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ORGANOBORON COMPOUNDS

XIV *. DIALKYLAMINOFLUOROPHENYLBORANES

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Summary

The preparation and properties of a series of dialkylaminofluorophenylboranes and their ^{1}H and ^{13}C NMR spectra are reported. Evidence is presented for restricted rotation about the boron—nitrogen bond and in the ^{13}C spectra $^{3}J(^{13}C—^{19}F)$ transfluorine coupling is observed.

There has been considerable interest in the possibility of restricted rotation about B—N bonds, especially in compounds of the type $PhB(NR_2)X$ (where X = halogen, dialkylamino or alkoxy). However, all the published work to date has been obtained using ^{1}H NMR [1—11]. This technique has a number of limitations, the main one being the difficulty of assignment in complex molecules, due to overlapping peaks. We have therefore used ^{13}C NMR as a probe to investigate the nature of the B—N bond in aminoboranes. A survey of the literature revealed that the synthesis and ^{1}H NMR of only one dialkylaminofluorophenylborane, namely dimethylaminofluorophenylborane, has been reported [2,8]. In this present paper we report the preparation and properties of a series of dialkylaminofluorophenylboranes as well as their ^{1}H and ^{13}C NMR spectra recorded at ambient temperature.

The series of dialkylaminofluorophenylboranes were prepared by mixing a chlorodialkylaminophenylborane with SbF_3, the reaction being exothermic, and stirring the mixture for three hours.

$$SbF_3 + 3\ PhB(NR_2)Cl \rightarrow SbCl_3 + 3\ PhB(NR_2)F$$

Care must be taken to prevent the mixture from overheating, otherwise a black polymer is obtained. The physical constants of the compounds prepared are given in Table 1. The compounds were mainly characterised by high resolution mass spectrometry due to their hydrolytic instability.

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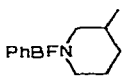
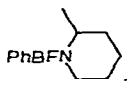
TABLE 1

DIALKYLAMINO(FLUORO)PHENYLBORANES

Compound	Yield (%)	B.p. (°C/mmHg)	Molecular weight (a.m.u.)		Error (ppm)	Ref.	Ref. b.p.
			Found	Calcd.			
$PhBFNMe_2$	70	40/1	151	151	—	2	62–6
$PhBFNEt_2$	75	45/1	179.1284872	179.1281548	2.08	—	—
$PhBFN(n\text{-}Pr)_2$	65	50/1	207.1585255	207.1494532	4.48	—	—
$PhBFN(i\text{-}Pr)_2$	65	50/1	207.1587214	207.1594532	3.89	—	—
$PhBFN(n\text{-}Bu)_2$	35	80/1	235.191511	235.1907516	3.23	—	—
$PhBFN(s\text{-}Bu)_2$ [a]	40	75/1	235	235	—	—	—
$PhBFN(i\text{-}Pent)_2$	40	90/1	263.2224350	263.2220500	1.58	—	—
PhBFNHt-Bu	70	35/1	179.128747	179.1281548	3.51	—	—
	35	65/1	205.1449036	205.1438040	5.36	—	—
	40	65/1	205.1441349	205.1438040	1.61	—	—

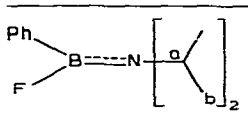
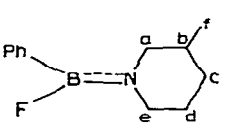
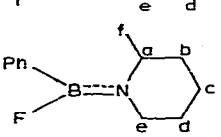
[a] Characterised by elemental analysis (see text).

^{1}H NMR spectra

The existence, in the ^{1}H NMR spectrum of $PhB(NMe_2)F$, of a single methyl band at temperatures as low as 223 K was assumed by Barfield [8] to be indicative of a low barrier to rotation resulting from substantial back donation from fluorine to boron. It is of interest that the ^{13}C NMR spectrum of the same compound shows a doublet at room temperature (separation 58 Hz) which coalesces to a singlet at 113°C to give a value of 19.1 kcal/mol for ΔG^*. Barfield rationa-

