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Intra- and inter-molecular carboranyl C–H · · · N hydrogen bonds in pyridyl-containing *ortho*-carboranes †

Elena S. Alekseyeva, Andrei S. Batsanov, Lynn A. Boyd, Mark A. Fox,* Thomas G. Hibbert, Judith A. K. Howard, J. A. Hugh MacBride, Angus Mackinnon and Kenneth Wade
Department of Chemistry, South Road, University of Durham, Durham, UK DH1 3LE. E-mail: m.a.fox@durham.ac.uk

Received 9th October 2002, Accepted 14th November 2002
First published as an Advance Article on the web 24th December 2002

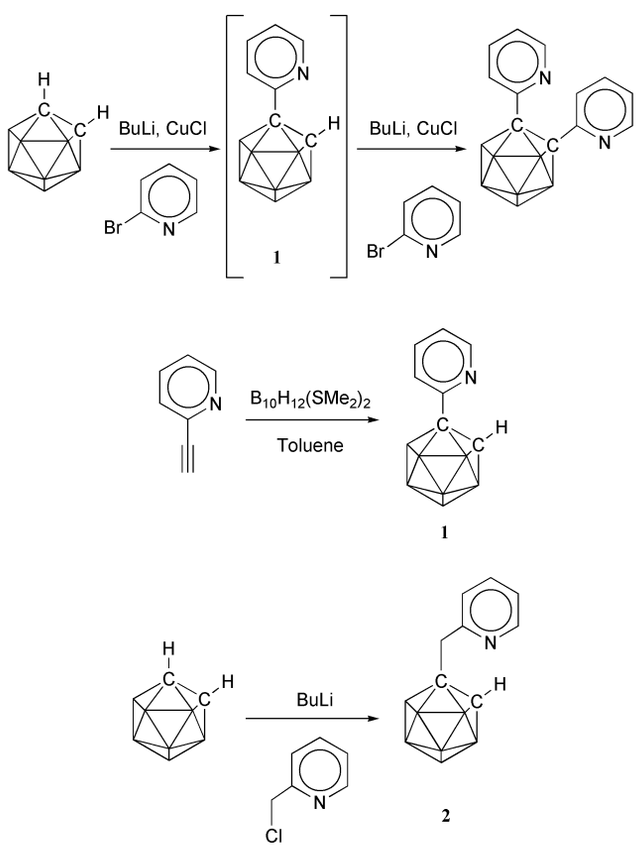
Four C-substituted derivatives of *ortho*-carborane, 1-R-1,2-$C_2B_{10}H_{11}$, where R = 2′-pyridyl (**1**), 2′-picolyl (**2**), 5′-bromo-2′-pyridyl (**3**) or 3′-pyridyl (**4**) have been prepared using adaptations of standard procedures, and structurally characterised by single crystal X-ray diffraction studies in an exploration of C–H · · · N hydrogen bonding effects involving their carborane CH units. Calculations at the MP2/6-31G* level of theory were used to assess the strength of the hydrogen bonding detected, and calculated NMR shifts at the GIAO-B3LYP/6-311G* level were compared with measured C–H shifts to show that intramolecular C–H · · · N hydrogen bonding persisted in solution in the case of compound **1**. The value of IR C–H stretching frequencies for probing hydrogen bonding in these systems was also studied. An unsuccessful attempt to convert compound **3** into a macrocyclic species $(C_2B_{10}H_{10}C_5H_3N)_3$ in which three *ortho*-carborane units are linked through 2,5-disubstituted pyridine rings is also described.

Introduction

Derivatives of the icosahedral carboranes have attracted considerable recent attention in both their fundamental properties and their wide-ranging potential applications.[1] The rigid geometries of the *ortho*, *meta* and *para* isomers of $C_2B_{10}H_{12}$, together with the relative ease of derivatisation at both the carbon and boron vertices make carboranes excellent candidates for crystal engineering.[2] For many of the potential applications of carborane derivatives an understanding of, and ideally control over, the solid-state structures of these compounds is vital. One way in which a degree of control over solid-state structure may be effected is by tailoring C–H · · · A hydrogen bonding involving the carboranyl cage C–H bond (A = acceptor).[3,4]

In 1997, the first examples containing carboranyl C–H · · · N hydrogen bonds, 1-(2′-pyridyl)- **1** and 1-(2′-picolyl)-*ortho*-carborane **2**, were demonstrated.[5] This type of hydrogen bonding was subsequently mentioned for 9-cyano-*ortho*-carborane,[6] $HNP(NMe_2)_3$ adducts of *meta*- and *para*-carborane[7] and the 1,10-phenanthroline adduct of *ortho*-carborane.[8] The pyridyl-containing carboranes **1** and **2** are interesting also as potential σ-bound carboranyl ligands possessing a pendant nitrogen donor group. C-Pyridyl carboranes can generally be prepared by the coupling of a copper(I) derivative of *ortho*-, *meta*- or *para*-carborane with a halopyridine.[9,10] However only 1,2-di-(2′-pyridyl)-*ortho*-carborane, and not 1-(2′-pyridyl)-*ortho*-carborane **1**, could be obtained from *ortho*-carborane (Scheme 1). This interesting reaction suggests that the pyridyl group in the presumed intermediate 1-(2′-pyridyl)-*ortho*-carborane increases significantly the reactivity of the adjacent unsubstituted cage carbon. The alkyne 2-ethynylpyridine must be prepared and then reacted with the dimethylsulfide complex of decaborane, 6,9-$(Me_2S)_2B_{10}H_{12}$, to give 1-(2′-pyridyl)-*ortho*-carborane **1** in low yield along with carborane side products.[9,11]

A compound closely related to **2**, 1-(dimethylaminomethyl)-*ortho*-carborane **6**, has recently been shown to be such a σ-bound carboranyl ligand.[12,13] Since compound **2** was prepared here by reaction of the lithio-*ortho*-carborane with picolyl chloride (Scheme 1), a report has appeared describing a similar preparation and an X-ray structure of **2**—identical to ours here—was determined.[14] The conversion of **2** by deboronation into a π-bound *nido*-carborane ligand with a pendant nitrogen donor group was also described.

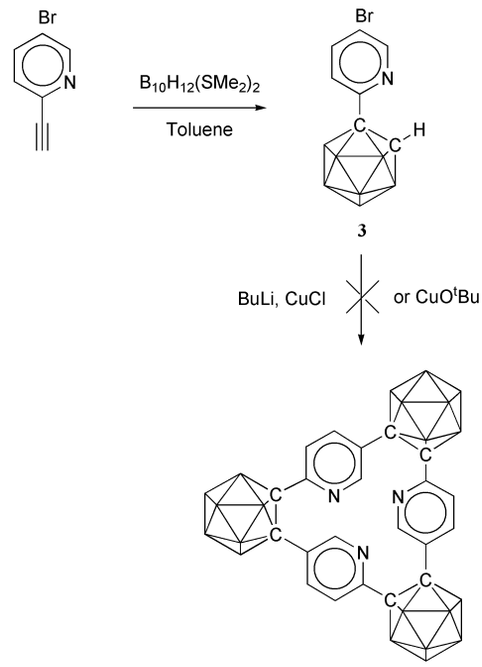


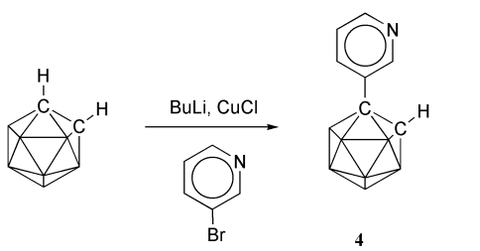
Scheme 1

Here we outline the preparation of new pyridyl derivatives of *ortho*-carborane, 1-(5′-bromo-2′-pyridyl)-*ortho*-carborane **3** and 1-(3′-pyridyl)-*ortho*-carborane **4** (Scheme 2) and discuss the various hydrogen bonds present in the crystal structures of all four compounds (**1**–**4**) determined by X-ray diffraction. We also demonstrate the accuracy of MP2-optimized geometries of **1**, **2**

