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Carboranes as model hypercarbon systems; structural and bonding patterns in selected isoelectronic *closo*-borane and carborane systems; $[B_nH_n]^{2-}$, $[1\text{-}CB_{n-1}H_n]^-$ and $1,n\text{-}C_2B_{n-2}H_n$ ($n = 5$, 6, 7, 10 or 12)

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Dedicated on the occasion of his 75th birthday to Professor Tom Fehlner, good friend, pioneering chemist, and long-time research partner of KW.

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ABSTRACT

Computations have been carried out on the title boranes and carboranes, model hypercarbon cluster systems chosen to explore how effectively an individual carbon atom, whilst bonding by a normal 2-electron 2-centre bond to an *exo*-hydrogen atom, can also bond to sets of three, four or five equivalent boron atoms within a series of carborane clusters which have carbon atoms in axial sites of C_{3v}, C_{4v} or C_{5v} local symmetry. The calculated interatomic distances and bond orders and CH and BH group charges are reported, and the manner in which the introduction of CH units to replace BH^- units in *closo*-borane cages perturbs the distribution of the skeletal electrons in these clusters is discussed.

1. Introduction

The deltahedral (or deltahedral fragment) shapes of borane and carborane clusters, and the way those shapes reflect formula types and skeletal electron numbers, have long been familiar [1–16]. Less familiar is how these skeletal electrons are distributed around the vertices, edges or faces of the deltahedra, though many calculations have been carried out to establish relative stabilities, probing group charges and showing the importance of skeletal connectivities [17–23]. Limited insight is provided by resonating localized 2-centre 2-electron (2c2e) and 3-centre 2-electron (3c2e) bond networks [24,25]. As carboranes can act as model hypercarbon systems to show how a carbon atom can form a single 2c2e bond to one (*exo*) atom whilst linked by fractional order bonds to three, four or five other atoms, it seemed profitable to explore and illustrate this by MP2/6-31G* calculations on a selected series of isoelectronic *closo*-borane dianions $[B_nH_n]^{2-}$, monocarba-borane mono-anions $[1\text{-}CB_{n-1}H_n]^-$ and neutral dicarba-boranes $1,n\text{-}C_2B_{n-2}H_n$, in order to explore how the distribution of the skeletal electrons over their pseudo-spherical cluster surfaces varies with the skeletal connectivities and nuclear charges of the cluster atoms.

The two sets of systems we chose to study, shown in Fig. 1, were:-

(i) bipyramidal systems with $n = 5$, 6 or 7 skeletal atoms, in which two axial boron or carbon atoms occupy capping sites above and below an equatorial belt of 3, 4 or 5 boron atoms, and
(ii) bicapped antiprismatic systems with $n = 10$ or 12 skeletal atoms, in which two boron or carbon atoms occupy the capping sites, above and below the staggered tropical belts of 4 or 5 boron atoms.

We deliberately selected the carborane isomers in which the carbon atoms occupied axial sites (a), rather than the equatorial (e) or tropical (t) sites that in certain cases are thermodynamically preferred, in order to place the carbon atoms in sites with as highly symmetrical environments as possible (C_{3v}, C_{4v} or C_{5v}). In the first set of bipyramidal systems, one can probe the effect of replacing one and then both of their axial anionic $[BH]^-$ units by (neutral) CH units above and below an equatorial belt of three, four or five boron

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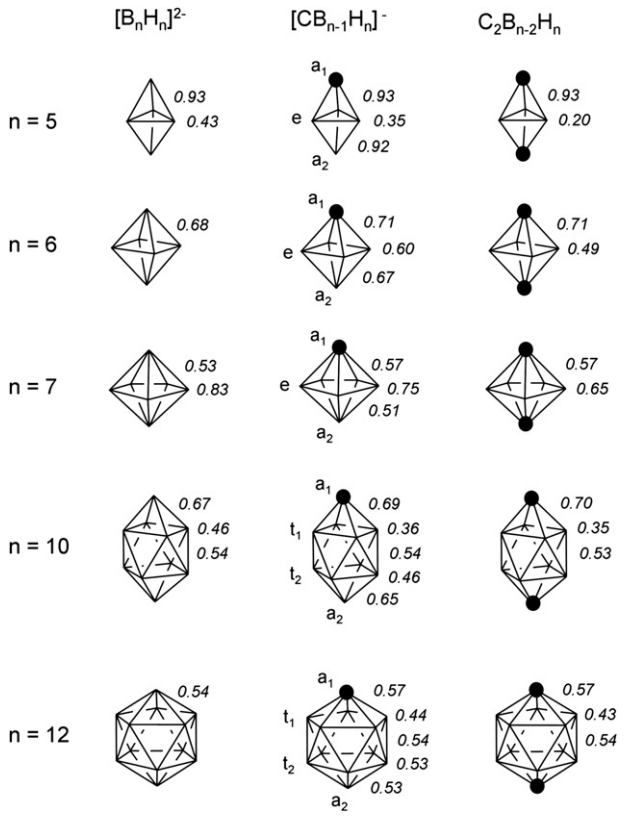

Fig. 1. Each naked vertex represents BH and each black dot represents a CH vertex. Bond order values are shown in italics.

atoms; in these carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$ and 1,7-$C_2B_5H_7$, the axial CH units compete with each other for electronic charge to bond to the same equatorial B_3H_3, B_4H_4 or B_5H_5 ring of atoms. In the second set, of bicapped antiprismatic systems 1,10-$C_2B_8H_{10}$ and 1,12-$C_2B_{10}H_{12}$, one can study how effectively the axial CH units bond to similar but distinct tropical B_4H_4 or B_5H_5 rings, each of which backs on to (and is staggered with respect to) another such tropical ring (with which it effectively shares an aromatic sextet of electrons).

