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Stabilization of tris(trifluoromethyl)borane in complexes with primary, secondary and tertiary amines. Crystal and molecular structure of $(CF_3)_3B \cdot NHEt_2$ and $(CF_3)_3B \cdot NH_2Et$

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Abstract

Various adducts $(CF_3)_3B \cdot NHR^1R^2$ of the unknown free Lewis acid tris(trifluoromethyl)borane with secondary amines have been prepared from $Cl_2BNR^1R^2$ by nucleophilic trifluoromethylation with $CF_3Br/P(NEt_2)_3$ and subsequent protonation: $R^1{=}R^2{=}Me$ (I), $R^1{=}R^2{=}Et$ (II), $R^1 + R^2{=}C_5H_{10}$ (III), $R^1{=}R^2{=}$cyclo-C_6H_{11} (IV), $R^1{=}Me$, $R^2{=}CH_2Ph$ (V), $R^1{=}Me$, $R^2{=}$t-Bu (VI). The primary amine derivatives $(CF_3)_3B \cdot NH_2R^1$, $R^1{=}Et$ (VII) and Me (VIII), have been isolated as by-products in the preparations of II and VI, respectively. Reactions of I, II and VII with KOH yield the corresponding salts $K[(CF_3)_3B \cdot NMe_2]$ (IX), $K[(CF_3)_3B \cdot NEt_2]$ (X) and $K[(CF_3)_3B \cdot NHEt]$ (XI). IX and X react with CH_3I, $CH_3OSO_2CF_3$ and allyl bromide to yield the tertiary amine adducts $(CF_3)_3B \cdot NR^1R^2R^3$, $R^1{=}R^2{=}R^3{=}Me$ (XII), $R^1{=}R^2{=}Me$, $R^3{=}C_3H_5$ (XIII), $R^1{=}R^2{=}Et$, $R^3{=}Me$ (XIV), $R^1{=}R^2{=}Et$, $R^3{=}C_3H_5$ (XV). The structure of II and VII were determined by an X-ray diffraction study. The strength of the B-N bonds in these compounds is reflected in their comparatively short average length (1.592(5) Å). The B-C bond lengths average 1.614(4) Å, and variations of the bond angles are consistent with considerable F strain in the adducts.

Introduction

Access to trifluoromethylboron derivatives has so far been restricted to neutral and anionic mono- and bis-(trifluoromethyl) derivatives with coordination numbers at boron of 3 (**A**,**B**) and 4 (**C**,**D**) [1-3].

$CF_3BX^1X^2$	$(CF_3)_2BX^2$	$CF_3BX^1X^2X^3$	$(CF_3)_2BX^1X^2$
(**A**)	(**B**)	(**C**)	(**D**)

While numerous ligands X (halogens, the hydroxy group and amines) have been incorporated into the tetracoordinate species [4], stabilization of the boranes A and

B appears to require at least one π donor such as $X^1 = NR_2$ [3]. Thus the preparation of the free Lewis acid $(CF_3)_3B$ (**E**) is a particular challenge, since the CF_3 group lacks π donor character.

$(CF_3)_3B$ (**E**) $(CF_3)_3B\cdot X$ (**F**)

In view of the inductive effect of the electronegative CF_3 groups on one hand and the presence of highly covalent B–C bonds on the other hand, **E** would be expected to be a very strong Lewis acid that is less prone to nucleophilic substitution of the CF_3 groups than e.g. BCl_3. Its complexes **F** with Lewis bases X would appear to be suitable models for the study of its properties as Lewis acid, and possibly to be precursors for its synthesis. The present contribution deals with the amine complexes $(CF_3)_3B\cdot NR^1R^2R^3$ (R^1, R^2, R^3 = H, alkyl, alkenyl, phenyl), which are the first species containing a tris(trifluoromethyl)boron unit.

Since liberation of $(CF_3)_3B$ from the adducts **F** would entail the rupture of the dative B–N bond, the steric and electronic effects of the nitrogen substituents on this linkage are very important. In order to provide a structural basis for delineating these effects, we have studied two of the adducts by single-crystal X-ray methods. The results provide evidence for steric interactions between the donor and acceptor fragments, and details are presented below.

Results

While preparing aminobis(trifluoromethyl)boranes by trifluoromethylation of some X_2BNR_2 (X = Cl, Br) species with the $CF_3Br/P(NEt_2)_3$ reagent [5], we noticed that CF_3^- readily becomes attached to the borane of type **B** according to eq. 1. Although ^{19}F and ^{11}B NMR spectra indicated that the yield of the $(CF_3)_3B\cdot NR_2^-$ anions could be as high as 90%, isolation of pure products proved to be difficult. Although the difficulties of work-up greatly exceeded those encountered when $CF_3I/C_2(NMe_2)_4$ was used instead of $CF_3Br/P(NEt_2)_3$ in trifluoromethylation of X_2BNR_2 derivatives [6], the use of the $CF_3Br/P(NEt_2)_3$ reagent rather than the expensive CF_3I was favoured for economic reasons.

