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Synthesis and solid state structure of α,α′-bis(2-phenyl-1,2-carboran-1-yl)lutidine

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Abstract

α,α′-Bis(2-phenyl-1,2-carboran-1-yl)lutidine has been prepared and the solid state structure characterised by X-ray diffraction. The structure reveals weak C–H···π interactions between molecules, forming a herringbone motif. Surprisingly, the pyridyl nitrogen atoms take part in no long-range interactions. © 2001 Published by Elsevier Science B.V.

Keywords: Carborane; Crystal structures; Intermolecular interactions C–H···π

1. Introduction

Compounds containing two or more carborane cages have attracted much interest recently, both as systems in their own right [1] and as precursors to macrocyclic [2] and polymeric [3] products. Hawthorne [2c] has demonstrated that carboranes linked by lutidine groups are excellent precursors for the preparation of carborane-containing macrocycles in high yield. In this paper the solid state structure and packing of α,α′-bis(2-phenyl-1,2-carboran-1-yl)lutidine (**1**) are described.

2. Experimental

All manipulations were carried out under anaerobic N_2 conditions using Schlenk-line apparatus. 1-Phenyl-1,2-carborane was prepared by a literature method [4] and 2,6-bis(chloromethyl)pyridine (Aldrich) was used as supplied. Et_2O was dried over sodium prior to use. The IR spectrum was recorded as a KBr disc on a Perkin–Elmer 1600 spectrophotometer. Elemental analyses were performed on an Exeter Analytical CE-440 system and the melting point was recorded on Electrothermal IA9100 apparatus. All NMR spectra were recorded at 25 °C in $CDCl_3$. ^{1}H- and ^{13}C-spectra were recorded on a Varian VXR 400 MHz spectrometer and the 11B spectrum was recorded on a Bruker AC 250 MHz machine. A $^{13}C\{^1H\}-^1H$ HETCOR spectrum was obtained in order to facilitate assignment of NMR spectra.

2.1. Preparation of **1**

1-Phenyl-1,2-carborane (1.10 g, 5.0 mmol) was dissolved in Et_2O (40 ml) and cooled to −78 °C. 2.38 M *n*-BuLi in hexanes (2.1 ml, 5.0 mmol) was added and the solution was stirred at −78 °C for 15 min. 2,6-Bis(chloromethyl)pyridine (0.44 g, 2.5 mmol) was then added via syringe, immediately forming a white precipitate (LiCl). The reaction was left to warm to room temperature (r.t.), whereupon the LiCl was removed by filtration. Removal of the solvent from the filtrate gave the desired product, **1**, as a white powder. Recrystallisation from Et_2O gave colourless crystals suitable for X-ray diffraction. Yield 1.07 g, 79%; ν_{max} (cm^{-1}) 3062 w (phenyl C–H), 2934 w (CH_2), 2862 w (CH_2), 2594 s,sh (B–H), 2584 vs (B–H), 2572 s,sh (B–H), 1592 m (pyridyl i.p.def.), 1576 m (pyridyl i.p.def.), 1456 m (pyridyl i.p.def.), 1448 (pyridyl i.p.def.), 1072 m (phenyl i.p.def.), 1030 w (phenyl i.p.def.), 882 w (phenyl o.o.p.def.), 758 (phenyl o.o.p.def.), 730 m (pyridyl o.o.p.def.), 691 s (B–H). Anal. Found: C, 50.8; H, 6.8; N, 2.6. Calc. for $C_{23}H_{37}B_{20}N$: C, 50.8; H, 6.9; N, 2.6%. ^{1}H-NMR ($CDCl_3$): δ 3.19 ppm (4H, s, H9); 6.73 ppm

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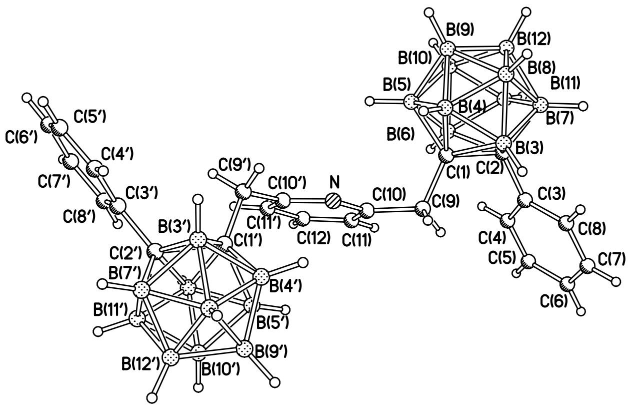

Fig. 1. Molecular structure of compound **1**. Primed and unprimed atoms of the same numbers are related by *non-crystallographic* twofold axis.

