

## PYRIDYL AND PICOLYL DERIVATIVES OF CARBORANE

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Carboranes containing a pendant pyridyl group are of interest in their own right and as precursors to novel metallocarboranes. 1-2'-pyridyl*orthocarborane*<sup>1,2</sup> and 1-2'-picolyl *orthocarborane*<sup>3</sup>, 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 intramolecular C-H-N hydrogen bond whereas the picolyl derivative (Fig. 2) displays intermolecular C-H-N bonding.

Fig. 1

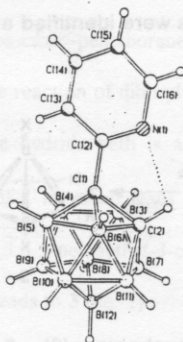
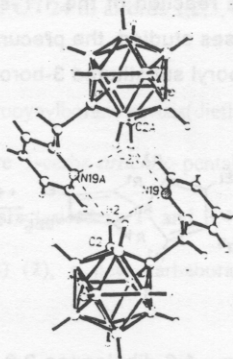


Fig. 2



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<sub>3</sub>SnCl gives the corresponding C-trimethyltin derivatives: the crystal structure of the pyridyl derivative reveals Sn-N interaction.

<sup>1</sup> R. Coult, M.A. Fox, W.R. Gill, P.L. Herbertson, J.A.H. MacBride and K. Wade, *J. Organometal. Chem.*, **1993**, *462*, 19.

<sup>2</sup> W.R. Gill, P.L. Herbertson, J.A.H. MacBride and K. Wade, *J. Organometal. Chem.*, **1996**, *507*, 249

<sup>3</sup> A.S. Batsanov, M.A. Fox, T.G. Hibbert, J.A.K. Howard, J.A.H. MacBride, N. Tinker and K. Wade, in preparation.

## 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-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> and a substituent oxygen<sup>1</sup>, sulphur<sup>2</sup> or nitrogen<sup>3</sup> 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 <sup>11</sup>B shift of the antipodal atom<sup>4</sup> 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.

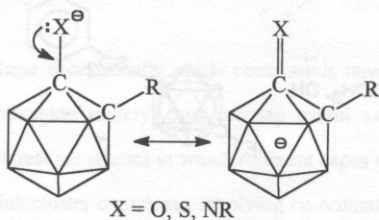


Figure 1

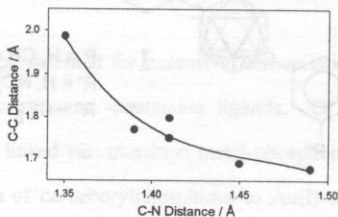


Figure 2

<sup>1</sup> D. A. Brown, W. Clegg, H. M. Colquhoun, J. A. Daniels, I. R. Stephenson and K. Wade, *J. Chem. Soc., Chem. Commun.*, **1987**, 889

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

<sup>3</sup> W. Clegg, V. C. Gibson, W. R. Gill, J. A. H. MacBride, R. J. Peace and K. Wade, *In preparation*

<sup>4</sup> S. Hermánek, J. Plešek, V. Gregor and B. Stíbr, *J. Chem. Soc. Chem. Commun.*, **1977**, 561