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Synthesis and structure of 1,12-diethynyl-*para*-carborane

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Abstract

Base desilylation of the novel compound, 1,12-bis(trimethylsilylethynyl)-*para*-carborane 1,12-($Me_3SiC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$, gave the previously unknown compound 1,12-bis(diethynyl)-*para*-carborane, 1,12-$(HC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$. In the structure of the latter carborane, determined by X-ray diffraction, the ethynyl substituents induce a distortion of the carborane icosahedron, lengthening the tropical B–B bonds. The structural parameters of the diethynyl carborane are compared with known structures of type 1,12-$(XE)_2B_{10}H_{10}$ bearing substituents on antipodal sites particularly the isostructural and isoelectronic 1,12-$B_{12}H_{10}(CO)_2$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structure; π-Conjugation; Cage distortion; Bond order; Carborane; Alkyne

1. Introduction

It is well known that an isolated $[B_{12}H_{12}]^{2-}$ anion is a regular icosahedron and very nearly retains the I_h symmetry in the crystal [1], unless a distortion is induced by a strongly polarising counterion as in $Ca[B_{12}H_{12}]$ [2]. A recent study [3] of 1,12-$B_{12}H_{10}(CO)_2$ (**1**) has shown that bonding with two carbonyl groups in para positions profoundly distorts the B_{12} cage, the 'polar-tropical' B–B bonds (type (i), see Scheme 1) contracting, the 'tropical' bonds (type (ii)) lengthening, and the cage as a whole being squashed along the B(1)···B(12) axis (see Table 1). Only two other *para*-disubstituted dodecaboranes have been structurally studied, 1,12-$B_{12}H_{10}\{C(OH)_2\}_2$ [3] and 1,12-$B_{12}H_{10}(SMe_2)_2$ [4]. They display similar distortions but of much smaller magnitude: bonds (ii) are longer than (i) by 0.02–0.03 Å, compared with 0.056 Å in **1**. In order to investigate how general is this effect in *closo*-deltahedra, in the present work we undertook the synthesis and single-crystal X-ray diffraction study of diethynyl-*para*-carborane 1,12-$(HC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$ (**2**), isostructural and isoelectronic with **1**, and itself a precursor/building block from which we propose to generate carborane assemblies.

There has been much recent interest in assemblies generated from carborane building blocks due to their capacity for use in anion complexation, supramolecular assembly and the formation of rigid rod molecules and polymers [5–7]. Most relevant to carborane **2** as a potential precursor/building block is the closely related isomer, 2,9-$(HC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$ with mutually para ethynyl groups on antipodally related pair of boron atoms [5,8]. The palladium-catalysed coupling reaction of the 2,9-diethynylcarborane with 2,9-I_2-1,12-$C_2B_{10}H_{10}$ resulted in 2,9-(2′-I-9′-C≡C-1′,12′-$C_2B_{10}H_{10})_2$-1,12-$C_2B_{10}H_{10}$, a three-cage product with the *para*-carborane cages linked by alkyne bridges [5].

2. Results and discussion

The bis(ethynyl)carborane **2** was prepared by base desilylation of another novel compound, 1,12-bis(trimethylsilylethynyl)-*para*-carborane 1,12-$(Me_3SiC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$ (**3**). The latter was synthesised from the 1,12-copper(I) derivative of *para*-carborane and bromotrimethylsilylacetylene in the presence of pyridine rather than in the ether–THF solution used previously for syntheses of C-trimethylsilylethynyl carboranes [9].