(2H, d $^{3}J_{(HH)} = 7.6$ Hz, H11); 7.44 ppm (1H, t $^{3}J_{(HH)} = 7.6$ Hz, H12); 7.45 ppm (4H, t $^{3}J_{(HH)} = 8.0$ Hz, H5/7); 7.52 ppm (2H, t $^{3}J_{(HH)} = 7.2$ Hz, H6); 7.75 ppm (4H, d $^{3}J_{(HH)} = 7.6$ Hz, H4/8). ^{13}C-NMR ($CDCl_3$) δ 42.7 ppm (C9), 80.5 ppm, 83.7 ppm (C1,C2), 123.5 ppm (C11), 129.0 ppm, 130.7 ppm, 130.8 ppm (C3,C5/7,C6), 131.5 ppm (C4/8), 136.7 ppm (C12), 154.9 ppm (C10). ^{11}B-NMR ($CDCl_3$) δ −3.08 ppm (4B; B9,B12), −9.65 ppm (16B; all other B). m.p. 231.7–233.2 °C; m^+/e (EI) M^+ 539.3–546.3, $M^+_{(max)}$ 543.3.

2.2. X-ray crystallography

The diffraction experiment was carried out at r.t. on a SMART 3-circle diffractometer with a 1K CCD area detector, using graphite-monochromated Mo–K_α radiation, $\bar{\lambda} = 0.71073$ Å. Crystal data: $C_{23}H_{37}B_{20}N$, $M = 543.74$, monoclinic, space group $C2/c$ (No. 15), $a = 33.910(2)$, $b = 7.764(1)$, $c = 27.005(2)$ Å, $\beta = 116.98(1)°$, $V = 6336(1)$ Å^3, $Z = 8$, $D_{calc} = 1.14$ g cm^{-3}, $\mu = 0.6$ cm^{-1}, colourless crystal of the 0.25 × 0.18 × 0.16 mm size. A full hemisphere of the reciprocal space was scanned by 0.3° steps in ω (25 s step^{-1}), $2\theta \leq 48°$, 15 267 total data, 4764 unique, 2430 observed with $I > 2\sigma(I)$, $R_{int} = 0.094$. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 of all data, using SHELXTL software [5]. All non-H atoms were refined anisotropically, carborane H atoms isotropically, other H atoms were treated as ‘riding’ (total of 418 variables), converging at wR (F^2, all data) = 0.195, goodness-of-fit 1.04; R (F, obs.data) = 0.067; residual $\Delta\rho_{max} = 0.16$, $\Delta\rho_{min} = -0.14$ e Å^{-3}.

3. Results and discussion

The molecule of **1** in crystal (Fig. 1, Table 1) has an approximate non-crystallographic twofold axis (through the N and C(12) atoms) parallel to the crystallographic [1 0 $\bar{1}$] direction. In either half of the molecule, the CH_2–C(py) bond adopts an orientation nearly eclipsed with B(5), with the torsion angles B(5)C(1)C(9)C(10) 9.7 and B(5′)C(1′)C(9′)C(10′) 7.4°, while the phenyl ring form a dihedral angle of 80.5° (average) with the C(9)C(1)C(2)C(3) plane.

The C(1)–C(2) distance (av. 1.715(4) Å) is significantly longer than in the parent *ortho*carborane (1.630(6) Å) [6] due to the steric and electronic influence of the substituents. Comparison with the corresponding distances in 1-phenyl-2-methyl- (1.696(5) Å) [7], 1,2-diphenyl- (1.726(6) Å) [8] and 1,2-bis-(*p*-acetylbenzyl)-1,2-carborane (1.682 Å) [9] shows an apparent correlation between the steric demands of the substituents and the C(1)–C(2) distance, suggesting that the latter atoms are driven apart by the inter-substituent repulsion. However, in fact the C(1)–C(9) and C(2)–C(3) bonds in **1** are leaning towards each other: the (mean) C(9)–X–C(3) angle (X is the centre of the cage) of 60.8° is smaller than C(1)–X–C(2) 64.8°. A similar effect has been observed in analogous systems [7,8], but it is not yet fully explained.