$$CF_3Br + (CF_3)_2BNR_2 + P(NEt_2)_3 \rightarrow (CF_3)_3B\cdot NR_2^- + BrP(NEt_2)_3^+ \qquad (1)$$

Such trifluoromethylation reactions of aminoboranes $Cl_2BNR^1R^2$ with various amine functions (R^1=R^2=Me, Et, i-Pr, Ph, cyclo-C_6H_{11}; R^1=Me, R^2=t-Bu, CH_2Ph, Ph; $R^1 + R^2$=C_5H_{10}) as starting materials showed that aminotris(trifluoromethyl)borates $(CF_3)_3B\cdot NR^1R^{2-}$ were formed unless the amine bore a phenyl substituent. Quantitative conversion was observed by NMR spectroscopy for all substituents except R=CH_2Ph (~ 10%), but salts of these anions could not be isolated from the complex reaction mixture. However, the borates can be protonated by concentrated hydrochloric acid, according to eq. 2, without cleavage of the B–C bonds.

$$(CF_3)_3B\cdot NR^1R^{2-} \underset{+OH^-/-H_2O}{\overset{+H^+}{\rightleftharpoons}} \underset{(I–VI)}{(CF_3)_3B\cdot NHR^1R^2} \qquad (2)$$

$(CF_3)_3B\cdot NHR^1R^2$	I	II	III	IV	V	VI
R^1 =	Me	Et	C_5H_{10}	cyclo-C_6H_{11}	Me	Me
R^2 =	Me	Et		cyclo-C_6H_{11}	CH_2Ph	t-Bu

The protonated form can be separated from the acidified reaction mixture by extraction with organic solvents. The borate anion may be regenerated by deprotonation of the amine adduct with concentrated aqueous KOH. During the work up of II, we isolated, in a yield of 1%, a second species, $(CF_3)_3B \cdot NH_2Et$ (VII). Formation of VII via trifluoromethylation of possible Cl_2BNHEt impurities in the starting material is unlikely for two reasons: first the monomeric form of Cl_2BNHEt, which is required for the reaction, is unstable, and second, the reaction of $Cl_2BNH(t\text{-}Bu)$ with $CF_3Br/P(NEt_2)_3$ yielded HCF_3 and no trifluoromethylboranes. We suggest that VII is formed by a Hofmann-type elimination of ethylene from $(CF_3)_3B \cdot NEt_2^-$ during the trifluoromethylation. This suggestion is strongly supported by the ease of thermal elimination of isobutene from VI (vide infra).

Properties

All the amine adducts of tris(trifluoromethyl)borane are colourless, airstable solids, soluble in most polar organic solvents but insoluble in cold water. Their thermal stability depends on the amine involved. Whereas II is stable up to 200 °C, VI loses isobutene to form $(CF_3)_3B \cdot NH_2Me$ (VIII) when heated to ca. 80 °C (eq. 3).

$$(CF_3)_3B \cdot NHMe(t\text{-}Bu) \xrightarrow{\Delta} (CF_3)_3B \cdot NH_2Me + (CH_3)_2C{=}CH_2 \qquad (3)$$

Furthermore, II is resistant to oxidation by alkaline solutions of 30% H_2O_2 at reflux temperature. It is not attacked at ambient temperature by acids such as concentrated hydrochloric acid or anhydrous HF.

Attempts to remove diethylamine from II by treatment with HF/SbF_5 (1/1) at room temperature resulted in decomposition with formation of HCF_3 and BF_3, while neat SbF_5 decomposed II with formation of BF_3 and $CF_3CF{=}CF_2$ accompanied by other perfluoroalkenes. When I, II and VI were treated in suspension with solid KOH in ether, the nitrogen was deprotonated and etheral solutions of the potassium salts IX, X and XI were obtained in quantitative yields. IX and X are sufficiently nucleophilic to react with MeI, CF_3SO_3Me, or allyl bromide according to eq. 4 to yield tris(trifluoromethyl)borane adducts of tertiary amines.

$$(CF_3)_3B \cdot NR^1{}_2^- + R^2X \rightarrow (CF_3)_3B \cdot NR^1{}_2R^2 + X^- \qquad (4)$$

The conditions for complete conversion are shown in Table 1. The particularly rapid alkylation of IX suggests that $(CF_3)_3B \cdot NMe_2$ groups may be readily attached to a variety of substrates.

