Mixed Boron Trihalide Adducts of Amines: A Multinuclear Nuclear Magnetic Resonance Study†

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The ^{19}F chemical shifts of mixed boron trihalide adducts of tertiary amines have a marked dependence on the steric effects of amine substituents, as estimated from the ' cone angle ' of the amines. Base strength of the amine has little effect on adduct ^{19}F shifts, but does have a pronounced effect on the rate of halogen redistribution. The ^{11}B and ^{13}C chemical shifts and ^{11}B–^{19}F coupling constants of the adducts are discussed. Amines NRR'R'' become chiral when complexed to Lewis acids, since complexation stops the rapid inversion process. Because of this the fluorines in R''R'RN·BF$_2$X (X = Cl, Br, or I) adducts are diastereotopic and magnetically non-equivalent, differing in chemical shift by up to 2 p.p.m. The four-adduct system of benzyl(ethyl)methylamine with BF$_n$I$_{3-n}$ (*n* = 0—3) gives rise to the cation B(PhCH$_2$NMeEt)$_2$F$_2$$^+$ which, because of the chirality of the co-ordinated amines, exists in *meso* and optically active forms distinguishable by ^{19}F n.m.r. spectroscopy.

OUR previous studies of mixed boron trihalide adducts [1] have dealt with a wide range of donor functional groups, but with only one or a very few representative donor molecules of each group. However, major differences in behaviour can occur as donor substituents are varied, while maintaining the same donor atom. Thus halogen-redistribution equilibria in phosphine–boron trihalide adducts are greatly dependent on the number of methyl substituents in PH$_n$Me$_{3-n}$,[2] and mixed boron trihalide adducts of benzoate and acetate esters differ in their ability to form difluoroboron cations BD$_2$F$_2$$^+$ (D = donor).[3]

Tertiary amines form the best-behaved mixed boron trihalide adducts studied to date,[1,4] and ambient-temperature n.m.r. studies are uncomplicated by either rapid chemical exchange reactions or by irreversible decomposition of the adducts, both of which are a problem in, for example, boron trihalide adducts of oxygen donors.[1,5,6] We have therefore chosen tertiary-amine adducts for a detailed study of steric and electronic effects on n.m.r. parameters. Furthermore, this work provides background knowledge for our studies of the much more reactive boron trihalide adducts of unsaturated nitrogen donors: enamines,[7] 1,1-enediamines,[8] amidines,[9] and imines.[9]

RESULTS AND DISCUSSION

(*a*) *General*.—Mixed boron trihalide adducts of tertiary amines are readily prepared by various methods; for our purposes they are not isolated but are made up directly in solution. The BF$_2$I and BFI$_2$ adducts of many tertiary amines can be detected by ^{19}F and ^{11}B n.m.r. spectroscopy, but are present only in small amounts because the halogen-redistribution equilibrium favours the BF$_3$ and BI$_3$ adducts.[1,4] Except for the BF$_3$ adducts, solutions of the adducts in CDCl$_3$ discolour slowly on standing at ambient temperature. No extra peaks could be detected in the ^{19}F, ^{11}B, or ^{13}C spectra of even very strongly discoloured solutions. No attempt was made to study these decomposition products. We note however that intense blue colours, possibly related to the aniline dyes, appeared in some of the *N*,*N*-dialkylaniline adduct samples.

Ethyldi-isopropylamine and *N*,*N*-diethylaniline gave especially reactive adducts. Any solutions in which BI$_3$ was present also tended to be especially reactive. In some cases precipitates appeared on standing; these were not further investigated.

Secondary-amine adducts of the boron trihalides are much more reactive than tertiary-amine adducts [6,10] and discoloration and precipitation were indeed more of a problem with such adducts. Although a wide range of products other than the simple adducts can form on direct addition of boron trihalides to secondary amines,[10] ^{19}F spectra of solutions of mixed boron trihalide adducts of secondary amines formed by direct addition of boron trihalides gave only the peaks expected for the mixed boron trihalide adducts. We were unable to detect BF$_2$I or BFI$_2$ adducts of any secondary amines, not surprisingly in view of the extreme reactivity of the B–I with the N–H linkages.

(*b*) ^{19}F *Chemical Shifts*.—The ^{19}F chemical shifts of tertiary-amine adducts of a given boron trihalide BF$_n$X$_{3-n}$ change by up to 23 p.p.m. with donor substituents (Table 1). Increasing steric hindrance of the amine corresponds to a shift to low field, *i.e.* towards the chemical shift value of the uncomplexed boron trihalide.[11] This is consistent with the expected weakening and lengthening of the donor–acceptor bond with increasing steric hindrance. Donor-substituent steric effects have, however, less effect on the ^{19}F chemical shift than do the number and type of heavy halogens attached to boron.

The concept of cone angle has been developed as an empirical description of the steric requirements of phosphine ligands in metal complexes.[12] Cone angle is defined as the minimum solid angle subtended at the acceptor site by the donor molecule (Figure 4b of ref. 12*b*). We have determined cone angles of amine–boron trihalide adducts, assuming an N–B bond length of 1.595 Å, as in the Me$_3$N·BF$_3$ adduct [13] (Table 1). A plot of cone angle *vs.* ^{19}F chemical shift of a series of aliphatic amines (Figure 1) confirms that steric effects do account