Table 1
Selected bond distances and angles in **1** [a]

Bond distances					
C(1)–C(2)	1.711(4)	1.718(4)	C(2)–B(3)	1.731(5)	1.735(5)
C(1)–B(3)	1.718(4)	1.725(5)	C(2)–B(6)	1.721(5)	1.729(5)
C(1)–B(4)	1.713(5)	1.707(5)	C(2)–B(7)	1.698(5)	1.701(5)
C(1)–B(5)	1.711(5)	1.705(5)	C(2)–B(11)	1.700(5)	1.703(5)
C(1)–B(6)	1.717(5)	1.723(5)	C(2)–C(3)	1.514(4)	1.513(5)
C(1)–C(9)	1.532(4)	1.527(4)	B–B, average	1.771(7)	
Bond angles					
C(9)C(1)C(2)	117.1(3)	117.3(3)	C(3)C(2)C(1)	119.2(3)	119.4(3)
C(9)C(1)B(3)	115.3(3)	115.6(3)	C(3)C(2)B(3)	116.8(3)	117.3(3)
C(9)C(1)B(4)	121.7(3)	121.7(3)	C(3)C(2)B(6)	119.5(3)	119.0(3)
C(9)C(1)B(5)	123.7(3)	124.2(3)	C(3)C(2)B(7)	120.6(3)	120.9(3)
C(9)C(1)B(6)	119.0(3)	118.9(3)	C(3)C(2)B(11)	122.0(3)	121.7(3)

[a] Left column for unprimed, right one for primed atoms.

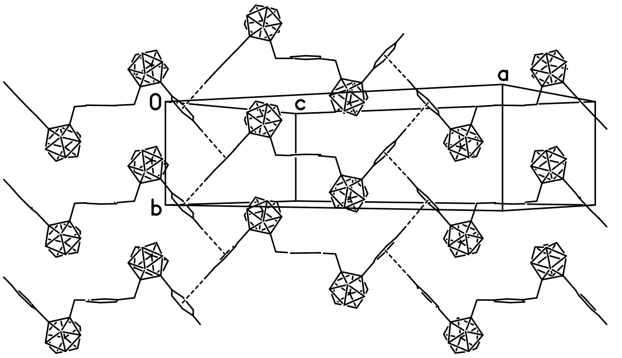

Fig. 2. Crystal packing of **1**; projection on the (1 0 $\bar{1}$) plane. H atoms are omitted, except those at C(6) and C(6′).

The molecules are packed in layers parallel to the (1 0 $\bar{1}$) plane (Fig. 2). The phenyl rings are nearly perpendicular to this plane and together form a herringbone motif (characteristic for benzene and some polyaromatic systems) [10], stabilized by weak intermolecular C–H···π interactions. Thus, C(6)H interacts with the π-electron system of the A′ ring, and C(6′)H with that of the A ring of the adjacent molecules, symmetrically related by the $1/2+x$, $1/2-y$, $1/2+z$ and $x-1/2$, $3/2-y$, $z-1/2$, respectively, to the original one (x, y, z). For the hydrogen atom positions calculated with the neutron-diffraction C–H distance of 1.08 Å, the above-mentioned H···π distances (where π is the ring centre) are 3.04 and 2.81 Å, C–H···π angles of 152 and 156°, respectively. The C–H bonds are inclined to the ring planes by 68 and 64°, while H atoms are slightly shifted from the ring centres, by 0.66 and 0.21 Å. Thus the configuration is close to the 'tilted T', found by Monte Carlo simulations to be the global minimum for the interactions between two isolated benzene molecules [11] (with the energy of -2.3 kcal mol^{-1}), though at longer distances (5.28 and 5.12 Å between the centres of the contacting rings, cf. the calculated 4.99 Å). Stronger interactions have been previously noted in a phenyl C–H···π(furan) system (H···π 2.79 Å, C–H···π angle 144°) [12]. It is noteworthy that the pyridyl nitrogen atom (possessing a lone pair) does not participate in any close N···H contacts whatsoever, unlike in other pyridyl and picolyl carborane species [13], probably due to steric overcrowding.

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 165191 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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