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## NUCLEAR MAGNETIC RESONANCE STUDIES OF BORON COMPOUNDS

### XVI \*. CARBON-13 STUDIES OF ORGANOBORANES: PHENYLBORANES AND BORON-SUBSTITUTED AROMATIC HETEROCYCLES

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#### Summary

$^{13}\text{C}$  and  $^{11}\text{B}$  NMR data of 29 phenylboranes and 9 boron-substituted aromatic heterocycles (thiophene, *N*-methylpyrrole and furan) are discussed. The observed  $^{13}\text{C}$  chemical shifts of the *para*-carbon atoms in phenylboranes and the corresponding carbon atoms in the aromatic heterocycles are consistent with mesomeric interactions of the boryl group with the aromatic system. The trend of  $\delta(^{13}\text{C}(\textit{para}))$  in phenylboranes corresponds to that observed for iso-electronic phenylcarbocations. Low temperature  $^{13}\text{C}$  NMR and/or  $^{13}\text{C}\{^{11}\text{B}, ^1\text{H}\}$  heteronuclear triple resonance experiments were employed to obtain the  $^{13}\text{C}$  chemical shifts of the boron-bonded carbon atoms.

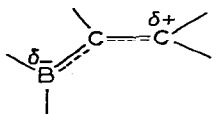
#### Introduction

A considerable amount of experimental data indicates that the electron deficiency of tricoordinate boron is compensated by  $p_{\pi}-p_{\pi}$  interactions between boron and  $\pi$  donor groups, such as  $-\text{NR}_2$  or  $-\text{OR}$  [2]. A similar situation has been suggested for alkynyl-, vinyl- and phenyl-boranes on the basis of NMR spectroscopy, vibrational spectroscopy, B—C bond distances, and chemical stabilities [2].

\* For Part XV, see ref. 1.

\*\* Taken in part from the thesis of T.F. Moore submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree, May, 1978.

Mesomeric interactions in tricoordinate organoboranes which contain one or more unsaturated organic moieties involve contributions from the structure



which could play a substantial role in the ground state properties of these molecules. NMR spectroscopy would appear to be a suitable technique with which to study these  $p_\pi-p_\pi$  interactions. Although the interpretation of  $^{11}\text{B}$  chemical shifts is not always straightforward due to the presence of various influences exerted by other substituents [3], the extensive data available to date strongly favor  $p_\pi-p_\pi$  interactions between boron and carbon [4]. Since  $^{11}\text{B}$  NMR data always represent the sum of all substituent effects, it has been found particularly useful (i) to study a series of compounds and (ii) to study NMR parameters of magnetically active nuclei in the substituent in order to obtain an idea of the extent of the  $\pi$ -donor properties of the groups which may be involved in  $\pi$  bonding to boron. This approach has been used extensively in the case of aminoboranes by means of  $^{14}\text{N}$  NMR spectroscopy [5] and was also successful in a study of a series of vinylboranes [6].

The quadrupolar nature of the boron nucleus ( $^{10}\text{B}$ :  $I = 3$ , 19.8%;  $^{11}\text{B}$ :  $I = 3/2$ , 81.2%) has hampered to some extent the application of  $^{13}\text{C}$  NMR spectroscopy to the study of organoboranes in that resonances representing the directly bonded carbon atoms are not easily detected. However, the data presented thus far indicate that  $^{13}\text{C}$  NMR can be a sensitive technique in studying the bonding in these molecules [7]. This has been demonstrated in a  $^{13}\text{C}$  NMR investigation of trivinylborane and vinylhaloboranes [6] where the resonance of the terminal carbon ( $C\beta$ ) of the vinyl group in each compound was found to be deshielded with respect to the carbon resonance in ethylene. This deshielding was interpreted as indicating that boron acts as a mesomeric acceptor and that  $\pi$ -conjugation between the vinyl groups and the boron atom occurs. Support for this interpretation came from the fact that complexation of boron in these compounds with a Lewis base resulted in a significant shielding of the  $C\beta$ -resonance in each compound. Similar observations were made in a series of 1-stanna-4-boracyclo-2,5-hexadienes [8] and  $^{13}\text{C}$  NMR data of several alkenyl- [9] and alkynyl-boranes [9–12] were also interpreted in terms of B–C  $\pi$  bonding. Therefore, it should be of considerable interest to study boron-substituted aromatic systems by  $^{13}\text{C}$  NMR spectroscopy.

Three reports of  $^{13}\text{C}$  NMR studies of phenylboranes have appeared recently [13–15]. Although a considerable number of compounds were studied, all reports have dealt primarily with the difficulties encountered in observing the boron-substituted aryl carbon resonances; moreover no attempt has been made to interpret the reported  $^{13}\text{C}$  chemical shifts in terms of B–C  $\pi$  bonding.

The present work contains additional  $^{13}\text{C}$  NMR data for phenylborane derivatives as well as borylated thiophenes, *N*-methylpyrroles and furans, and discusses these data in terms of electron delocalization involving the boron atom and the aromatic ring systems.

## Results and discussion

### *Phenylborane derivatives*

The carbon-13 and boron-11 chemical shift data for the phenylborane derivatives are presented in Table 1. Assignment of the resonances of the boron-substituted aryl carbon atoms was made on the basis of their being broad, low intensity resonances and/or on the basis of their being sharpened by irradiating at the appropriate  $^{11}\text{B}$  resonance frequency. For many of these compounds this  $^{13}\text{C}$  resonance was not observed at ambient temperature in the proton decoupled  $^{13}\text{C}$  NMR spectrum; however, acquisition of spectra of low temperatures [13,14] or simultaneous  $^{11}\text{B}$ -decoupling enabled assignments to be made.