† Electronic supplementary information (ESI) available: rotatable 3-D molecular structure diagrams of experimental structures of **1**–**4** and of MP2/6-31G* optimised geometries **1a**–**7b** in CHIME format. Computed GIAO NMR data for **1b**–**4c**. See http://www.rsc.org/suppdata/dt/b2/b209931d/

DOI: 10.1039/b209931d





Scheme 2

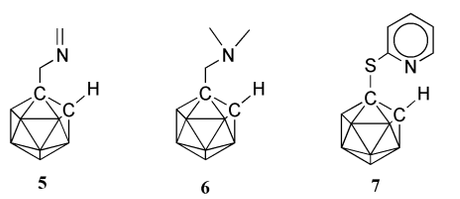


Fig. 1 Related carborane derivatives **5**–**7**

and **4** and compare experimental and theoretical NMR data for **1**, **2** and **4** and the related carboranes **5**–**7** (see Fig. 1) in order to show the presence of an intramolecular carboranyl C–H ⋯ N bond in solution for **1**.

Experimental

All manipulations were carried out under dry, oxygen-free N_2. Commercial grade acetonitrile, pentane, *n*-butyllithium solution and 2-picolyl chloride hydrochloride were used without further purification. Commercial *ortho*-carborane was purified by vacuum sublimation (50 °C, 0.01 mmHg). Dry Et_2O, toluene and dimethoxyethane (DME) were obtained by reflux and distillation over Na wire. Dry CH_2Cl_2 was obtained by reflux and distillation over CaH_2. Demineralised water was used in aqueous stages of syntheses. Compound **1** was prepared by the literature method.[9]

Infrared spectra were recorded as KBr discs using a Perkin Elmer 1720X FTIR spectrometer. Mass spectra were recorded on a VG Micromass 7070E instrument under EI conditions at 70 eV. Elemental analyses were performed using Exeter Analytical CE-440 apparatus. NMR spectra including ^1H–^{13}C correlation, 2D ^{11}B–$^{11}B\{^1H\}$ COSY and $^1H\{^{11}B$ selective$\}$ were recorded as room temperature solutions on a Varian Unity 300 MHz (^1H, ^{11}B, ^{13}C) spectrometer. ^1H NMR spectra were referenced to residual protio impurity in the solvent ($CDCl_3$, 7.26 ppm; C_6D_6, 7.15 ppm; C_5D_5N, 8.71, 7.56, 7.20 ppm). ^{13}C NMR spectra were referenced to the solvent resonance ($CDCl_3$, 77.0 ppm; C_6D_6, 128.0 ppm; C_5D_5N, 149.9, 135.5, 123.5 ppm). ^{11}B NMR spectra were referenced externally to $Et_2O{\cdot}BF_3$, $\delta = 0.0$ ppm.

Spectroscopic data for 1-(2′-pyridyl)-*ortho*-carborane 1

NMR ($CDCl_3$); δ $^1H\{^{11}B\}$: 8.41 (1H, d, *J* 4.5, H6′), 7.70 (1H, dd, *J* ~8.2, H4′), 7.50 (1H, d, *J* 8.0, H3′), 7.30 (1H, dd, *J* 8.5, 4.5 Hz, H5′), 5.00 (1H, s, C2H), 2.48 (s, 2H, B4,5H), 2.37 (s, 1H, B9H), 2.33 (s, 5H, B3,6,8,10,12H), 2.25 (s, 2H, B7,11H): δ ^{11}B: −2.9 (d, 1B, *J* 148, B9), −3.7 (d, 1B, *J* 151, B12), −8.2 (d, 2B, *J* ~149, B8,10), −10.3 (d, 2B, B3,6), −11.1 (d, 2B, B4,5), −13.0 (d, 2B, *J*~164 Hz, B7,11). δ ^{13}C: 151.0 (C2′), 148.7 (C6′), 137.3 (C4′), 124.3 (C5′), 121.5 (C3′), 75.3 (C1), 56.8 (C2).

Preparation of 1-(2′-picolyl)-*ortho*-carborane 2

To a solution of *ortho*-carborane (302 mg, 2.1 mmol) in dry Et_2O (30 cm^3) at −78 °C was added 1.46 M of n-BuLi in hexanes (1.45 cm^3, 2.1 mmol) and the reaction mixture was stirred for 1 h at –78 °C. In a separate vessel 2-picolyl chloride hydrochloride (508 mg, 3.1 mmol) was dissolved in Et_2O (80 cm^3) and $NaHCO_3$ (430 mg, 5.0 mmol, 60% excess) was added to neutralise the HCl. After stirring for 1 h, the unreacted $NaHCO_3$ was removed by filtration and the solution dried over Na_2SO_4. Ether was then removed *in vacuo* to give 2-picolyl chloride (319 mg, 2.5 mmol) as pale pink oil. To the previously formed suspension of 1-lithio-*o*-carborane in Et_2O was added, at −78 °C, 2-picolyl chloride (268 mg, 2.1 mmol) and the stirred reaction mixture was allowed to warm to room temperature for 1 h. Addition of water (30 cm^3) dissolved the nascent LiCl and the separated Et_2O layer was further washed with water (2 × 30 cm^3) before being isolated and dried over Na_2SO_4. Filtration, followed by removal of the solvent *in vacuo* gave a white solid. Unreacted *ortho*-carborane was removed by slow vacuum sublimation (40 °C, 0.01 mmHg) to give analytically pure **2** (280 mg, 57% yield (94% conversion allowing for recovered *ortho*-carborane)). Mp 79.5–80.0 °C. Found: C, 41.1; H, 7.5; N 6.0. $C_8B_{10}H_{17}N$ requires: C, 40.8; H, 7.3; N, 6.0%. EI-MS: *m*/*z* 233–237, $M^+_{(max)}$ 235. ν_{max}/cm^{-1}: 3017m (br) (carborane CH), 2916w, 2848w (pyridyl/CH_2 str.); 2596vs, 2576s (BH); 1593s, 1571m, 1476s, 1438s (pyridyl skel.) 1095m, 1063m, 1022m, 771s, 750m (CH o.o.p. and carborane skel.) 729s (br) (BH wag). NMR ($CDCl_3$); δ $^1H\{^{11}B\}$: 8.56 (1H, d, *J* 4.5, H6′), 7.71 (1H, dd, *J* ~ 8.0, H4′), 7.28 (1H, dd, *J* 8.5, 4.5, H5′), 7.17 (1H, d, *J* 7.5 Hz, H3′), 4.07 (1H, s, C2H), 3.66 (s, 2H, CH_2), 2.34 (s, 1H, B9H), 2.23 (s, 2H, B4,5H), 2.13 (s, 5H, B3,6,8,10,12H), 2.10 (s, 2H, B7,11H). δ ^{11}B: −1.5 (d, 1B, *J* 154, B9), −4.0 (d, 1B, *J* 146, B12), −9.3 (d, 2B, *J* ~149, B8,10), −10.5 (d, 2B, B4,5), −11.5 (d, 2B, B3,6), −12.4 (d, 2B, *J* ~161 Hz, B7,11). δ ^{13}C: 155.2 (C2′), 149.8 (C6′), 137.2 (C4′), 124.4 (C5′), 123.0 (C3′), 73.3 (C1), 58.4 (C2), 45.0 (CH_2).

