

Intra- and inter-molecular C–H···F–C and N–H···F–C hydrogen bonding in secondary amine adducts of B(C₆F₅)₃: relevance to key interactions in alkene polymerisation catalysis

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The reactions between the cyclic *sec.* amines pyrrolidine and piperidine with B(C₆F₅)₃ yield Lewis acid-base adducts with both intra- and inter-molecular hydrogen bonding interactions between C–H and N–H groups and aryl-fluorines in the solid state.

Perfluoroaryl boranes and borates have attracted considerable interest in the field of 1-alkene polymerisation catalysis.¹ In this context we recently reported the synthesis of [NH₂{B(C₆F₅)₃}₂][–] from NH₂[–] and 2 equivalents of B(C₆F₅)₃.² The stability of this anion appears to be enhanced by a number of N–H···F–C hydrogen bonding interactions. In the solid state these hydrogen bonds vary in length between 1.90(2) and 2.42(2) Å. Hydrogen bonding to covalently bonded organic fluorine is regarded as rare but is of significance in crystal engineering and enzyme substrate recognition and has been the subject of detailed studies.³ O–H···F–C hydrogen bonding is found in (C₆F₅)₃B(OH₂)[–] and the anion [(C₆F₅)₃B(OH)B(C₆F₅)₃][–].⁴ Very recently intra- and inter-molecular O–H···F–C hydrogen bonding interactions have been identified in the H₂O and MeOH adducts of Al(C₆F₅)₃.⁵

C–H···F–C interactions and their designation as hydrogen bonds have until recently been the subject of particular controversy but are believed to play a role in determining the crystal structure of fluorobenzenes and fluorine substituted ribonucleic acids.^{3b,d,6} They have also been invoked to explain the behaviour of fluorine substituted polymerisation catalysts.⁷ Dunitz and Taylor have laid down criteria for designation as hydrogen bonds, *i.e.* the H···F–C interaction should be significantly shorter than the sum of the van der Waals radii (*ca.* 2.55 Å) and preferably no longer than *ca.* 2.2–2.3 Å, with obtuse X–H–F angles.^{3a,8,9}

In the course of studies designed to gauge the extent of hydrogen bonding in B(C₆F₅)₃ adducts we prepared the *sec.* amine adducts (cyclo-C₄H₈NH)B(C₆F₅)₃ (**1**) and (cyclo-C₅H₁₀NH)B(C₆F₅)₃ (**2**).[†] The molecular structures[‡] of **1** (Fig. 1) and **2** have a number of similarities: in both cases the amino-hydrogen is *ca.* 2.1 Å from two *o*-F atoms and is involved in a bifurcated, intramolecular F···H···F hydrogen bonding system (Table 1).

Evidence that the N–H···F–C interactions in **1** and **2** are maintained in solution is provided by VT ¹⁹F NMR spectroscopy. At room temperature the ¹⁹F NMR spectra of **1** and **2** are complex, with highfield resonances for the hydrogen bonded *o*-F atoms. The *o*-F resonances coalesce only on warming to 80 °C. This cannot be dismissed as hindered rotation about the B–N and/or B–C bonds on steric grounds alone since (Et₂MeN)B(C₆F₅)₃, which is of greater steric bulk but cannot participate in N–H···F–C hydrogen bonding, gives no indication in the ¹⁹F NMR spectrum for hindered rotation down to –60 °C.¹⁰

Unexpectedly, the crystal structure of **1** also shows a close contact between an α -hydrogen of the cyclic amine and an aryl *o*-F atom on the third C₆F₅ group. This intramolecular interaction (Chart 1) appears to be more than a weak van der Waals interaction brought about by the proximity of the C–H and F–C groups after complex formation. The large C–H···F angle (151°) and short H···F distance (2.20 Å) places it within

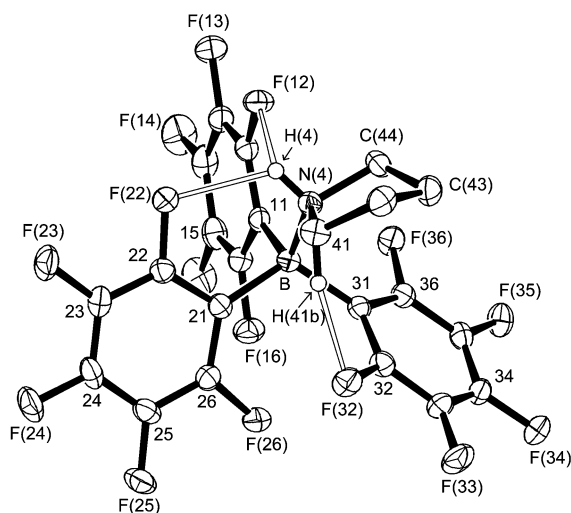


Fig. 1 Molecular structure of **1**, showing intramolecular N–H···F–C and C–H···F–C interactions.