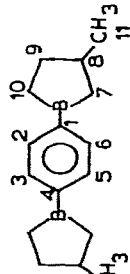
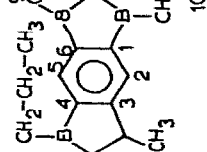
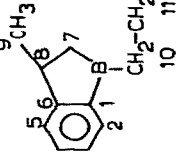
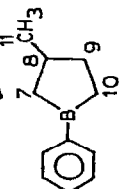
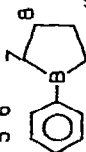
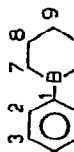
Brown and coworkers [15] recently reported that acquisition of  $^{13}\text{C}$  NMR spectra on neat samples at room temperature made it possible to assign the boron-substituted phenyl carbon resonances which were not detected in spectra obtained on solutions at room temperature. However, we were unable to detect the resonance of the boron bonded carbon atom in phenyldichloroborane (25) in the neat liquid at room temperature. Therefore, one cannot be assured that acquisition of a spectrum of a neat sample will always enable observation of the substituted aryl carbon resonance in a phenylborane. Thus,  $^{11}\text{B}$  decoupling appears to be the reliable method of choice\*.


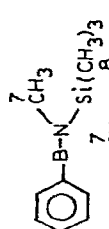
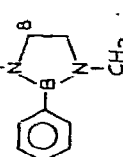
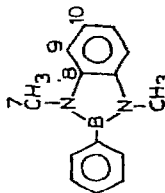
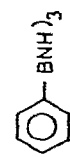
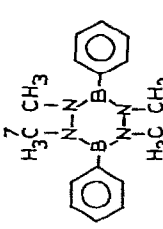
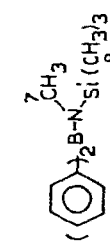
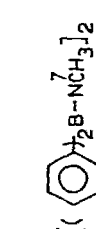
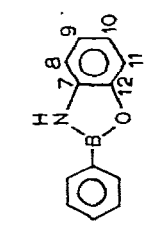
It has been shown for a series of methylboranes that the  $^{13}\text{C}$  chemical shifts of the boron bonded methyl carbons are sensitive to  $p_{\pi}-p_{\pi}$  interactions between boron and other substituents [16]. In agreement with Niedenzu et al. [13,14] the data in Table 1 indicate that this trend does not hold for the directly bound carbon atoms of the phenylboranes studied here. Examination of  $\delta(^{13}\text{C})$  for the boron-substituted aryl carbon resonance shows no obvious relationship between these shieldings and the electronic nature of the other boron substituents. This is not entirely surprising because of the potential delocalization of the phenyl  $\pi$  electron density onto boron. The shielding of the boron bonded phenyl carbon must be a function of the extent of this delocalization as well as of the  $\pi$  interactions between boron and other substituents. In addition, it appears that the shielding of a boron bonded carbon atom depends greatly upon the bond angles at boron, reflecting both electronic and steric effects. Thus, a substantial increase in shielding has been observed when the boron atom is part of a five-membered ring as compared to a six-membered ring or an analogous sterically unstrained noncyclic compound [7]. A comparison of  $\delta(^{13}\text{C}(1))$  of compounds 1 and 2, 8 and 10, 11 and 13, or 20 and 21 clearly shows that this trend also holds for phenylboranes. The fact that 18 and 19 have similar  $^{13}\text{C}(1)$  shifts is puzzling only at first sight. A thorough study of all NMR data for 19 suggests that ring opening and closure occurs rapidly compared to the NMR time scale. This conclusion is based on the observation that the  $^1\text{H}$  NMR signal of the  $-\text{OCH}_2$  group cannot be sharpened in  $^1\text{H}\{^{11}\text{B}\}$  heteronuclear decoupling experiments\*\*. Analogous  $^1\text{H}$  resonances of other alkoxyboranes are significantly

\* The factors which govern  $^{11}\text{B}$  and  $^{13}\text{C}$  relaxation in these compounds have not been fully investigated, and there is clearly a need for study in this area.

\*\* It is not clear at present whether the exchange reaction found for 19 is due to impurities in the compound (traces of glycol), to the solvent or traces of water in the solvent. Further studies of compound 19 will, therefore, be necessary.

No. Compound	$\delta(^{13}\text{C})$ (ppm)												$\delta(^{11}\text{B})$ (ppm)	
	1	2	3	4	5	6	7	8	9	10	11	12		
1	140.7	133.6	127.6	131.9	127.6	133.6	23.4	24.4	28.2					77.5 <sup>a</sup>
2	138.1	136.5	127.7	132.4	127.7	136.5	26.4	27.4						84.5 <sup>a</sup>
3	138.3	136.4	127.8	132.5	127.8	136.4	35.7	36.1	35.6	25.4	22.4			84.5 <sup>a</sup>
4	143.3	138.4	127.3	131.1	127.3	138.4								68.0
5	143.4	131.9	124.5	133.0	125.5	169.1	35.0	39.4	23.4	25.2	19.2	17.6		82.5
6	148.5	127.3 <sup>b</sup> 127.2	166.0 165.7	148.5	127.3 127.2	166.0 165.7	36.0	38.8	23.7 23.6	25.4	19.1	17.5		83.4
7	142.0	135.4	135.4	142.0	135.4	135.4	36.2	36.1	35.5	25.8	22.4			86.4

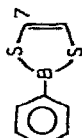
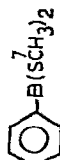
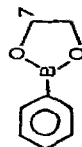
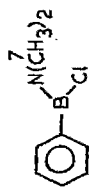