Table 1

Conditions for the alkylation of $(CF_3)_3B \cdot NR^1{}_2^-$ with R^2X

R^1	R^2	X	T (°C)	t (min)	Product
Me	Me	CF_3SO_3	21	12	XII
		I	21	18	XII
Me	C_3H_5	Br	21	60	XIII
Et	Me	CF_3SO_3	21	30	XIV
		I	21	300	XIV
Et	C_3H_5	Br	35	10080	XV

Table 2. Physical properties and NMR spectra of I–XV (δ in ppm, J in Hz) [a]

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV
M.p. (°C)	99	137	112	142	133	61	52	87	153 (dec.)	135	171	210	100	147	96
$\delta(NC\mathit{H}_3)$	2.98				2.83	2.93		2.94	2.36			3.03	2.88	2.85	
$\delta(CC\mathit{H}_2C)$			1.45 2.10	1.05 2.20											
$\delta(CC\mathit{H}_3)$		1.46				1.54	1.45			0.93	1.00			1.35	1.41
$\delta(NC\mathit{H}_{(2)})$		3.07 3.73	3.05 3.75		3.74 4.87		3.31			2.77 2.80	2.70			3.46	3.49
$\delta(C_6\mathit{H}_5)$					7.37 7.52										
$\delta(C{=}C\mathit{H}H(Z))$													~ 5.75		~ 5.53
$\delta(C{=}CH\mathit{H}(E))$														~ 5.61	~ 5.52
$\delta(C\mathit{H})$				3.55										5.96	6.08
$\delta(C\mathit{H}_2CH{=}C)$														3.91	3.99
$\delta(N\mathit{H})$	~ 3	3.3	3.59	~ 3.6	4.07	3.9	4.0	4.54			0.9				
$^2J(\mathit{H}C\mathit{H})$		13.5			13.4										
$^3J(C\mathit{H}_2C\mathit{H}_3)$		7.2					7.2			6.8	7.1			7.3	7.3
$^3J(\mathit{H}NC\mathit{H})$	5.3	6.6			5.6 10.0	5.9	3.3 11.2	6.1							
$^3J(\mathit{H}C{=}C\mathit{H}_{cis})$														~ 9.4	~ 9.2
$^3J(\mathit{H}C{=}C\mathit{H}_{trans})$														~ 16.5	~ 16.0
$^3J(C\mathit{H}_2C\mathit{H}{=}C)$														7.4	7.5
$\delta(C\mathit{F}_3)$	−63.9	−62.0	−63.1	−61.2	−62.7	−59.5	−66.4	−65.6	−61.2	−61.3	−64.2	−62.4	−61.3	−60.5	−59.5
$^2J(BF)$	31.0	30.0				27.0	~ 31	27.8	23.7	23.7	24.8	27.1	~ 25	29.9	~ 28
$\delta(\mathit{B})$	−11.4	−11.1	−11.3	−10.4	−11.1	−10.2	−12.9	−13.0	−11.7	−11.3	−12.8	−9.2	−8.8	−8.1	−7.5
$\delta(N\mathit{C}H_3)$	41.8				36.7	36.0		30.1	41.7			52.9	46.8	41.3	
$\delta(C\mathit{C}H_3)$		14.0				27.5	14.9			15.8	19.5			9.6	11.3
$\delta(\mathit{C}CH_3)$						67.1									
$\delta(N\mathit{C}H_{(2)})$		48.9	51.0	64.6	57.9		40.4			43.4	38.7			54.1	52.4
$\delta(C\mathit{C}H_2C)$			21.9 25.6	24.6 33.3											
$\delta(\mathit{C}_6H_5)$					129.6 131.4										
$\delta(C{=}\mathit{C}H_2)$													124.0		126.0
$\delta(CH_2\mathit{C}H{=}C)$													129.4		128.6
$\delta(\mathit{C}H_2CH{=}C)$													63.0		60.1
$^4J(CF)$	1.7	1.8	1.7		1.8	2.3	1.1				0.8	2.2	2.0	2.1	1.8

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[a] I to VIII and XII to XV in $CDCl_3$. IX to XI in CD_3CN. ^1H: 250.13 MHz, int. std. $CHCl_3$ = 7.27 ppm/CHD_2CN = 1.95 ppm. ^{13}C: 62.9 MHz, int. std. $CDCl_3$ = 77.0 ppm/CD_3CN = 1.3 ppm. ^{19}F: 84.67 MHz, int. std. $CFCl_3$. ^{11}B: 25.52 MHz, ext. std. $BF_3 \cdot OEt_2$.

Spectra

The physical properties and the ^1H, ^{19}F, ^{11}B and ^{13}C NMR spectra of I to XV are set out in Table 2. The ^1H spectra confirm the proposed structures and only a few comments are necessary. The CH_2NH_2 group of VII gives rise to an AA′XX′ spin system in $CDCl_3$, while in more polar solvents such as CD_3CN there is no coupling with the NH_2 protons. AB spin systems are observed for the CH_2 groups in II and V, while first order coupling patterns for the ethyl groups are found in XIV and XV. The CH_2 and phenyl resonances of III, IV and V were not assigned.