Table 1 Hydrogen atom contacts (Å and °); esds are in parentheses

D–H···A	D···A	H···A	D–H···A
Structure 1:			
Intramolecular contacts:			
N(4)–H(4)···F(12)	2.736(2)	2.15	122
N(4)–H(4)···F(22)	2.766(2)	2.18	122
C(41)–H(41b)···F(32)	3.085(2)	2.20	151
Intermolecular contacts:			
C(41)–H(41a)···F(16 [′])	3.181(2)	2.43	134
C(42)–H(42b)···F(13 [″])	3.351(2)	2.48	149
Structure 2:			
Intramolecular contacts:			
N(4)–H(4)···F(12)	2.747(2)	2.10	127
N(4)–H(4)···F(26)	2.733(2)	2.10	126
N(8)–H(8)···F(52)	2.758(2)	2.11	128
N(8)–H(8)···F(66)	2.745(2)	2.14	123
Intermolecular contact:			
C(85)–H(85a)···F(25 ^{″″})	3.175(3)	2.34	143
Symmetry ops.: [′] : $x - \frac{1}{2}, 1\frac{1}{2} - y, z - \frac{1}{2}$; [″] : $1 - x, 2 - y, -z$; ^{″″} : $x - \frac{1}{2}, 1 - y, \frac{1}{2} + z$.			

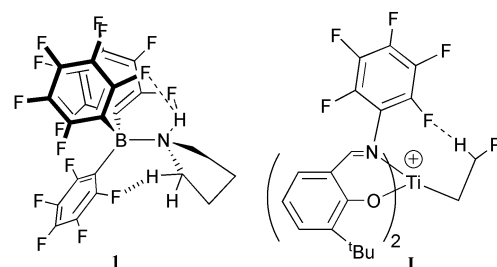


Chart 1

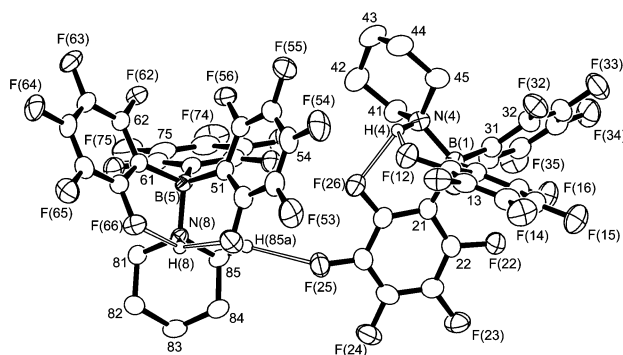


Fig. 2 Structure of **2** indicating intramolecular N-H...F-C and intermolecular C-H...F-C interactions.

the Dunitz criteria for X-H...F-C hydrogen bonds. It is significantly shorter than any previously reported intra- or intermolecular C-H...F-C bond.⁶

There are also weak intermolecular C-H...F-C interactions (Table 1) linking molecules of **1** in planar nets. By contrast, **2** does not adopt an extended supramolecular structure. There are two independent molecules in the crystal, linked by a C-H...F-C interaction (Fig. 2).

Intramolecular C-H...F-C interactions, similar to that observed for **1**, between the *o*-F atoms of fluorinated phenyl groups and the β -H of the polymeryl chain (Structure **I**, Chart 1) have recently been proposed as being responsible for decreasing the likelihood of β -H transfer and causing the observed differences in molecular weight between polyalkenes prepared with phenyl and perfluorophenyl substituted phenoxy-imine catalysts. The F-H β distance predicted by the DFT calculations for this interaction was 2.28 Å.⁷ However; there was little structural precedence for bonding between a C-H group and the *o*-F of a C₆F₅ ring. Chan *et al.* have very recently reported a model complex with an intramolecular interaction between a methylene hydrogen atom on a zirconium bonded benzyl group and a (sp³)-CF₃ ligand substituent (H...F 2.47 Å and C-H...F 114°).¹¹ **1** and **2** exhibit intra- and inter-molecular hydrogen bonding to a (sp²)-C₆F₅ group with structural parameters suggesting a significantly stronger interaction, comparable to that found in the DFT studies.

The electron-withdrawing properties of organofluorine substituents are employed widely, both in ligand design and in the preparation of least coordinating anions.^{1,12} Our observations and those of Fujita and Chan suggest that subtle interactions between X-H groups and organofluorines may have a significant influence on catalytic behaviour.