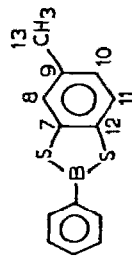
8		141.7	134.8	127.1	127.2	127.1	127.1	134.8	40.8		32.4 <sup>c</sup>		
9		144.0	134.2	127.0	138.2	127.0	127.0	134.2	34.5	0.4	39.5 <sup>d</sup>		
10		133.9	132.9	127.5	127.9	127.5	127.5	132.9	34.1	51.2	32.2 <sup>e</sup>		
11		132.7	133.9	127.9	128.6	127.9	127.9	133.9	29.5	138.4	108.2	29.4	
12		138.0	133.3	127.6	129.6	127.6	127.6	133.3				33.8 <sup>f</sup>	
13		138.0	134.2	127.5	128.6	127.5	127.5	134.2	36.1			32.5 <sup>g</sup>	
14		145.6 <sup>b</sup> 143.6	133.2 132.3	127.1 127.1	127.8 127.8	127.1 127.1	127.1 127.1	133.2 132.3	36.6	1.0		47.6 <sup>d</sup>	
15		141.7 <sup>b</sup> 140.5	133.0 132.1	127.1 126.8	128.1 127.4	127.1 126.8	127.1 126.8	133.0 132.1	39.6			39.5 <sup>h</sup>	
16		128.9	133.7	128.1	130.9	128.1	128.1	133.7	136.2	120.2	111.2	149.7	32.4

(Continued)

TABLE 1 (continued)

No. Compound	$\delta(^{13}\text{C})$ (ppm)												$\delta(^{11}\text{B})$ (ppm)	
	1	2	3	4	5	6	7	8	9	10	11	12		
17	137.0	132.6	127.3	128.7	127.3	132.6	40.3 37.7							32.4
18	131.7	133.1	127.6	129.0	127.6	131.1	52.0							28.6
19	132.2	134.5	127.5	131.1	127.5	134.5	65.6							31.2
20	138.0	131.1	127.6	129.0	127.6	131.1	12.7							65.0 <sup>i</sup>
21	132.6	134.4	127.4	131.4	127.4	134.4	37.6							66.2
22	132.7	133.9	128.1	130.8	128.1	133.9	127.2							59.1

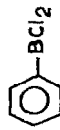




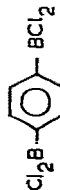
23 133.2 134.1 128.2 131.5 128.2 134.1 141.2 126.8 135.5 126.7 126.7 137.8<sup>k</sup> 59.8



24 124.0 136.3<sup>j</sup> 128.3 134.0 128.3 136.3 25.1



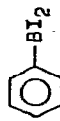
25 134.0 136.8 128.0 134.9 128.0 136.8 54.8<sup>c</sup>



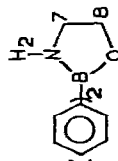
26 139.1 135.7 135.7 139.1 135.7 135.7 55.3



27 137.3 137.7 128.1 135.2 128.1 137.7 57.8



28 143.4 138.7 128.1 135.1 128.1 138.7 48.1



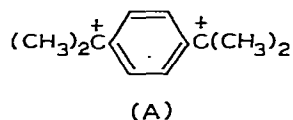
29 137.5 131.7 127.6 126.5 127.6 131.7 42.5 63.3 6.5

<sup>a</sup> Ref. 4. <sup>b</sup> Two isomers, see text. <sup>c</sup> Ref. 29a. <sup>d</sup> Ref. 38. <sup>e</sup> Ref. 45. <sup>f</sup> Ref. 46. <sup>g</sup> Ref. 41. <sup>h</sup> Ref. 42. <sup>i</sup> Ref. 47. <sup>j</sup> <sup>3j</sup>(<sup>19</sup>FBC<sup>13</sup>C) = 5.2 Hz. <sup>k</sup> 8(C(13)) 20.9 ppm.

broadened by partially relaxed coupling to boron but can be sharpened by  $^{11}\text{B}$  decoupling.

It has been previously shown that strong electronegative groups attached to the aryl substituent do not necessarily cause shifts to low field for C(1). This is demonstrated by a comparison of the  $\delta(^{13}\text{C}(1))$  data of toluene with trifluoromethylbenzene [17], acetophenone with benzoylfluoride [17,18] or benzoylchloride [17], or by examining  $\delta(^{13}\text{C}(1))$  data of many phenylcarbocations [18,19]. This also holds for the  $\delta(^{13}\text{C}(1))$  data of the phenylboranes examined here, indicating the influence of various parameters on this carbon shielding.

It has been reported that the concept of additive substituent parameters [20] for predicting  $\delta(^{13}\text{C})$  data of disubstituted (1,4 or 1,3) or trisubstituted (1,3,5) benzenes breaks down for A [21]. This has been explained in terms of charge—



charge repulsions leading to a greater demand of hyperconjugative delocalization of electron density from the methyl groups [21]. Although in many cases a striking resemblance of NMR parameters for carbocations and their isoelectronic and isostructural counterparts, the boranes, is observed, the  $\delta(^{13}\text{C})$  data of 1,4-diborylated benzenes (6, 7, 26) are in good agreement with the additivity concept (deviation  $<1$  ppm). Another difference in the trends of NMR parameters between A and the corresponding boranes is evidenced by the  $^{13}\text{C}$  resonance of  $\text{C}^+$  in A which is significantly more shielded than the corresponding resonance in monosubstituted phenylcarbocations [21], while the boron atoms in the 1,4-diborylated benzenes are slightly deshielded with respect to the phenylboranes.

There is currently some confusion regarding the assignment of *ortho*-, *meta*- and *para*-carbon resonances in phenylboranes. Niedenzu et al. [13,14] did not discuss the criteria by which they assigned the resonances of the *ortho*- and *meta*-carbons, and Brown and coworkers [15] stated that their assignments of the *ortho*- and *para*-carbon resonances are in conflict with those reported by Niedenzu et al. However, the data presented by Brown et al. indicate that the conflicting assignments involve the *ortho*- and *meta*- and not the *ortho*- and *para*-carbon resonances.