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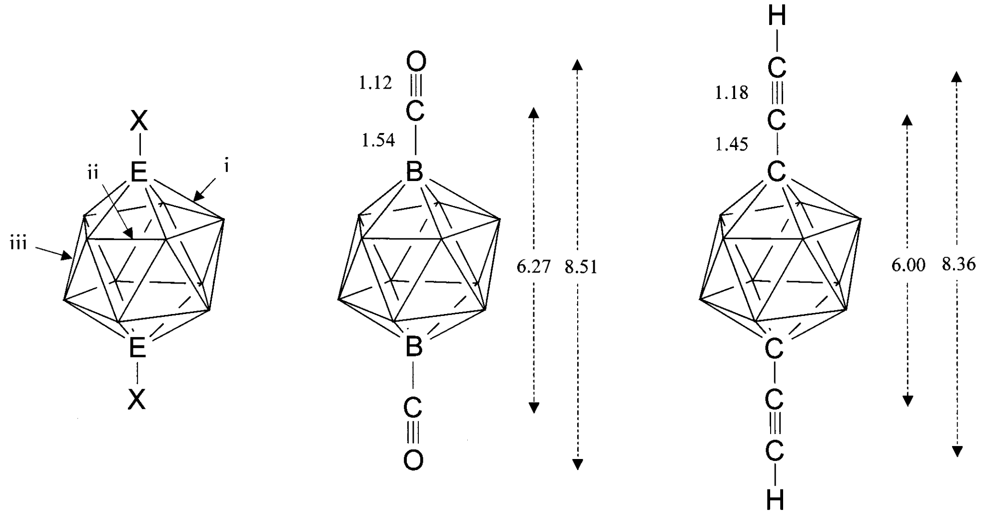
The crystal structure of **2** contains two crystallographically non-equivalent molecules (A and B), both situated at inversion centres and having essentially the same geometry (Fig. 1, Table 2). The displacement ellipsoids of all atoms in molecule A are systematically elongated in the direction parallel to the ethynyl bonds, while those in molecule B are consistent with the expected vibrational motion. This anomaly was not eliminated by the absorption correction, which proved negligible (from ψ-scans, $T_{\min}:T_{\max} = 0.97$). An investigation of the crystal packing (Fig. 2) shows that molecules of type A are arranged sequentially in a 'channel', parallel to the crystallographic $[1\bar{1}0]$ direction and surrounded by molecules of type B. The diethynyl axis of molecule A forms a very acute angle (20°) with the direction of the channel, hence a (concerted) shift of this molecule and its translational equivalents along the channel will not affect molecules B, while a similar shift of molecule B will bring its ethynyl group into a collision with molecule A. All molecules are considered to be discrete with the shortest intermolecular distances of 3.14 and 3.15 Å found between H(18) of molecule A and the carbon atoms, C(27) and C(28) of molecule B [10]. This is based on the idealised H(18) position, i.e. C(18)–H(18) = 1.06 Å.

The C(cage)–C(ethynyl) and C≡C bond lengths in **2** average 1.451(2) and 1.180(3) Å, respectively, compared to 1.433(2) and 1.194(2) Å, respectively in the only previously studied C-ethynyl-carborane, the ortho carborane derivative 1-(PhC≡C)-2-Ph-1,2-$C_2B_{10}H_{10}$ [11]. Thus, the *para*-carborane cage in **2** is seen to be less π-conjugated with the ethynyl groups than the *ortho*-cage, in accordance with the lower electron-withdrawing ability of the cage C atom in *para*-carboranes. Although the orbital used by a cage C atom to form an *exo* σ-bond is commonly regarded as sp hybridised, the C(cage)–C(ethynyl) bond is understandably much longer than the standard C(sp)–C(sp) single bond (1.38 Å) and is, in fact, intermediate in length between standard C(sp^2)–C(sp) and C(sp^3)–C(sp) bonds (1.43 and 1.47 Å) [12,13]. A slightly longer *exo* C–C bond distance might have been expected in **2** due to the higher coordination number of the cage carbon. Significantly, comparison of the reported [14] ^{13}C-NMR chemical

Table 1
Average distances (Å) in 1,12-$X_2E_2B_{10}H_{10}$ derivatives

E	X	i	ii	iii	E···E	Reference
B	H	1.783(4)	1.783(4)	1.783(4)	3.39(1)	[1]
B	CO	1.768(2)	1.824(2)	1.779(2)	3.193(2)	[3]
C	H	1.704(5)	1.781(7)	1.762(5)	3.056(4)	[16]
C	C≡CH	1.726(3)	1.793(3)	1.761(2)	3.104(2)	This work
C	CO_2H	1.711(3)	1.784(5)	1.758(3)	3.065(2)	[17]
C	H	1.706(3)	1.782(3)	1.766(5)	3.105(1)	[7]
	$C_6H_4C{\equiv}CPh$	1.725(3)	1.780(3)			



1 **2**

Scheme 1.

