# Crystallographic evidence for the diene character of $C_2B_{10}H_{10}C_4H_4$ ('benzocarborane') and a Diels–Alder reaction of its anionic *nido*-analogue, $[C_2B_9H_{10}C_4H_4]^-$: crystal structures of $C_2B_{10}H_{10}C_4H_4$ and $C_2B_{10}H_{10}C_4H_6$

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**Single-crystal X-ray diffraction studies on $C_2B_{10}H_{10}C_4H_4$ ('benzocarborane') and $C_2B_{10}H_{10}C_4H_6$ ('dihydrobenzocarborane') show that the $C_6$ rings of each possess localised double bonds and this has been confirmed by bond-order calculations; the *nido*-anion, $[C_2B_9H_{10}C_4H_4]^-$ synthesised from $C_2B_{10}H_{10}C_4H_4$, with maleic anhydride forms a Diels–Alder adduct.**

Polyhedral boranes, carboranes and related clusters, including many metal clusters, are often treated as three-dimensional aromatic systems[1,2] because their delocalised skeletal bonding involves σ- and π-bonding interactions between tangentially orientated p (or pd hybrid) orbitals on sets of atoms around their circumferences; indeed, aromatic ring systems in general are formally *arachno* members of the borane cluster family. As a result, much interest attaches to the extent to which such clusters can interact electronically with unsaturated substituents,[3] and so transmit π-electron donor/acceptor effects from one substituent to another,[4] or participate in extended π-delocalised systems containing alternating cluster units and conjugated unsaturated chains or rings,[5] or π-bond to suitable π-donor substituents.[6] Compounds in which potentially aromatic rings are fused to carborane clusters provide convenient systems with which to probe such interactions. This paper describes the first definitive structural study of such a system, 'benzocarborane' **1**, 1,2-(buta-1′,3′-diene-1′,4′-diyl)-1,2-dicarbadodecaborane(12), a compound first described in 1968[7] and subsequently the subject of detailed reactivity and NMR studies[8] that nevertheless left uncertainty about the degree of electronic delocalisation in the $C_6$ ring, although it was recognized to be small, which our own study has confirmed. We also report the structure of compound **2**, 1,2-(but-2′-ene-1′,4′-diyl)-1,2-dicarbadodecaborane(12), an intermediate in the synthesis of **1**, and describe a Diels–Alder reaction of the anionic system **3**, preparable from **1** by a standard deboronation reaction.

Compounds **1** and **2** were prepared by the literature method,[8] starting from the dilithiocarborane and 1,4-dichlorobut-2-ene. Recrystallisation of $C_2B_{10}H_{10}C_4H_4$ **1** from methanol containing a little water produced colourless needles. $C_2B_{10}H_{10}C_4H_6$ **2** was recrystallised from methanol as colourless needles. X-ray studies on **1** proved particularly difficult as the crystal decomposed when exposed to X-rays at room temperature and also, without X-ray exposure, as the sample temperature was progressively lowered in preparation for analysis. The problem was overcome by flash-cooling a crystal to 100 K. The diffraction study of **1**[†] shows a well ordered structure in space group $Pca2_1$ (no. 29), with two independent molecules in the asymmetric unit. The molecular structure with significant bond lengths and angles is shown in Fig. 1. The cage interatomic distances are comparable with those found in unperturbed carborane cages.[9] The non-cage C–C bond lengths in the $C_6$ ring (Table 1) show alternating values consistent with the localised single and double bonds found in cyclohexa-1,3-diene and related compounds.[10] The $C_6$ ring is planar, with the largest deviation from a least-squares plane being 0.016 Å for C(24). Compound **2** crystallizes in a well ordered manner in space group *Pbca* (no. 61),[‡] and, as with **1** there are two independent molecules in the asymmetric unit; Fig. 2 shows the molecular structure with significant bond lengths and bond angles. The cage distances for **2** are not significantly different from those of **1**. The four single bonds and one double bond in the $C_6$ ring of **2** are clearly identified from the bond lengths. As with **1** the