Preparation of 1-(5′-bromo-2′-pyridyl)-*ortho*-carborane 3

5-Bromo-2-ethynylpyridine[15] (7.1 g) in toluene (83 cm^3) was added over 7 h to a solution of decaborane–dimethylsulfide complex (11.63 g) in toluene (67 cm^3) with stirring at bath temperature 80–82 °C. After a further 3 h at this temperature the solution was allowed to stand at room temperature for 7 days, decanted from resinous insoluble matter, and evaporated. The semi-solid residue (*ca*. 14 g) was extracted with ether (6 × 30 cm^3) and the residue after evaporation of ether was slowly sublimed at bath temperature (75–80 °C, 0.005 mmHg). The sublimate (5.56 g) was dissolved in hot ethanol, with effervescence, and the carborane (3.80 g, 32%), mp 137–138 °C, which crystallised on standing was dried *in vacuo* at room

temperature. Found: C, 27.2; H, 4.8; N, 4.5. $C_7H_{14}B_{10}BrN$ requires: C, 28.0; H, 4.7; N, 4.7%. ν_{max}/cm^{-1}: 3064 (carborane CH); 2958w, 2924w, 2856w (pyridine CH); 2656, 2623, 2609, 2591vs, 2566vs (BH); 1570, 1558, 1453, 1363 (pyridine skel.); 1283; 1156; 1130w; 1093; 1070; 1023; 1007; 885; 839 (pyridyl CH o.o.p.); 725 (carborane skel.); 631w; 491. NMR ($CDCl_3$); $\delta^1H\{^{11}B\}$: 8.47 (d, 1H, *J* 2.0, H6′), 7.83 (dd, 1H, *J* 8.5, 2.0, H4′); 7.43 (d, 1H, *J* 8.5 Hz, H3′); 4.88 (C2H); 2.43 (2H, B4,5H), 2.37 (1H, B9H), 2.33 (5H, B3,6,8,10,12H), 2.25 (B7,11H). δ $^{11}B\{^1H\}$: −3.0 (1B, B9), −3.8 (1B, B12), −8.3 (2B, B8,10), −10.6 (2B, B3,6), −11.4 (2B, B4,5), −13.1 (2B, B7,11). δ $^{13}C\{^1H\}$: 149.9 (C6′), 149.6 (C2′), 139.9 (C4′), 122.8 (C3′), 121.8 (C5′), 74.4 (C1), 56.8 (C2). EI-MS: 292–304, 300.30 and 301.30 (100%), M^+.

Attempted cyclotrimerisation of 3

(a) Using butyllithium. A solution of bromopyridylcarborane (2.03 g) in dimethoxyethane (50 cm^3) was cooled to −70 °C and butyllithium (2.75cm^3, 2.5 M) was added dropwise. The mixture was allowed to warm to 0 °C and pyridine (4.0 cm^3) followed by copper(I) chloride (1.13 g) added. The red–brown solution was heated to 70–72 °C (bath temperature) for 3 h, cooled and the products isolated using ether and aqueous acid, followed by chromatography on silica eluted with 15% v/v dichloromethane in cyclohexane to give 1-(2′-pyridyl)-*ortho*-carborane **1** with traces of two more polar compounds.

(b) Using copper(I) *tert*-butoxide. Copper(I) chloride (804 mg) was added to a stirred solution of potassium *tert*-butoxide (793 mg) in dimethoxyethane (40 cm^3). After 4 h the solution was cooled to −45 °C, pyridine (1.8 cm^3) was added followed after 15 h by the bromopyridylcarborane (2.01 g) in dimethoxyethane (20 cm^3) dropwise during 8 min. The mixture was allowed to warm to room temperature during 1.5 h, heated to *ca.* 80 °C for 15 h and refluxed for 24 h. Isolation as before gave a 1:1 mixture (IR, TLC) of the starting carborane **3** and 1-(2′-pyridyl)-*ortho*-carborane **1** (1.42 g) with traces of more polar material.

Preparation of 1-(3′-pyridyl)-*ortho*-carborane 4

Under nitrogen, *ortho*-carborane (1.44 g; 10 mmol) was dissolved in 100 ml of DME and lithiated with a 2.5 M solution of butyllithium in hexanes (9.5 ml, 24 mmol). After 40 min copper(I) chloride (2.23 g, 22 mmol) and pyridine (13 ml) were added to the cloudy solution which turned black. After 1 h refluxing, the 3-bromopyridine (2 ml, 21 mmol) was added and the solution left to reflux under nitrogen for 7 days. The resulting deep red cloudy solution was cooled and stirred with ether (100 ml). The precipitate was filtered off and the green filtrate was washed with 2 M HCl (3 × 70 ml) and water (3 × 50 ml). The organic layer was dried over $MgSO_4$, filtered and pumped to dryness. The pale yellow solid was purified by column chromatography on silica with chloroform as eluent to give 0.74 g (33%) of **4**. Mp 129 °C. ν_{max}/cm^{-1}:3024m (carboranyl C–H), 2963m; 2640m, 2629m, 2616m, 2590s, 2555s (BH); 1476m, 1420m, 1261s, 1097s, 1075s, 1020s, 800s, 704m. Found: C, 36.6; H, 7.0; N, 4.7. $C_7H_{15}B_{10}N$ requires: C, 38.0; H, 6.8; N, 6.3%. NMR ($CDCl_3$); δ $^1H\{^{11}B\}$: 8.75 (s, 1H, H2′), 8.73 (d, 1H, *J* 4.5, H6′), 7.81 (d, 1H, *J* 8.5 Hz, H4′), 7.28 (1H, dd, *J* 8.5, 4.5, H5′), 3.96 (C2H), 2.62 (2H, B3,6H), 2.47 (3H, B4,5,9H), 2.35 (3H, B8,10,12H), 2.30 (2H, B7,11H). δ $^{11}B\{^1H\}$: −1.5 (1B, B9), −3.6 (1B, B12), −8.6 (2B, B8,10), −10.7 (2B, B4,5), −11.5 (2B, B3,6), −12.4 (2B, B7,11). δ $^{13}C\{^1H\}$: 151.0 (C6′), 148.3 (C2′), 135.4 (C4′), 129.6 (C3′), 123.3 (C5′), 73.6 (C1), 60.1 (C2).

NMR data for *ortho*-carborane

δ ^1H (C_5D_5N): 4.93 (C1,2H), 2.68 (B9,12H), 2.53 (B8,10H), 2.49 (B3,6H), 2.34 (B4,5,7,11H). δ ^1H ($CDCl_3$): 3.55 (C1,2H), 2.31 (B3,6,9,12H), 2.21 (B8,10H), 2.12 (B4,5,7,11H). δ ^1H (C_6D_6): 2.84 (B9,12H), 2.63 (B8,10H), 2.13 (B4,5,7,11H), 2.04 (C1,2H), 1.86 (B3,6H).

δ ^{11}B ($CDCl_3$):[16] −2.9 (B9,12), −9.6 (B8,10), −14.0 (B4,5,7,11), −15.1 (B3,6). δ ^{11}B (C_5D_5N): −2.6 (B9,12), −9.1 (B8,10), −13.2 (B4,5,7,11), −14.1 (B3,6). δ ^{11}B (C_6D_6): −2.2 (B9,12), −9.1 (B8,10), −13.6 (B4,5,7,11), −14.9 (B3,6).