TABLE 2

^{1}H NMR ISOMER SHIFTS OF $PhBNR_2F$

Compound	Isomer shifts (Hz)					
	a	b	c	d	e	f
	70	22				
						10
						10

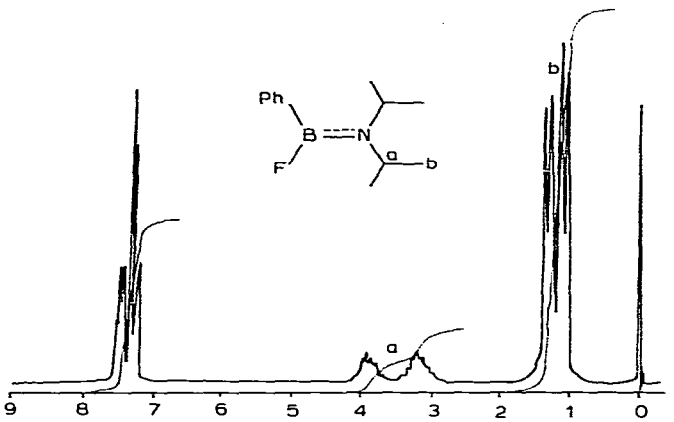


Fig. 1. ^{1}H NMR spectrum of PhBN-i-Pr$_2$F.

lised the observance of a single line in the ^{1}H NMR in terms of rapid internal rotation about the B—N bond, as he considered a small internal chemical shift unlikely in view of the anisotropy of the phenyl group. It is worth noting that the magnitude of the doublet splitting (i.e. internal chemical shift or isomer shift) $\Delta\nu$, for a particular hydrogen or carbon is determined mainly by the difference in environment of a given ^{1}H or ^{13}C nucleus in the *cis* and *trans* rotomers. The magnitude of $\Delta\nu$ is not dependent on the strength of the B—N π bond, but if the π bond is weak and rotation at $\succeq$B═N$\preceq$ becomes more rapid, time averaging results in broadening and reduction in $\Delta\nu$ followed, at higher temperature, by coalescence. The ^{1}H NMR spectra have been recorded on all ten compounds and, with the exception of PhB(NMe$_2$)F, all spectra indicated restricted rotation about the B—N bond. In three cases the spectra were simple enough to obtain isomer shifts (Table 2). The ^{1}H NMR spectrum of di-i-propylaminofluorophenylborane (Fig. 1) contains two septets for the methine hydrogens and two doublets for the methyl hydrogens, indicative of restricted rotation about the B—N bond.

^{13}C NMR spectra

In order to interpret the NMR spectra of phenylboranes of the type PhBNR$_2$X, (X = F, Cl, Br, OMe, SEt, NR$_2$', Ph), it must be appreciated that at ambient temperatures these compounds exist as a mixture of *cis* and *trans* isomers. This is because back donation of the nitrogen lone pair towards boron (p_π—p_π bonding) results in partial double bond character:

R *cis* to Ph

R *trans* to Ph

These isomers can interconvert by 180° rotation about the B—N bond, but the barrier to rotation is usually high enough at ambient temperatures to permit the observation of separate absorptions from the rotational isomers. It is therefore generally found that the resonances for the alkyl groups 'double up' and unless the alkyl group is simple the ^{1}H NMR spectrum can be very complicated, with many overlapping peaks. The corresponding ^{13}C NMR spectra are much more simplified with 'doublets' being observed for each unique carbon. The frequency separation of the separate absorptions originating from the *cis* and *trans* isomers is known as the isomer shift and is sometimes referred to as the internal chemical shift. It is a measure of the difference in environment of an alkyl group in the *cis* and *trans* isomers.

Assignment of ortho, meta and para carbon resonances in phenylboranes

There has been some confusion regarding the assignment of *ortho*, *meta* and *para* carbon resonances in phenylboranes. Niedenzu [12] did not discuss the criteria by which he assigned the resonances of the *ortho* and *meta* carbons, and Cragg [13] has reported that his assignments are in conflict with Niedenzu's. However, the latter assignments which are more reasonable from the point of view of accepted substituent effects, were confirmed by off-resonance decoupled and selectively decoupled $^{13}C(^{1}H)$ and by undecoupled ^{13}C spectral measurements. The assignments have recently been corroberated by Wrackmeyer [14] who used gated ^{1}H decoupled ^{13}C NMR to assign the aromatic resonances.