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TABLE 1

Fluorine-19 chemical shifts [a] of amine-boron trihalide adducts

Amine	Amine pK_b	Amine cone angle (±2°)	^{19}F Chemical shifts							
			D·BF$_3$	D·BF$_2$Cl	D·BFCl$_2$	D·BF$_2$Br	D·BFBr$_2$	D·BF$_2$I	D·BFI$_2$	D·BFClBr
Quinuclidine	2.9 [c]	134	−163.2	−141.9	−131.7	−133.0	−120.4			−125.5
NMe$_3$ [b]	4.24 [d]	138	−164.1	−143.4	−132.6	−134.0	−120.8	−119.6		−126.0
NMe$_2$Et	4.01 [d]	144	−161.4	−139.7	−129.2	−130.8	−117.6	−117.4		−123.5
NMeEt$_2$	3.71 [d]	149	−156.0	−133.9	−121.2	−125.0	−109.5	−111.8	−97.2	−114.8
NEt$_3$	3.35 [d]	161	−150.5	−127.8	−115.2	−119.6	−104.2	−105.9	−92.5	−108.0
NPr$^n_3$	3.35 [d]	165	−151.5	−128.3	−115.4	−119.5	−104.1	−106.3	−91.8	−109.4
NBu$^n_3$	3.11 [d]	161	−151.0	−128.2	−115.2	−119.3	−103.7	−106.2	−91.9	
NEtPr$^i_2$		205	−142.4	−119.6	−108.6	−110.3				
NMe$_2$Ph	8.9 [c]	143	−158.3	−137.4	−126.3	−128.7	−115.1	−115.0	−102.0	−120.3
p-CH$_3$C$_6$H$_4$NMe$_2$	8.4 [c]		−158.5	−137.3	−126.3	−128.8	−115.2	−115.6	−102.6	−120.3
p-O$_2$NC$_6$H$_4$NMe$_2$	13.2 [c]		−150.5							
NMeEtPh	7.99 [c]	142	−157.1	−136.5	−125.8	*e*	−114.3	*e*	−102.0	−119.4, −120.3 [f]
NEt$_2$Ph	7.4 [c]	144	−147.4	−127.5	−117.3	−119.3	−106.8			−111.6
PhCH$_2$NMeEt	4.3 [g]		−156.4	−134.0 [e]	−121.2	*e*	−109.7	*e*	−97.6	−115.0, −115.4 [f]
NMe$_2$(n-C$_{12}$H$_{25}$)			−161.0	−139.5	−128.9	−130.6	−117.4	−117.4	−105.3	−123.1
N(CH$_2$CH=CH$_2$)$_3$	5.69 [c]		−151.1	−128.2	−116.5	−120.1	−106.1	−106.8		−110.8
NHPr$^n_2$	3.1 [c]		−154.0	−134.1	−124.3	−126.2	−113.5			
NHBu$^n_2$	2.7 [c]		−153.6	−134.1	−124.4	−126.2	−112.8			
NHMePh	9.2 [c]		−153.7	−134.7 [h]	−125.7	−125.8 [h]	−115.6			
NHEtPh	8.88 [c]		−151.8	−132.8	−124.3	−124.6	−115.1			
4-Methylpyridine [b]	7.98 [c]		−142.4	−125.4	−118.8	−117.3	−110.5			
Uncomplexed BF$_n$X$_{3-n}$ [i]			−125.0	−73.5	−26.0	−56.6	+5.4			−10.2

[a] In p.p.m. to low field of CFCl$_3$; obtained using C$_6$F$_6$ (−162.7 p.p.m. from CFCl$_3$) as a secondary standard. [b] Ref. 4. [c] Ref. 15. [d] Ref. 16. [e] Magnetically non-equivalent fluorines. See section (*c*) and Table 2. [f] Each diastereomer has a distinct chemical shift. [g] Estimate: pK_b values of PhCH$_2$NMe$_2$ and PhCH$_2$NEt$_2$ are 5.09 and 4.56, respectively.[15] [h] Centre of the multiplet arising from the two magnetically non-equivalent fluorines. [i] Ref. 11; converted into the CFCl$_3$ scale by subtracting 125 p.p.m.

for most of the variations in chemical shift with amine substituents. The qualitative or at best semi-quantitative nature of cone angles should be kept in mind. Boron–nitrogen bond distances are unlikely to remain constant as the amine substituents increase in size or as the halogens change. The appreciable differences between gas-phase and solid-state B–N bond lengths in Me$_3$N·BX$_3$ (X = Cl, Br, or I)[14] provide further uncertainty as to the most appropriate solution value for the B–N bond length. It is noteworthy however that steric effects come into play even when the amine substituents are quite small. This is in contrast to metal–phosphine complexes in which the phosphorus–metal bond is considerably longer and steric effects on ^{31}P chemical shift remain negligible until the cone angle exceeds 120°.[12]

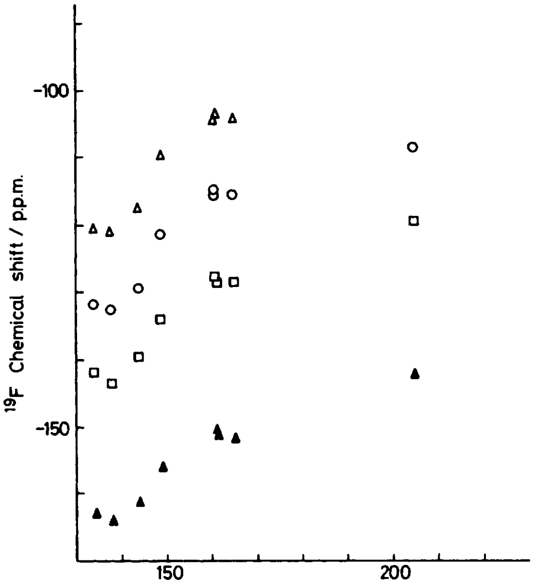


FIGURE 1 Dependence of ^{19}F chemical shift on the amine cone angle in a series of aliphatic tertiary amine–boron trihalide adducts D·BFBr$_2$ (△), D·BFCl$_2$ (○), D·BF$_2$Cl (□), and D·BF$_3$ (▲)

Cone angles of the *N*,*N*-dialkylanilines do not correlate well with ^{19}F chemical shifts if the most tightly packed conformation is used (Table 1). Comparison with Tolman's work[12] indicates a similar discrepancy with phenylphosphine ligands. Better chemical shift correlations appear to have been obtained by neglecting these conformations, but the rationale for this is not clear.