δ ^{13}C (C_5D_5N): 57.0. δ ^{13}C ($CDCl_3$): 54.5. δ ^{13}C (C_6D_6): 54.5.

NMR data for 1-methyl-*ortho*-carborane

δ ^1H (C_5D_5N): 5.03 (C2H), 2.68 (B9H), 2.50 (B8,10,12H), 2.40 (B3,6H), 2.36 (B4,5,7,11H), 1.96 (CH_3). δ ^1H ($CDCl_3$): 3.58 (C2H), 2.35 (B3,6H), 2.31 (B9H), 2.22 (B4,5H), 2.18 (B7,8,10,11H), 2.10 (B12H), 2.05 (CH_3). δ ^1H (C_6D_6): 2.90 (B9H), 2.70 (B12H), 2.66 (B8,10H), 2.27 (B4,5H), 2.22 (B7,11H), 2.12 (C2H), 1.93 (B3,6H), 1.07 (CH_3).

δ ^{11}B (C_5D_5N): −1.9 (B9), −6.5 (B12), −9.0 (B8,10), −10.2 (B4,5), −10.9 (B3,6), −12.3 (B7,11). δ ^{11}B ($CDCl_3$): −1.7 (B9), −6.7 (B12), −9.1 (B8,10), −10.5 (B4,5), −11.2 (B3,6), −12.6 (B7,11). δ ^{11}B (C_6D_6): −1.4 (B9), −6.2 (B12), −8.8 (B8,10), −10.4 (B4,5), −11.4 (B3,6), −12.5 (B7,11).

δ ^{13}C (C_5D_5N): 71.7 (C1), 63.4 (C2), 25.2 (CH_3). δ ^{13}C ($CDCl_3$): 70.4 (C1), 61.5 (C2), 25.8 (CH_3). δ ^{13}C (C_6D_6): 70.1 (C1), 61.5 (C2), 24.9 (CH_3).

NMR data for 1-phenyl-*ortho*-carborane

δ ^1H (C_5D_5N): 7.67 (C2′,6′H), 7.34 (C3′,4′,5′H), 5.69 (C2H), 2.78 (B9H), 2.68 (B3,4,5,6,12H), 2.64 (B8,10H), 2.48 (B7,11H). δ ^1H ($CDCl_3$): 7.50 (C2′,6′H), 7.38 (C4′H), 7.34 (C3′,5′H), 3.97 (C2H), 2.62 (B3,6H), 2.53 (B4,5H), 2.46 (B9H), 2.35 (B8,10,12H), 2.30 (B7,11H). δ ^1H (C_6D_6): 6.90 (C2′,6′H), 6.88 (C4′H), 6.77 (C3′,5′H), 3.02 (B9H), 2.86 (C2H, B12H), 2.80 (B8,10H), 2.64 (B4,5H), 2.34 (B3,6,7,11H).

δ ^{11}B (C_5D_5N): −0.9 (B9), −2.7 (B12), −7.1 (B8,10), −9.0 (B3,6,4,5), −10.9 (B7,11). δ ^{11}B ($CDCl_3$):[17] −1.2 (B9), −3.5 (B12), −8.1 (B8,10), −9.9 (B4,5), −10.3 (B3,6), −11.9 (B7,11). δ ^{11}B (C_6D_6): –1.7 (B9), −3.9 (B12), −8.6 (B8,10), −10.5 (B4,5), −11.2 (B3,6), −12.5 (B7,11).

δ ^{13}C (C_5D_5N): 134.0 (C1′), 130.2 (C4′), 129.3 (C3′,5′), 127.9 (C2′,6′), 77.5 (C2), 61.7 (C2). δ ^{13}C ($CDCl_3$): 133.4 (C1′), 129.9 (C4′), 128.8 (C3′,5′), 127.5 (C2′,6′), 76.5 (C1), 60.1 (C2). δ ^{13}C (C_6D_6): 133.5 (C1′), 129.6 (C4′), 128.6 (C3′,5′), 127.6 (C2′,6′), 76.6 (C1), 60.2 (C2).

X-Ray crystallography

Single crystals of **1** (colourless) were grown from acetonitrile at 4 °C, of **2** from Et_2O, **3** from Et_2O–CH_2Cl_2 and **4** from ethanol at room temperature. X-Ray diffraction experiments for **1** and **2** were carried out on a Rigaku AFC6S diffractometer (graphite-monochromated Cu-Kα radiation), for **3** and **4** on a SMART 3-circle diffractometer with a 1K CCD area detector (graphite-monochromated Mo-Kα radiation). A Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat was used for low-temperature experiments. All structures were solved by direct methods and refined by full-matrix least squares against F^2 of all reflections, using SHELXTL software.[18] Carbon atoms in the carborane cages could be clearly distinguished from boron by the bond distances and electron density concentration. H atoms were located in difference Fourier syntheses; in all of **1**–**4** their refinement showed a significant difference between the C–H and B–H bond lengths in the carborane moiety, *e.g.* 0.96(2) Å and (the average) 1.14 Å, respectively, in **4**. This also confirms the location of the cage carbon atoms. In the final refinement, the H atoms participating in hydrogen bonds were refined in isotropic approximation. The crystal data and experimental details are listed in Table 1.

CCDC reference numbers 162846, 162847, 195131 and 195132.

Table 1 Crystal data

Compound	**1**	**2**	**3**	**4**
Formula	$C_7H_{15}B_{10}N$	$C_8H_{17}B_{10}N$	$C_7H_{14}B_{10}BrN$	$C_7H_{15}B_{10}N$
M	221.30	235.33	300.20	221.30
T/K	150	295	150	150
λ/Å	1.54178	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P2/c$ (no. 13)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	7.057(3)	8.887(1)	7.147(1)	7.239(1)
b/Å	18.029(3)	7.170(2)	18.867(4)	7.700(1)
c/Å	9.899(4)	21.945(3)	10.082(2)	11.198(2)
α/°	90	90	90	100.05(1)
β/°	92.54(4)	90.22(1)	91.38(3)	92.30(1)
γ/°	90	90	90	90.57(1)
U/Å^3	1258.2(8)	1398.3(4)	1359.1(5)	614.0(2)
Z	4	4	4	2
D_c/g cm^{-3}	1.168	1.118	1.467	1.197
μ/mm^{-1}	0.39	0.38	3.00	0.06
Reflections measured	1984	2742	14930	4529
Unique reflections	1780	2598	3599	2783
R_{int}	0.028	0.023	0.068	0.020
R [$F^2 \geq 2\sigma(F^2)$]	0.047	0.056	0.049	0.049
$wR(F^2)$, all data	0.136	0.184	0.126	0.145

See http://www.rsc.org/suppdata/dt/b2/b209931d/ for crystallographic data in CIF or other electronic format.

