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 found 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.
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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. characterize each hydrogen-bond pattern with respect to the range, frequencies, and metrical aspects of chemical functional groups that display that pattern;
3. 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?