We have used proton decoupled  $^{13}\text{C}$  NMR spectra to confirm our assignments and spectra of compounds 13 and 22 are shown in Figs. 1 and 2. Since it is well established that in benzene rings the coupling constants  $^3J(^{13}\text{C}^1\text{H}) \gg ^2J(^{13}\text{C}^1\text{H})$  the assignment of the phenyl carbon resonances in 13 is straightforward. In compound 22 the  $^{13}\text{C}$  resonance of the  $-\text{SCH}=\text{CHS}-$  group also gives rise to a doublet of doublets in the aromatic region of its proton coupled  $^{13}\text{C}$  NMR spectrum which can be easily assigned owing to the larger coupling constant  $^1J(^{13}\text{C}^1\text{H})$ . Compounds 11, 16 and 23 exhibit additional signals in the aromatic region due to the benzo rings and the assignment was made on the basis of the proton coupled  $^{13}\text{C}$  NMR spectra and on the basis of accepted substituent effects. In compound 24 the presence of the coupling constant  $^3J(^{19}\text{F}^{13}\text{C})$  lends additional support to the correct assignment of the *ortho*-carbon resonance.

The chemical shifts of the *meta*-carbon atoms for the compounds studied



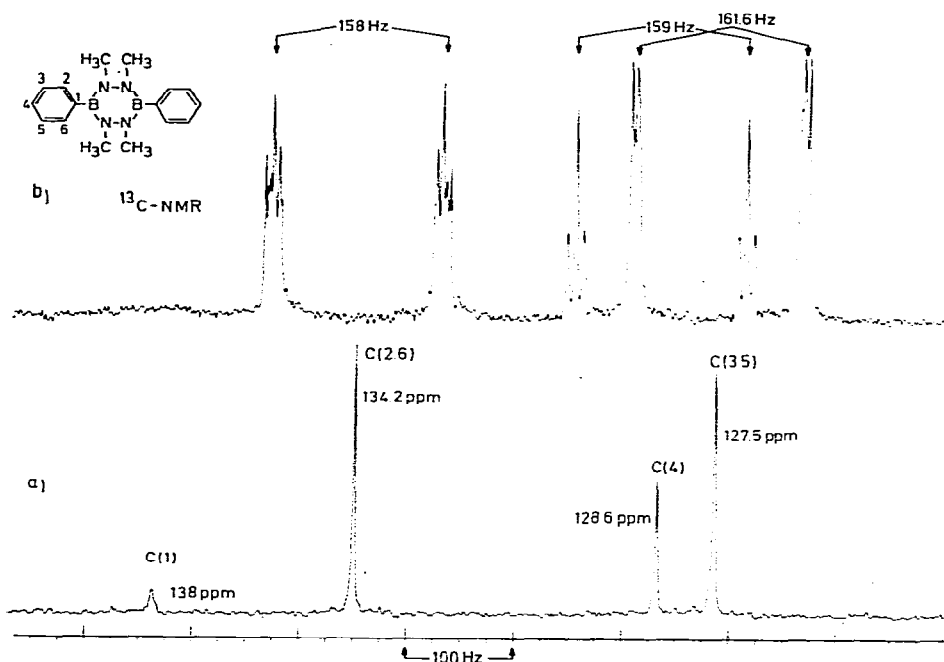


Fig. 1. (a)  $^{13}\text{C}\{^1\text{H}, ^{11}\text{B}\}$  NMR spectrum of compound 13. (b)  $^{13}\text{C}\{^{11}\text{B}\}$  NMR spectrum of compound 13.

(Table 1), including the tetra-coordinate boron molecule 29, fall into a small range ( $<1$  ppm). These shifts are obviously neither indicative of the nature of boron substituents nor sensitive to mesomeric interactions. The *ortho*- and *para*-carbon resonances in the molecules cover relatively broad ranges; how-

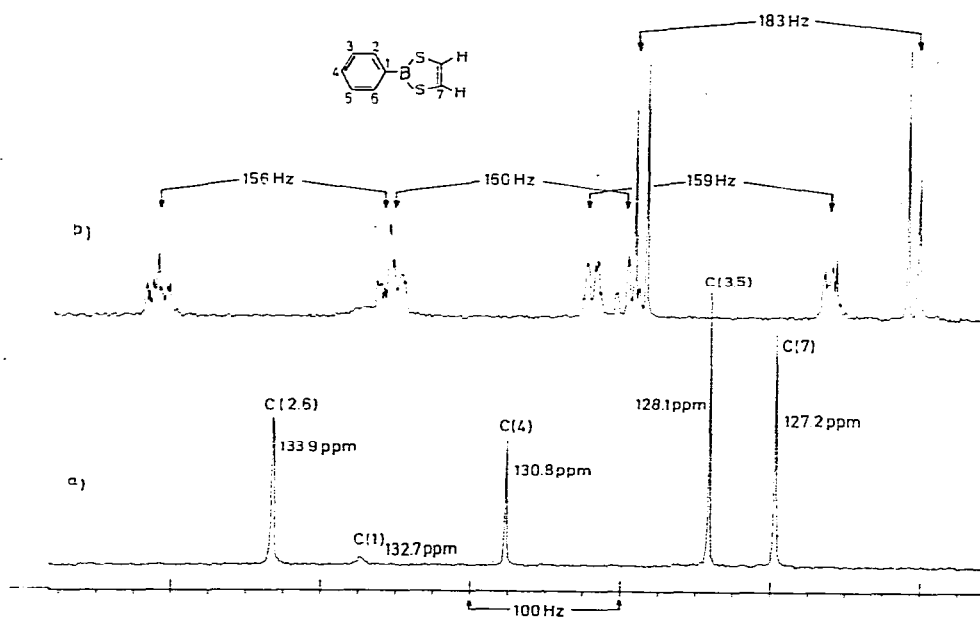


Fig. 2. (a)  $^{13}\text{C}\{^1\text{H}, ^{11}\text{B}\}$  NMR spectrum of 22. (b)  $^{13}\text{C}\{^{11}\text{B}\}$  NMR spectrum of 22.

