Carborane Derivatives and Polymer Synthesis

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INTRODUCTION

The icosahedral carboranes 1,2-, 1,7- and 1,12-C₂B₁₀H₁₂ are chemical building blocks of high boron content and remarkable thermal and chemical stability, resistant to attack by acids and oxidising agents and generally inactive towards biological systems. Despite their cost, such properties make them suitable for various specialised applications. These include the incorporation of large concentrations of boron atoms in tumour-seeking drugs for boron neutron capture therapy (BNCT),¹ and the synthesis of polymers for high temperature² or neutron shielding³ purposes or for firing to form ceramics related to boron carbide.⁴ Their exceptional hydrophobic character, and the unusual solubility characteristics of their ionic derivatives,⁵ together with their ability to form nido anionic species with remarkable ligand properties by treatment with nucleophiles, has led to their use in metal complexing agents for solvent extraction, particularly of fissionable metals where neutron capture is desirable,⁶ in radiochemical drugs⁷ and in new catalysts.⁸ The non-linear optical (NLO) properties of selected derivatives are also attracting attention.⁹

Our own recent interest in such systems has focussed on the synthesis of new types of thermally stable or electronically interesting polymers incorporating icosahedral carboranes, and of ceramic materials related to boron carbide accessible through precursor polymers.²,¹⁰ Particular attention has been paid to polymers of the poly-ether-ketone (PEK) or poly-ether-ether-ketone (PEEK) type in which ortho, meta or para carborane units and phenylene rings are linked through such functional groups. We are also exploring related oxygen-free systems, including macrocycles, in which carborane icosahedra are linked through benzene or other aromatic rings, and are investigating the capacity of carborane icosahedra to interact electronically with sources of π-bonding electrons attached to their carbon atoms. Our findings are summarized below.
Studies on model systems ROR' or RCOR' containing carboranyl groups R attached directly to ether or ketone units showed them to be susceptible to hydrolytic cleavage of their C-O or C-CO bonds.\(^2\) We have therefore, in our polymer work, used phenylene spacers to separate the carborane icosahedra from the ether or ketone units. Illustrative routes to representative polymers are shown in Figure 1. For ortho-carborane systems 1,2-C\(_2\)R\(_2\)B\(_{10}\)H\(_{10}\), it was possible to attach suitable substituents to an alkyne before forming the carborane polyhedron.\(^10\) For meta- and para-systems 1,7- and 1,12-C\(_2\)R\(_2\)B\(_{10}\)H\(_{10}\), it proved to be more convenient to attach suitable substituents R to the icosahedron by exploiting the reactivity of copper derivatives Cu\(_2\)C\(_2\)B\(_{10}\)H\(_{10}\) towards aryl iodides in the presence of pyridine.\(^11\) Polymers were made by acylation reactions between appropriate carboxylic acids and phenoxypyphenyl derivatives in triflic acid as both solvent and catalyst, from which the soluble product polymers were recovered by pouring into water.

Figure 1    Routes to PEEK- and PEK-type carborane polymers

Products could be cast as films from CH\(_2\)Cl\(_2\) or CHCl\(_3\) solution, and were generally amorphous, with T\(_g\) in the region 180-220°C. Thermogravimetric analysis showed that evolution of volatiles began at about 350-400°C without melting, the total weight loss even at 1000°C being only some 10-15%, suggesting that inert atmosphere pyrolysis might lead to a ceramic residue of boron carbide dispersed in a graphite matrix.
Following our discovery\textsuperscript{12} that deprotonation of the C-hydroxy ortho-carborane 1-Ph-2-OH-1,2-C\textsubscript{2}B\textsubscript{10}H\textsubscript{10} gave an anion RO\textsuperscript{-} in which the negative charge was delocalised into the carborane cage, to which the oxygen atom was attached by a double bond (length 1.25\textdegree A), we have prepared and characterised several other systems that offered scope for related exo \pi-bonding (Figure 2).

![Figure 2 Ortho carborane systems showing exo \pi-bonding](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>RO\textsuperscript{-}</th>
<th>RS\textsuperscript{-}</th>
<th>R\textsubscript{2}S</th>
<th>R\textsubscript{2}NH</th>
<th>R\textsubscript{2}N\textsuperscript{-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(C---C)/\textdegree A</td>
<td>2.00</td>
<td>1.86</td>
<td>1.76</td>
<td>1.80</td>
<td>1.99</td>
</tr>
<tr>
<td>d(C---X)/\textdegree A</td>
<td>1.25</td>
<td>1.73</td>
<td>1.79</td>
<td>1.40</td>
<td>1.35</td>
</tr>
</tbody>
</table>

They include the sulphur analogue of the original anion,\textsuperscript{13} RS\textsuperscript{-}, the bis(carboranyl)sulphide R\textsubscript{2}S and amine R\textsubscript{2}NH, and the anion R\textsubscript{2}N\textsuperscript{-} (R=1-Ph-1,2-C\textsubscript{2}B\textsubscript{10}H\textsubscript{10}).\textsuperscript{14} All have relatively short exo C---X bonds and long C1---C2 bonds, and the CXC' planes in the systems R\textsubscript{2}X (X=S, NH, N') show that the exo \pi-bonding uses the p AO on C2 that lies in the C1-C2-X plane. Apart from revealing a hitherto unprecedented capacity of carbon atoms to form a multiple bond to one atom whilst bonding simultaneously to four or five other atoms (when the skeletal C---C distance increases to ca 2.0\textdegree A, this link hardly counts as a bond) these systems effectively show that carborane polyhedra attached directly to sources of \pi-bonding electrons can in principle participate in extended conjugative interactions that may lead to exploitable bulk properties.

MACROCYCLES INCORPORATING CARBORANE ICOSAHEDRA

During an exploration of the feasibility of preparing polymers in which carborane polyhedra were linked through arylene rings, we have also developed synthetic routes to macrocyclic systems in which meta-carborane units were linked by 1,3-disubstituted benzene rings or 2,6-disubstituted pyridine rings (Figure 3).\textsuperscript{15} Such systems promise to have a rich chemistry themselves.
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REFERENCES