DECLARATION

The work described in this thesis was carried out in the University of Durham between October 1988 and September 1991. It has not been submitted, either completely or in part, for another degree in this or any other University and is the original work of the author except where acknowledged by reference.

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ICOSAHEDRAL

CARBORANE

DERIVATIVES

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To Mum and Dad.....

ABSTRACT

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This thesis describes some new derivative chemistry of the icosahedral carboranes, 1,2- and 1,7-$C_2B_{10}H_{12}$, related to the incorporation of carborane polyhedra in Victrex-type polymers (polymers incorporating para-disubstituted benzene rings linked through ether and ketone functional units).

It begins with a survey of relevant carborane literature, and reviews the spectroscopic techniques by which carborane derivatives can be characterized. The syntheses of a range of boron-iodo carboranes by reaction of iodine, nitric acid and sulphuric acid with the parent carboranes are described, and the ^{11}B and ^{13}C n.m.r. spectra of the products are discussed.

Syntheses and model reactions of series of diarylcarboranes $R'R''C_2B_{10}H_{10}$ (in which the aryl substituents R′ and R″ have functional groups suitable for their incorporation in polymers) are described, including the previously unknown 1,9- and 1,12-bis(4-carboxyphenyl)-*ortho*-carborane, 1,7-bis(phenoxyphenyl)-*meta*-carborane and 1,7-bis(4-carboxyphenyl-*meta*-carborane - 4,4′-diphenoxybiphenyl polymer. A new and efficient method of 1,7-diaryl-*meta*-carboranes from *meta*-carborane with butyllithium, copper (I) chloride and aryldiazonium tetrafluoroborate as reagents is described.

Several C-substituted hydroxy, mercapto and amino derivatives of *ortho*- and *meta*-carborane have been prepared and deprotonated using triethylamine of N,N,N′,N′-tetramethyl-1,8-diaminonaphthalene (proton sponge). The molecular structure of the proton sponge salt of 1-phenyl-2-mercapto-*ortho*-carborane, $[PhCB_{10}H_{10}CS]^-[C_{10}H_6(NMe_2)_2H]^+$, has been determined and found to contain cage distortions which are rationalized by frontier molecular orbital considerations. Structures of 1-phenyl-2-phenylethynyl-*ortho*-carborane, 1-phenyl-2-(4-methylphenyl)azo-*ortho*-carborane, 1-phenyl-2-(4-methoxyphenyl)-*ortho*-carborane and 2,2′-bis(1-phenyl-*ortho*-carboranyl) trisulphide, determined by X-ray crystallography, are reported.

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