The ^{11}B and ^{19}F resonances of all tris(trifluoromethyl)borane derivatives vary only marginally, $\delta(B) = -10 \pm 3$ ppm and $\delta(F) = -63 \pm 3$ ppm. Except for IX–XI, which give sharp lines, the $^2J(BF)$ coupling constant cannot be evaluated precisely and varies between 20 and 30 Hz. The three borate anions IX–XI belong to the small number of trifluoromethylboranes whose C atoms of the CF_3 groups can be detected by ^{13}C NMR spectroscopy: $^1J(CF) \sim 315$ Hz, $^3J(CF) \sim 3.7$ Hz, $^1J(CB) \sim 71.5$ Hz. In most cases a small $^4J(CF)$ coupling constant of ~ 1.8 Hz is observed for the carbon atoms bonded to nitrogen, and the patterns of the multiplets are indicative of the number of CF_3 groups attached to boron. All other ^{13}C resonances are in line with the proposed structures.

The EI mass spectra of trifluoromethylborane derivatives are of limited diagnostic value owing to the ease of F and CF_2 elimination. Accordingly M^+ peaks were not observed, and the peaks with the highest m/e values $(M^+ - F)$ or $(M^+ - CF_2)$ have only 1% of the intensity of the base peaks. The latter are usually associated with the $(F_2BNR_2H^+)$ ion unless more stable cations can be formed, e.g. $(CH_2-CH_2{=}CH_2{}^+)$ from XIII and XV.

Along with dominating nonspecific IR bands and Raman lines the vibrational spectra reveal some typical strong IR absorptions of the $(CF_3)_3BN$ group, e.g. $\nu(CF_3)$ 1100–1150 cm^{-1} and $\delta_s(CF_3)$ 695 cm^{-1}. The intense Raman line at ~ 724 cm^{-1} assigned to $\delta_s(CF_3)$ is characteristic.

X-ray structural analyses

Crystals of II and VII were grown by sublimation. Intensity data and lattice constants were measured as described previously [7] with a Siemens AED 1 diffractometer employing Zr-filtered Mo-K_α radiation (λ 0.71073 Å). The structures were solved by direct methods and refined to convergence by least-squares techniques with the program SHELX-76 [8]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned group isotropic temperature factors and placed in calculated positions (N–H, C–H: 0.95 Å) except for that bonded to the N atom of II, which was unconstrained. Crystal data and details of the refinements are given in Table 3, and the final coordinates are listed in Tables 4 and 5 for II and VII, respectively. Relevant bond distances and angles are presented in Tables 6 and 7. The numbering schemes are defined in Figs. 1 and 2 [9*].

With apparent root-mean-square displacements as large as 0.70 Å, the F atoms of II appear to be disordered. Our inability to model this disorder, which probably involves moderate rotations of the CF_3 groups about the B–C bonds, is the cause of

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* Reference number with asterisk indicates a note in the list of references.

Table 3

Crystal data and details of the data collection at refinement for II and VII

	II	VII
Formula	$(CF_3)_3B\cdot NHEt_2$	$(CF_3)_3B\cdot NH_2Et$
Space group	*Pnma*	$P2_1/c$
a (Å)	13.015(3)	7.761(3)
b (Å)	12.428(3)	10.893(3)
c (Å)	7.156(1)	12.020(4)
β (°)	90	100.21(3)
Z	4	4
D_C (g cm^{-3})	1.670	1.746
2θ limits (°)	4–55	4–60
Forms	$h \pm k \pm l$	$\pm h\ k\ l$
Measured reflections	5528	3168
Unique reflections	1388	2895
Observed ($F_o > 4\sigma(F_o)$)	1070	1173
Monitor correction	0.990–1.003	0.992–1.141
Crystal size (mm)	0.174×0.551×0.696	0.075×0.377×0.580
μ (Mo–K$_\alpha$) (cm^{-1})	1.90	2.11
Absorption correction	1.034–1.092	–
R [a]	0.121	0.067
R_w [a]	0.156	0.070
ρ (e/Å^3) [b]	0.66 to −0.55	0.34 to −0.29
Parameters	93	148
g	0.0002	0.0003

[a] $R = \Sigma\Delta/\Sigma|F_o|$, $R_w = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$ where $\Delta = ||F_o| - |F_c||$ and $w = 1/(\sigma^2(F_o) + gF_o^2)$. [b] Densities in final difference Fourier map.

the high R factors for this structure (55% of the electrons in the compound come from the F atoms).

