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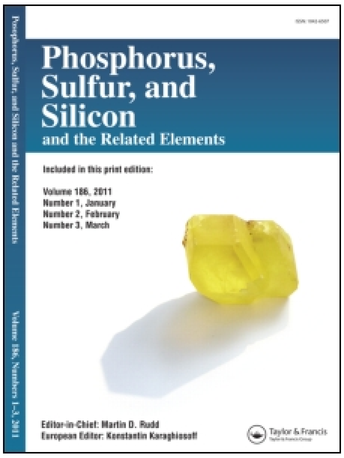

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SOME BORON-CONTAINING RING SYSTEMS

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The synthesis and characterisation of series of new types of boron-containing ring systems are described. They include:
(a) carborane systems containing C-H--X (X = O or N) hydrogen bonds;
(b) systems in which C_n rings share C-C links with *o*-carborane units;
(c) macrocycles containing 2,3 or 4 carborane icosahedra linked through benzene or pyridine rings, and
(d) 'new types of 'carborazacycles' containing one carbon, two boron and three nitrogen atoms in a single 6-membered ring system.

Keywords carborane assemblies/ macrocycles; carborazacycles; hydrogen-bonding.

INTRODUCTION

This paper is concerned primarily with ring systems incorporating carborane icosahedra. The icosahedral carboranes $C_2B_{10}H_{12}$ are interesting as thermally and chemically very stable species that have an extensive derivative chemistry.[1,2] Of particular concern to us here are derivatives bearing substituents on the two carbon atoms, which can occupy adjacent (*ortho*), alternate (*meta*) or opposing (*para*) sites on the icosahedral molecular framework (Fig. 1), when the angles between the bonds to the substituents resemble those of comparable benzene derivatives (*ca* 63 °, 117 ° and 180 ° for carborane derivatives, 60 °, 120 ° and 180 ° for benzene derivatives). Although the carborane icosahedron has a greater diameter than the benzene ring (3.37 pm *cf* 2.8 pm) it can in principle replace a benzene or similar hexagonal ring system in a molecule with relatively little change in the positions and orientations of substituents. Moreover, the *closo*-$C_2B_{10}H_{12}$ icosahedron is capable of being converted into a *nido*-icosahedral fragment structure by removal of a BH unit (formally as BH^{2+}, by the action of nucleophilic reagents) from a site adjacent to the two carbon atoms (Fig. 1), leaving a C_2B_3 pentagonal open face that has a capacity to bond metal ions similar to that of a cyclopentadienyl ligand.

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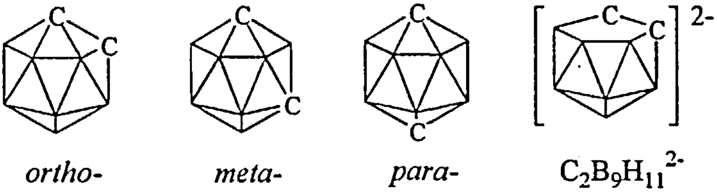

Figure 1 The three $C_2B_{10}H_{12}$ carborane skeletons, and one *nido* C_2B_9 isomer.

These structural and bonding features of icosahedral and icosahedral-fragment carboranes have been exploited by us in the present work, which stemmed from a study of carborane polymers which had revealed the chemical and thermal stability of diarylcarboranes in general and the phenylene-carborane-phenylene unit

$-C_6H_4CB_{10}H_{10}CC_6H_4-$ in particular as a convenient linking unit in thermally stable poly-ether-ketones of the type shown in Fig 2.[3]