Base strength has little effect on ^{19}F chemical shift. Dialkylanilines are far weaker bases (by several pK_b units,[15,16] Table 1) than trialkylamines, yet ^{19}F shifts of the adducts do not reflect this. While basicity toward the proton, with its small steric requirements, can be misleading as a guide to Lewis basicities,[17] other evidence, based on faster halogen redistribution in PhMe$_2$N·BF$_n$Cl$_{3-n}$ adducts than in the corresponding trimethylamine adducts,[4] indicates that *N*,*N*-dimethylaniline is indeed a far weaker Lewis base than trimethylamine.

The BF$_3$ adduct of *N*,*N*-dimethyl-*p*-nitroaniline, an extremely weak base,[18] has a chemical shift 7.8 p.p.m. to low field of $PhMe_2N{\cdot}BF_3$. This is consistent with electron withdrawal from the donor site by the *p*-nitro-group. The *para*-substituent has a larger effect here than in the $PhCO_2Me{\cdot}BF_3$ adducts.[3]

The ^{19}F spectra of adducts of secondary amines with BF_nX_{3-n} (n = 1—3, X = Cl or Br) are similar to those of the tertiary-amine adducts. There is a shift to high field, consistent with the low steric requirement of the N–H proton.

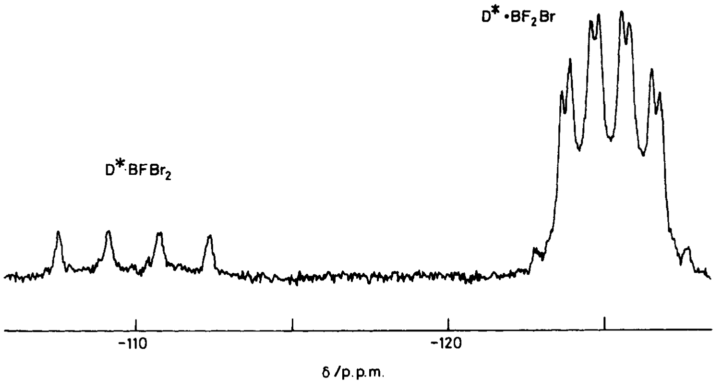


FIGURE 2 56.4-MHz ^{19}F n.m.r. spectrum of the BF_2Br and $BFBr_2$ adducts of benzyl(ethyl)methylamine, showing the effect of magnetically non-equivalent fluorine atoms

(*c*) ^{19}F *N.M.R. Effects of a Chiral Donor.*—Complexation ' freezes ' amines NRR'R" into *R* and *S* forms by stopping the rapid inversion process; BF_2X adducts of such amines, $D^*{\cdot}BF_2X$ (X = Cl, Br, or I), have diastereotopic and hence magnetically non-equivalent fluorines. The ^{19}F spectra of the BF_3 and BFX_2 adducts of such amines show the usual 1 : 1 : 1 : 1 quartet due to ^{11}B–^{19}F coupling (^{11}B: 80% abundant, $I = \frac{3}{2}$), but the BF_2X adducts give more complex patterns (Figure 2). Confirmation of BF_2 non-equivalence comes from ^{11}B decoupling, which simplifies the complex multiplet to an AB pattern, from which the ^{19}F chemical shifts of the individual fluorines, and $^2J_{FBF}$, are readily determined (Table 2). Loss of resolution in our decoupled spectra (peak width at half height ≈6 Hz; see the Experimental section) prevented resolution of AB patterns from $D^*{\cdot}BF_2Cl$ adducts. For D* = benzyl(ethyl)methylamine and *N*-methylaniline there is indeed a small chemical shift difference of the diastereotopic fluorines (>0.13 and >0.18 p.p.m., from the coupled spectra) but for D* = *N*-ethyl-*N*-methylaniline there is apparently an accidental chemical shift equivalence.

TABLE 2

N.m.r. parameters of diastereotopic fluorines in $D^*{\cdot}BF_2X$ adducts

		^{19}F Chemical shifts (p.p.m. from $CFCl_3$)	
Adduct	$^2J_{FBF}$/Hz	F_A	F_B
(*a*) D* = $C_6H_5CH_2NMeEt$			
$D^*{\cdot}BF_2I$	39.7	−110.8	−112.8
$D^*{\cdot}BF_2Br$	48.5	−121.8	−122.5
$D^*{\cdot}BF_2Cl$ [a]	—	—	—
(*b*) D* = C_6H_5NMeEt			
$D^*{\cdot}BF_2I$	33.8	−114.0	−115.8
$D^*{\cdot}BF_2Br$	44.1	−127.4	−128.1
$D^*{\cdot}BF_2Cl$ [b]	—	—	—

[a] Not resolved in ^{19}F-{^{11}B} spectra; however, better resolved ^{19}F spectra showed a further splitting (0.13 p.p.m.) of the 1 : 1 : 1 : 1 quartet peaks. [b] No BF_2 non-equivalence detected.

