group act as a weak mesomeric donor.





These results therefore indicate of the compounds measured that B–C p_π–p_π bonding is strongest for $PhBBr_2$. This is supported by the observation that the *para* carbon atom in $PhBBr_2$ is mesomerically deshielded by 7 ppm relative to benzene.

Caminati [17] has measured the barrier to interval rotation about the B–C bond in $PhBCl_2$ as 14 kJ mol^{-1} using microwave spectroscopy.

All the δ^{13}C (*para*) values for the phenylboranes measured fall between the above extremes but most boryl groups act as mesomeric acceptors. It was general found that the shielding of the *para* carbons decreased as the boron substituents were changed in the order NHR > NR_2 > SR > OR > organyl > halogens.

Trends in δ^{13}C (para)

Compounds of the type $PhBX_2$. Table 4 lists some δ^{13}C (*para*) values for this class of compound. It is interesting to note that the chemical shifts do not vary very much when the alkyl groups are changed from methyl to more branched hydrocarbon chains. The results indicate that with the exception of bis-alkylamino- and bis-dialkylamino groups all other act as mesomeric acceptors.

Compounds of the type $PhBNR_2X$. The range of δ^{13}C (*para*) values is much smaller when one substituent is varied and the other held constant, than when both substituents are varied as in the $PhBX_2$ systems. However, the same general trend in δ^{13}C(*para*) was observed when the group X was varied as obtained for the series $PhBX_2$ i.e. halogen substituents on boron deshielded the *para* carbon atom whilst amino groups shielded them. Typical examples are given in Table 5.

However for some amino groups including the BNR_2Cl and BNR_2Br groups act as weak mesomeric donors as evidenced by δ^{13}C (*para*) values which are shielded relative to benzene.

Although there are only very small changes in the δ^{13}C (*para*) upon changing the halogens it is interesting to note that in the series BBr_2, BCl_2 and BF_2 the BBr_2 group is the strongest mesomeric acceptor and the BF_2 group the weakest. However, in the BNR_2X (X = F, Cl, Br) the reverse trend is observed with the BNR_2F group always the best acceptor irrespective of the nature of the amino group. The order of mesomeric acceptor strength BBr_2 > BCl_2 > BF_2 is easily rationalised in terms of accepted substituent effects since B–F back donation is recognised to be strongest and therefore the BF_2 group is the weakest mesomeric acceptor. However, these arguments do not hold for the BNR_2F grouping which behaves as the strongest mesomeric acceptor of all $PhBNR_2X$ groupings while in some cases the $PhBNR_2Br$

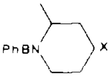
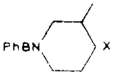
TABLE 4

δ^{13}C (*para*) VALUES FOR SOME $PhBX_2$ COMPOUNDS

Compound	δ^{13}C (*para*) (ppm)	Compound	δ^{13}C (*para*) (ppm)
$PhBBr_2$	135.2	$PhB(NMe_2)_2$	127.2
$PhBCl_2$	135.0	$PhB(NEt_2)_2$	127.7
$PhBF_2$	134.0(9)		
		$PhB(NHBu^n)_2$	127.5
$PhB(OMe)_2$	129.7	$PhB(NHBu^i)_2$	127.5
$PhB(OPent^n)_2$	129.5	$PhB(NHBu^s)_2$	127.4
$PhB(SMe)_2$	129		
$PhB(SEt)_2$	129.1		

TABLE 5

$\delta^{13}C$ (*para*) VALUES FOR SOME $PhBNR_2X$ COMPOUNDS

X	$PhBNMe_2X$	$PhBNPr^i_2X$	$PhBNBu^s_2X$		
F	129.5	129.1	128.9	129.4	130.0
Cl	129.0	128.1	128.0	128.6	128.7
Br	128.9	127.9	127.8	128.4	128.6
OMe	127.8	127.1	126.8	127.9	127.9
SEt	127.8	126.8	126.8	127.3	127.3
NMe_2	127.2	–	126.8	127.3	–
$NHBu^t$	126.5	126.3	–	126.4	–

group behaves as a weak mesomeric donor. This behaviour could be tentatively accounted for in the following way. Mesomeric back donation from bromine to boron is smallest and this induces greater back donation from nitrogen to boron in compounds of the type $PhBNR_2BR$. Conversely back donation from fluorine to boron is greatest and this results in a reduction in the back donation from nitrogen in the corresponding fluoro compounds. Consequently the BNR_2Br group has the strongest back donation from nitrogen and appears therefore to be the best mesomeric donor. It must be emphasised that these differences are very small, being reflected in only a 1 ppm change in $\delta^{13}C$ (*para*), and the rationalisation is only tentative. Hall [11] has also observed only a small (~ 1 ppm) change in the mesomeric shielding of $C\beta$, with the interchange of halogens (F, Cl, Br), in a series of halovinylboranes.

