

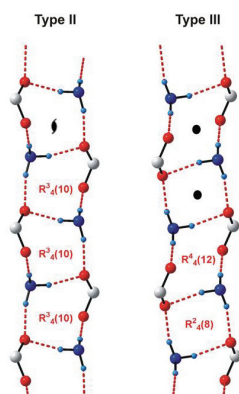
FA4-MS07-O1

A Robust Supramolecular Synthon: Effect on Melting Points and Wallach's Rule. Susan A. Bourne. *Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa.*

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One of the aims of crystal engineering is to produce crystalline materials with predictable and reproducible supramolecular interactions. Although a number of other interactions are possible, the most common supramolecular "glue" used in crystal engineering is the hydrogen bond.

We have recently undertaken a systematic survey of the charge-assisted supramolecular heterosynthons that occur in ammonium carboxylate salts. Most structures reported previously incorporate either regularly repeating hydrogen-bonded rings propagated by a 2-fold screw axis or alternating hydrogen bonded rings propagated by a centre of inversion. We set out to examine how robust these supramolecular synthons would be under the influence of various molecular interferences. In doing so, we also considered the validity of the empirical "Wallach's rule" which suggested that racemates have more stable crystal structures than their related enantiomorphs.



Compounds have been characterised by single crystal and powder X-ray diffraction. Their thermal stability and decomposition behaviour have been studied using Differential Scanning Calorimetry, Thermogravimetry and Hot Stage Microscopy.

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Keywords: crystal engineering; supramolecular synthon; ammonium carboxylates

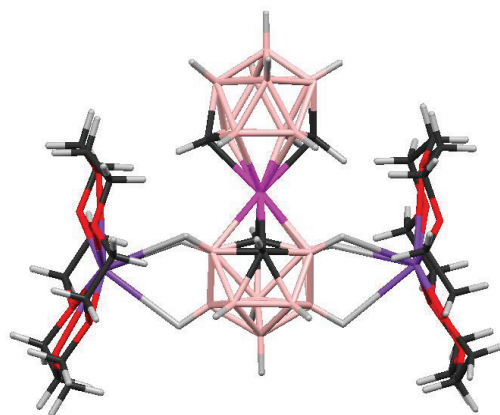
FA4-MS07-O2

Employing Intermolecular Interactions in Metallocarboranes to Overcome Exo Polyhedral and Polyhedral Disorder. Georgina M. Rosair^a, David Ellis^a, Alan J. Welch^a. ^a*School of Engineering & Physical Sciences, Heriot Watt University, Edinburgh, UK EH14 4AS.*

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Carborane cages generally are pseudo-spherical and supraicosahedral cages in particular can be prone to disorder [1]. However, to understand the mechanisms of isomerisation and cage expansion it is essential to determine the precise location of the carbon atoms in the cage. Therefore various strategies have been employed to discourage these species from packing in a random way.

It is well known that cage H atoms make B-H^{δ-} · M^{δ+} "reverse" hydrogen bonds with metals. This interaction was employed in the investigation of a series of transition metal salts of the supraicosahedral metallocarborane sandwich anions [4,4'-*M*-(1,10-*closo*-C₂B₁₀H₁₂)₂]ⁿ⁻ [2] with two dicosahedral 13-vertex cages joined at the central metal atom (below).



B-H · K⁺ interactions were found involving either one or both cages. By holding the cage in place these interactions enabled location of the C atoms. In cases where only one cage was involved this allowed the relative conformations of the two cages to be rationalised by simple bonding arguments.

Another method, that of changing the substituents on the cage itself, has also enabled us to overcome disorder. The use of the *p*-cymene ligand instead of benzene breaks the symmetry of the ring by the isopropyl and methyl substituents [3]. We considered *p*-cymene a fairly innocent ligand but recently uncovered unusual *p*-cymene reactivity involving breaking of an aromatic C-C bond and formation of two allyl units linked by a single C-C bond [4].

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