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Notes and references

† Synthesis: (cyclo-C₄H₈NH)B(C₆F₅)₃ (**1**). To a solution of B(C₆F₅)₃ (1.46 g, 2.9 mmol) in toluene (40 cm³) HNC₄H₈ (0.24 cm³, 2.9 mmol) was added. After stirring for 1 h the toluene was removed under reduced pressure. The product was isolated as colourless crystals after recrystallisation from a light petroleum-dichloromethane mixture (1.21 g, 72%). Anal. found: C, 45.27; H, 1.54; N, 2.40%. Calcd. for C₂₂H₉BF₁₅N: C, 45.32; H, 1.56; N, 2.40%. δ_{H} (300 MHz, C₆D₆, 20 °C) 5.80 (br. s, 1H, NH), 2.31 (dt, 4H, *J* 158.1 and 8.3 Hz, CH₂), 0.84 (t, 4H, *J* 4.0 Hz, CH₂); δ_{C} (75.47 MHz; C₆D₆, 20 °C) 49.56, 23.08; δ_{B} (96.29 MHz, C₆D₆, 20 °C) -3.1; δ_{F} (282.40 MHz, C₆D₆, 20 °C) -127.90 (br. 4F, *o*-F), -143.37 (br. 2F, *o*-F), -155.95 (br. 3F, *p*-F), -162.81 (br. 6F, *m*-F).

(Cyclo-C₅H₁₀NH)B(C₆F₅)₃ **2** was prepared from B(C₆F₅)₃ (1.60 g, 3.1 mmol) and HNC₅H₁₀ (0.31 cm³, 3.1 mmol) following the same procedure as **1** (1.55 g, 84%). Anal. found: C, 45.74; H, 1.99; N, 2.22%. Calcd. for C₂₃H₁₁BF₁₅N: C, 46.26; H, 1.86; N, 2.35%. δ_{H} (300 MHz, C₆D₆, 20 °C) 5.24 (br. m, 1H, NH), 2.94 (d, 4H, *J* 12.5 Hz, CH₂), 1.76 (q, 4H, *J* 11.7 Hz, CH₂), 1.07 (m, 2H, *J* 12.5 Hz, CH₂); δ_{C} (75.47 MHz, C₆D₆, 20 °C) 50.2, 25.5, 22.5; δ_{B} (96.29 MHz, C₆D₆, 20 °C) -2.1; δ_{F} (282.40 MHz, C₆D₆, 20 °C) -127.69 (s, 2F, *o*-F), -127.76 (s, 2F, *o*-F), -142.91 (s, 2F, *o*-F), -154.22 (t, 1F, *J* 19.8 Hz, *p*-F), -156.39 (t, 2F, *J* 22.6 Hz, *p*-F), -161.08 (s, 2F, *m*-F), -162.72 (m, 2F, *m*-F), -163.02 (m, 2F, *m*-F).

‡ Crystal data for **1**: C₂₂H₉BF₁₅N, *M* = 583.1, monoclinic, space group *P*2₁/*n* (equiv. to no. 14), *a* = 14.232(1), *b* = 11.510(1), *c* = 14.543(1) Å, β = 117.22(1)°, *V* = 2118.5(3) Å³, *Z* = 4, *D*_c = 1.828 Mg m⁻³, *F*(000) = 1152, *T* = 140(1) K, μ (MoK α) = 0.200 mm⁻¹, λ (MoK α) = 0.71073 Å, 12139 reflections measured, 3616 unique (*R*_{int} = 0.060), *F*² refinement, *R*_i = 0.033 [*I* > 2 σ (*I*)], *wR*₂ = 0.095 (all data).

Crystal data for **2**: C₂₃H₁₁BF₁₅N, *M* = 597.1, monoclinic, space group *Pn* (equiv. to no. 7), *a* = 10.186(2), *b* = 13.026(3), *c* = 17.501(4) Å, β = 96.63(3)°, *V* = 2306.5(8) Å³, *Z* = 4, *D*_c = 1.720 Mg m⁻³, *F*(000) = 1184, *T* = 140(1) K, μ (MoK α) = 0.186 mm⁻¹, λ (MoK α) = 0.71073 Å, 12844 reflections measured, 7190 unique (*R*_{int} = 0.042), *F*² refinement, *R*_i = 0.031 [*I* > 2 σ (*I*)], *wR*₂ = 0.075 (all data). CCDC 211286 and 211287. See <http://www.rsc.org/suppdata/cc/b3/b305613a/> for crystallographic data in cif or other electronic format.

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