

Organic Compounds

MS06.00.01 THE ROLE OF INTERMOLECULAR INTERACTIONS IN THE CRYSTALLISATION OF RACEMATES.

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Crystallisation of a 1:1 mixture of enantiomers will most frequently lead to the formation of a racemic compound, crystals containing molecules of opposite chirality. In other cases a spontaneous resolution can occur, leading to a conglomerate of enantiomerically pure crystals. This difference in crystallisation behaviour of racemates reflects the difference in the free energy between the crystals of the racemic compound and the conglomerate of enantiomers.

We have found that the type of racemate obtained by crystallization can be related to differences in the intermolecular interactions. The results are based on an analysis of the crystal packing and physico-chemical properties of some closely related compounds.

The systems investigated are the ortho-, meta- and para-substituted fluoromandelic acids and some of the halogen-substituted 3-hydroxy-3-phenylpropionic acids. Racemates of the first class of acids crystallize as racemic compounds whereas racemates of the last class crystallize as conglomerates and racemic compounds depending on the type of halogen-substitution.

A variety of (O-H...O) hydrogen bond motifs are observed in the crystal structures of the racemic and enantiomerically pure fluoromandelic acids. Identical hydrogen bond motifs are found in the investigated 3-hydroxy-3-phenylpropionic acids. In these systems where conglomerate crystallization occurs frequently, the differences can be related to differences in weaker interactions e.g. C-H...O hydrogen bonds and electrostatic interactions. We have noticed that the racemates which form a cyclic carboxylic acid dimers tend to be higher melting than the pure enantiomer. The thermodynamic differences reflected in their binary phase diagrams are related to the observed differences in the crystal packings.

MS06.00.02 HYDROGEN-BOND PATTERNS. Raymond E. Davis, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712-1167, USA

Our study of hydrogen-bond patterns has the following broad aims:

1. identify and describe hydrogen-bond patterns (HBPs) that persist across traditional boundaries of chemical functionality;
2. investigate the possibility of hydrogen-bond pattern functionalities by which molecules "recognize" each other;
3. characterize each hydrogen-bond pattern with respect to the range, frequencies, and metrical aspects of chemical functional groups that display that pattern;
4. provide and elaborate protocols, including the graph-set methodology originated by Etter, to facilitate the recognition, characterization, and cataloguing of common hydrogen-bond patterns.

Current work is focused in these areas:

- *Diversity of chemical functionalities.* Which chemical functional groups are observed to display a particular hydrogen-bond pattern?
- *Frequency of occurrence of chemical functionalities.* For a given chemical functional group, how common or how unusual is a particular hydrogen-bond pattern? Can structural features be identified — in terms of chemical groupings, metrical aspects, or accompanying HBPs — that correlate with the frequency of occurrence of a particular HBP for a given chemical functional group?

- *Variability of metrical aspects.* Over what range of geometric constraints does a particular HBP vary?

- *Pattern cofunctionality.* Do certain patterns often occur together? Could such pairs of patterns be considered to be cofunctional?

We will discuss our recent work in these areas, including an introduction to the graph-set methodology for describing hydrogen-bond patterns.

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MS06.00.03 HYDROGEN-BONDED SCAFFOLDING FOR CRYSTAL ENGINEERING. Christer B. Aakerøy, Mark Nieuwenhuyzen, School of Chemistry, The Queen's University of Belfast, Belfast, Northern Ireland

The intentional design and synthesis of specific structural aggregates in the solid state, crystal engineering, continue to attract considerable attention, since the controlled assembly of structural units into a crystal may result in the development of new materials with *cf.* improved electrical, optical or catalytic properties. Unfortunately, the task of directing the orientation of individual molecules into one, two and, finally, three-dimensional architectures is extremely difficult, as they can adopt a vast number of conformations in the crystal.

We have combined the strength and directionality of the hydrogen bond with suitable carboxylic acids, e.g. tartaric acid¹ and malic acid,² in the design of predictable, two-dimensional ionic architectures. In these structures, the anionic building blocks provide structural consistency and rigidity by creating anionic layers held together by several directional O-H...O hydrogen bonds. The infinite layers then act as 'scaffolding', thereby restricting the possible packing options for the cations. Within this structural framework, the cation can act either as a 'bridge' between neighbouring layers, or as a 'spacer', depending upon its chemical characteristics, thereby providing an extension from 2-D to 3-D motifs.

The close similarity between the structural behaviour of the two acids, and the complementarity and selectivity of their respective hydrogen-bond sites, has also enabled us to incorporate tartaric acid and malic acid within the same solid framework as one cocrystal.³

1. C. B. Aakerøy; P. B. Hitchcock, *J. Mat. Chem.*, 1993, **3**, 1129.
2. C. B. Aakerøy; M. Nieuwenhuyzen, *J. Am. Chem. Soc.*, 1994, **116**, 10983.
3. C. B. Aakerøy; T. I. Cooke; M. Nieuwenhuyzen, *Supramolecular Chemistry*, 1996, in the press.