The ^{13}C NMR spectra, recorded at ambient temperature, exhibited isomer shifts and fluorine coupling, $^{3}J(^{19}F—^{13}C)$, for all compounds. The proton noise-decoupled ^{13}C NMR spectrum of 3-methylpiperidinofluorophenylborane (Fig. 2) illustrates the main features of the spectra of this class of compound.

In the aliphatic region of the spectrum 6 'doublets' are observed, correspondin to the 6 unique carbons of the 3-methylpiperidine ring. One set of signals originates from each rotomer. In addition the 2 'doublets' at lowest field show a splitting of their highfield lines. This splitting is about 7 Hz in both cases and is

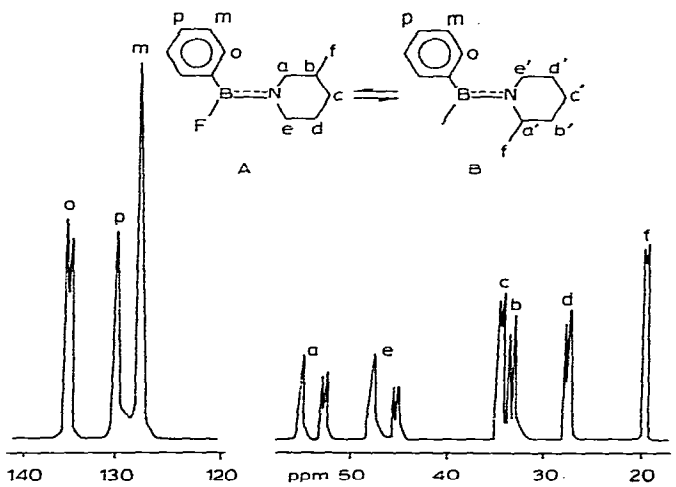


Fig. 2. ^{13}C NMR spectrum of 3-methylpiperidinofluorophenylborane.

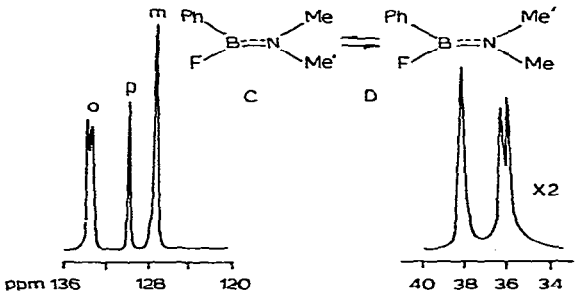


Fig. 3. ^{13}C NMR spectrum of $PhBNMe_2F$.

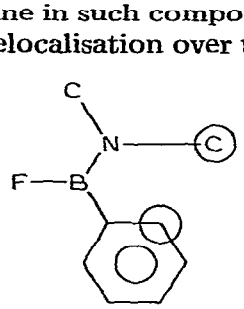
attributed to $^{19}F—^{13}C$ coupling. The *ortho* carbons of the phenyl group also show fluorine coupling. By analogy with olefins, *trans* coupling constants, $^3J(^{19}F—^{13}C)_{trans}$, are much larger than *cis* coupling constants. This would account for the splitting of only one of the lines in the low-field 'doublets'. If the analogy with olefins holds, then the line showing fluorine coupling may be assigned to one rotomer. For example, carbon a in rotomer A (Fig. 2) would be coupled to fluorine, but carbon a' in rotomer B would not. However, this is a tentative assignment since it assumes that coupling constants in olefins and aminoboranes are governed by the same factors.

The ^{13}C NMR data for all the fluoro compounds studied are collected in Table 2 and were obtained using 30% V/V solutions in $CDCl_3$ at room temperature (23°C).

Fluorine coupling

This observation may be taken as further evidence of restricted rotation. It is observed, in all 10 compounds, between fluorine and the α carbons of the amino groups [^3J(F—C) ~ 7 Hz] and also between fluorine and the *ortho* carbons of the phenyl group [^3J(C—F) ~ 4 Hz]. Furthermore, fluorine coupling is observed for the α carbon of only one rotomer (Fig. 2). This behaviour is indicative of restricted rotation about both the B—N and B—C bonds. It is also known that there is $p_\pi—p_\pi$ back-donation from fluorine in such compounds, [2,8] and it is therefore likely that there is electronic delocalisation over three bonds:

◯ — ringed atoms show *trans* fluorine coupling



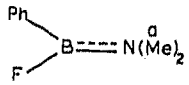
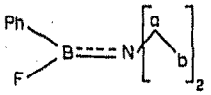
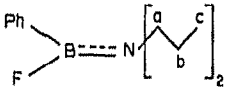
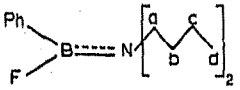
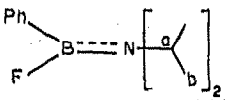
B—C, B—N and B—F $p_\pi—p_\pi$ bonds are all well established but models indicate that simultaneous B—N and B—C π bonding, resulting in a flat molecule, is unlikely on steric grounds.