ever, for each compound the *para*-carbon resonance is shielded with respect to the *ortho*-carbon resonance. For the aminoboranes 9, 10 and 14–16, the *para*-carbon resonance is shielded as compared to the analogous resonance in benzene whereas the *ortho*-carbon resonances are significantly deshielded ( $>4$  ppm). This is in accord with  $^{13}\text{C}$  NMR data of monosubstituted benzenes where the *para*-carbon resonance is sensitive to the electronic nature of the substituents while the shielding of the *ortho*-carbon resonances is undoubtedly affected by this *and* other contributions [20].

Delocalization of the nitrogen lone pair of electrons into the vacant  $p$  orbital on boron is well documented for aminoboranes. In fact two sets of phenyl carbon resonances are observed for each of the compounds 14 and 15. Restricted rotation about the B–N bond yields one set of phenyl group(s) *cis* to the *N*-methyl and the other set *trans* to the *N*-methyl group. This restricted rotation about the B–N bond has been observed also for less crowded aminoboranes and implies significant B–N  $p_{\pi}$ – $p_{\pi}$  interactions. These interactions together with potential twisting of the phenyl groups relative to the  $\text{BNR}_2$  plane should substantially reduce or eliminate any mesomeric acceptance by boron of the phenyl  $\pi$  electron density. The finding of the increased shielding of the *para*-carbon atom in aminophenylboranes with respect to benzene leads to the conclusion that  $-\text{B}(\text{NR}_2)_2$  or  $-\text{B}(\text{NR}_2)\text{X}$  groups may even act as weak mesomeric donors. This suggestion is supported by  $^{14}\text{N}$  chemical shifts of dialkylaminophenylboranes [5a]. The deshielding of the nitrogen atom in these compounds as compared to  $\text{RB}(\text{NR}_2)_2$  and  $\text{RB}(\text{NR}_2)\text{X}$  ( $\text{R} = \text{alkyl}$ ) can now be interpreted in terms of delocalization of the nitrogen lone pair beyond boron onto the boron bonded phenyl group.

The *para*-carbon chemical shifts  $\delta(^{13}\text{C}(4))$  of the phenylboranes studied indicate significant B–C  $p_{\pi}$ – $p_{\pi}$  interactions decreasing in the following order for substituents attached to boron: halogens  $>$  organyls  $>$  OR  $>$  SR  $>$   $\text{NR}_2$ . With the possible exception of amino groups this sequence is not directly related to the observed  $^{11}\text{B}$  chemical shifts. In the absence of groups which are known to exert strong neighbouring anisotropic effects (e.g.,  $-\text{I}$ ,  $-\text{Br}$ ,  $-\text{C}\equiv\text{C}-\text{R}$ ),  $^{11}\text{B}$  chemical shifts in tricoordinate boranes are linearly related to the calculated  $\pi$  electron density on boron [22]. Thus, they reflect the sum of all  $\pi$  interactions. Therefore, NMR parameters of potential  $\pi$  donor groups bonded to boron supply valuable information regarding their contribution to the  $\pi$  electron density on boron. However, the  $\pi$  acceptor strength of boron must also be considered. This increases with increasing polarization of the  $\sigma$  bonding framework by electronegative ligands. Consequently, the observed shielding sequence of the *para*-carbon atoms is a function of the  $\pi$  acceptor potential of boron in the compounds under consideration and its  $\pi$  interaction with other ligands, the latter depending also upon steric hindrance.

The  $\delta(^{13}\text{C}(4))$  data of the dihalogenophenylboranes parallel those of dihalogenovinylboranes [6]. This indicates that the dihalogenoboryl group is the stronger  $\pi$  acceptor as compared to the diorganylboryl group, although the  $^{11}\text{B}$  chemical shifts of boranes  $\text{R}_2\text{BR}'$  and  $\text{Hal}_2\text{BR}'$  ( $\text{R}' = \text{C}_6\text{H}_5$ ) indicate that the boron  $\pi$  electron density is less in the  $\text{R}_2\text{BR}'$  molecules. Obviously, the halogens withdraw more  $\sigma$  charge density from boron than the organyl groups and this is compensated by increased B–C ( $p_{\pi}$ – $p_{\pi}$ ) interactions with the phenyl

groups. Together with B—Hal ( $p_\pi-p_\pi$ ) interactions [23] (Hal = F, Cl) an overall increase of shielding for the boron atom in  $\text{Hal}_2\text{BR}'$  with respect to  $\text{R}_2\text{BR}'$  results.

Similar considerations apply to explain the close range of  $\delta(^{13}\text{C}(4))$  data for organyloxo- and organylthiophenylboranes (Table 1). The  $-\text{B}(\text{OR})_2$  group may be a stronger  $\pi$  acceptor as compared to the  $-\text{B}(\text{SR})_2$  group. However, B—O  $\pi$  bonding is believed to be more efficient than B—S  $\pi$  bonding.

