

Poster Presentation

MS35.P09

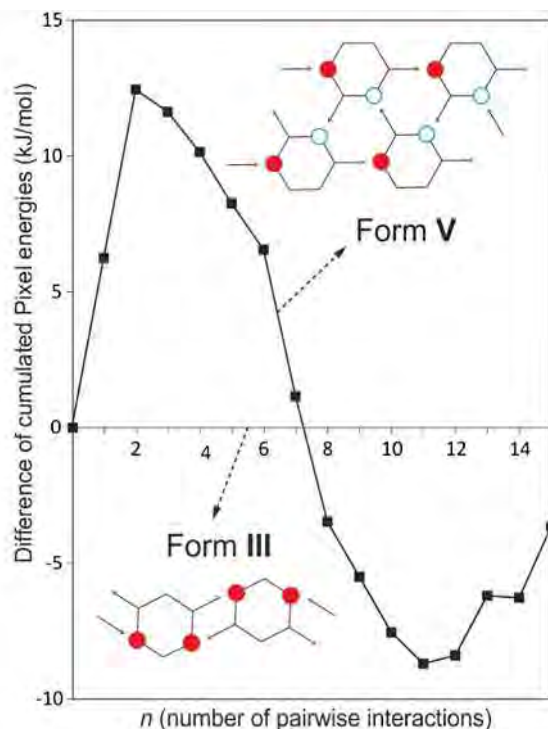
Specific energy contributions associated with competing hydrogen bond motifs

T. Gelbrich¹, U. Griesser¹

¹University of Innsbruck, Department of Pharmacy, Innsbruck, Austria

The semi-classical density sums (SCDS-Pixel) method [1] was used to study the intermolecular interaction energies in six polymorphs of phenobarbital, a model system for the barbiturate class of compounds.[2] Barbiturates display a rigid pyrimidinetrione ring whose two N–H and three C=O functions can be employed in H-bonding. The ensuing intermolecular N–H···O=C interactions result in a small set of standard H-bonded chain, layer and framework motifs.[3] Even though the average number of N–H···O=C bonds per molecule is always two, the standard barbiturate H-bond motifs differ in the number of intermolecular two-point and one-point N–H···O=C connections per molecule, i.e. (1; 0), ($\frac{1}{2}$; 1), (0; 2). For each polymorph (I, II, III, V, VI, X), cumulated Pixel energies, $E(n)$, were calculated for the first n ($n = 1, 2, 3, \dots$) interactions associated with the highest individual contributions to the lattice energy. The obtained sets of $E(n)$ values were compared to one another to establish the differences associated with the formation of the alternate N–H···O=C motifs. Those polymorphs whose N–H···O bonded structures are dominated by two-point connections have superior $E(n)$ values for small clusters of molecules (low n). However, this advantage diminishes gradually if larger clusters of molecules are considered and is completely compensated at $n = 8$. This indicates that crystal packing on the basis of one-point connection N–H···O=C motifs is viable only because the latter enable the formation of more advantageous weaker interactions which are dominated by dispersion forces. This case illustrates that an assessment of competing H-bond motifs cannot be restricted to just those molecules that are directly involved in H-bond interactions. Rather, the complete crystal packing has to be taken into account. [Figure: Evolution of the difference between $E(n)$ (form V; one-point connections) and $E(n)'$ (form III; two-point connections) with n].

[1] A. Gavezzotti, *Molecular Aggregation: Structure Analysis and Molecular Simulation of Crystals and Liquids*, Oxford University Press, 2007, [2] N. Zencirci, T. Gelbrich, D. C. Apperley et al., *Cryst. Growth Des.*, 2010, 10, 302-313, [3] T. Gelbrich, D. Rossi, C. A. Häfele et al., *CrystEngComm*, 2011, 13, 5502-5509



Keywords: hydrogen bonding, energy calculations, polymorphism