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THE RELATIONSHIP BETWEEN CYCLIC HYDROCARBONS AND BORANES: CYCLOBUTANE AS A HYPHO CLUSTER

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Summary: The close structural relationship that exists between many cyclic hydrocarbons and borane clusters is noted. Treatment of cyclobutane as a member of the $B_7H_7^{2-}$, $C_6Me_6^{2+}$ $C_5H_5^-$ family allows a rationalisation of its puckered structure.

The puckering of the cyclobutane ring (Fig. 1(a)) is usually discussed in terms of distortion from an expected square planar structure (Fig. 1(b)). The puckering reduces the nonbonding repulsive interactions between the hydrogen atoms of adjacent methylene groups, though at the expense of increased ring bond angle strain as the ring angles decrease. The dihedral angle, α, between the two halves of the ring, ca. 35° (1-5), is that at which the puckering-promoting and -resisting forces presumably balance. Here, we show how a puckered structure, with α = 36°, is seen to be appropriate for cyclobutane if one treats it as a member of the family of cluster and ring compounds to which the species $B_7H_7^{2-}$, $C_2B_5H_7$, $C_6Me_6^{2+}$ (6) and $C_5H_5^-$ (7,8) also belong.

Fig.1 (a) (b)

The manner in which the structures of borane-type clusters reflect the numbers of electrons available to hold their skeletal atoms together is now well-established (8-13), and a few hydrocarbon systems such as $C_5H_5^+$ (9-11, 14-18), $C_6Me_6^{2+}$ (6) and benzvalene (8) have been seen to conform to the same pattern. However, it is by no means commonly recognized that many other hydrocarbons adopt structures clearly related to those of boranes, so a secondary objective of this note is to give some indication of the large range of hydrocarbon systems to which the pattern applies.

To illustrate the pattern, it is convenient to focus attention on the number of atoms, *n*, in the molecular skeleton, and the number of skeletal electron pairs, *s*, available to hold these atoms together (19). Borane clusters $B_nH_n^{2-}$, B_nH_{n+4}, B_nH_{n+6} *etc.* and isoelectronic systems such as carboranes $C_2B_{n-2}H_n$, $C_2B_{n-2}H_n^{2-}$, $C_4B_{n-4}H_n^{2-}$ *etc.* may be regarded as clusters of *n* BH (or CH) units held together by the electrons they themselves contribute (2 from each BH unit, 3 from each CH unit) together with extra electrons from any extra hydrogen atoms or

Table 1. Systems formally containing 8 skeletal bond pairs

Structural type		*n**	Examples†
closo	2(a)	7	$B_7H_7^{2-}$; $C_2B_5H_7$; $MeGaC_2B_4H_6$; $(OC)_3MnC_3B_3H_5Me$; $Fe_3(CO)_8C_4Ph_4$; various triple-decker sandwich systems (20,22)
nido	2(b)	6	B_6H_{10}; $C_xB_{6-x}H_{10-x}$ (X = 1-4); $C_6Me_6^{2+}$ (6); $C_5Me_5BI^+$ (21) η^5-C_5H_5 complexes, e.g. $(\eta^5\text{-}C_5H_5)Mn(CO)_3$
arachno	2(c)	5	B_5H_{11}; η^4-butadiene complexes, e.g. $(\eta^4\text{-}C_4H_6)Fe(CO)_3$
arachno	2(d)	5	$C_5H_5^-$ and related pentagonal aromatic systems
hypho	2(e)	4	C_4H_8 (cyclobutane) (1-5)

* number of skeletal atoms; † for references, see refs. (8,9) unless otherwise cited.

Table 2. Cyclic hydrocarbons as borane-type clusters

Species	Formula	*n*	*s*	Structural type	
cyclopropane	C_3H_6	3	6	arachno	3(a)
tetrahedrane	C_4H_4	4	6	nido	3(b)
cyclobutadiene dianion	$C_4H_4^{2-}$	4	7	arachno	3(c)
bicyclo[1.1.0]butane	C_4H_6	4	7	arachno	3(d)
cyclopentadienyl cation	$C_5H_5^+$	5	7	nido	3(c)
cyclobutane	C_4H_8	4	8	hypho	2(e)
cyclopentadienyl anion	$C_5H_5^-$	5	8	arachno	2(d)
hexamethylbenzene dication	$C_6Me_6^{2+}$	6	8	nido	2(b)
cyclopentene	C_5H_8	5	9	hypho	4(a)
bicyclo[2.1.0]pentane	C_5H_8	5	9	hypho	4(b)
benzvalene	C_6H_6	6	9	arachno	4(c)
hexamethylbicyclo[2.1.1]hexenyl cation	$C_6Me_6H^+$	6	9	arachno	4(d)

Fig. 2 Systems formally containing 8 skeletal bond pairs, (see Table 1)