The twisting of the phenyl rings out of the  $\text{C}_3\text{B}$  plane [24] may partly account for the relatively high shielding of the *para*-carbon atom in triphenylborane (4). In the absence of solution structural data for this compound as well as for compounds 9, 14, and 15, a detailed discussion of the  $^{13}\text{C}$  NMR data does not appear appropriate. However, it should be noted here that the  $\delta(^{11}\text{B})$  data reported for triphenylborane [25,26] are incorrect. Several independent measurements of 4 gave a broad resonance centered at 68.0 ( $\pm 1$ ) ppm which is 8 ppm deshielded with respect to the chemical shift in previous reports.

An interesting situation arises when two or more groups compete for the lone pair of an atom attached to boron. This situation exists for 9, 11, 12, 14 and 16 where the  $(\text{CH}_3)_3\text{Si}$  groups (9, 14), another boron (12), or the benzo ring (11, 16) are linked to the nitrogen(s) or oxygen (16) attached to boron. We will exclude 9 and 14 from our discussion since steric crowding complicates the situation. However, the *para*-carbon resonance of *B*-triphenylborazine (12) is the most deshielded resonance with respect to all other aminophenylboranes studied. This indicates that in the case of two boron atoms competing for the nitrogen lone pair, mesomeric acceptance by boron of the phenyl  $\pi$  electron density has to be taken into account. As is apparent from the  $\delta(^{13}\text{C})$  data of the benzo groups in 11 and 16, the nitrogen and oxygen atoms are still acting as mesomeric donors in spite of their being linked to trivalent boron. Therefore, an increased  $\pi$  acceptor strength of boron is expected which will result in more efficient  $\pi$  interaction between boron and the phenyl group. Indeed, the *para*-carbon resonance of 11 is deshielded with respect to the *para*-carbon resonance of 10 and the analogous resonance of 16 is also markedly deshielded with respect to 10, 11, 18 and even 17.

It has been very helpful in many respects to compare NMR parameters of isoelectronic and isostructural compounds. Thus, linear relationships exist between  $\delta(^{11}\text{B})$  of tricoordinate boranes and  $\delta(^{13}\text{C})$  of carbocations [27,28], between  $\delta(^{11}\text{B})$  of tetravalent boron compounds and  $\delta(^{13}\text{C})$  of corresponding substituted saturated hydrocarbons [29], as well as between  $\delta(^{11}\text{B})$  of polyboranes and  $\delta(^{13}\text{C})$  of non-classical carbocations [30] and  $\delta(^{11}\text{B})$  and  $\delta(^{13}\text{C})$  of isoelectronic polyboranes and carboranes [31]. A strictly linear relationship between  $\delta(^{13}\text{C})$  of phenylboranes and the corresponding phenylcarbocations may not be expected owing to the differing  $\overset{\cdot}{\text{C}}-\text{C}$  and  $\overset{\cdot}{\text{B}}-\text{C}$  bond polarities and consequently differing inductive effects on the  $^{13}\text{C}$  resonances of the phenyl carbon atoms. However, since the *para*-carbon resonance is the least susceptible one to these influences, a similar trend of carbon shielding may result provided the shielding of C(4) in both classes of compounds is governed by the same mechanism. At present five pairs of  $\delta(^{13}\text{C}(4))$  data are available for comparison and the result is graphically depicted in Fig. 3. The roughly linear relationship thus obtained suggests that for phenylcarbocations and phenylboranes the mesomeric

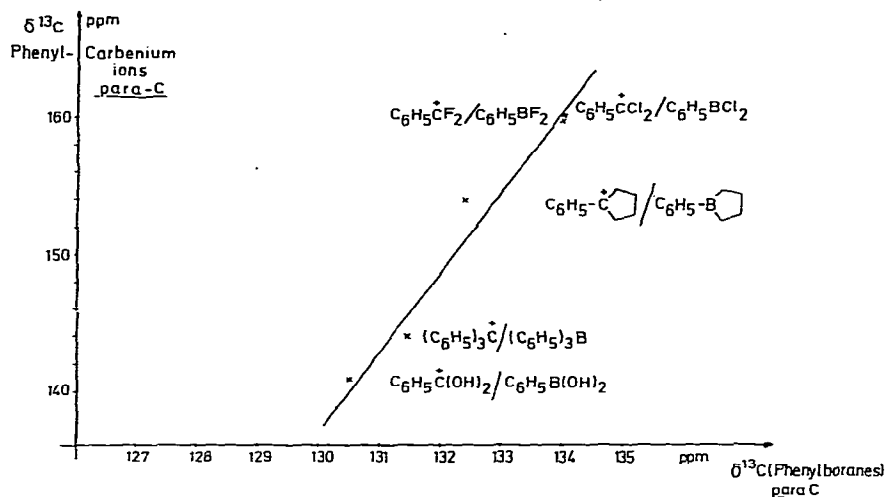
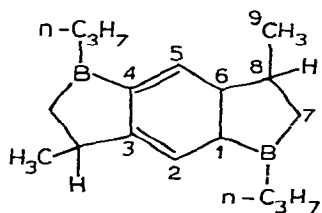


Fig. 3. Correlation of  $^{13}\text{C}$  chemical shifts of the *para*-carbon resonance of phenylcarbocations and phenylboranes.

withdrawal of  $\pi$  electron density from the phenyl groups by the  $\pi$  acceptors  $\overset{+}{\text{C}}$  and  $\text{B}^-$  dominates the *para*-carbon shielding. Not surprisingly the shift differences for the *para*-carbon resonances are ca. six times greater for the phenylcarbocations than for phenylboranes.