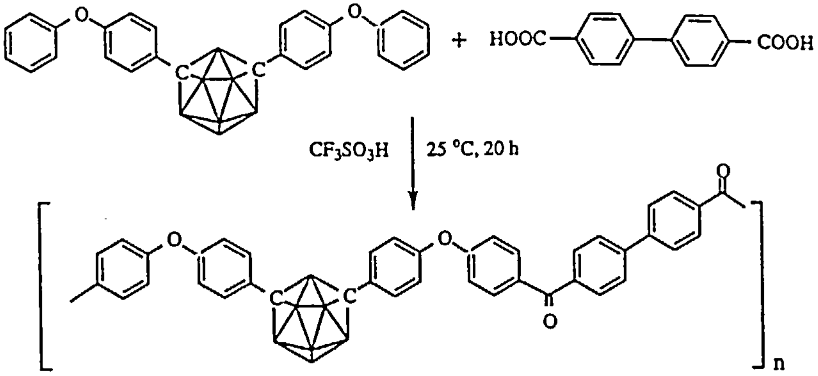

FIGURE 2 Preparation of a poly-ether-ketone incorporating carborane icosahedra.

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The cyclic systems that are the subject of the present paper are described below. Some systems held together by hydrogen bonds involving unsubstituted carboranyl C-H--O or C-H--N units are discussed first.[4,5] A section follows on benzocarborane, in which four CH units as a 1,3-butadiene residue link the two carbon atoms of *ortho*-carborane.[6] Macrocyclic systems in which two, three or four carborane icosahedra are linked through benzene or pyridine rings are described next,[5,7] and this survey ends with an outline of our work on carborazacyclic systems directly preparable by hydroboration of nitriles.[8]

SOME HYDROGEN-BONDED SYSTEMS

The C-H bonds of the icosahedral carboranes are relatively acidic. Although the acidity decreases in the sequence *ortho* > *meta* > *para*, all three types of carboranyl C-H bonds can participate in hydrogen bonds to sources of lone pairs of electrons. This had been detected by decreases in ν(C-H) in their vibrational spectra[9] though not documented structurally until we discovered that *ortho*, *meta* and *para*- carborane formed C-H--O hydrogen bonds to the oxygen atom of HMPA (hexamethylphosphoramide, $(Me_2N)_3PO$) molecules of sufficient strength to allow crystalline 1:1 adducts HMPA:$C_2B_{10}H_{12}$ to be isolated and structurally characterised.[4]

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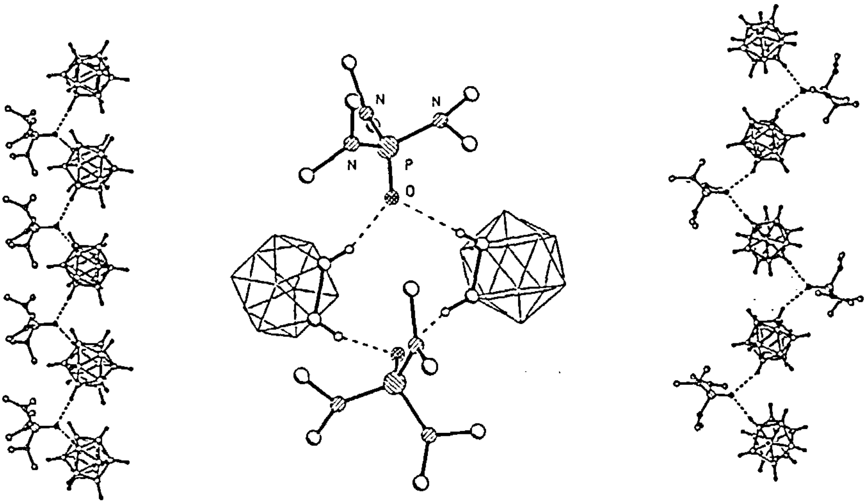

Figure 3 H-bonding in adducts of $(Me_2N)_3PO$ with 1,7-, 1,2- and 1,12-$C_2B_{10}H_{12}$

These adducts have chain structures in the case of *meta* and *para*-carborane but a macrocyclic dimeric structure in the case of *ortho*-carborane. (Fig. 3) presumably because the acute angle between the C-H bonds of *ortho*-carborane makes a cyclic structure preferable to a polymeric one. These HMPA adducts are of particular interest because their C-H--O hydrogen bonds lock the carborane icosahedra into orientations that define the positions of the skeletal carbon and boron atoms so allowing precise determination of their skeletal bond lengths and angles which all too often, in structural studies of unsubstituted carboranes, are average values because of disordering between carbon and boron sites.