The chemical shift differences between the diastereotopic fluorines, increasing from near zero to 2 p.p.m. in the series X = Cl, Br, I, are in accord with ^{19}F chemical shift differences previously observed in C^*–CF_2X compounds (0—6.4 p.p.m.).[19] They also correspond approximately to the range of errors observed when ^{19}F chemical shifts of mixed boron trihalide adducts are calculated by ' pairwise interaction ' n.m.r. parameters, which do not take into account neighbour anisotropy effects.[20]

Geminal FBF coupling constants increase in magnitude as the heavy halogen changes from iodine to bromine (Table 2). The only previously reported geminal FBF coupling ($B_2F_7^-$: 95 ± 10 Hz between the bridging and terminal fluorines [21]) continues this trend to larger values as the remaining halogens change in the series I, Br, Cl, F. The J_{FBF} value of 74 Hz for $B(PhCH_2NMeEt)_2F_2^+$ [section (*g*)] is in accord with this trend to larger coupling constants when the atoms about boron are all first-short-period atoms. These coupling constants can be compared to geminal F–C–F coupling constants in saturated fluorocarbons (160—290 Hz).[22]

We can exclude the possibility that these effects arise from slow rotation about the donor–acceptor bond, which would cause increased multiplicity in all of the adduct ^{19}F resonances, rather than only in the $D^*{\cdot}BF_2X$ resonances. We note however that adduct peaks in the ^{19}F-{^{11}B} spectra, fairly sharp at ambient temperature, are much broader at −40 °C, indicating that rotation about the donor–acceptor bond is becoming slow on the n.m.r. time-scale in this temperature range. Fluorinated ethanes, somewhat analogous to these adducts, do show restricted rotation about carbon–carbon single bonds in this temperature range.[23] Restricted rotation in trimethylamine adducts has been studied by solid-state n.m.r.[24] and by gas-phase electron diffraction,[14,25] and seems consistent with our results. Without ^{11}B decoupling the low-temperature ^{19}F spectra are so broadened by coupling to ^{11}B, which is undergoing intermediate rates of quadrupole relaxation,[26] that the additional broadening due to restricted rotation cannot be distinguished.

TABLE 3

^{11}B–^{19}F Coupling constants (Hz) [a]

Amine	D·BF_3	D·BF_2Cl	D·$BFCl_2$	D·BF_2Br	D·$BFBr_2$	D·BF_2I	D·BFI_2	D·BFClBr
Quinuclidine	15.2	43.5	68.6	53.9	89.6			78.9
NMe_3 [b]	15.1	44.8	69.5	54.2	89.3	65.8		78.0
NMe_2Et	15.7	44.1	70.1	54.9	90.8	68.6		80.5
$NMeEt_2$	17.7	45.6	72.1	55.9	93.2	68.6	116.7	82.4
NEt_3	18.2	46.9	72.9	56.8	93.6	69.6	118.1	83.3
NPr^n_3	19.1	46.2	72.9	56.2	93.8	68.1	118.6	82.4
NBu^n_3	17.7	46.5	72.6	54.9	92.2	64.7	117.7	
$NEtPr^i_2$	20.1	49.5	75.9	60.3				
NMe_2Ph	13.2	44.1	67.5	54.4	91.2	66.3	116.8	79.4
p-$CH_3C_6H_4NMe_2$	12.8	43.0	67.7	54.9	90.2	67.2	115.7	79.4
NMeEtPh	12.8	43.1	69.1	54.2	90.2	68.7	116.2	79.9
NEt_2Ph	*c*	45.1	70.6	55.4	94.1			84.8
$PhCH_2NMeEt$	16.7	45.6	72.1	55.6	92.7	66.8	116.6	81.9
$NMe_2(n\text{-}C_{12}H_{25})$	16.2	43.7	69.6	52.9	89.2	66.7	114.7	80.4
$N(CH_2CH{=}CH_2)_3$	16.7	47.5	72.3	56.9	94.1	69.1		82.4
$NHPr^n_2$	16.7	43.0	69.0	52.5	89.2			
$NHBu^n_2$	16.7	43.2	67.7	51.0	87.3			
NHMePh	13.2	40.7	66.7		88.2			
NHEtPh	13.8	40.7	69.1	50.0	87.8			
4-Methylpyridine [b]	11.8	38.3	62.8	49.2	82.2			
Uncomplexed BF_nX_{3-n} [d]	14.5	33	78	58	121			95

[a] ±1 Hz. [b] Ref. 4. [c] Not resolved. [d] Ref. 28.

We conclude that ^{19}F n.m.r. spectroscopy allows reliable detection of donor-atom chirality in BF_2Br and BF_2I adducts, but not in BF_2Cl adducts, of donors in which a highly magnetically anisotropic phenyl group is present. We are applying this in attempts to detect donor-atom chirality in ambiguous systems.[27]

Similar effects of a chiral donor molecule are seen in the doubling of the ^{19}F resonance of the ternary-halogen adducts D*·BFClBr. These adducts consist of a pair of diastereomers, each of which gives rise to a 1 : 1 : 1 : 1 quartet due to ^{11}B–^{19}F coupling. Chemical shift differences between the diastereomers (D* = $PhCH_2NMe$-Et, 0.4 p.p.m.; PhNMeEt, 0.9 p.p.m.) are consistent with the predominance of neighbour anisotropy effects. The ^{11}B–^{19}F coupling constants of the diastereomers are not detectably different.

The BF_2X (X = Cl or Br) adducts of *N*-methylaniline also give complex ^{19}F multiplets due to BF_2 fluorine non-equivalence.

(*d*) *^{11}B–^{19}F Coupling Constants and ^{11}B Chemical Shifts.*—These parameters are primarily determined by the number and type of heavy halogens present,[20] and amine substituents have only small effects. The ^{11}B–^{19}F coupling constants increase somewhat in magnitude with increasing steric hindrance of the amine (Table 3); there is no obvious relationship to the corresponding values for the uncomplexed boron trihalides.[28]

Adduct ^{11}B resonances are sufficiently broadened, both at 19.25 and at 128.38 MHz, that separate resonances cannot be resolved for the diastereomeric D*·BFClBr adducts. There are pronounced deviations from direct additivity of substituent effects in determining ^{11}B chemical shifts in BF_nBr_{3-n} adducts, in which both mixed-halogen adducts absorb to low field of the BF_3 and BBr_3 adducts (Table 4). In such situations a ' pairwise additivity ' calculation [20] can be helpful in assigning chemical shifts.