Thermal motion calculations were made with the program THMA 11 [10]. The 84 U_{ij}'s of the $(CF_3)_3BN$ fragment in VII were fit to a 23 parameter model which augments the usual rigid-body-motion parameters by allowing for torsional motion

Table 4

Positional and equivalent isotropic temperature factors [a] for $(CF_3)_3B\cdot NHEt_2$

Atom	x	y	z	U
B	0.4772(5)	0.2500	0.1994(8)	0.044(2)
N	0.3871(4)	0.2500	0.0480(7)	0.048(2)
C(1)	0.5898(5)	0.2500	0.103(1)	0.064(2)
C(2)	0.4652(4)	0.1455(4)	0.3306(7)	0.068(2)
C(3)	0.3834(6)	0.1520(8)	−0.076(1)	0.121(3)
C(4)	0.2798(5)	0.1114(6)	−0.119(1)	0.107(3)
F(1)	0.6662(3)	0.2500	0.2259(7)	0.109(2)
F(2)	0.6106(3)	0.1674(5)	−0.0060(7)	0.148(2)
F(3)	0.3715(3)	0.1331(3)	0.4011(5)	0.100(2)
F(4)	0.5229(4)	0.1487(5)	0.4843(7)	0.164(3)
F(5)	0.4909(7)	0.0556(4)	0.257(1)	0.216(4)

[a] $U = \frac{1}{3}\Sigma_i\Sigma_j \bar{a}_i \cdot \bar{a}_j a_i^* a_j^* U_{ij}$.

Table 5

Positional and equivalent isotropic temperature factors [a] for $(CF_3)_3B\cdot NH_2Et$

Atom	*x*	*y*	*z*	*U*
B	0.1608(6)	−0.1496(4)	0.2525(4)	0.041(2)
N	−0.0049(4)	−0.2159(3)	0.1808(3)	0.046(1)
C(1)	0.2210(6)	−0.0382(4)	0.1789(4)	0.056(2)
C(2)	0.1167(7)	−0.1021(4)	0.3716(4)	0.059(2)
C(3)	0.3106(5)	−0.2540(4)	0.2727(4)	0.055(2)
C(4)	−0.1772(6)	−0.1494(5)	0.1509(5)	0.071(2)
C(5)	−0.3062(5)	−0.2193(5)	0.0695(4)	0.076(2)
F(1)	0.1139(4)	0.0598(2)	0.1653(3)	0.092(1)
F(2)	0.2324(5)	−0.0714(3)	0.0741(2)	0.101(2)
F(3)	0.3745(5)	0.0083(3)	0.2216(3)	0.118(2)
F(4)	0.0087(4)	−0.0033(3)	0.3634(2)	0.090(1)
F(5)	0.0354(4)	−0.1873(3)	0.4247(2)	0.087(1)
F(6)	0.2566(4)	−0.0685(3)	0.4451(2)	0.101(1)
F(7)	0.2751(4)	−0.3450(3)	0.3409(3)	0.092(1)
F(8)	0.3305(4)	−0.3097(3)	0.1766(3)	0.087(1)
F(9)	0.4706(3)	−0.2155(3)	0.3182(3)	0.094(1)

[a] See Table 4.

Table 6

Selected bond distances (Å) and angles (°) in $(CF_3)_3B\cdot NHEt_2$

B–C(1)	1.620(9)	N–C(3)	1.509(8)	C(2)–F(3)	1.329(6)
B–C(2)	1.610(6)	C(3)–C(4)	1.472(9)	C(2)–F(4)	1.331(6)
B–N	1.596(8)	C(1)–F(1)	1.326(8)	C(2)–F(5)	1.280(7)
N–H(N)	0.79(6)	C(1)–F(2)	1.318(6)		
C(1)–B–C(2)	109.6(3)	C(3)–N–H(N)	108(2)		
C(2)–B–C(2′) [a]	107.5(5)	B–C(1)–F(1)	113.4(5)		
C(1)–B–N	112.1(4)	B–C(1)–F(2)	116.0(4)		
C(2)–B–N	109.0(3)	B–C(2)–F(3)	113.8(4)		
B–N–H(N)	103(4)	B–C(2)–F(4)	113.8(5)		
B–N–C(3)	115.0(4)	B–C(2)–F(5)	116.1(4)		
C(3)–N–C(3′)	107.7(9)	N–C(3)–C(4)	115.4(6)		

[a] $x', y', z' = x, 0.5-y, z$.

Table 7

Selected bond distances (Å) and angles (°) in $(CF_3)_3B\cdot NH_2Et$

B–C(1)	1.617(6)	C(1)–F(1)	1.345(5)	C(2)–F(6)	1.324(5)
B–C(2)	1.616(6)	C(1)–F(2)	1.329(5)	C(3)–F(7)	1.346(5)
B–C(3)	1.613(6)	C(1)–F(3)	1.312(5)	C(3)–F(8)	1.338(5)
B–N	1.589(5)	C(2)–F(4)	1.357(5)	C(3)–F(9)	1.333(5)
N–C(4)	1.507(5)	C(2)–F(5)	1.345(5)	C(4)–C(5)	1.481(6)
C(1)–B–C(2)	111.9(3)	B–C(1)–F(1)	115.4(4)		
C(1)–B–C(3)	109.9(3)	B–C(1)–F(2)	112.9(4)		
C(2)–B–C(3)	110.6(3)	B–C(1)–F(3)	113.9(4)		
C(1)–B–N	109.2(3)	B–C(2)–F(4)	114.5(4)		
C(2)–B–N	110.3(3)	B–C(2)–F(5)	113.1(4)		
C(3)–B–N	104.7(3)	B–C(2)–F(6)	113.8(4)		
B–N–C(4)	120.6(3)	B–C(3)–F(7)	113.0(3)		
N–C(4)–C(5)	112.2(4)	B–C(3)–F(8)	112.3(3)		
		B–C(3)–F(9)	115.7(4)		

