ChemComm

Supramolecular self-assembly directed by carborane C–H···F interactions

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Received (in Columbia, MO, USA) 21st August 2000, Accepted 31st October 2000
First published as an Advance Article on the web

The synthesis and crystallization of 9,12-bis-(4-fluorophenyl)-1,2-carborane 1 and 9,12-bis-(3,5-difluorophenyl)-1,2-carborane 2 provide the first examples of a supramolecular assemblage directed by C–H$_{\text{carborane}}$···F interactions.

The potential utilization of the isomeric icosahedral carborane ($C_2B_{10}H_{12}$) cages as building blocks for macromolecules and supramolecular assemblies has only recently been explored.[1–3] The versatile chemistry available at the carborane C–H and B–H vertices makes carborane derivatives attractive candidates for crystal engineering.[4] Intermolecular hydrogen bonding is an important factor involved in supramolecular self-assembly motifs. Consequently, the participation of the acidic carborane C–H vertices in hydrogen bonding generates supramolecular structures. The established intermolecular interactions involving carboranes are: classical C–H···O hydrogen bonds,[5] bifurcated C–H···$(O)_2$ hydrogen bonds,[6] non-classical C–H···π hydrogen bonds[7] and B–H···H–N interactions.[1,8] Thus far, known C–H carborane interactions are limited to C–H···Y (Y= O, N, π) systems.[1,9] Fluorocarbon sites (C–F) are poor hydrogen bond components and cannot compete with O and N, although weak C–H···F interactions contribute to crystal-packing organization.[10] We report here the novel *ortho*-carborane derivatives: 9,12-bis-(4-fluorophenyl)-*o*-carborane **1**, and 9,12-bis-(3,5-difluorophenyl)-*o*-carborane **2**. Compounds **1** and **2** provide the first examples of a supramolecular assemblage directed by carborane C–H···F interactions.

Electron-rich boron vertices of *ortho*-carborane were easily functionalized by electrophilic iodination followed by palladium-catalyzed reactions of the regioselectively iodinated carborane with the appropriate fluorophenyl or difluorophenyl Grignard reagent.[11] Colorless crystals of **1** and **2** were grown from a methylene chloride–hexane solution and Et_2O, respectively,† by slow evaporation of the solvent. The structures of compounds **1** and **2** were determined by single-crystal X-ray diffraction analysis.

Crystal structures of both **1** and **2**‡ show intermolecular carborane C–H···F interactions. The unit cell of the solid-state structure of **1** contains four crystallographically unrelated, yet similar carboranes. Carborane C–H···F intermolecular distances lie in the range 2.49–3.05 Å and non-classical C–H···π hydrogen bonds with carborane C–H···aromatic centroid separations of 2.48 and 2.46 Å are observed (see caption to Fig. 1). The observed carborane C–H···F distances are consistent with phenyl C–H···F interactions reported for various fluorobenzene compounds (H···F 2.36–2.86 Å).[10] Also, close phenyl C–H···F distances (H···F 2.25–2.70 Å) are observed. All carborane C–H vertices are in close proximity to either a fluorine atom or π centroid, with the majority participating in C–H···F interactions. The solid-state IR spectrum of **1** exhibits two distinct stretching frequencies for carboranyl C–H at 3088 and 3060 cm^{-1}. These unassigned stretching frequencies represent either a carborane C–H···(F or π) interaction. The C–H stretching frequencies of the *o*-carborane C–H···π bond were reported[7] between 3066 and 3059 cm^{-1} which suggests that the lower energy stretching mode (3060 cm^{-1}) corresponds to those carborane C–H bonds involved in C–H···π interactions.

