Carboranes containing a pendant pyridyl group are of interest in their own right and as precursors to novel metallacarboranes. 1-2'-pyridylherencearene\textsuperscript{1,2} and 1-2'-picolyl \textit{ortho}carbonarene\textsuperscript{3}, although structurally similar, show significant differences in their IR and NMR spectra. These are rationalised by their crystal structures: the pyridyl derivative (Fig. 1) shows an \textit{intra}molecular C-H-N hydrogen bond whereas the picolyl compound (Fig. 2) displays \textit{inter}molecular C-H-N bonding.

This difference causes very different crystal packing, presenting the possibility of crystal engineering by minor changes in the pendant group. Reaction of the C-lithio derivatives of these compounds with Me\textsubscript{3}SnCl gives the corresponding C-trimethyltin derivatives: the crystal structure of the pyridyl derivative reveals Sn-N interaction.

ANTIPODAL EFFECTS AND EXO PI-BONDING IN ICOSAHEDRAL CARBORANES

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Since our discovery of the possibility of exo multiple bonding between a carbon atom of 2-R-1,2-C₂B₁₀H₁₀ and a substituent oxygen₁, sulphur² or nitrogen³ atom (Figure 1) we have structurally characterised a range of nitrogen-substituted carboranes to investigate the effect further.

In all the compounds bond lengths and orientations indicate a varying degree of exo multiple bonding due to a C-N dative pi-bond. The lengthening of the C-C skeletal bond is found to be dependent on the degree of exo pi-bonding and is hence related to the C-N distance (Figure 2).

The ¹¹B shift of the antipodal atom⁴ is found to be a good indication of the degree of exo pi-bonding. Similar trends in both the oxygen and sulphur systems will be illustrated.

Figure 1

Figure 2

2 R. Coult, M. A. Fox, W. R. Gill and K. Wade, Polyhedron, 1992, 11(20), 2717