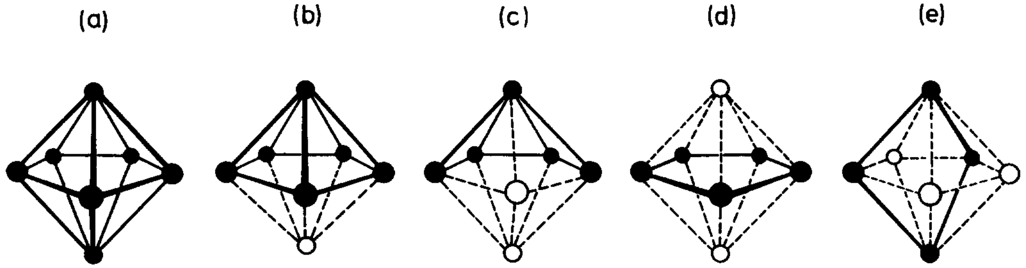


Fig. 3 Structures of cyclic hydrocarbons with s=6 or 7 related to parent polyhedra; (see Table 2).

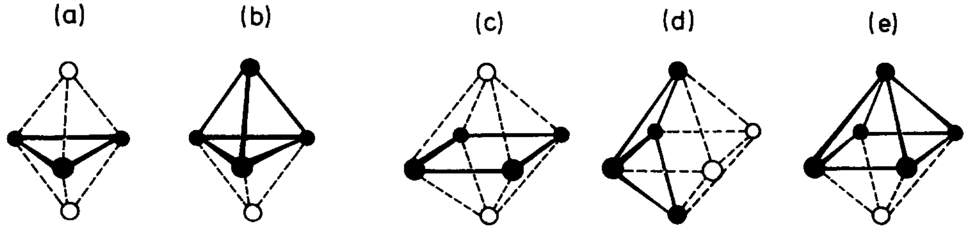
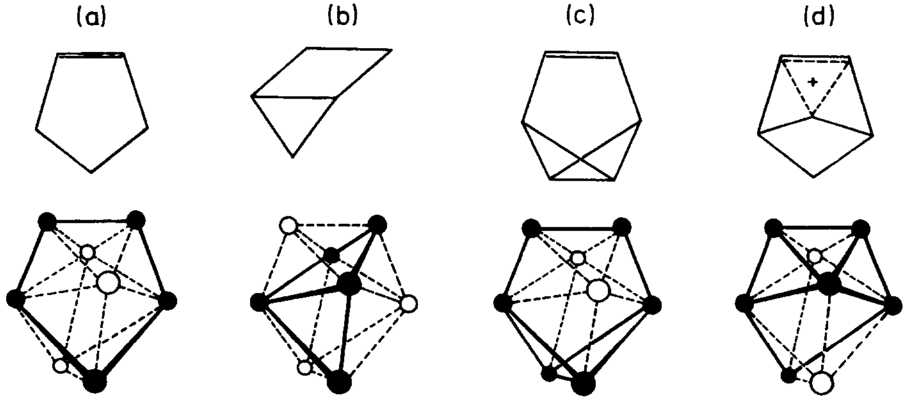


Fig 4 Structures of cyclic hydrocarbons with s=9 related to parent polyhedra, (see Table 2)



any overall negative charge. Their structures reflect the number of skeletal bond pairs, $\underline{s}$, as follows. The polyhedron on which the structure is based has ($\underline{s}$-1) vertices, of which all are occupied (a '<u>closo</u>' structure) if $\underline{n}$ = $\underline{s}$-1, all but one ('<u>nido</u>') if $\underline{n}$ = $\underline{s}$-2, all but two ('<u>arachno</u>') if $\underline{n}$ = $\underline{s}$-3, and all but three ('<u>hypho</u>') if $\underline{n}$ = $\underline{s}$-4. Table 1 and Figure 2 illustrate the structural pattern for systems with $\underline{s}$ = 8.

Cyclobutane, C_4H_8, treated as four CH units held together by the electrons they contribute (4 x 3 = 12) together with one from each of the four extra hydrogen atoms, formally has $\underline{n}$ = 4, $\underline{s}$ = 8, i.e. it is a <u>hypho</u> member of this series. Its puckered structure is readily rationalized as shown in Fig. 2(e) by assuming that its four carbon atoms occupy the axial vertices and two nonadjacent equatorial vertices of a pentagonal bipyramid, the D_{5h} symmetry of which leads to an expected dihedral angle, α, of 36°, in remarkably good agreement with the measured value of <u>ca</u>. 35° (1-5).

Other cyclic hydrocarbons with structures related to the same 5- to 8-vertex polyhedra as borane clusters are listed in Table 2 and shown in Figs. 3 and 4. A detailed discussion of their relationship to boranes, including bond length, bond order, bond energy, and orbital correlations will be published elsewhere, together with a consideration of systems related to higher polyhedra, and predictions about new species.

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