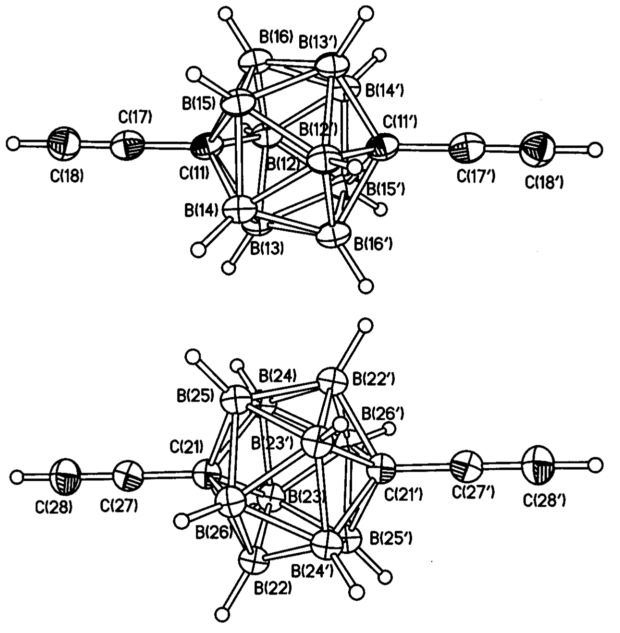


Fig. 1. Molecular structure of **2** (independent molecules A and B), showing 50% displacement ellipsoids. Primed atoms are symmetrically related via inversion centres.

Table 2
Bond distances (Å) in **2**

Molecule A		Molecule B	
C(11)–C(17)	1.449(2)	C(21)–C(27)	1.452(2)
C(17)–C(18)	1.179(3)	C(27)–C(28)	1.180(3)
C(11)–B(12)	1.722(2)	C(21)–B(22)	1.728(2)
C(11)–B(13)	1.726(2)	C(21)–B(23)	1.723(2)
C(11)–B(14)	1.724(2)	C(21)–B(24)	1.732(3)
C(11)–B(15)	1.732(2)	C(21)–B(25)	1.725(2)
C(11)–B(16)	1.727(3)	C(21)–B(26)	1.724(2)
B(12)–B(13)	1.789(3)	B(22)–B(23)	1.791(3)
B(13)–B(14)	1.794(3)	B(23)–B(24)	1.791(3)
B(14)–B(15)	1.792(3)	B(24)–B(25)	1.794(2)
B(15)–B(16)	1.792(3)	B(25)–B(26)	1.793(3)
B(16)–B(12)	1.796(2)	B(26)–B(22)	1.799(3)
B(12)–B(14′)	1.764(3)	B(22)–B(24′)	1.761(3)
B(12)–B(15′)	1.758(3)	B(22)–B(25′)	1.759(3)
B(13)–B(15′)	1.759(3)	B(23)–B(25′)	1.761(3)
B(13)–B(16′)	1.766(3)	B(23)–B(26′)	1.759(3)
B(14)–B(16′)	1.762(3)	B(24)–B(26′)	1.762(3)

shifts of the ethynyl carbons in known terminal alkynes RC≡CH with the bis(ethynyl)carborane **2** reveals the effect of the carborane substituent on the shifts of the ethynyl carbons to be more like that of an alkyl substituent rather than an aryl one. For example, the ^{13}C-NMR chemical shifts for the substituted ethynyl carbons in **2**, 1-pentyne and ethynylbenzene are 79.5, 83.6 and 83.6 ppm, respectively, and for the unsubstituted ethynyl carbons are 69.1, 68.2 and 77.2, respectively. These experimental observations suggest that π-conjugation in the C(cage)–C(ethynyl) *exo* bond of **2** is negligible. This conclusion is supported by AM1 calculations [15] which give the total bond orders of the C(cage)–C(ethynyl) and C≡C bonds as 1.02 and 2.88, and the π bond orders as 0.08 and 1.92, respectively.

In the C_2B_{10} cage of **2**, the C–B bonds (i), the tropical B–B bonds (ii) and the antipodal cross-cage C···C distance are longer than in the unsubstituted *para*-carborane $C_2B_{10}H_{12}$ [16], while the 'meridianal' B–B bonds (iii) remain essentially unaltered (see Table 1). The lengthening of C–B bonds in carboranes caused by substituents at the carbon atoms is well known, but the effect on the B–B bonds has not been observed before. Most conspicuously, in a monosubstituted *para*-carborane 1-PhC≡CC$_6$H$_4$-1,12-C$_2$B$_{10}$H$_{11}$ [7] the C–B distances to the substituted carbon atom are 0.02 Å longer than those to the unsubstituted one, but the adjacent B–B bonds (ii) are essentially equal. Thus, the effect of unsaturated substituents on the tropical B–B bonds in **2**, similar to that in **1**, is intriguing and *para*-carboranes deserve further experimental and theoretical investigation, which is currently in progress. Although crystallographic studies of boranes and carboranes abound, the simplest systems have never been studied systematically. Particularly regrettable is the scarcity of low-temperature data, since the thermal motion in *para*-carboranes mostly takes the form of rotation around the C(1)···C(12) axis and the resulting systematic error (spurious bond shortening) is the largest precisely for the tropical B–B bonds.