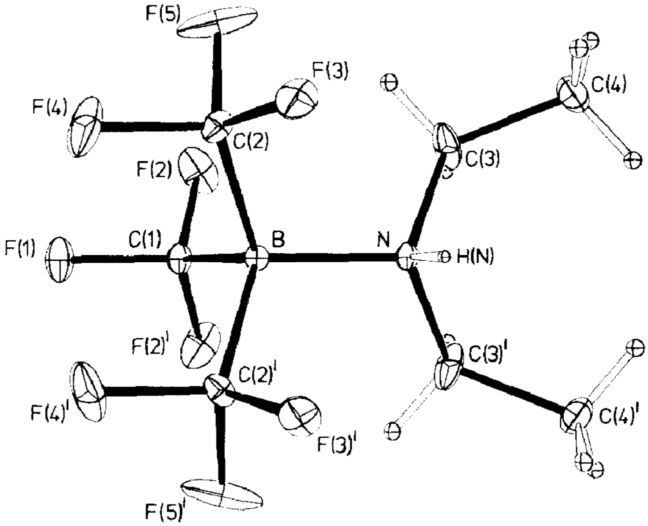

Fig. 1. A perspective drawing of $(CF_3)_3B \cdot NHEt_2$.

of the F atoms about each of the three B–C bonds [11]. The average barrier calculated for these torsions is 4(1) kcal/mol. Thermal corrections to the interatomic distances appear to be reliable, the average F $\cdots$ F separation in a CF_3 group being lengthened from an unreasonably short 2.117(13) Å value to a more typical 2.172(6) Å distance [12]. Unless otherwise specified, uncorrected distances are used in the discussion below.

Description of the crystal structures

As can be seen from Figs. 1 and 2, the groups bonded to the boron atoms are mutually staggered. Owing to the substitution of the nitrogen atoms, the highest possible symmetry for these molecules is C_s. This symmetry applies strictly to II;

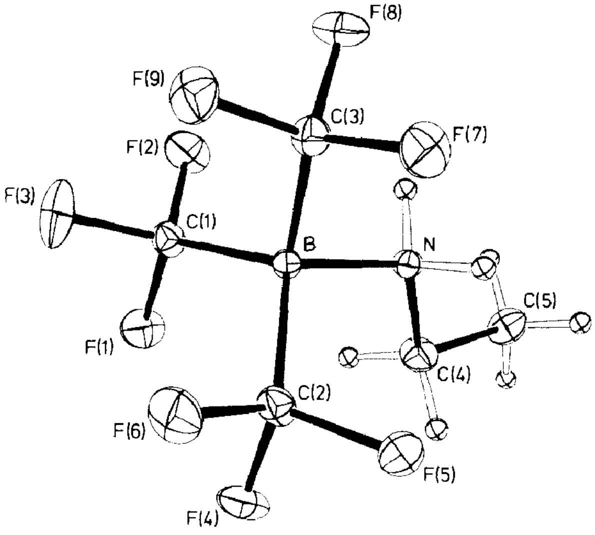

Fig. 2. A perspective drawing of $(CF_3)_3B \cdot NH_2Et$.

that is, the B–C(1) and N–H(N) bonds, which exhibit a *trans* conformation, lie on a crystallographic mirror plane. No crystallographic symmetry is imposed on VII. Here the only possible plane of symmetry would contain the C(3)–B–N–C(4) torsion angle (176.2(6)°), which is close to the ideal 180° value.

The bond lengths involving the boron atoms are very similar in these structures. The B–C bond distances average 1.613(6) and 1.615(6) Å in II and VII, respectively. They are comparable with those found for $(CF_3)_2BF \cdot NHMe_2$ (**G**) (1.612(8) Å) and $(CF_3)_2BOH \cdot NHMe_2$ (**H**) (1.624(4) Å) [4]. In addition, the B–N distances in II (1.596(8) Å) and VII (1.589(5) Å) are statistically indistinguishable from those of **G** (1.584(7) Å) and **H** (1.602(3) Å). Librational corrections increase the average B–C and B–N distances of VII to 1.627(6) and 1.602(5) Å, respectively.

The bond angles of II and VII may be correlated with the size and orientation of the amines, which possess both N–H and sterically more demanding N–C bonds. As a result, the B–C bonds may be differentiated by the number (0, 1 or 2) of associated *gauche* N–C bonds. Thus the C(1)–B–N bond angle of II (112.1(4)°) is the largest C–B–N angle since the corresponding B–C(1) bond has two *gauche* N–C bonds, and the smallest of the angles (C(3)–B–N of VII, 104.7(3)°) has no *gauche* N–C bonds. Each remaining B–C bond has only one *gauche* N–C bond, and the corresponding C–B–N angles have an intermediate value (ave. 109.4(6)°). As the C–B–N angles increase, the C–B–C angles must decrease; therefore, the average C–B–C angle of II is 1.9° smaller than that of VII because II has more ethyl groups.