Computational section

All *ab initio* computations were carried out with the Gaussian 98 package.[19] The geometries **1a**–**7b** discussed here were optimised at the HF/6-31G* level with no symmetry constraints. Frequency calculations were computed on these optimised geometries at the HF/6-31G* level for imaginary frequencies. Optimisation of these geometries were then carried out at the MP2/6-31G* level. Calculated NMR shifts at the GIAO-B3LYP/6-311G* level were then obtained from these MP2-optimized geometries. Theoretical ^{11}B chemical shifts at the GIAO-B3LYP/6-311G*//MP2/6-31G* level were referenced to B_2H_6 (16.6 ppm[20]) and converted to the usual $BF_3{\cdot}OEt_2$ scale: $\delta(^{11}B) = 102.83 - \sigma(^{11}B)$. The ^{13}C and ^{1}H chemical shifts were referenced to TMS: $\delta(^{13}C) = 184.81 - \sigma(^{13}C)$; $\delta(^1H) = 32.28 - \sigma(^1H)$. Relative energies were computed at the MP2/6-31G* level with ZPE (calculated at HF/6-31G*) corrections scaled by 0.89.

Calculated NMR data for **1a**: δ ^{1}H: 8.62 (H6′), 7.78 (H4′), 7.65 (H3′), 7.28 (H5′), 5.08 (C2H), 2.97 (B9,12H), 2.96 (B4,5H), 2.95 (B8,10H), 2.78 (B7,11H), 2.74 (B3,6H): δ ^{11}B: −3.0 (B9), −3.2 (B12), −8.2 (B8,10), −11.9 (B3,6), −12.3 (B4,5), −14.3 (B7,11). δ ^{13}C: 163.2 (C2′), 155.9 (C6′), 142.8 (C4′), 129.0 (C5′), 128.3 (C3′), 81.0 (C1), 61.5 (C2). Calculated NMR data for **1b**–**7b** are available in the ESI.†

Calculated NMR data for *ortho*-carborane: δ ^{1}H: 3.26 (C1,2H), 2.97 (B9,12H), 2.82 (B8,10H), 2.75 (B3,6H), 2.65 (B4,5,7,11): δ ^{11}B:[16] −2.0 (B9,12), −9.3 (B8,10), −14.7 (B4,5,7,11), −16.7 (B3,6). δ ^{13}C: 59.3.

Results and discussion

Preparative aspects

While the 2-pyridyl carborane **1** was prepared as described previously,[9] the synthesis of picolyl carborane **2** here differs from the reported method[14] by using ether instead of THF as solvent and using picolyl chloride instead of picolyl chloride hydrochloride. The yields and characterization data for **2** between the two methods are similar.

The carborane 1-(5′-bromo-2′-pyridyl)-*ortho*-carborane **3** was prepared as a potential precursor for the "triangular" system containing three *para*-pyridylene units (Scheme 2). The bromo carborane **3** was made in 32% yield from the decaborane–dimethylsulfide adduct and the alkyne, 5-bromo-2-ethynylpyridine.[15] Metallation of the bromopyridylcarborane **3** with equimolar proportions of either butyllithium and copper(I) chloride, or copper(I) *tert*-butoxide, gave (after acid work-up) the debrominated pyridyl carborane **1** and the starting carborane **3** rather than the "triangular" system. Metallation probably occurs on the pyridine ring with displacement of bromine. The iodinated analogue, 1-(5′-iodo-2′-pyridyl)-*ortho*-carborane, may be a better precursor to the "triangular" system but the alkyne, 5-iodo-2-ethynylpyridine, needed to make the carborane is not known.

Compound **4**, 1-(3′-pyridyl)-*ortho*-carborane, was obtained by the general Ullman-type coupling between a copper derivative of *ortho*-carborane and 3-bromopyridine. No disubstituted product 1,2-di-(3′-pyridyl)-*ortho*-carborane was found even with the appropriate ratio of reagents.

Structural aspects

The X-ray crystal structure of a molecule of **1** (Fig. 2) reveals an intramolecular C–H ⋯ N hydrogen bond (see Table 2). The

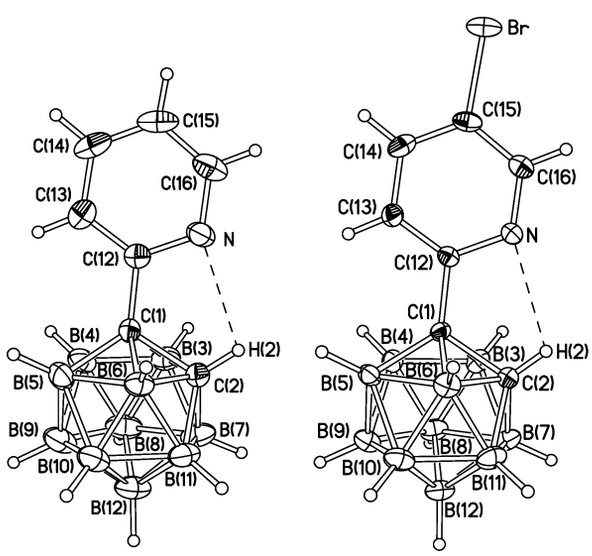


Fig. 2 Molecules of **1** (left) and **3** (right) in crystal. Here and forthwith thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths in Å for **1**: C(1)–C(2) 1.632(3), N–C(12) 1.335(3), N–C(16) 1.342(3), C(1)–C(12) 1.513(3), C(2)–H(2) 0.98(2), H(2) ⋯ N 2.42(2); for **3**: C(1)–C(2) 1.639(5), N–C(12) 1.339(4), N–C(16) 1.340(4), C(1)–C(12) 1.515(3), Br(1)–C(6) 1.896(3), C(2)–H(2) 0.93(4), H(2) ⋯ N 2.43(4).

Table 2 Energies of minima **1a**–**7b** and carboranyl C–H proton NMR peak shifts[a]

Optimized geometry	ZPE/ kcal mol^{-1}	MP2/a.u.	Relative energy/ kcal mol^{-1}	Calculated C–H shift/ppm	Observed C–H shift/ppm
1-(2′-C_5H_4N)-*ortho*-$C_2B_{10}H_{11}$ **1a**	164.07(0)	−577.17304	0	5.08	5.00 (**1**)
1-(2′-C_5H_4N)-*ortho*-$C_2B_{10}H_{11}$ **1b**	163.91(0)	−577.16422	5.4	3.62	
Av. **1a/1b**				*4.35*	
1-(2′-$C_5H_4NCH_2$)-*ortho*-$C_2B_{10}H_{11}$ **2a**	183.50(0)	−616.33906	0	4.76	
1-(2′-$C_5H_4NCH_2$)-*ortho*-$C_2B_{10}H_{11}$ **2b**	183.37(0)	−616.33508	2.4	3.45	
Av. **2a/2b**				*4.10*	4.07 (**2**)
1-(3′-C_5H_4N)-*ortho*-$C_2B_{10}H_{11}$ **4a**	164.17(0)	−577.16243	0	4.03	
1-(3′-C_5H_4N)-*ortho*-$C_2B_{10}H_{11}$ **4b**	164.24(0)	−577.16168	0.5	3.35	
1-(3′-C_5H_4N)-*ortho*-$C_2B_{10}H_{11}$ **4c**	164.14(0)	−577.16157	0.5	3.82	
Av. **4a/4b/4c**				*3.73*	3.96 (**4**)
1-(H_2C=NCH_2)-*ortho*-$C_2B_{10}H_{11}$ **5a**	151.40(0)	−463.15991	0	4.08	4.44[22,b]
1-(H_2C=NCH_2)-*ortho*-$C_2B_{10}H_{11}$ **5b**	151.22(0)	−463.15467	3.1	3.01	
Av. **5a/5b**				*3.55*	
1-(Me_2NCH_2)-*ortho*-$C_2B_{10}H_{11}$ **6a**	186.20(0)	−503.50799	0	4.42	
1-(Me_2NCH_2)-*ortho*-$C_2B_{10}H_{11}$ **6b**	186.09(0)	−503.50397	2.4	3.24	
Av. **6a/6b**				*3.83*	3.99[13] (**6**)
1-(2′-C_5H_4NS)-*ortho*-$C_2B_{10}H_{11}$ **7a**	164.68(0)	−974.79577	0	4.97	
1-(2′-C_5H_4NS)-*ortho*-$C_2B_{10}H_{11}$ **7b**	164.56(0)	−974.79163	2.5	3.42	
Av. **7a/7b**				*4.20*	4.41[24] (**7**)