Examination of the distances between the atoms on the molecular 5-fold axes of the two isoelectronic compounds, O≡CB(B$_{10}$H$_{10}$)BC≡O (**1**) and HC≡CC-(B$_{10}$H$_{10}$)CC≡CH (**2**) is instructive, illustrating dramatically the consequences of effectively transferring one unit of nuclear charge from the substituted skeletal atom to the terminal atom(s) of the substituents going from the bis(ethynyl)carborane **2** to the bis(carbonyl)borane **1**. The antipodal cross-cage distance between the carbon atoms of the carborane icosahedron is understandably shorter, at 3.10 Å, than that between the substituted boron atoms in the bis(carbonyl)borane (3.19 Å) (Table 1). However, the substantially greater

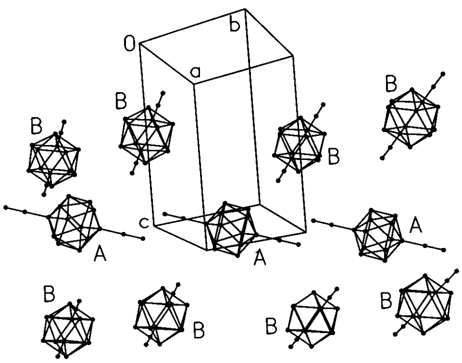


Fig. 2. Crystal packing of **2**.

length of the essentially single *exo* B–C bonds (1.54 Å) to the carbonyl substituents in **1**, when compared with the *exo* C–C bonds (1.45 Å) in **2** increases the separation between the substituent carbon atoms in the former (6.27 Å) compared with that (6.00 Å) in the latter. As the triple C≡O (1.12 Å) and C≡C (1.18 Å) bonds differ but little in length, in the manner consistent with the smaller radius of oxygen than carbon, the separation between the wing-tip oxygen atoms in the bis(carbonyl)borane **1** (8.51 Å) exceeds by some 0.15 Å that between the wing-tip carbon atoms (8.36 Å) in **2**.

Though it lacks the five-fold symmetry of compounds **1** and **2**, the structure of the reported B-bis(ethynyl)carborane 2,9-$(HC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$ closely related to **2** is worthy of comparison [5,8]. The molecular structure of its silyl derivative 2,9-$(Me_3SiC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$ determined by X-ray crystallography revealed bond distances of 3.405, 1.532 and 1.206 Å for the antipodal cross-cage distance B(2)···B(9), *exo* B–C bonds and the triple C≡C bonds, respectively [8]. These distances imply that the distance between the wing-tip carbons in 2,9-$(HC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$ will be about 8.88 Å, exceeding that in our C-bis(ethynyl)carborane **2** by some 0.52 Å.

3. Experimental

NMR spectra were recorded on a Varian Unity 300 (299.9 MHz ^{1}H, 96.2 MHz ^{11}B and 75.4 MHz ^{13}C) instrument. $CDCl_3$ was used as solvent in all NMR spectra recorded here and chemical shifts were referenced to $SiMe_4 = 0.00$ ppm for ^{1}H and ^{13}C and externally to $BF_3{\cdot}Et_2O = 0.0$ ppm for ^{11}B. Infrared spectra were recorded as potassium bromide discs using a Perkin–Elmer 1720X FTIR spectrometer. Mass spectra were recorded on a VG Micromass 7070E instrument operating in the EI mode at 70 eV. Calculated values of M_r show the full isotope range $^{10}B_n$ to $^{11}B_n$ including a ^{13}C contribution where this is likely to have observable intensity; the less-probable combinations are seldom observed in practice. Monoglyme was dried by refluxing and distillation over potassium and storage over sodium wire, and pyridine by distillation after standing over potassium hydroxide. Bromotrimethylsilylacetylene was prepared as described in the literature [18]. *para*-Carborane (Katchem), butyllithium solution (Aldrich) and diethyl ether were used as supplied.

