

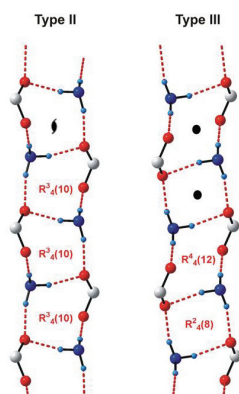
FA4-MS07-O1

A Robust Supramolecular Synthron: 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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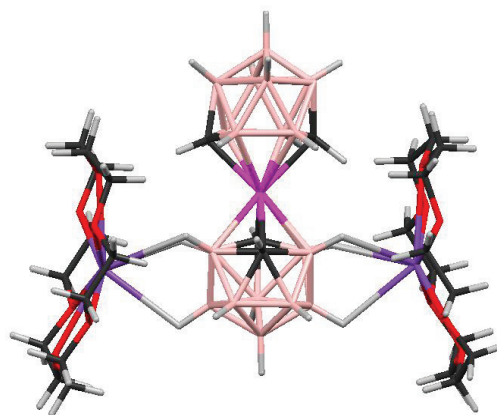
Keywords: crystal engineering; supramolecular synthron; ammonium carboxylates

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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Keywords: boron compounds; bonding intermolecular; chemical reactivity and structure; metal-hydrogen interactions

FA4-MS07-O3

Intermolecular Interactions and Nano-Segregation in the Modulation of Liquid Crystalline Properties of Molecular Materials. Alessandra Crispini^a, Daniela Pucci^b, Iolinda Aiello^b, Anna Bellusci^b, Mauro Ghedini^b. ^a*Department of Pharmaceutical Science, University of Calabria Italy.* ^b*Centro di Eccellenza CEMIF.CAL-LASCAMM, CR-INSTM Unità della Calabria; Department of Chemistry, University of Calabria, Italy.*

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The self-assembly of suitable building-blocks, through inter- or intra-molecular interactions of different nature, is a current approach to get new nanostructure materials, amongst which liquid crystals are particularly intriguing due to their ordered yet dynamic structures [1]. Significant progress has been made by modulating factors such as nano-segregation, molecular motifs functional to specific intermolecular interactions and molecular shapes [2]. The synthesis of liquid crystals based on metal complexes (metallomesogens) has received great attention since the metal centre is able to promote mesomorphism in non mesogenic ligands, introduce interesting electrical, optical and magnetic properties in the system and allow the formation of molecular motifs and inter-molecular interactions unapproachable in organic liquid crystals [3]. In this context, we have recently reported that, by a careful choice of suitable molecular frameworks, it is possible to modulate the interactions responsible for the supramolecular architecture. In this manner, liquid crystalline properties in metal-containing molecular materials may be attained [4]. This communication will illustrate examples proving that a basic step for the analysis of newly synthesized materials is the recognition of the non covalent interactions from systematic structural studies. In particular, the determination of the solid state crystalline structure, provides rich information also for the comprehension and control of the organization in the related liquid crystalline state.

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Keywords: liquid-crystal structures; intermolecular interactions

FA4-MS07-O4

Structural Properties of Hybrid Compounds based on Aniline Derivatives. Nouredine Benali-Cherif. *Laboratoire des Structures, Propriétés et Interactions*

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We are interested past ten years to hydrogen bonding, hydrogen atoms and their localization by X-ray diffraction. We have synthesized many original compounds and published their structures [1-5]. Our prepared hybrids compounds are generally combination of organic matrix and mineral anions, we obtain original structures with strong, medium and weak hydrogen bonds, with two, three and four centers: OH ... O, NH ... O and NH ... N, OH ... N and CH ... O.

Compounds based on aniline and its derivatives contain hydrogen bonds stabilizing crystal structure. We studied a series of these compounds and observed sequence similarities in the networks of hydrogen bonding.

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Keywords: aniline; structure determination, X-ray; hybrid compounds; hydrogen bonding

FA4-MS07-O5

Weak Intermolecular Interactions of Fluorinated Benzenes and Pyridines. Vera Vasylyeva^a, Klaus Merz^a. ^a*Department of Inorganic Chemistry I, Ruhr-University Bochum, Bochum, Germany.*

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One challenge in chemical engineering is the lack of correlation between crystal packing and the molecular structure. The nature of self-organisation in the solid state is complicated and depends on different parameters such as symmetry, secondary interactions and supramolecular synthons. Our strategy for analysing weak dipole-dipole-interactions is to reduce the complexity of parameters and investigate small molecules, such as fluoro-substituted benzenes and pyridines. The *in situ* crystallisation with an IR-laser and a low temperature device allows a crystallisation of compounds with a low melting point under the direct control of the crystal growth via X-ray analysis. A comparison of fluoro-substituted benzonitriles shows, in opposite to Cl-, Br- and I-substituted benzenes[1,2], no supramolecular synthons with weak intermolecular interactions on participation of fluorine or nitrogen. Nevertheless the changes in the crystal packing of fluorobenzonitriles were observed to alter from T-shape conformation by o-fluorobenzonitrile to coplanar layers with alternated arrangement of geared F- and CN-groups by p-fluorobenzonitrile[3]. In contrast, several F-substituted pyridines show different intermolecular interactions