[a] ZPE = zero point energy at HF/6-31G* level, number of imaginary frequencies in brackets. Non-SI unit employed: 1 kcal mol^{-1} = 4.184 kJ mol^{-1}. Calculated shifts at GIAO-B3LYP/6-311G*//MP2/6-31G* level. Observed shifts in $CDCl_3$. [b] For 1-(Ph_2C=N)CH_2-*ortho*-carborane.

pyridine ring turns its nitrogen atom towards the unsubstituted carbon atom C(2) of the cage: the N(1)–C(12)–C(1)–C(2) torsion angle is 8.3(3)°. In the two crystalline polymorphs of the similarly structured 1-phenyl-*ortho*-carborane, the smaller C(2)–C(1)–C(Ph)–C(Ph) torsion angles are 22.3(3) and 18.3(2)°.[17,21]The pyridyl group tilts slightly towards the cage CH unit with the C(12)–C(1)–C(2) angle of 117.1(3)°. Compound **1** is monomeric in the crystal—the distances between the cage C–H unit of one molecule and the pyridyl nitrogen atom of neighbouring molecules are too great (H ··· N > 5.7 Å) to be compatible with intermolecular hydrogen bonding. The pyridyl rings in crystals of **1** lie in parallel planes (Fig. 3) and are

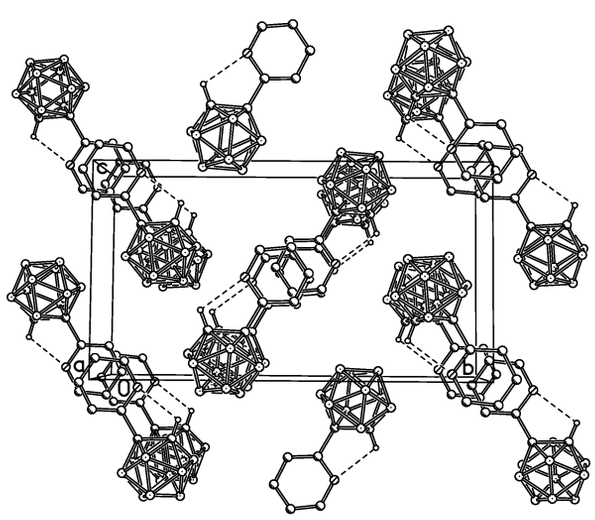


Fig. 3 Crystal packing of **1**.

partially overlapped, with alternating inter-plane distances of 3.44 and 3.53 Å, consistent with π-stacking.

The X-ray crystal structure of **2** showed it to be dimeric in the solid state (Fig. 4), the monomer units being held together by a peculiar bifurcated hydrogen bond (intermolecular H ··· N 2.40(3) Å; intramolecular H ··· N 2.61(4) Å). The carboranyl

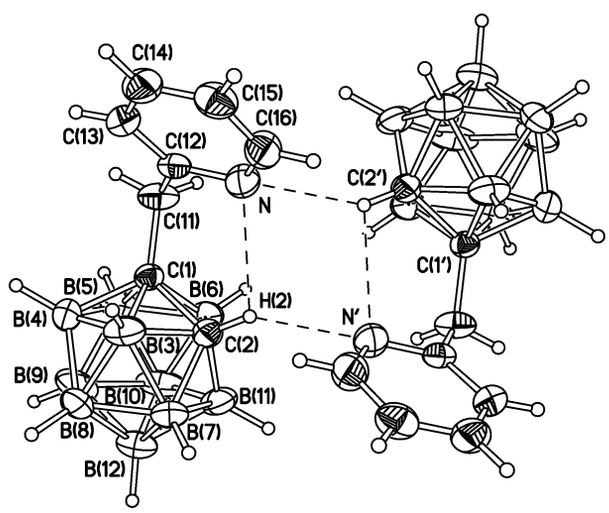


Fig. 4 Molecule of **2** and its equivalent, generated by twofold axis (primed atoms). Selected bond lengths in Å for **2**: C(1)–C(2) 1.622(4), N–C(12) 1.332(3), N–C(16) 1.331(4), C(1)–C(11) 1.535(3), C(11)–C(12) 1.501(4), C(2)–H(2) 0.98(3), H(2) ··· N 2.61(4), H(2) ··· N′ 2.40(3).

C–H unit interacts at comparable distances with the nitrogen atom of the same molecule (which is brought to the proximity of H(2) by the torsion angles C(2)–C(1)–C(11)–C(12) –49.4(4)° and C(1)–C(11)–C(12)–N 70.6(3)°) and with that of another molecule, related to the former by the twofold axis.

The crystal structure of **3** (Fig. 2) is pseudo-isomorphous with that of **1**. It displays a similar molecular conformation (the N(1)–C(12)–C(1)–C(2) torsion angle of 12.6(4)°), substituent tilt (C(2)–C(1)–C(12) 117.1(3)°) and hydrogen bonding (H ··· N 2.42(2) Å). The bromine atom forms no shortened intermolecular contacts and apparently does not affect the packing mode in any significant way.

A different pattern exists in the crystal structure of **4**, where similar intramolecular hydrogen bonding is sterically impossible. Thus the two molecules symmetrically related by an inversion centre, form a pair of *intermolecular* C–H ··· N hydrogen bonds (Fig. 5), while the C(2)–C(1)–C(13)–C(12) torsion angle is increased to 92.6(2)° in contrast to the range of torsion angles

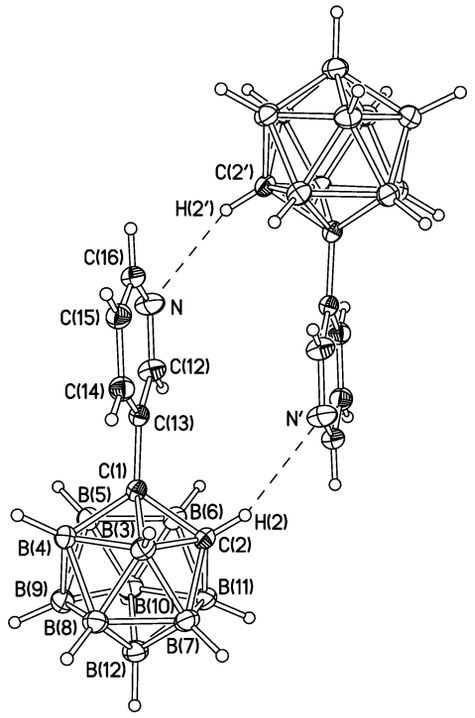


Fig. 5 Molecule of **4** and its equivalent, generated by an inversion centre (primed atoms). Selected bond lengths in Å: C(1)–C(2) 1.663(2), C(2)–H(2) 0.95(2), H(2) · · · N′ 2.53(2).

between 8.3 and 22.3° found for **1**, **3** and 1-phenyl-*ortho*-carborane. These torsion angles are required to accommodate the intermolecular hydrogen bonds (H · · · N 2.53(2) Å) in the dimer.