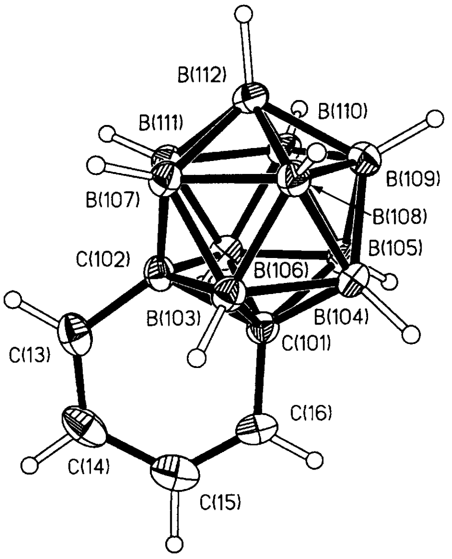


**Fig. 1** Molecular structure of **1** (50% ellipsoids). A second independent molecule is numbered in a similar fashion, with the first digit of the serial number being changed from 1 to 2. Important interatomic distances (Å) are: C(101)–C(102) 1.654(3), C(201)–C(202) 1.647(3), C(101)–C(16) 1.478(3), C(201)–C(26) 1.479(3); C(102)–C(13) 1.478(3), C(202)–C(23) 1.488(3); C(13)–C(14) 1.340(4), C(23)–C(24) 1.332(4); C(15)–C(16) 1.331(4), C(25)–C(26) 1.348(4); C(14)–C(15) 1.452(4), C(24)–C(25) 1.441(4); B–B for B(103) to B(112) range between 1.760(4) and 1.791(4); B–B for B(203) to B(212) range between 1.755(3) and 1.792(4); B–C for B(103) to B(112) and C(101) and C(102) range between 1.707(4) and 1.751(4); B–C for B(203) to B(212) and C(201) and C(202) range between 1.708(4) and 1.745(4).

**Table 1** Bond lengths and bond orders for the $C_6$ ring in **1** and **2**

| | Length[a]/Å | | Total bond order | | π-Bond order[a] | |
|---|---|---|---|---|---|---|
| Bond | **1** | **2** | **1** | **2** | **1** | **2** |
| C(101)–C(102) | 1.651 | 1.662 | 0.679 | 0.645 | 0.023 | 0.020 |
| C(2)–C(13), C(1)–C(16) | 1.481 | 1.521 | 1.003 | 0.975 | 0.060 | 0.025 |
| C(13)–C(14), C(15)–C(16) | 1.338 | 1.499 | 1.846 | 0.987 | 0.881 | 0.036 |
| C(14)–C(15) | 1.447 | 1.325 | 1.064 | 1.939 | 0.109 | 0.969 |

[a] Minor differences in length between chemically equivalent bonds in the two molecules in the asymmetric unit are averaged; the greatest difference, and the standard deviation, in the bond order is 0.005.

carbocyclic ring is essentially planar, the largest deviation from a least-squares plane being 0.033 Å for C(26). Bond order calculations carried out on the molecular geometries of **1** and **2** using the AM1 molecular-orbital program[11] support their essentially localised double-bond character (see Table 1).

Removal of one boron atom [B(103) or B(106)] from **1** is conveniently effected by tetrabutylammonium fluoride in the presence of water[12] (Scheme 1) and gives the anionic *nido*-analogue of benzocarborane, $[C_2B_9H_{10}C_4H_4]^-$ **3**,[8] which formed colourless crystals after recrystallization from propan-2-ol–acetonitrile (90:10). We have been unable to grow crystals of salts of anion **3** suitable for X-ray diffraction but have tested the diene character of **1** (*closo*) and **3** (*nido*) by treating each with maleic anhydride in triglyme. Compound **1** did not react at temperatures < 150 °C, probably for steric and electronic reasons. However, at 80 °C the tetrabutylammonium salt of **3** gave one isomer of the tetrabutylammonium salt of the adduct $[C_2B_9H_{10}C_4H_4C_4H_2O_3]^-$ **4**, probably with the configuration shown in Scheme 1. The $^{13}C$ NMR chemical shifts of the non-cage atoms correspond closely with those of the parent compound $C_6H_8C_4H_2O_3$ **5**, prepared from maleic anhydride and cyclohexa-1,3-diene[13] as do the $^1H$ NMR resonances except for the pair [H(13), H(16); see Scheme 1] adjacent to the cage which are 0.68 ppm to higher frequency. Similar deshielding by the cage probably contributes to the relatively high frequency resonances of the C protons in **1**. Models of the transition states for each of the other three possible orientations of addition indicate decisively greater steric repulsion.