The additional  $^{13}\text{C}$  resonances of ligands other than the phenyl group attached to boron deserve a mention,  $^{13}\text{C}\{^1\text{H}, ^{11}\text{B}\}$  triple resonance experiments enabled us to observe all boron-bonded carbons for compounds 1–7, and even those resonances could be observed which overlap with other intense  $^{13}\text{C}$  resonances (e.g., C(7,8) of 3, or C(7,8) of 7). There are still too few organoboranes studied by  $^{13}\text{C}$  NMR to be able to establish substituent effects for saturated carbons attached to boron. It seems worth mentioning that the resonance of the boron bonded carbon of the propyl group in 5 and 6 is shielded by ca. 6.5 ppm with respect to the corresponding resonance in tripropylborane. This may again reflect the influence of the bond angles at boron upon  $\delta(^{13}\text{C})$ . Most of the additional  $\delta(^{13}\text{C})$  data are in the expected range and a greater body of data will certainly help to stimulate the use of  $^{13}\text{C}$  NMR in organoboron chemistry.

We observe a splitting of three carbon resonances for compound 6 into doublets of unequal intensity (C(2,5), C(3,6) and C(9)). The obvious explanation is the presence of two isomers having the methyl substituents (C(9)) either in *cis*- or in *trans*-positions.



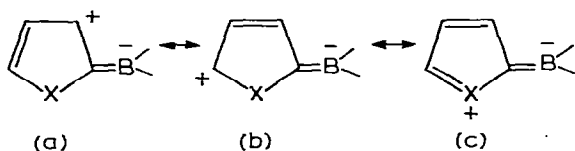
(6)

### Boron-substituted aromatic heterocyclic compounds

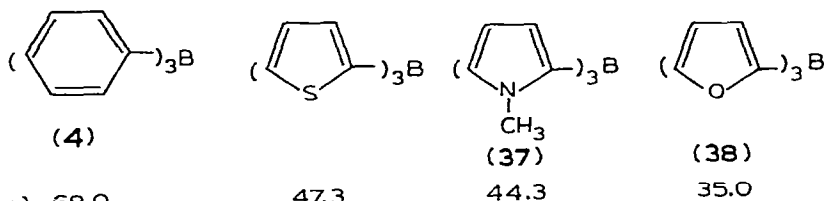
Carbon-13 and boron-11 chemical shift data for the boron-substituted thiophene, *N*-methylpyrrole and furan compounds 30–38 are presented in Table 2. The assignment of the aromatic carbon bonded to boron was made in analogy to the phenylboranes. Again the acquisition of spectra of a neat sample of 34, or low temperature  $^{13}\text{C}$  NMR experiments were not successful in detecting the resonance of the boron bonded carbon, whereas  $^{11}\text{B}$  decoupling readily yields this parameter. As with phenylboranes the  $\delta(^{13}\text{C})$  data of the boron bonded carbons are surely influenced by several factors and the set of data collected in this study is too small to reach any firm conclusions in delineating these factors.

The assignments of the other carbon resonances is straightforward on the basis of chemical shift differences relative to the parent compounds and/or the magnitude of the coupling constant  $^1J(^{13}\text{C}^1\text{H})$  which is larger for carbon atoms in 2,5 positions with respect to those in 3,4 positions [20].

Chemical reactivity and molecular orbital calculations of the three, five-membered aromatic heterocycles suggest that their  $\pi$  electron system is much more readily affected by substituents capable of mesomeric interactions than benzene. Resonance structures analogous to phenylboranes can be drawn:

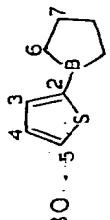
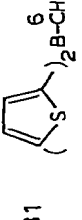
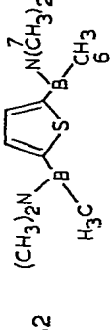
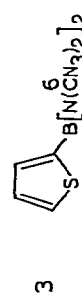


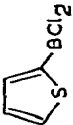
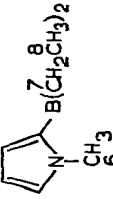
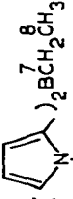
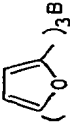
Accordingly, contributions of the valence bond structures a–c to the chemical shift of the ring carbons should result in a significant deshielding of C(3) and C(5) for substituents in the 2 position which act as mesomeric acceptors. The resonance of C(4) should remain fairly constant. This was found to be the case in studies of substituted five-membered aromatic heterocycles [20,32]. The  $\delta(^{13}\text{C})$  data in Table 2 are also in good agreement with this concept. The strong deshielding of C(3) and C(5) in dichloro-2-thienylborane (34) again indicates that the  $-\text{BCl}_2$  group is a strong  $\pi$  acceptor in agreement with our results for the dichlorophenylborane molecule. The  $\text{B}-\text{C}(p_\pi-p_\pi)$  interactions become less efficient in compounds 30 and 31 as compared to 34; however, the deshielding of the relevant carbon atoms is still much greater than in the analogous phenylboranes. Interestingly, there appears to be some mesomeric acceptance by boron from the thienyl  $\pi$  electron density in 33, in contrast to bis(dimethylamino)phenylborane (8) where the  $-\text{B}(\text{N}(\text{CH}_3)_2)_2$  group seems to have weak mesomeric donor properties. This lends further credence to the assumption that the five-membered aromatic heterocycles are better  $\pi$  donors than the phenyl group, a conclusion obtained independently by  $^{11}\text{B}$  NMR studies [4]. This is evidenced by the  $^{11}\text{B}$  chemical shifts of the following series:



(Continued on p. 30)