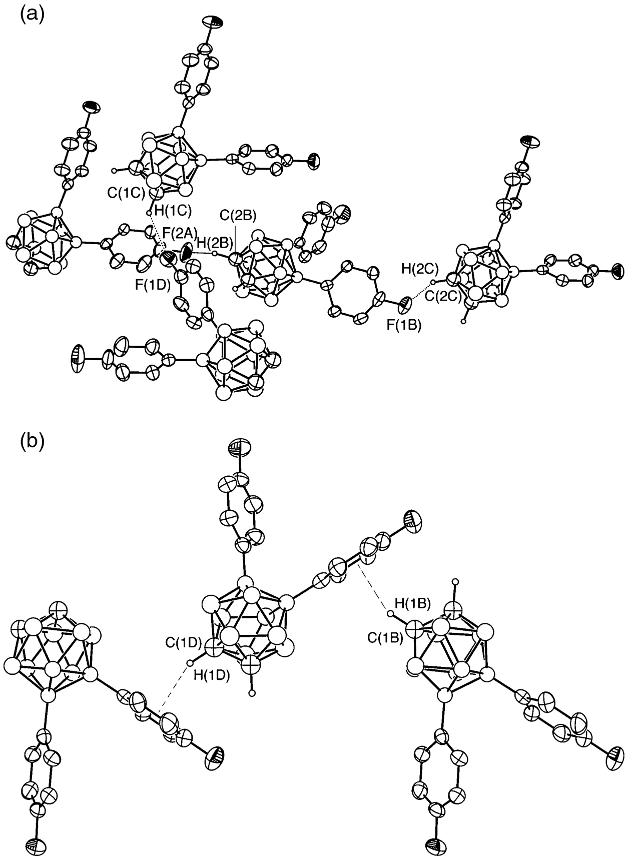

Fig. 1 Crystal packing diagram of **1**. (a) View of carborane C–H···F interactions. Selected distances (Å) and angles (°): C(1C)···F(1D) 3.593(8), H(1C)···F(1D) 2.91, C(2B)···F(2A) 3.416(7), H(2B)···F(2A) 2.49, C(2C)···F(1B) 3.557(8), H(2C)···F(1B) 2.69; C(1C)–H(1C)–F(1D) 120, C(2B)–H(2B)–F(2A) 146, C(2C)–H(2C)–F(1B) 136. (b) View of carborane C–H···π interactions. Selected distances (Å) and angles (°): H(1D)···aromatic centroid(π) 2.48, H(1B)···π 2.46; C(1D)–H(1D)–π 24.3, C(1B)–H(1B)–π 24.7. For clarity, the remaining phenyl and carborane H atoms are not shown.

In the solid state structure, molecules of **2** form a one-dimensional polymeric chain linked by two different carborane interactions having characteristic C–H···F distances. Directionality of both C–H vertices toward the fluorine atoms differ with angles of C(1)–H(1)–F(3P) 160° and C(2)–H(2)–F(11P) 124°. Intermolecular interactions of C(1)–H(1)···F(3P) 2.47 Å and C(2)–H(2)···F(11P) 2.35 Å demonstrate that the hydrogen atom bonded to C(2) interacts more strongly with fluorine than the hydrogen atom bonded to C(1) (Fig. 2). Close phenyl C–H···F interactions are not observed in **2**. The solid-state IR spectrum exhibits two different carborane C–H stretching frequencies of equal intensity (3077 and 3098 cm^{-1}). This observation is consistent with the presence of the two discrete sets of such interactions observed in the X-ray diffraction study. The position of the 3,5-difluorophenyl group in **2** allows the

DOI: 10.1039/b007353i

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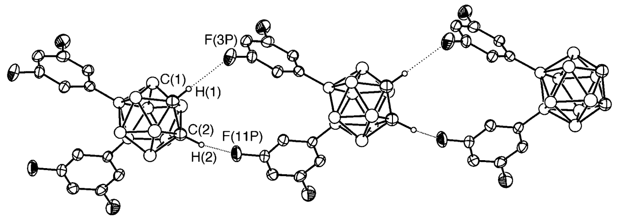

Fig. 2 Crystal packing diagram of **2**. The three molecules are related by translation. Selected distances (Å) and angles (°): C(1)···F(3P) 3.462(5), H(1)···F(3P) 2.47, C(2)···F(11P) 3.107(5), H(2)···F(11P) 2.35; C(1)–H(1)–F(3P) 160, C(2)–H(2)–F(11P) 124. For clarity, the remaining phenyl and carborane H atoms are not shown.

orientation of both carborane C–H vertices to simultaneously be in close proximity to fluorine atoms present on the neighboring molecule. This orientation leads to formation of the observed one-dimensional polymeric structure.

The crystal lattices of **1** and **2** are directed by a network of weak carborane C–H···F and/or C–H···π contacts. Although these C–H···F interactions are weak, their sum in lattice networks provides stabilization. This study demonstrates an additional motif for carboranes in supramolecular self-assembly chemistry.

We are grateful to the National Science Foundation (Grant No. CHE-9730006) for their support of this research.

Notes and references

† *Synthetic procedure* for **1**: to a dry THF (300 ml) solution of 9,12-I$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (4.12 g, 10.4 mmol) was added 52 ml of 4-fluorophenylmagnesium bromide (1 M, in THF) at 0 °C. At 25 °C, *trans*-[PdCl$_2$(PPh$_3$)$_2$] (120 mg, 0.17 mmol) was added to the solution. The mixture was heated at the reflux temperature under nitrogen for 2 days, resulting in a black solution. Aqueous 10% HCl was added cautiously to destroy residual Grignard reagent, and all volatiles were removed *in vacuo*. The residue was dissolved in 200 ml of diethyl ether and 10% HCl (aq). The organic phase was separated and the aqueous layer was extracted with diethyl ether (2 × 100 ml). The organic phases were combined, dried over MgSO$_4$, and filtered. The solvent was removed under reduced pressure to yield a red solid. Purification by chromatography on basic aluminum oxide (toluene) gave a white solid. Crystallization from a methylene chloride–hexane solution afforded **1** (2.98 g, 8.95 mmol, 86%).