TABLE 4

Boron-11 chemical shifts [a]

	Donor					
Acceptor	*b*	Quinuclidine	$NEtPr^i_2$	NMe_2Ph	NMeEtPh	$PhCH_2NMeEt$
BF_3	10.0	−0.5	0.2	−0.1	0.1	−0.1
BF_2Cl	19.8	4.1	4.9	4.3	4.3	4.6
$BFCl_2$	32.3	7.7	8.8	8.0	8.0	8.3
BCl_3	46.5	9.2		10.0	10.1	9.8
BF_2Br	19.5	3.6	3.3	3.6	3.9	3.8
$BFBr_2$	29.0	3.1		3.0	3.3	3.2
BBr_3	38.7	−3.9		−3.5	−3.4	−3.7
BF_2I	*c*				2.3	1.3
BFI_2	*c*			−17.3	−16.9	−16.0
BI_3	−7.9	−53.1		−54.0	−54.0	−53.3
BCl_2Br	44.7	5.8		6.4	6.7	6.3
$BClBr_2$	42.3	1.4		1.8	2.3	1.8

[a] In p.p.m. to low field of $Et_2O·BF_3$; $CDCl_3$ solution. External trimethoxyboron (+18.1 p.p.m. from $Et_2O·BF_3$) was used as a secondary standard. [b] Uncomplexed boron trihalide; ref. 28. [c] Not detectable.

Collapse of a ^{19}F (or ^{1}H) 1 : 1 : 1 : 1 quartet arising from coupling to ^{11}B can occur at high ***and*** at low temperatures,[29-32] and is indicative of chemical exchange (high temperatures) and of more efficient quadrupole relaxation of boron [26] (low temperatures). The aliphatic amine ^{19}F quartets are well resolved, indicating a symmetrical environment about boron and slow fluorine exchange. The *N*,*N*-dialkylaniline adducts give less well resolved quartets or no splitting at all in certain cases (the BF_3 adducts of *N*,*N*-diethylaniline and *N*,*N*-dimethyl-*p*-nitroaniline). Excess of boron trihalide causes collapse of all splittings, due to rapid fluorine exchange.[1,4] We note also that the presence of BBr_3 or BI_3 can collapse the moderately well resolved ^{19}F 1 : 1 : 1 : 1 quartet splittings of the $PhMe_2N{\cdot}BF_3$ adduct, even when the amine is present in excess. The heavy-halogen adduct, or a trace impurity, is apparently inducing B–F bond breaking; such halogen redistribution reactions can be complex.[29] The anilines, in keeping with their weaker basicity, are more prone to halogen-exchange reactions than the aliphatic amines. This was confirmed by a study of halogen exchange between BF_3 and BCl_3 adducts of *N*,*N*-dimethylaniline in the presence of a large excess of the uncomplexed base in $CDCl_3$. After several minutes at 60 °C the BF_2Cl and $BFCl_2$ adducts could be detected. This contrasts with the far more drastic conditions required to induce halogen exchange in the corresponding trimethylamine adducts.[4,33]

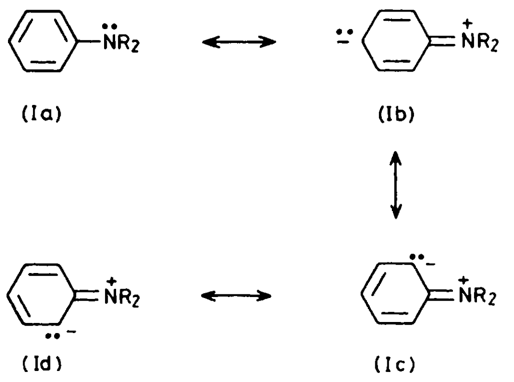
(*e*) ^{13}C *Chemical Shifts*.—The ^{13}C complexation shifts of amines need not be large or consistently in one direction, as Table 5 indicates. Nevertheless there are regularities. Once the amines are complexed to the boron trihalides the α-carbon shifts are consistently to lower field as the Lewis acid becomes stronger ($BF_3 < BCl_3 < BBr_3 < BI_3$), in accord with increasing electron withdrawal from the amine by the stronger Lewis acids. A similar trend is seen in the β-carbon shifts but with less regularity, indicating that other effects are competitive with the charge-density effect in determining the complexation shift. Other studies of ^{13}C complexation shifts of similar donors with the boron trihalides [34,35] and with a variety of metals [36] are consistent with ours. Considerably larger shifts can occur when the carbonyl oxygen (or thiocarbonyl sulphur) is the donor.[36-38]

The ^{13}C chemical shifts are affected by a number of factors,[39-41] and in general they do not correlate with charge density unless other factors are held constant. Considerable use can be made of ^{13}C n.m.r. to study electronic structure, provided that appropriate model systems are used.[42] Changes in shifts relative to an appropriate model compound are more meaningful than the shifts *per se*, since geometry changes or substituent changes may result in the predominance of other factors in determining chemical shift.

The shift to high field of many amine ^{13}C resonances on complexation has features in common with protonation shifts of amines,[43-45] in particular the especially large shift to high field for the β-carbons. Protonation shifts of amines show marked structural and conformational dependences,[44] and in keeping with this we find considerable variations in the magnitudes of the complexation shifts of the various amines.