The C–B–C angles in each compound correlate with the orientation of the amine. In II, the angle C(1)–B–C(2) is 2.1(6)° larger than the C(2)–B–C(2)′ angle, and in VII the C(1)–B–C(2) angle is 1.6(6)° larger than the average of the other two C–B–C angles. In both cases the larger angles are those which are bisected by N–C bonds when the molecules are viewed along their B–N linkage.

Steric interactions between the CF_3 and ethyl groups are also relieved by tipping the amine so as to open the B–N–C angles at the expense of the B–N–H angles. Obviously the tilt angle must lie in the B,N,H(N) plane of II and in the B,N,C(4) plane of VII; consequently the B–N–C(4) angle of VII is widened 5.6(5)° further than the B–N–C(3) angle of II.

Some tilting of the CF_3 groups is also evident from the distribution of the B–C–F angles. Of these, the larger involve the fluorine atoms closest to the ethyl groups. The large B–C(3)–F(9) angle in VII is an understandable exception since tilting of the CF_3 group of C(3) towards the NH_2 group relieves the F(3) · · · F(9) and F(6) · · · F(9) repulsions. Furthermore, those CF_3 groups which are *gauche* to both N–H and N–C bonds are rotated by 8–10° away from the perfectly staggered conformation so as to reduce F · · · Et repulsions.

In VII the C–F bonds *gauche* to the B–N bond are probably longer than those *trans* to the B–N bond, the averages of the thermally corrected distances being 1.374(7) and 1.354(6) Å, respectively. Obviously better X-ray data are required in order to define this difference more precisely.

Discussion

The concept of F strain was developed in part to explain the reduction in the dissociation energies of trimethylborane-amine adducts as the steric bulk of the amine increases [13]. The corresponding F strain in adducts of $(CF_3)_3B$ derivatives must be much larger, since the CF_3 group is bulkier than a CH_3 group; for example, from the observed borane-amine geometries [14*] and van der Waals radii [17], ligand cone angles of 132 and 117 °, respectively, can be estimated by assuming free rotation about the B–C bonds. Nevertheless, despite the considerable steric strain in the $(CF_3)_3B$ adducts (vide supra), these compounds are apparently much more stable than the corresponding $(CH_3)_3B$ derivatives. The additional stability is also supported by the observed bond lengths, the B–N bonds in II and VII being 0.06(1) Å shorter than those in $(CH_3)_3B \cdot NHMe_2$ (**J**) [15]. This shortening must be ascribed to the inductive effect of the CF_3 groups, which should enhance electron transfer from the amine to the $(CF_3)_3B$ entity. Perhaps this additional electron transfer is responsible for the fact that N–C bonds in II and VII are 0.04(1) Å longer than those in **J**.

If **E** is an electropositive main group element, the **E**–CF_3 bonds tend to be longer than **E**–CH_3 linkages [18]. This rule is obeyed well by trigonal boranes; thus the B–CF_3 bonds in $CF_3B(NMe_2)_2$ and $(CF_3)_2BNMe_2$ were shown to be 0.062(8) and 0.037(4) Å longer, respectively, than the B–CH_3 bonds in similar aminomethylboranes [19]. The need to compare analogous compounds can not be over-emphasised; for example, the B–C bond of $K[CF_3BF_3]$ (1.625(6) Å [20]) is essentially equal to that in $Li[B(CH_3)_4]$ (1.634(7) Å [21]) but significantly longer than that in $K[CH_3BF_3]$ (1.575(3) Å [23]). Thus while the structures of several four-coordinate bis(trifluoromethyl)boranes are known [2,4], they have limited relevance to the CH_3/CF_3 substitution effect because of the lack of structurally studied four-coordinate dimethylboranes. Thus comparison of the average B–C bond length of II and VII (1.614(4) Å) with that of **J** (1.618(9) Å) gains special importance. The similarity of these distances places a constraint on theories which rationalize differences in **E**–CF_3 and **E**–CH_3 linkages.

Such differences have been explained in terms of the polar interaction model which considers the electrostatic interactions along the **E**–C bond. These are repulsive for the **E**–CF_3 fragment since both the **E** and C atoms carry a positive charge; on the other hand a weak attractive effect might be expected for the **E**–CH_3 fragment because of the small negative charge of the carbon atom [18]. Of course a CF_3 group will enhance the positive charge on **E** more than a CH_3 group will, but in the adducts II, VII and **J** electron transfer from the amines appears to counteract this effect. Conceivably donation could effectively neutralize the boron atoms, which possess a formal charge of −1, and thus negate the electrostatic interactions.