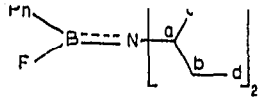
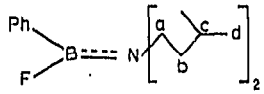
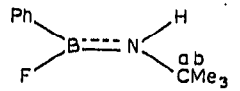
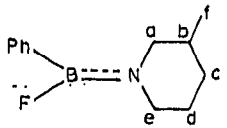
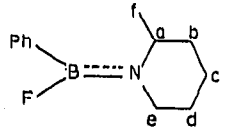
Trans spin-spin coupling constants of olefins are much larger than *cis* coupling constants:

(continued on p. 8)

TABLE 3

^{13}C NMR DATA OF DIALKYLAMINO(FLUORO)PHENYLBORANES

Compound [a]	o	p	m	a	b	c	d	e	f
	133.6 133.4 4	129.5 129.5 0	127.7 127.7 0	38.1 35.9 [b] 58					
	133.1 132.9 4	129.5 129.5 0	127.8 127.8 0	40.9 39.0 [b] 43	15.5 15.3 4				
	133.1 132.9 4	129.4 129.4 0	127.7 127.7 0	48.4 46.5 [b] 43	22.9 22.4 12	11.2 11.0 4			
	133.1 132.9 4	129.4 129.5 0	127.7 127.7 0	46.5 44.6 [b] 46	32.2 31.7 10	20.3 20.1 4	14.0 14.0 0		
	132.7 132.5 4	129.1 129.1 0	127.7 127.1 0	48.2 43.8 110	24.1 21.9 55				

	132.6 132.4 4	128.9 128.9 0	127.6 127.5 0	54.5 50.5 [c] 100	30.7 28.3 60	21.4 20.1 [c] 31	12.3 11.5 20		
	133.1 132.9 4	129.4 129.4 0	127.5 127.5 0	45.0 43.1 [b] 46	35.8 35.4 10	26.3 26.0 8	27.7 27.7 0		
	132.7 132.5 4	130.4 130.4 0	127.9 127.9 0	49.4 49.4 0	32.0 32.0 0				
	134.0 133.8 4	130.0 130.0 0	128.3 128.3 0	54.0 51.7 [b] 57	33.0 32.5 12	33.7 33.5 3	27.3 27.0 7	46.7 44.2 [b] 57	19.4 19.2 3
	133.1 132.9 4	129.4 129.4 0	127.8 127.8 0	47.2 45.1 [b] 52	31.7 31.4 7	19.3 19.3 0	27.8 27.5 9	40.5 37.5 [b] 73	17.7 17.7 0

[a] The chemical shift (in ppm) of a signal arising from a particular carbon in one rotomer, (δr_1), is given first, followed by the chemical shift of the same nucleus in the other rotomer (δr_2) and the isomer shift, $\Delta\nu$, in Hz. [b] These signals are split due to fluorine coupling which is about 6—7 Hz in all cases. [c] This signal is further split due to the chirality of $N(s\text{-}Bu)_2$.

	^3J(H—H)	^3J(H—F)	^3J(F—F)
cis C=C	6—13	1—8	35—58
trans C=C	12—18	12—40	115—124

(coupling constants in Hz). Aminoboranes, being analogous systems, may also have *trans* coupling constants much larger than *cis* coupling constants.

The ^{13}C NMR spectrum of $PhMNMe_2F$ is typical of this class of compound and can be used to illustrate these points (Fig. 3).

The methyl resonance of $PhBNMe_2F$ is 'split' into a 'doublet', since restricted rotation about B—N results in one methyl group *cis* and one *trans* to F. However, only one of these lines shows fluorine coupling, and this line is thought, by analogy with olefin coupling constants, to arise from the methyl group *trans* to F. *Cis* $^{19}F—^{13}C$ coupling is assumed to be too small to resolve, and if there were free rotation about B—N no fluorine coupling would be observed at all. Indeed the fluorine coupling is lost, together with restricted rotation, at 113°C, when a single peak results.