The $\delta^{13}C$ (*para*) values for compounds of the series $PhBN(i\text{-}Pr)_2X$ are all about 1 ppm more shielded than those of other series where the amino group is less branched. This phenomenon is also found for compounds of the type $PhB(NR_2)_2$ and Ph_2BNR_2 [2]. In all cases the *para* carbon atoms are more shielded when the amino group is most hindered. The high degree of branching of the $N(i\text{-}Pr)_2$ group makes it difficult to get the planarity about the B–N bond necessary for effective p_π–p_π B–N bonding. Consequently this π bonding is weakened and the bond becomes more freely rotating. The B–C bond, however, is much less hindered and B–C p_π–p_π bonding could become established at the expense of B–N p_π–p_π bonding. Models show that when the $N(i\text{-}Pr)_2$ group is twisted out of the plane B–C p_π–p_π bonding is sterically favoured. These effects might increase the mesomeric shielding of the *para* carbons by the boryl group resulting in lower $\delta^{13}C$ (*para*) values.

Uses of $\delta^{13}C$ (para)

The $\delta^{13}C$ (*para*) is a relatively reliable quantitative parameter which measures the mesomeric acceptor, or donor properties of a boryl group attached to a phenyl group. The $\delta^{13}C$ (*para*) values of the following pairs of phenylboranes is instructive.

The *para* carbon atoms in the $Ph_2BNHSiMe_3$ [2] and $PhBNMe_2NHSiMe_3$ are deshielded by about 1 ppm relative to $Ph_2BNHCMe_3$ and $PhBNMe_2NHCMe_3$, respectively. This observation could tentatively be rationalised in terms of competition between boron and silicon for the nitrogen lone pair resulting in increased mesomeric withdrawal of electron density by boron from the phenyl group.

Conclusions about $\delta^{13}C$ (*para*) values in phenylboranes

The $\delta^{13}C$ (*para*) values are consistent with mesomeric interactions of the boryl group with the phenyl group and thus provide good evidence for B–C p_π–p_π bonding. If $\delta^{13}C$ (*para*) is larger than $\delta^{13}C$ of benzene (128.3 ppm) then the boryl group is a mesomeric acceptor, but if it is lower than 128.3 ppm mesomeric donation is indicated.

The magnitude of $\delta^{13}C$ (*para*) may be used as a quantitative measure of the amount of B–C p_π–p_π bonding. Large deshielded values indicating strong delocalisation of phenyl π electron density on to boron via p_π–p_π interaction. $\delta^{13}C$ (*para*) values for the phenylboranes studied show significant B–C p_π–p_π bonding decreasing in the following order for substituents attached to boron: halogens > organyls > OR > SR > NR_2 ~ NHR.

$\delta^{13}C$ *(ortho) of phenylboranes*

These chemical shifts range from 130–139 ppm and would be expected to parallel $\delta^{13}C$ (*para*) if the mesomeric effect was the only factor affecting shielding of the *ortho* carbon atoms. However, while $\delta^{13}C$ (*para*) is sensitive to the electronic nature of the boron substituents $\delta^{13}C$ (*ortho*) is affected by this and other factors because of its closeness to boron. Indeed the factors governing the magnitude of $\delta^{13}C$ (*ortho*) are probably composite of those affecting $\delta^{13}C$ (*ortho*) and $\delta^{13}C$ (C(1)). Consequently there is no simple relationship between $\delta^{13}C$ (*ortho*) and the nature of the boryl group. It is noteable that for every phenylborane studied ^{13}C (*ortho*) is deshielded relative to $\delta^{13}C$ (*para*) and benzene.

$\delta^{13}C$ *(meta) of phenylboranes*

These chemical shifts span a range from only 126.7–128.3 ppm. $\delta^{13}C$ (*meta*) is always marginally deshielded relative to benzene, but all $\delta^{13}C$ (*meta*) values fall into a very narrow range (1.6 ppm) and are therefore neither indicative of the nature of the boron substituents nor sensitive to mesomeric interactions of the boryl group with the phenyl group.

Experimental

The spectra were recorded on a JEOL-PS-100 NMR spectrometer. The ^{13}C NMR were recorded using the FT mode. Tetramethylsilane was used as an internal standard and the compounds were recorded as solutions in CCl_4, $CDCl_3$ or as neat samples. Chemical shifts quoted are correct to 0.5 ppm. An internal DMSO capillary lock was used when measured the ^{13}C NMR spectra of neat samples and the temperature of the sample was varied by passing a stream of heated air or cold nitrogen over the probe.

Acknowledgement

We thank Dr. C. Brown for helpful discussion, D.O'N Smith for recording the spectra, and the SERC for grant to T.J.M.

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