A survey of the Cambridge Crystallographic Database (October 2001 release) revealed three more structures of 1-substituted *ortho*-carboranes, that contain carboranyl C–H · · · N bonds shorter than 2.8 Å where these bonds were not mentioned in the papers cited. The compound 1-(Ph_2C=NCH_2)-*ortho*-carborane[22] forms an intramolecular hydrogen bond (C–H 0.92, H · · · N 2.48 Å) similar to **1** and **3** whereas intermolecular hydrogen bonds are present in 1-(terpyridyl)-*ortho*-carborane[23] (C–H 0.99, H · · · N 2.50 Å) similar to **4**. Interestingly 1-(2′-pyridylmercapto)-*ortho*-carborane[24] **7** is pseudo-isomorphous with **2** and contains a bifurcated hydrogen bond with the distances C–H 0.85 Å, intramolecular H · · · N 2.53 Å and intermolecular H · · · N 2.66 Å.

Computational aspects

The strengths of the carboranyl C–H · · · N hydrogen bonds investigated here may be calculated by looking at relative energies of minima located within the same compound. Fig. 6 shows the MP2-optimized geometries **1a**–**7b** carried out in this study and Table 2 lists their absolute and relative energies.

For the pyridyl compound **1**, two minima are found with **1a** being lower in energy than **1b** by *ca.* 5.4 kcal mol^{-1}. The torsional angles of cage C–cage C–aryl C–nitrogen are 0 and 146.8° for **1a** and **1b**, respectively. Clearly the geometry permitting the intramolecular C–H · · · N hydrogen bond is highly favourable and the pyridyl group is very likely to adopt a particular conformation in the solid and solution state. The X-ray geometry of **1** is similar to **1a** but has a slightly different torsional angle of 8.3°—presumably due to crystal packing.

Two minima, **2a** and **2b**, were located for the picolyl carborane **2**, the geometry **2a** with a carboranyl C–H · · · N bond is only 2.4 kcal mol^{-1} lower in energy compared to **2b**. As clearly shown between Fig. 3 and minimum **2a** in Fig. 5, the experimental X-ray geometry of **2** and the optimized geometry **2a** are similar. However the intermolecular N · · · H bonds present in the crystal lengthen the intramolecular C–H · · · N bond in **2** compared to the latter bond in the optimised geometry **2a**.

For compound **4**, where an intramolecular C–H · · · N bond is geometrically impossible, three minima were located: **4a**, **4b** and **4c**—with **4a** as the lowest energy minimum with an energy difference of only 0.5 kcal mol^{-1} compared to **4b** and **4c**. This is expected as the phenyl group in the related 1-phenyl-*ortho*-carborane also has a low rotation barrier with two minima located (similar conformations to **4a/4c** and **4b**) with an energy difference of only 0.3 kcal mol^{-1} (at HF/6-31G*).[17] The intermolecular C–H · · · N bonds play an important role in the conformation of **4** in the solid state. The experimental geometry found is very similar to minimum **4b**. An interesting observation in these geometries is the substantially longer cage C–cage C bond lengths of 1.663(2) Å in **4** and 1.655 Å in **4b** compared to others discussed with values ranging from 1.622(2) to 1.639(5) for experimental data of **1**–**3** and from 1.626 to 1.638 for minima **1a**–**4a** and **4c**.

As other compounds containing the expected carboranyl C–H · · · N intramolecular bond have been reported it was of interest to calculate their hydrogen bond strengths by the same principle. For 1-(Ph_2C=NCH_2)-*ortho*-carborane,[22] a model geometry 1-(H_2C=NCH_2)-*ortho*-carborane **5** was optimised and two minima, **5a** and **5b**, were located. A difference of 3.1 kcal mol^{-1} in energy between these minima is found with the minimum containing the C–H · · · N bond being lower in energy. Differences in energy for the minima in 1-(Me_2NCH_2)-*ortho*-carborane[12,13] (**6a** and **6b**) and 1-(2′-C_5H_4N)S-*ortho*-carborane[24] (**7a** and **7b**) were 2.4–2.5 kcal mol^{-1} with the carboranyl C–H · · · N bonds present in the lower energy minima (**6a** and **7a**). Similarly for **2a** and **2**, a good agreement is found between geometries of the minimum **7a** and the X-ray structure of 1-(2′-C_5H_4N)S-*ortho*-carborane **7**.

Spectroscopic aspects

IR spectroscopy has long been demonstrated as a tool for evidence of carboranyl C–H · · · A bonding by comparison of the shifts assigned to the characteristic carboranyl C–H stretching mode in the 3100–3000 cm^{-1} region between the IR spectra of the free carborane and the carborane adduct.[25–27] However the presence of carboranyl C–H · · · A hydrogen bonding cannot be confirmed by comparing the C–H shifts of substituted carboranes with the parent carborane, reported in several papers,[4,6] as the substituents themselves can also be responsible for the change in the shifts. The carboranyl C–H stretch frequencies of **1** (3070 cm^{-1}) and **3** (3064 cm^{-1}) with intramolecular C–H · · · A hydrogen bonding are very similar to that of *ortho*-carborane (3070 cm^{-1}) whereas those of **2** (3017 cm^{-1}) and **4** (3024 cm^{-1}) are quite different.

A significant change in the carboranyl C–H stretch frequencies between solid-state and solution-state IR spectra indicates evidence of intermolecular C–H · · · A hydrogen bonding. For **2** and **4** the shift differences to lower energies are 46 and 45 cm^{-1}, respectively, whereas for **1** and **3** they are 10 and 14 cm^{-1}. Allowing for solvent effects, compounds **2** and **4** do contain intermolecular hydrogen bonds in the solid state whereas compounds **1** and **3** do not.

Unlike IR spectroscopy, NMR spectroscopy has not been widely used to investigate carboranyl C–H · · · A hydrogen bonding in carborane derivatives. It is well known that the proton shift of the carboranyl C–H proton peak is very sensitive to the solvent used. In a study on proton NMR shifts of *closo*-carboranes $C_2B_nH_{n+2}$ (n = 3–10) using the non-coordinating solvent CCl_4, and the coordinating aromatic solvents C_6H_6 and C_6F_6,[28] the largest proton shift change was found for the proton attached to the cage carbon in *ortho*-carborane and attributed to carboranyl C–H · · · π-arene hydrogen bonds[26] present in benzene. A study on proton NMR shifts of