Selected data for **1**: mp 132–133 °C; ν(KBr)/cm^{-1} 3060, 3088 (carborane C–H); δ_H(400 MHz, CDCl$_3$, *J*/Hz) 1.5–3.4 (BH), 3.68 (br s, 2H), 6.80 (tt, *J* 9.0, 2.3, 4H), 7.13 (br dd, *J* 8, 6, 4H); δ_C(100 MHz, CDCl$_3$, *J*/Hz) 162.8 (d, J_{CF} 245.5, CF), 134.6 (d, J_{CF} 7.3, CH), 114.3 (d, J_{CF} 19.9, CH), 49.4; δ_B(160 MHz, BF$_3$·Et$_2$O external standard, *J*/Hz) 8.4 (s, 2B), −8.3 (d, J_{BH} 138, 2B), −13.0 (d, J_{BH} 151, 4B), −15.6 (d, J_{BH} 167, 2B); δ_F(376 MHz, CDCl$_3$, external Freon-113/C$_6$D$_6$ solution referenced at −68.0 ppm[12] relative to CFCl$_3$) −116.5; HR-EIMS: *m/z*: found 332.2376; calc. 332.2387.

Synthetic procedure for **2**: the synthesis and separation procedure was similar to that of **1**. Crystallization from Et$_2$O afforded **2** (79%).

Selected data for **2**: mp 189–190 °C; ν(KBr)/cm^{-1} 3077, 3098 (carborane C–H); δ_H(400 MHz, CDCl$_3$, *J*/Hz) 6.61 (br d, *J* 6.6, 4H), 6.52 (tt, *J* 9.1, 2.4, 2H), 3.74 (2H), 1.5–3.4 (BH); δ_C(100 MHz, CDCl$_3$, *J*/Hz) 50.1, 102.7 (t, J_{CF} 25.2), 115.1 (dd, J_{CF} 17.2), 162.2 (dd, J_{CF} 251.5); δ_F(376 MHz, CDCl$_3$, external Freon-113/C$_6$D$_6$ solution referenced at −68.0 ppm[12] relative to CFCl$_3$) −112.4; δ_B(160 MHz, Et$_2$O, BF$_3$·Et$_2$O external standard, *J*/Hz) 7.4 (s, 2B), −8.6 (d, J_{BH} 140, 2B), −13.0 (d, J_{BH} 154, 4B), −15.5 (d, J_{BH} 168, 2B); HR-EIMS: *m/z*: found 368.2196; calc. 368.2191.

‡ Single crystals of 9,12-bis-(4-C$_6$H$_4$F)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ **1** were crystallized from methylene chloride–hexane, placed on a fiber and mounted on a Syntex P-1 diffractometer.

Crystal data for **1**: C$_{56}$B$_{40}$H$_{72}$F$_8$, M = 1329.54, monoclinic, space group $P2_1/n$, a = 17.504(8), b = 15.015(7), c = 27.57(1) Å, β = 91.16(1)°, V = 7244(6) Å^3, T = 293 K, Z = 4, λ(Cu-Kα) = 1.5418 Å, μ = 0.592 mm^{-1}, 7440 reflections measured, 7440 unique, which were used in all calculations. The final $R1(F^2)$ was 0.0746 [4642 reflections, $I > 2\sigma(I)$].

Single crystals of 9,12-bis-(3,5-C$_6$H$_3$F$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ **2** were crystallized from Et$_2$O, placed on a fiber and mounted on a Syntex P-1 diffractometer.

Crystal data for **2**: C$_{14}$B$_{10}$H$_{18}$F$_2$, M = 332.38, triclinic, space group $P\bar{1}$, a = 6.882(4), b = 9.710(5), c = 13.926(7) Å, α = 84.80(2), β = 81.41(2), γ = 78.50(2)°, V = 900 Å^3, T = 298 K, Z = 2, λ(Cu-Kα) = 1.5418 Å, μ = 0.793 mm^{-1}, 2468 reflections measured. The final $R1(F^2)$ was 0.0616 [1540 reflections, $I > 2\sigma$(I)].

CCDC 182/1844. See http://www.rsc.org/suppdata/cc/b0/b007353i/ for crystallographic files in .cif format.

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