We have studied protonation of NPr^n_3 and NBu^n_3 with trifluoroacetic acid (tfa) in $CDCl_3$ in order to compare protonation shifts with our complexation shifts under the same conditions. However, we find that excess of tfa has a major effect on ^{13}C chemical shifts. The high-field protonation shifts reach a maximum at about 1 : 1 proportions of amine and tfa as expected, but there is a shift of up to 2 p.p.m. back to lower field with excess of tfa. These large medium effects probably relate to the very strong hydrogen bonding possible between tfa and its anion,[46] which should displace NHR_3^+ from hydrogen bonding with trifluoroacetate when excess of tfa is present. Samoilenko *et al.*[47] have also observed complex interactions between amines and tfa, which they have attributed to hydrogen-bonding effects. Magnitudes of amine ^{13}C protonation shifts are different in D_2O and in $CDCl_3$, perhaps due to extensive hydrogen bonding in aqueous solution.[43] Similarly, ^{15}N protonation shifts of pyridines correlate with the solvent's hydrogen-bonding capacity.[48]

Anilines undergo large complexation (and protonation [47,49,50]) shifts due to the elimination of all mesomeric forms but (Ia) in the *N*-donor adducts. The *ortho*-carbons have complexation shifts similar to those of other carbons β to nitrogen. The large high-field complexation shift of the C^1 carbon is similar to the protonation shifts of aniline [49] and substituted anilines [47,50] and the methylation shift on formation of NMe_3Ph^+.[51]


(Ia) (Ib) (Ic) (Id)

The BBr_3 adduct of *N*,*N*-diethylaniline gives anomalous ^{13}C chemical shifts. We cannot yet exclude donation to BBr_3 from the aniline *para*-carbon [structure (Ib)]. Protonation of aniline is well known to occur at either nitrogen or the *para*-carbon, depending on the conditions,[52] and *N*,*N*-dimethylaniline behaves similarly.[53] *N*,*N*-Dialkylanilines have been reported to be ambidentate nucleophiles toward hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$,[54] and they may behave similarly toward the boron trihalides under appropriate conditions.

Adducts of $NEtPr^i_2$ have non-equivalent isopropyl methyl ^{13}C resonances, as does the protonated amine,[43] because the methyls are intrinsically diastereotopic.

TABLE 5

Carbon-13 complexation shifts[a]

Base	Acceptor						
		C_α	C_β	C_γ			
Quinuclidine	free	48.0	27.0	21.1			
	BF_3	−1.3	−3.0	−1.0			
	BCl_3	+1.0	−2.9	−0.6			
	BBr_3	+2.2	−2.7	−0.4			
	BI_3	+3.4	−2.5	+0.1			
NMe_3[b]	free	47.7					
	BF_3	−0.6					
	BCl_3	+2.1					
	BBr_3	+3.2					
	BI_3	+4.2					
		N–Me	N–CH_2	C–Me			
NMe_2Et	free	45.1	53.7	13.0			
	BF_3	−1.9	−0.5	−5.0			
	BCl_3	−0.9	0.0	−4.8			
	BBr_3	+0.1	+0.8	−4.4			
	BI_3	+0.8	+1.5	−3.5			
$NMeEt_2$	free	41.0	50.9	12.3			
	BF_3	+0.6	−1.0	−3.9			
	BCl_3	+2.7	+1.4	−2.2			
	BBr_3	+2.9	+2.7	−1.7			
		C_α	C_β	C_γ			
NEt_3	free	46.5	11.9				
	BF_3	+1.9	−3.3				
	BCl_3	+6.1	−1.6				
	BBr_3	+7.7	−1.1				
	BI_3	+9.3	−0.1				
NPr^n_3	free	56.6	20.6	12.0			
	BF_3	+0.1	−4.2	−0.3			
	BCl_3	+3.8	−2.8	−0.2			
	BBr_3	+5.4	−2.3	−0.2			
	BI_3	+7.1	−1.5	−0.2			
		C_α	C_β	C_γ	C_δ		
NBu^n_3	free	54.2	29.6	20.9	14.1		
	BF_3	+0.7	−4.5	−0.1	−0.3		
	BCl_3	+4.5	−3.3	0.0	−0.4		
	BBr_3	+5.9	−2.9	−0.1	−0.5		
	BI_3	+7.6	−2.1	−0.1	−0.4		
		Ethyl		Isopropyl			
		α	β	α	β		
$NEtPr^i_2$	free	39.1	17.2	48.6	20.8		
	BF_3	+2.6	−7.5	+5.1	−2.0, −1.4[c]		
	BCl_3	+5.0	−3.9	+7.5	−3.1, −1.6[c]		
	BBr_3	+4.9	−3.9	+7.2	−3.1, −1.6[c]		
		N–CH_3	C^1	$C^{2,6}$	$C^{3,5}$	C^4	
NMe_2Ph	free	40.1	150.6	112.6	129.0	116.6	
	BF_3	+7.3	−4.5	+9.3	+0.5	+11.6	
	BF_2Cl	+8.0	*d*	+9.7	*d*	*d*	
	$BFCl_2$	+8.5	*d*	+10.2	*d*	*d*	
	BCl_3	+10.1	−5.3	+11.3	−0.5	+11.9	
	BF_2Br	+8.3	−5.3	+9.6	*d*	*d*	
	$BFBr_2$	+9.8	−5.6	+10.3	*d*	*d*	
	BBr_3	+11.7	−5.9	+12.0	−0.7	+12.2	
	BI_3	+12.9	−6.9	+12.8	−1.0	+12.4	
	Me^+[e]		−13.3	+7.7	−0.3	+14.9	
		N–CH_2	CH_3	C^1	$C^{1,6}$	$C^{3,5}$	C^4
NEt_2Ph	free	44.4	12.7	148.0	112.2	129.3	115.7
	BF_3	+8.1	−3.1	−5.7	+11.4	+0.2	+12.1
	BCl_3	+7.5	−2.0	−7.1	+14.0	−1.0	+15.5
	BBr_3	+9.2	−1.0	−16.7	+14.8	−1.4	+12.8

[a] Chemical shifts of free bases are in p.p.m. to low field of $SiMe_4$ in $CDCl_3$ solution. Positive values of complexation shifts are to low field. [b] Ref. 35. [c] Non-equivalent methyl resonances. [d] Not resolved. From the chemical shift of $NMe_3Ph^+I^-$, ref. 51.