If the analogy with olefins is good, fluorine coupling allows the assignment of bands to each rotomer. The line showing fluorine coupling results from absorption by the methyl group which is *trans* to fluorine, but *cis* to phenyl. The methyl group *cis* to fluorine is therefore assigned to the line showing no fluorine coupling.

Having tentatively assigned the absorptions to each isomer it is interesting to note that the methyl group *trans* to fluorine, and therefore *cis* to phenyl, appears at higher field than the methyl *cis* to fluorine. The methyl group *trans* to fluorine is evidently shielded with respect to the methyl group *trans* to phenyl. This behaviour was observed in all the fluoro compounds studied.

Further evidence that flucrine coupling observed is *trans* is provided by the ^{13}C NMR spectrum of PhBNH-t-BuF (Fig. 4).

In unsymmetrical compounds of the type PhBNRR'X it has been established that the rotomer having the two bulky groups *trans* predominates [10]. Since there was no 'doubling up' of the resonances for the t-butyl group this indicates that the rotomer with the bulky t-butyl and phenyl groups *trans* is much more

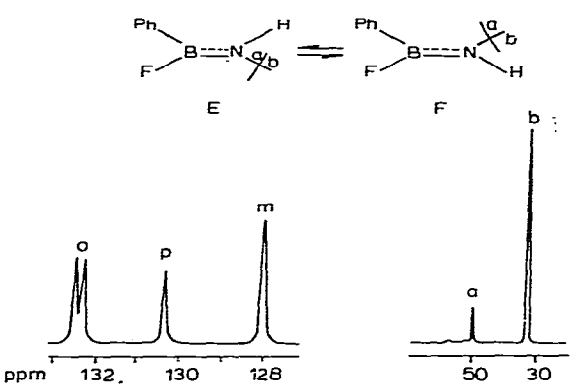


Fig. 4. ^{13}C NMR spectrum of PhBNH-t-BuF.

abundant than the other rotomer. So the spectrum is effectively that of rotomer E, where the t-butyl group is *cis* to fluorine. No fluorine coupling was observed for this rotomer and it was concluded that $^3J(F—C)_{cis}$ is much smaller than $^3J(F—C)_{trans}$ because fluorine coupling was still observed for the *ortho* carbons of the phenyl group, which are *trans* to fluorine.

Experimental

Nuclear magnetic resonance spectra

The spectra were recorded on a JEOL-PS-100 NMR spectrometer; ^1H NMR spectra with the instrument on the continuous wave mode while ^{13}C NMR spectra were recorded using the Fourier transform mode. Tetramethylsilane was used as an internal reference and compounds were studied as solutions in $CDCl_3$ or as neat samples. Chemical shifts quoted are correct to ±0.05 ppm.

An internal DMSO capillary lock was used when measuring the ^{13}C NMR spectra of neat samples.

Mass spectrometric measurements

The spectra were measured on an A.E.I. MS 902 mass spectrometer at 20°C and 70 eV. The source was maintained at 70 ± 20°C. The compounds were introduced as neat liquids using a direct insertion probe. The instrument was calibrated against heptacosafluorotributylamine to give a resolution of 1 in 10,000 for precise mass measurements.

Preparation of di-s-butylamino(fluoro)phenylborane

Antimony trifluoride (2 g, 0.011 mol) was ground into a fine powder, placed in a small flask and cooled. Chloro(di-s-butylamino)phenylborane (7.3 g, 0.03 mol) was slowly added with cooling and stirring. The mixture was allowed to warm up to room temperature slowly, with continuous stirring, but not permitted to overheat. It was then left stirring at room temperature for 3 hours. Vacuum distillation of the resultant mixture yielded di-s-butylamino(fluoro)-phenylborane (2.82 g, 40%), b.p. 75°C/1 mmHg. (Found: C, 70.13; H, 9.61; N, 5.76. $C_{14}H_{23}NBF$ calcd.: C, 71.49; H, 9.79; N, 5.96%). All the dialkylamino-(fluoro)phenylboranes listed in Table 1 were prepared using this technique.

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