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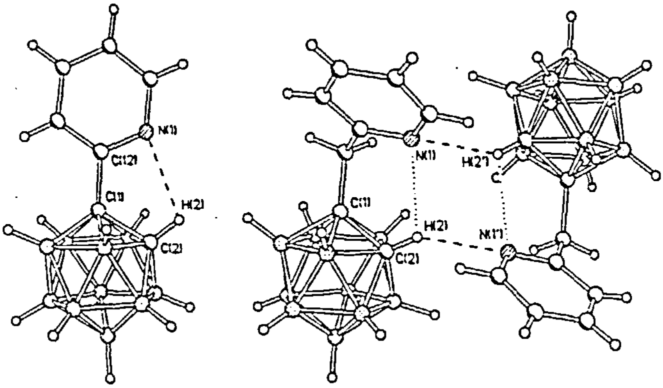

Figure 4 H-bonding in 2-pyridyl and 2-picolyl derivatives of 1,2-$C_2B_{10}H_{12}$

Having shown that C-H--X hydrogen bonds involving carboranyl C-H units can be strong enough to account for adduct formation with

HMPA, we sought further structural evidence of such bonding in other systems. Fig. 4 shows 2-pyridyl- and 2-picolyl-*ortho*-carborane as examples of systems in which intramolecular C-H--N hydrogen bonding occurs.[5]

BENZOCARBORANE AND RELATED SPECIES

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Benzocarborane, the compound in which four CH units as a 1,3-butadiene system bridge the two skeletal carbon atoms of ortho-carborane (Fig. 5) was first prepared some thirty years ago and deduced to have a diene structure from its reactions and spectra.[10] We have confirmed this by X-ray crystallographic studies of the compound itself and the 2-butene-1,4-diyl precursor through which benzocarborane can be prepared.[6] One puzzling feature of benzocarborane was that it did not undergo a Diels-Alder reaction with maleic anhydride, despite its diene character. We conclude that this unreactivity is attributable to a combination of steric and electronic factors. Deboronation of benzocarborane using tetrabutylammonium fluoride in the presence of water[11] affords the analogous *nido* anion which does undergo Diels-Alder addition to maleic anhydride.

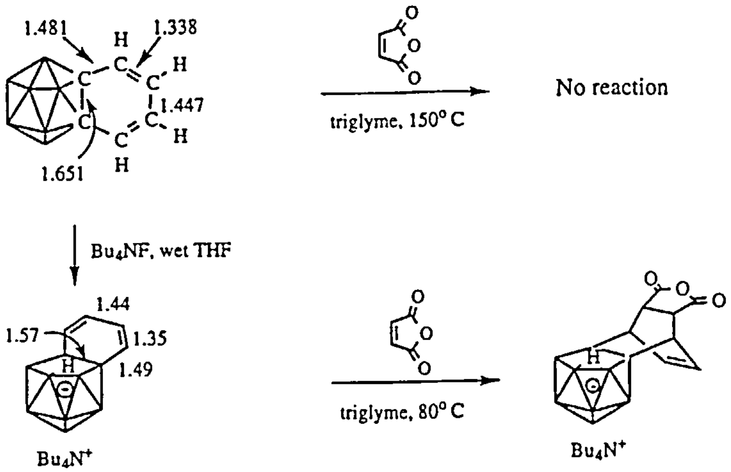

Figure 5 Carbon-carbon bond lengths in benzocarborane, and a Diels-Alder reaction of the *nido*-benzocarborane anion.