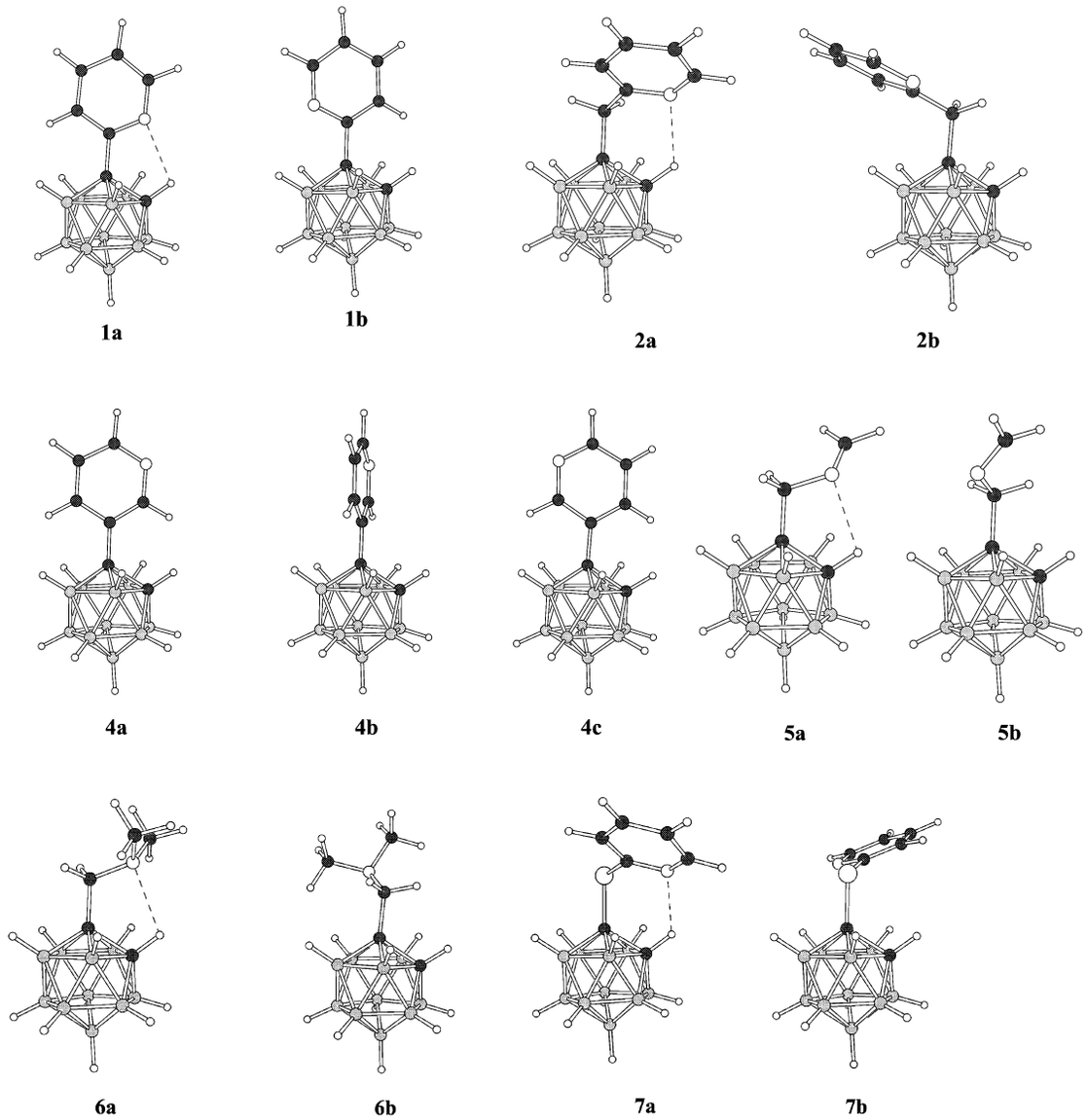


Fig. 6 MP2/6-31G* optimised geometries.

methyl-*ortho*-carborane derivatives using CCl_4, C_6H_6 and C_5H_5N as solvents indicated that carboranyl C–H ··· N hydrogen bonds occur in the pyridine solutions.[29]

Here we show that in d_5-pyridine, the carboranyl C–H proton shifts of *ortho*-carborane, 1-methyl-*ortho*-carborane and 1-phenyl-*ortho*-carborane are 4.93, 5.02 and 5.69 ppm whereas in $CDCl_3$ they are 3.55, 3.58 and 3.97 ppm, respectively, and in C_6D_6 they are 2.04, 2.12 and 2.86 ppm (see Experimental section for detailed NMR data) with the shift differences largely attributable to carboranyl C–H ··· N bonds in pyridine and C–H ··· π-arene bonds in benzene. Table 2 lists the observed proton shifts in the common non-coordinating solvent $CDCl_3$ for the nitrogen-containing compounds discussed here. As there is a large proton shift difference of 1.04 ppm for the carboranyl C–H peak between 1-(2′-pyridyl)-*ortho*-carborane **1** and the closely related 1-(3′-pyridyl)-*ortho*-carborane **4**, the carboranyl C–H ··· N bond appears to be intact in solutions of **1**.

While calculated ^{11}B NMR shifts generated from MP2-optimized geometries can confidently be used to determine solution-state geometries of carboranes,[30] calculated ^{1}H NMR shifts are not so accurate due to the solvent effects and the typically small ppm range (*ca.* 10 ppm compared with 100 ppm for ^{11}B NMR). Nevertheless there are reasonable agreements between calculated and observed proton NMR shifts for *closo*-carboranes in $CDCl_3$ and discrete *nido*-carborane monoanions in CD_3CN but not for *closo*-carboranes in the coordinating solvent C_6D_6.[31]

Here agreement between the calculated and observed proton NMR shifts of *ortho*-carborane in $CDCl_3$ is good particularly for the shift of the proton attached to carbon: calculated 3.26 ppm, observed 3.55 ppm. Carboranyl C–H NMR shifts at the B3LYP/6-311G* level for all minima **1a**–**7b** were computed and listed in Table 2. By comparison of observed and calculated shifts of carboranyl C–H protons, the carboranyl C–H ··· N bond appears to be retained in solution for **1** (and by implication for **3**) and possibly 1-(Ph_2C=NCH_2)-*ortho*-carborane (as a model geometry was used) but not for the other compounds discussed here. This assumption is supported by the larger energy differences between minima **1a** and **1b** for **1** and **5a** and **5b** for 1-(Ph_2C=NCH_2)-*ortho*-carborane due to favourable intramolecular carboranyl C–H ··· N bonds.

While the proton NMR shifts of carboranes are clearly solvent-dependent, the ^{11}B and ^{13}C NMR shifts shown for *ortho*-carborane, 1-methyl-*ortho*-carborane and 1-phenyl-*ortho*-carborane in various solvents are not so dependent on solvent. There are subtle changes observed in the ^{11}B NMR spectrum of 1-phenyl-*ortho*-carborane; the two peaks corresponding to B4,5 and B3,6 are observed in chloroform and benzene but they overlap in pyridine. Similar ^{11}B NMR differences are found between **1** and **4** further supporting the presence of

intramolecular hydrogen bonding for **1** in solution. In addition, calculated ^{1}H, ^{11}B and ^{13}C NMR data (see Experimental section) generated from the low-energy geometry **1a** are in good agreement with the experimental values of 1-(2′-pyridyl)-*ortho*-carborane **1** in $CDCl_3$.

Conclusions

The crystal structures of **1**–**4** demonstrate how minor variations in the molecular structure of pyridyl-containing *ortho*-carborane derivatives have a profound influence on the supramolecular structure of these species. In combination with the Lewis basic ring nitrogen, the acidic carboranyl C–H hydrogen may form *intra*- and/or *inter*-molecular hydrogen bonds to give highly ordered systems. The relative geometries of these acid/base pairs determine the precise nature of these hydrogen bonds and thus the supramolecular architecture of the crystal. That intramolecular hydrogen bonding is also retained in solutions of **1** and **3** is shown by NMR spectroscopy and supported by *ab initio* NMR computations. This study also shows that solution-state NMR spectroscopy is a good diagnostic tool for evidence of strong intramolecular carboranyl C–H ··· N hydrogen bonds (and presumably for other C–H ··· A hydrogen bonds) with a non-coordinating solvent. Calculated NMR shifts from optimised geometries are also useful in this connection.

Acknowledgements

We thank the EPSRC for the awards of an Advanced Research Fellowship (M. A. F.) and Senior Research Fellowship (J. A. K. H.) and Prof. Matthew G. Davidson (University of Bath) for useful discussions.

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