The resonances of the BF_3 adduct coalesce between 30 and 48 °C. Breaking and reforming of the donor–acceptor bond seems the most likely explanation for the coalescence, which requires inversion of the amine. Sufficient weakening of the donor–acceptor bond by steric strain in this highly sterically hindered amine would lead to donor–acceptor bond breaking. We note that this amine is unusual in other respects: the mixed boron trihalide adducts are less stable than expected, and $BFBr_2$, BF_2I, and BFI_2 adducts could not be detected.

(*f*) *Other Nuclei*.—We have not extended our previous studies [4] of ^1H complexation shifts of amine adducts. Many ^1H n.m.r. studies of adducts have been carried out and in general, for a particular donor, a stronger donor–acceptor bond shifts the ^1H signal further to low field. It is widely accepted that inductive effects explain this, although other factors can have an effect.[1] We note however that Myers *et al.*[55] have concluded from a study of diethylamine–halogenoborane adducts that steric interactions between halogen on boron and alkyl groups on nitrogen are predominant in determining ^1H chemical shifts. However, since the same order of successively larger low-field shifts ($BF_3 < BCl_3 < BBr_3 < BI_3$) is found even when such steric interaction is not possible,[56,57] this conclusion cannot be valid for boron trihalide adducts in general.

A preliminary study at 40.53 MHz makes it clear that ^{15}N enrichment will be required if ^{15}N n.m.r. is to be applied to these systems.

(*g*) *A Diastereomeric* $B(amine)_2F_2^+$ *Cation*.—We have been attempting to prepare difluoroboron cations by the displacement of heavy halogen (X = Cl, Br, or I) from the BF_2X adducts of a range of donor molecules [equation (1)]. This reaction, analogous to that used by Ryschkewitsch [58] to form dihydroboron cations and related species, is successful with donors which can delocalize negative charge toward the donor site, *e.g.* esters,[3] ureas,[59] and amidines,[9] but has not been successful with amines. In the course of this work we have observed a case of spontaneous formation of a $B(amine)_2F_2^+$ cation.

$$D{\cdot}BF_2X + D \rightleftharpoons BF_2D_2^+ + X^- \qquad (1)$$

Benzyl(ethyl)methylamine forms a typical series of mixed boron trihalide adducts. Its BF_nI_{3-n} (n = 0—3) adducts are typical of mixed fluorine–iodine adduct systems in that the equilibrium very much favours the BF_3 and BI_3 adducts over the BF_2I and BFI_2 adducts. However, in addition to all of these a major species giving a ^{19}F multiplet and an ^{11}B 1:2:1 triplet is present and on standing increases at the expense of the mixed halogen adducts. We attribute this to $B(PhCH_2NMeEt)_2F_2^+$ on the basis of the following evidence.

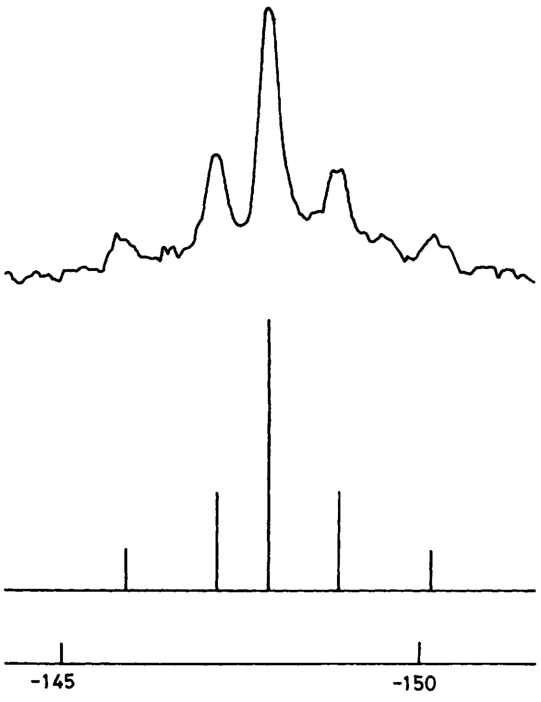
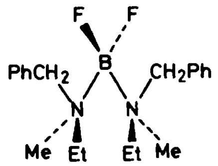
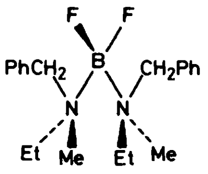


FIGURE 3 56.4-MHz ^{19}F-{^{11}B} n.m.r. spectrum of $B(PhCH_2NMeEt)_2F_2^+$, showing the overlapping patterns of the *meso* and optically active forms

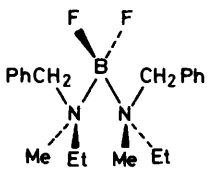
On ^{11}B broad-band decoupling the ^{19}F multiplet simplifies to a five-line pattern, which can be interpreted as a superimposed singlet and AB pattern, of equal intensities, with the singlet slightly displaced from the centre of the AB pattern (Figure 3). The key to interpretation is the chirality of complexed $PhCH_2NMeEt$. The donor molecule has equal probability of being 'frozen' in the *R* or the *S* configuration, leading to the formation of a *meso* form (*RS*·BF_2^+) and an optically active form (*RR*·BF_2^+ and *SS*·BF_2^+) with equal probability. The *meso* form (II) has magnetically non-equivalent fluorines which give rise to the AB pattern.