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MACROCYCLIC SYTEMS INCORPORATING CARBORANES

We have already alluded to our studies of poly-ether-ketone systems, incorporating phenylene-carborane-phenylene linking units, which have remarkably high chemical and thermal stability.[3] Such studies prompted us to explore also the synthesis of polymeric or oligomeric systems in which carborane icosahedra are linked solely through benzene (or occasionally pyridine) rings. Cyclic oligomers have been isolated as minor products of some of these studies. Representative stuctures are shown in Fig. 6. Most have been prepared by reactions between appropriate metalla-carboranes and aryl halides.[7,12] Structures of some related acyclic species are also included for purposes of comparison.

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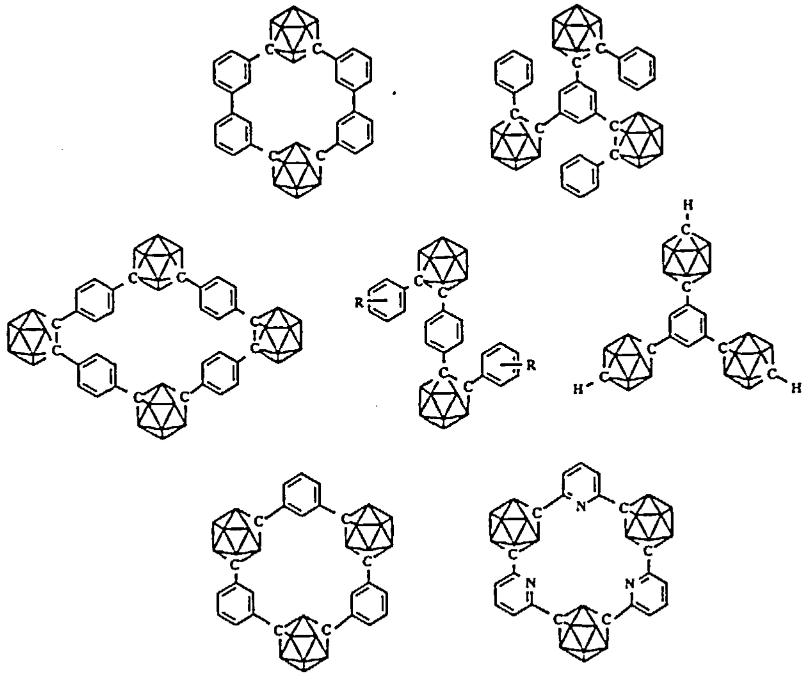

Figure 6 Examples of cyclic and acyclic carborane assemblies

CARBORAZACYCLES MADE BY NITRILE-HYDROBORATION REACTIONS.

Many years ago, studies of the hydroboration of nitriles RCN showed that such reactions can afford substantial yields of N-trialkylborazines $(RCH_2NBH)_3$, and indeed provide the simplest route to such products from commercially available starting materials.[13] A reinvestigation of such reactions,[8] which were known to afford higher molecular weight materials as byproducts has shown that under some conditions a second unexpected product can be isolated in astonishingly high yields, comparable to those of the N-trialkylborazine. This second product has been deduced by multinuclear NMR studies to have the structure shown in Fig. 7, a structure formally related to dihydronaphthalene and intelligible in terms of nucleophilic attack by one nitrile nitrogen on the carbon atom of a second nitrile at some stage during hydroboration. Its formula corresponds to a reagent ratio of $5RCN:4BH_3$

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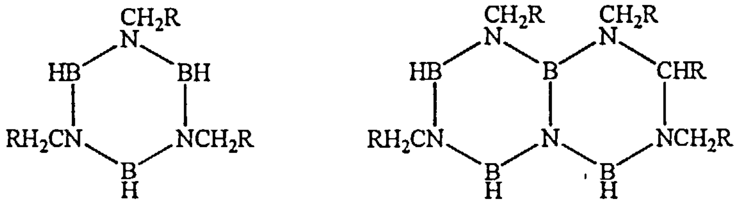

R = Me, Et, *t*-Bu, CH_2F

Figure 7 Products formed during RCN/B_2H_6 reactions

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