2. Results and discussion

2.1. The calculational method

As we wished to consider series of compounds that included hypothetical unknown species as well as systems that have been prepared and well characterised analytically, spectroscopically, structurally and computationally, and wanted to explore variations in structural and bonding characteristics across series, we used MP2/6-31G* calculations throughout to monitor such variations which were likely to have been distorted if we had used a mix of experimental and computed data. MP2/6-31G* calculations have been shown by many studies of boranes and carboranes to afford optimised structures with interatomic distances of comparable precision to experimentally determined structures [26]. Indeed, such calculations are being increasingly used in borane and carborane chemistry to predict the structures and stabilities of ever more exotic systems, and routes thereto [17–27].

We carried out MP2/6-31G* calculations on the fifteen systems $[B_nH_n]^{2-}$, $[1\text{-}CB_{n-1}H_n]^-$ and 1,*n*-$C_2B_{n-2}H_n$ (n = 5, 6, 7, 10, and 12) with the Gaussian09 computational package [28]. Our bond orders/indices were calculated by the Wiberg Bond Index method and the atomic and group charges by Natural Population Analysis (NPA) using the NBO 3.1 program within Gaussian09. These afforded the optimised geometries with the B–B and B–C bond distances and indices and atomic charges. Frequency calculations for all optimised geometries with symmetry constraints at MP2/6-31G* including the unfavourable high-energy isomers, $[1\text{-}CB_6H_7]^-$ and 1,7-$C_2B_5H_7$, showed no imaginary frequencies. Each triad of three isoelectronic species is considered in turn below.

2.2. The trigonal bipyramidal species $[B_5H_5]^{2-}$, $[1\text{-}CB_4H_5]^-$ and 1,5-$C_2B_3H_5$

Bond lengths and indices, total bond indices at particular atoms, and CH and BH group charges for these systems are listed in Table 1. The parent dianion $[B_5H_5]^{2-}$, though as yet unknown, has been the subject of earlier calculations [3,19,20,29] which have shown the bonding between the axial and equatorial boron atoms to be far stronger than that between the equatorial atoms, as revealed again here, reinforcing the simplistic picture given by a localized bond description in which three 2c2e BB bonds along axial–equatorial edges in one hemisphere, and three 3c2e BBB bonds in adjacent faces in the other hemisphere, but resonating between the two hemispheres, imply bond orders of 0.833′ and 0.333′ for the axial–equatorial and equatorial–equatorial bonds respectively [13,30]. A description of the bonding in terms of six axial–equatorial 2c2e bonds, and no bonding around the equator, with the equatorial boron atoms using only three AOs (one for the *exo*-hydrogen, one each for the axial boron neighbours), can be ruled out.

The effect of replacing one and then both of the axial boron atoms of $[B_5H_5]^{2-}$, formally as B^- anions, by neutral carbon atoms, is reflected in the data in Table 1 for $[1\text{-}CB_4H_5]^-$ and 1,5-$C_2B_3H_5$ [31,32]. The most marked bonding effect is on that between the equatorial boron atoms, which move only slightly further apart though the bond index between them decreases dramatically, from 0.43 to 0.35 then 0.20 as successive axial carbon atoms are introduced. The total skeletal bond indices of the equatorial set of boron atoms decrease in the same sequence from 2.72 to 2.54 to 2.26, markedly lower values than those (2.79, 2.76) of the axially-located boron atoms. No significant change occurs in the bond indices of the axial–equatorial bonds, which are essentially the same for BC bonds as BB bonds.

Drainage of electronic charge from the equatorial BH units as axial CH units are introduced is reflected in the stepwise change in the charge on each equatorial BH unit from −0.32 to +0.03 to +0.41 a.u.. The equatorial B_3H_3 ring in $[B_5H_5]^{2-}$ bears a formal negative charge of −0.96; this changes dramatically to +0.09 in $[CB_4H_5]^-$, becoming +1.23 a.u. in $C_2B_3H_5$, as axial BH units, each bearing charges of −0.53 a.u. in the dianion, are replaced by CH units each bearing charges of −0.62 a.u. in the neutral carborane $C_2B_3H_5$.

Table 1
Calculated BB and BC bond distances and bond orders, and BH and CH group charges, for the trigonal bipyramidal *closo*-cluster systems $[B_5H_5]^{2-}$, $[1\text{-}CB_4H_5]^-$ and 1,5-$C_2B_3H_5$. Subscripts a and e identify axial and equatorial sites.

(a) Bond distances/pm (bond orders in parentheses)

System	$C_{a_1}B_e$	B_eB_e	$B_{a_2}B_e$
$[B_5H_5]^{2-}$	–	181 (0.43)	167 (0.93)
$[1\text{-}CB_4H_5]^-$	155 (0.93)	182 (0.35)	167 (0.92)
1,5-$C_2B_3H_5$	155 (0.93)	184 (0.20)	–

(b) Group charges/a.u. (total order of skeletal bonds to that group)

System	$C_{a1}H$	B_eH	$B_{a2}H$
$[B_5H_5]^{2-}$	–	−0.32 (2.72)	−0.53 (2.79)
$[1\text{-}CB_4H_5]^-$	−0.66 (2.79)	+0.03 (2.54)	−0.42 (2.76)
1,5-$C_2B_3H_5$	−0.62 (2.79)	+0.41 (2.26)	–