Experimental

Tris(trifluoromethyl)borane-dimethylamine (I), Tris(trifluoromethyl)borane-diethylamine (II), Tris(trifluoromethyl)borane-piperidine (III), Tris(trifluoromethyl)borane-dicyclohexylamine (IV), Tris(trifluoromethyl)borane-methyl(benzyl)amine (V), Tris(trifluoromethyl)borane-methyl(t-butyl)amine (VI), Tris(trifluoromethyl)borane-ethylamine (VII), Tris(trifluoromethyl)borane-methylamine (VIII)

General procedure: A stirred solution containing 1 mol of the dichloroborane ($Cl_2BNR^1R^2$) in 400 ml of dry CH_2Cl_2 was saturated with gaseous CF_3Br at 0 °C, and a stream of CF_3Br was passed through as 3.2–3.4 mol $P(NEt_2)_3$ were added dropwise. When no further CF_3Br was being consumed, the mixture was stirred for

Table 8

Elemental analyses

Compound	Formula	Analyses (found (calc.) (%))		
		C	H	F
I	$C_5H_7BF_9N$	23.0	2.8	64.6
		(22.84)	(2.68)	(65.03)
II	$C_7H_{11}BF_9N$	29.3	3.7	57.9
		(28.89)	(3.81)	(58.75)
III	$C_8H_{11}BF_9N$	32.1	3.7	55.8
		(31.71)	(3.67)	(56.43)
IV	$C_{15}H_{23}BF_9N$	45.35	5.7	42.3
		(45.13)	(5.82)	(42.84)
V	$C_{11}H_{11}BF_9N$	39.1	3.3	50.0
		(38.97)	(3.28)	(50.44)
VI	$C_8H_{13}BF_9N$	31.5	4.4	55.5
		(31.50)	(4.30)	(56.06)
VII	$C_5H_7BF_9N$	23.0	2.8	65.8
		(22.84)	(2.68)	(65.03)
VIII	$C_4H_5BF_9N$	19.5	2.2	67.7
		(19.30)	(2.03)	(68.70)
IX	$C_5H_6BF_9KN$	20.1	2.2	55.0
		(19.95)	(2.01)	(56.80)
X	$C_7H_{10}BF_9KN$	25.6	2.9	51.5
		(25.55)	(3.06)	(51.96)
XI	$C_5H_6BF_9KN$	20.3	2.2	55.5
		(19.95)	(2.01)	(56.80)
XII	$C_6H_9BF_9N$	26.2	3.3	61.3
		(26.02)	(3.28)	(61.74)
XIII	$C_{10}H_{15}BF_9N$	31.7	3.6	56.0
		(31.71)	(3.66)	(56.43)
XIV	$C_8H_{13}BF_9N$	31.7	4.4	55.7
		(31.51)	(4.30)	(56.06)
XV	$C_{11}H_{13}BF_9N$	36.3	4.6	51.5
		(36.28)	(4.57)	(51.65)

1 h at room temperature, the solvent and other volatile material were removed in vacuo, and the viscous residue treated with ~ 400 ml of conc. HCl with stirring. II, IV and VII, which separated out spontaneously, were filtered off and recrystallized from $CHCl_3$, while VII was isolated from the mother liquor of II and purified by repeated fractional crystallization. I was extracted from the acidified reaction mixture with two 200 ml portions of ether. III, V and VI, which separated from the acidified solution as oils, were first repeatedly sublimed or distilled and then recrystallized from $CHCl_3$/hexane mixtures. VIII, which is less volatile than VI, was formed during the sublimation of VI by decomposition.

	I	II	III	IV	V	VI	VII	VIII
Yields %:	35	77	15	18	1	5	1	7

The low yields of V and VI are due to decomposition during sublimation. For elemental analyses see Table 8.

Potassium dimethylaminotris(trifluoromethyl)borate (IX), Potassium diethylaminotris (trifluoromethyl)borate (X), Potassium ethylaminotris(trifluoromethyl)borate (XI)

10 mmol of I, II or VII were stirred with 35 mmol (2g) of powdered KOH in 10 ml of ether for 10 min at room temperature. The solution was filtered and IX, X and XI obtained quantitatively by evaporation of the solvent in vacuo.

Tris(trifluoromethyl)borane-trimethylamine (XII), Tris(trifluoromethyl)borane-allyl(dimethyl)amine (XIII), Tris(trifluoromethyl)borane-methyl(diethyl)amine (XIV), Tris(trifluoromethyl)borane-allyl(diethyl)amine (XV)

A solution of 10 mmol VIII or IX in 10 ml ether was stirred with 30 mmol MeI, $MeOSO_2CF_3$ or allyl bromide. Details are given in Table 1. After removal of the solvent and of unchanged alkylating agent, XII, XIII, XIV and XV were obtained by sublimation in vacuo in essentially quantitative yield.

Acknowledgements

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