TABLE 2  
 $^{13}\text{C}$  AND  $^{11}\text{B}$  CHEMICAL SHIFTS OF BORON-SUBSTITUTED FIVE-MEMBERED HETEROCYCLES

No.	Compound	$\delta(^{13}\text{C})$ (ppm) <sup>a</sup>								$\delta(^{11}\text{B})$ <sup>b</sup> (ppm)
		2	3	4	5	6	7	8		
30		143.2 (17.6)	139.5 (12.1)	128.8 (1.4)	136.2 (10.6)	26.1	27.5		76.0	
31		144.8 (19.2)	139.5 (12.1)	128.9 (1.5)	136.7 (10.1)	9.5			57.0	
32		147.6 (22.0)	134.0 (6.6)	134.0 (6.6)	147.6 (22.0)	5.2	40.3 41.2		39.7	
33		139.2 (13.6)	128.0 (0.6)	127.0 (-0.4)	132.6 (7.0)	41.1			30.0	

34		139.1 (13.5)	143.0 (15.6)	129.6 (2.2)	140.2 (14.6)	48.5
35		139.3 (18.3)	126.4 (18.7)	108.8 (1.1)	131.9 (10.9)	66.4
36		140.8 (19.8)	125.2 (17.5)	108.2 (0.5)	129.8 (8.8)	54.7
37		140.5 (19.5)	123.3 (15.6)	108.2 (0.5)	129.6 (8.6)	44.3
38		160.7 (17.9)	130.6 (20.8)	111.5 (1.7)	148.7 (5.9)	35.0

<sup>a</sup> Numbers in brackets refer to the differences in <sup>13</sup>C chemical shifts relative to the parent compounds, <sup>b</sup> Ref. 4.

The increase of the  $\pi$  donor strength in going from the phenyl- to the 2-furyl group has been suggested on the basis of  $\delta(^{11}\text{B})$  data [4]. However, the  $\delta(^{13}\text{C})$  data presently available do not allow us to distinguish between the aromatic heterocycles as far as their  $\pi$  donor strength is concerned since the influence of the heteroatoms S, N, and O on the carbon resonances is not yet fully understood.

## Conclusions

The data for the organoboranes reported here show that the carbon-13 chemical shifts of aromatic carbons are sensitive to  $\pi$  interactions with boron. They are in complete agreement with the accepted model of tricoordinate boron acting as a  $\pi$  electron acceptor with the acceptor strength depending on the electronic nature of the substituents at boron. Furthermore, it is satisfying to note that many of the  $^{13}\text{C}$  NMR parameters reported in this study contribute to a verification of the picture of B—C bonding which was derived hitherto only in part from other physical methods.

The failure to observe B—C coupling of boron-substituted aromatic compounds is both disappointing and interesting. These B—C coupling constants [11,33,34] should provide useful information for analyzing the bonding in these molecules. The fact that the resonances of the boron bonded carbon atoms appear as broad, low intensity singlets or are not observed at all at room temperature prevent measurement of this parameter. However, with a thorough understanding of  $^{11}\text{B}$  and  $^{13}\text{C}$  relaxation in these compounds, it might be possible to extract B—C coupling constants from the broad, low intensity resonances which are observed at lower temperatures or by partial  $^{11}\text{B}$  decoupling. Work aimed in this direction is currently in progress in these laboratories.

## Experimental

The compounds studied are shown in Tables 1 and 2. The  $^{13}\text{C}$  NMR spectra were recorded on a Varian Associates CFT-20 and/or a Bruker WP-200 spectrometer. The latter was equipped with a double tuned  $^1\text{H}$  decoupling coil to carry out  $^{13}\text{C}\{^1\text{H}, ^{11}\text{B}\}$  heteronuclear triple resonance experiments. Spectra were obtained on samples in 8 mm and 10 mm O.D. NMR tubes as ca. 30% (v/v) solutions in  $\text{CDCl}_3$  which provided the deuterium lock signal and also served as an internal reference. For measurements at temperatures below  $-55^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$  was used as the solvent. Carbon-13 chemical shifts were recorded directly from the spectrometer and were converted from secondary references to TMS reference by the following equations:

$$\delta(\text{TMS}) = \delta(\text{CDCl}_3) + 76.9; \quad \delta(\text{TMS}) = \delta(\text{CD}_2\text{Cl}_2) + 53.6$$

Unless otherwise noted chemical shifts are accurate to  $\pm 0.1$  ppm.

Observation of the boron-substituted carbons was accomplished either by recording the spectra at low temperature or by simultaneous  $^{11}\text{B}$  decoupling at room temperature. In either case small pulse angles ( $\leq 20^\circ$ ) or long delay times (10–40 s) were required to obtain these signals.

$^{11}\text{B}$  NMR spectra were recorded on Varian HA-100, Varian XL-100-15



(32.1 MHz) and Bruker WP-200 (64.2 MHz) NMR spectrometers. Spectra were referenced to external  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  using the same sign convention as for  $^{13}\text{C}$  chemical shifts. The compounds studied have been prepared according to methods reported in the literature: 1, 3, 30–38 [4]; 2, 25 and 27 by the reaction of the respective halogenoboranes with tetraphenyltin; 4 [35]; 5 and 6 were kindly supplied by Dr. R. Köster [36]; 7 and 26 by reaction of the respective halogenoboranes with 1,4-bis(trimethylstannyl)benzene; 8 and 10 [37]; 9 and 14 [38]; 11, 16, 21–23 [39]; 12 [40]; 13 [41]; 15 [42]; 17 by reaction of equimolar amounts of 8 and 25; 19 by reaction of 25 with glycol (1 : 1 ratio); 20 by reaction of 25 with an excess of  $\text{Pb}(\text{SCH}_3)_2$ ; 24 by reaction of 8 with  $\text{BF}_3$ ; 28 [43]; 29 [44]. The purity of the compounds was checked by  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectroscopy prior to the recording of the  $^{13}\text{C}$  NMR spectra. A detailed description for new compounds will be given elsewhere.

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