(II) (*meso*)



(III) (*SS*)



(III) (*RR*)

The optically active forms (III) have magnetically equivalent fluorines which give rise to the singlet.

The ^{19}F chemical shifts (*meso*, −146.6 and −149.3 p.p.m.; optically active, −147.8 p.p.m.) are all within a range of 3 p.p.m., and are consistent with ^{19}F chemical shifts of known $BD_2F_2^+$ ions.[3,9,59] The ^{11}B 1 : 2 : 1

triplet [$J(^{11}B-^{19}F) = 42.6$ Hz] and chemical shift (+2.4 p.p.m.) confirm the structure. The broadening of the ^{11}B lines, typical of a quadrupolar nucleus, prevents resolution of any chemical shift difference between borons in the *meso* and optically active cations. The value of J_{FBF} is consistent with those discussed in section (*c*).

It is not yet clear why we have obtained the $BD_2F_2^+$ cation in this system and in the $PhMe_2N{\cdot}BF_nI_{3-n}$ system [^{19}F 1 : 1 : 1 : 1 quartet, −155.3 p.p.m. $J(^{11}B-^{19}F) = 37.2$ Hz] but not in corresponding systems in which the tertiary amine has only aliphatic substituents. The BF_nI_{3-n} adducts are clearly the most likely to give the cation in reluctant systems, due to the weakness of the B–I bond and the ease of I^- displacement by a second donor molecule. Our work does not support previous reports[60] that non-iodine-containing tertiary amine–boron trihalide adducts readily give rise to boron cations in solution.

The absence of any ^{11}B resonance for a tetrahalogenoborate ion such as BI_4^- confirms our suggestion[3] that the counter ion of $BD_2F_2^+$ can be halide ion rather than, or in addition to, tetrahalogenoborate ion.

EXPERIMENTAL

Most of the amines were commercial samples, which were dried over activated Lindé 3A or 4A molecular sieves and distilled before use, the initial and final cuts being rejected. Benzyl(ethyl)methylamine was synthesized from benzylmethylamine and ethyl iodide by reflux in benzene. The hydroiodide, which separated as an oil, was made basic with potassium hydroxide solution, extracted with diethyl ether, and washed with water. After drying and removal of the ether the residue was chromatographed on a silica gel column with ethyl acetate to remove traces of starting material. The ethyl acetate was removed and vacuum fractionation of the residue yielded pure benzyl(ethyl)methylamine.

Deuteriochloroform (Merck Sharp and Dohme Silanor, with a trace of C_6F_6 added as a ^{19}F n.m.r. reference) was stored over activated Lindé molecular sieve 3A before use.

The boron trihalides were purified as described previously.[5] Solutions of mixed boron trihalide adducts were prepared by the following methods.

(*i*) Addition of already equilibrated mixtures BX_nY_{3-n} (n = 0—3) to $CDCl_3$ solutions of the amine, frozen and degassed on a high-vacuum system, and sealing off the samples. (This method is not suitable for the preparation of BF_2I and BFI_2 adducts, as no detectable amounts of these mixed boron trihalides form spontaneously from uncomplexed BF_3 and BI_3.)

(*ii*) Passage of a gaseous boron trihalide (BF_3 or BCl_3) through a solution of the amine in dry $CDCl_3$ at −50 °C. The heavier boron trihalide, dissolved in dry $CDCl_3$ in a nitrogen-filled glove-bag, was then transferred to the amine–BF_3 solution by syringe/septum cap techniques. Sufficient total boron trihalide must be added to be in excess over the amine, as only under these conditions does rapid halogen exchange take place. Before n.m.r. spectra are obtained an excess of the amine must be added to 'quench' the uncomplexed boron trihalide; otherwise exchange reactions would remain rapid on the n.m.r. time-scale.

(*iii*) Successively passing BF_3 and BCl_3 gases through a solution of the amine in $CDCl_3$ at −50 °C, followed by adding excess of amine to 'quench' the uncomplexed boron trihalide. This is a rapid but crude method to obtain BF_nCl_{3-n} (n = 0—3) adducts.

The ^{19}F, ^{11}B, and ^{13}C n.m.r. spectra were obtained on a Bruker WP-60 Fourier–transform n.m.r. spectrometer operating at 56.45, 19.25, and 15.08 MHz, respectively, using fixed-frequency probes, an internal deuterium lock, and quadrature detection. Sweep widths of 6 024 Hz (^{19}F) and 3 759 Hz (^{11}B and ^{13}C) were normally used. The ^{11}B and ^{13}C spectra were obtained with broad-band ^1H decoupling. The transformed spectra contained 4 K data points. Thirty-degree pulses were used. Some ^{11}B spectra were obtained on a Bruker WH-400 Fourier-transform n.m.r. spectrometer operating at 128.38 MHz, with broad-band ^1H decoupling. The transformed spectra contained 8 K data points.

The ^{19}F-{^{11}B} spectra were obtained on the Bruker WP-60 spectrometer using an ^{11}B fixed-frequency probe, in which the ^{11}B 'observe' coil was used to provide the ^{11}B decoupling, while the ^1H decoupling coil was retuned to 56.4 MHz and used to observe ^{19}F. The ^{11}B frequency was provided by a Hewlett-Packard model 8654B signal generator and model 8655A synchronized counter, and amplified with an ENI model 320L RF power amplifier. An external deuterium lock was used. Under these conditions ^{19}F peak widths at half-height were about 6 Hz: far from ideal, but adequate to resolve the splittings.

Cone angles were determined using Taylor-Hirschfelder models of donor molecules, arranged in their most tightly packed conformations. These were mounted to facilitate easy rotation about the scaled B–N bond axis (1.595 Å).[13] Substituent angles at the acceptor atom were measured by projecting the image of each substituent onto a screen placed immediately behind the model.

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