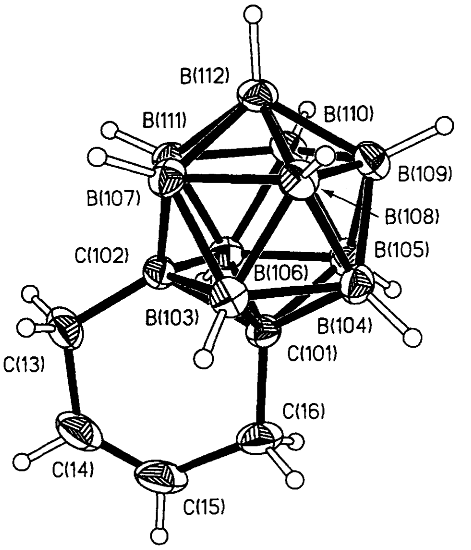
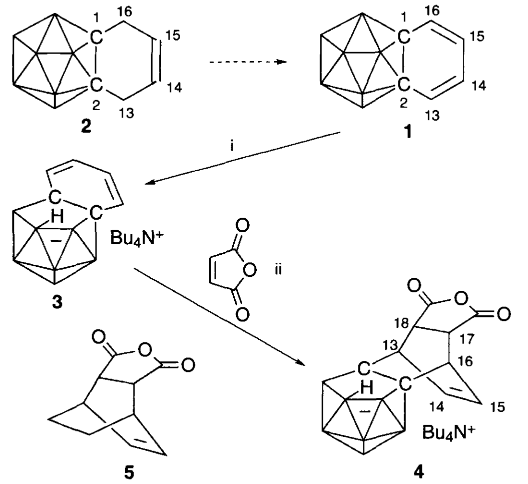


**Fig. 2** Molecular structure of **2** (50% ellipsoids). A second independent molecule is numbered in a similar fashion, with the first digit of the serial number being changed from 1 to 2. Important interatomic distances (Å) are: C(101)–C(102) 1.662(1), C(201)–C(202) 1.661(1); C(101)–C(16) 1.522(1), C(201)–C(26) 1.520(1); C(102)–C(13) 1.520(1), C(202)–C(23) 1.520(1); C(13)–C(14) 1.498(2), C(23)–C(24) 1.497(2); C(15)–C(16) 1.500(2), C(25)–C(26) 1.502(2); C(14)–C(15) 1.326(2), C(24)–C(25) 1.324(2); B–B for B(103) to B(112) range between 1.770(2) and 1.790(2); B–B for B(203) to B(212) range between 1.766(2) and 1.791(2); B–C for B(103) to B(112) and C(101) and C(102) range between 1.706(1) and 1.725(1); B–C for B(203) to B(212) and C(201) and C(202) range between 1.706(1) and 1.723(2).



**Scheme 1** Synthesis of the Diels–Alder product **4** from **1**. *Reagents and conditions*: i, $Bu_4NF$, $H_2O$, thf; ii, triglyme, 80 °C.

Participation in Diels–Alder reaction does not necessarily preclude significant aromatic delocalisation and we hope to obtain a single crystal structure of a salt of the *nido*-anion **3**. Meanwhile we contend that our results have established the diene character of **1**, confirming Matteson's and Jones's earlier conclusions.[8] The name 'benzocarborane' may remain a convenient label for this interesting molecule but should not be interpreted as implying substantial π-delocalistion in the $C_6$ ring.

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## Footnotes

† *Crystal data* for **1**: $C_6H_{14}B_{10}$, $M$ = 194.27, orthorhombic, space group $Pca2_1$ (no.29), $a$ = 18.113(9), $b$ = 8.961(7), $c$ = 14.165(8) Å, $U$ = 2299(3) Å$^3$, 100 K; final $R$, $wR$ and $S$ are 0.0358, 0.0401 and 1.18 for 376 variables.

‡ *Crystal data* for **2**: $C_6H_{16}B_{10}$, $M$ = 196.29, orthorhombic, space group $Pbca$ (no. 61), $a$ = 14.226(4), $b$ = 18.203(5), $c$ = 18.339(5) Å, $U$ = 4749(2) Å$^3$, T = 150 K; final $R$, $wR$ and $S$ are 0.0422, 0.0506 and 1.10 for 388 variables.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/188.

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