3.1. Preparation of 1,12-bis(trimethylsilylethynyl)-para-carborane (3)

Under nitrogen, *para*-carborane (2.87 g, 20 mmol) in dry monoglyme (80 ml) was treated dropwise with butyllithium in hexanes (16.5 ml, 2.5 M, 41 mmol). Pyridine (12 ml) and copper (I) chloride (4.50 g, 45 mmol) were added and the mixture was heated under reflux for 30 min, cooled briefly during addition of bromotrimethylsilylacetylene (7.96 g, 45 mmol), heated for a further 19 h, cooled and diluted with ether (400 ml). After standing for 4 h the mixture was filtered and the filtrate was washed with dilute hydrochloric acid (250 ml, 2.5 M) and water (2 × 500 ml), dried over magnesium sulphate and evaporated. The brown semi-solid residue was dissolved in cyclohexane (30 ml) and passed through a column of chromatographic silica (20 g), which was eluted with cyclohexane collected in two portions of 50 ml. The second portion was evaporated to give a yellow semi-solid (4.00 g) which was triturated with ethanol and the resulting finely divided white solid was separated, washed with ethanol and dried at 20°C/0.005 mmHg to give **3** (993 mg, 15%). Recrystallisation from ethanol gave ragged blades m.p. 140–141°C. Found: C, 41.9; H, 8.5, MS (EI): typical carborane pattern at m/z 317–325 [322, $M-CH_3$, 100%], 332–340, [337, M, 6%] $C_{12}H_{28}B_{10}Si_2$ requires: C, 42.8; H, 8.4; M = 337. IR: ν(CH) 2961, 2926, ν(BH) 2620, ν(C≡C) 2178. ^{11}B-NMR (298 K, $CDCl_3$): δ 11.9 (d, 169 Hz). $^{1}H\{^{11}B\}$-NMR: δ 2.44 (10H, BH), 0.08 (18H, CH). $^{13}C\{^{1}H\}$-NMR: δ 100.3 (C–Si), 85.9 (*C*≡CSi), 66.0 (cage C), −0.6 (CH_3).

3.2. Preparation of 1, 12-diethynyl-para-carborane (2)

Compound **3** (250 mg, 0.74 mmol) was suspended in methanol (2.5 ml) and a methanol solution (0.25 ml) of potassium hydroxide (2% w/v) containing water (5% w/v) was added. The resulting homogeneous solution was stirred at room temperature for 50 min, diluted with ether (20 ml), washed with water (2 × 20 ml), and dried over sodium sulphate. Evaporation at room temperature gave a crystalline solid (150 mg) which was sublimed at 45–50°C/0.01 mmHg to give 1, 12-diethynyl-*para*-carborane (140 mg, 0.73 mmol, 99%). Found, C, 37.4; H, 6.1. MS (EI): 186–194 [192, M, 100%]. $C_6H_{12}B_{10}$ requires C, 37.5; H, 6.3, M = 192. IR: ν(CH) 3305, 3294, ν(BH) 2623, 2606. ^{11}B-NMR (298 K, $CDCl_3$): δ 11.9 (d, 169 Hz). $^{1}H\{^{11}B$-NMR: δ 2.49 (10H, BH), 2.12 (2H, CH). $^{13}C\{^{1}H\}$-NMR: δ 79.5 (*C*≡CH), 69.1 (CH), 65.3 (cage C). Recrystallisation from ethanol and sublimation at room temperature in a sealed evacuated tube gave large colourless crystals suitable for X-ray structural determination, m.p. 135–136°C.

3.3. Crystal structure determination of **2**

The experiment for was carried out on a Rigaku AFC6S 4-circle diffractometer, using graphite-monochromated Cu–K$_\alpha$ radiation ($\lambda = 1.54184$ Å) at $T = 150$ K. Crystal data: $C_6H_{12}B_{10}$, M = 192.26, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.287(2)$, $b = 7.579(1)$, $c = 10.953(3)$ Å, $\alpha = 82.73(2)$, $\beta = 72.96(2)$,

$\gamma = 80.01(2)°$, $V = 567.7(2)$ Å^3, $Z = 2$, $D_{calc} = 1.125$ g cm^{-3}, $\mu = 0.34$ mm^{-1}, crystal size 0.2 × 0.2 × 0.1 mm. A total of 2517 reflections (2064 unique, $R_{int} = 0.012$) with $2\theta < 150°$ were measured in $2\theta/\omega$ scan mode. The structure was solved by direct methods and refined by full-matrix least squares (non-H atoms in anisotropic approximation, all H atoms refined freely in isotropic approximation) against F^2 of all data, using SHELXTL software [19], to $R = 0.045$ [for 1766 data with $F^2 \geq 2\sigma(F^2)$], $wR(F^2) = 0.181$, $\Delta\rho_{max/min} = 0.21, -0.23$ e Å^{-3}.

4. Supplementary material

Crystallographic data for **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC-135249. 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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