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Hydrogen Bond Motifs in Polymorphs and Cocrystals. László Fábián, Simon Lawrence, Humphrey Moynihan, Anita Maguire. *Department of Chemistry, University College Cork, Ireland.*
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Software tools to automatically survey extended hydrogen bond motifs in a large set of crystal structures have recently become available [1,2]. When applied to structures stored in the Cambridge Structural Database [3], these tools allow discrimination between common and unusual hydrogen bond motifs. Complete hydrogen bond networks can be described and common substructures can be identified by using the list of motifs present in each structure as a fingerprint [1]. The results from such an analysis are particularly useful for the comparison of polymorphs and in the design of cocrystals. The application of automated motif analysis will be demonstrated by discussing results obtained for amino acids, sulfonamides, sulfinamides and for cocrystals containing the corresponding functional groups. We will show that common packing arrangements in different forms can be readily identified by using motif fingerprints. The presence of unusual hydrogen bond motifs will be related to polymorph stability and to unusual experimental conditions. The relevance of data from homomolecular crystals to the design of cocrystals will be assessed by comparing frequent motifs in crystals that contain the same donor and acceptor group either as part of a single molecule or in two components of a cocrystal.

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Effect of crystal packing on the static polarizability and first-hyperpolarizability of crystalline urea: An ab-initio computational study. Bartolomeo Civalleri^a, Mauro Ferrero^a, Michel Rerat^b, Roberto Orlando^c, Roberto Dovesi^a. ^a*Università di Torino, Torino, Italy.* ^b*Université de Pau, Pau, France.* ^c*Università del Piemonte Orientale, Alessandria, Italy.*
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Static dielectric properties of crystalline urea, an archetypal compound for its optical properties, have been recently studied by means of ab-initio calculations [1]. Here, the effect of the crystal packing and hydrogen bonding (HB) on the static polarizability and first-hyperpolarizability tensors is investigated. Within a rigid body approach, molecules are first assembled along the *c*-axis to form infinite chains and then the chains are put in interaction by reducing the *a*-axis till the crystal packing is complete. This allows us to explore the role of the long-range dipolar interactions and short-range polarization and charge transfer effects due to HB. Both polarizability and hyper-polarizability of the molecule are markedly enhanced during crystal assembling with the hyper-polarizability being particularly sensitive to crystal packing. Largest enhancement occurs when the molecules interact at a

medium/short-range and hydrogen bonding starts playing a relevant role. The role of HB is also analyzed in terms of changes in the electronic structure and through a topological analysis of the electron charge density. Overall, effects are more pronounced at short-range when all interaction forces occur and cooperative effects take place. Calculations were carried out at the B3LYP level of theory with a TZPP basis set by using the CPKS scheme for periodic systems [2,3] recently implemented in the CRYSTAL09 code [4].

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High-pressure / low-temperature polymorphism in chiral and racemic cysteine. Vasily S. Minkov^a, Boris Kolesov^b, Sergei Goryainov^c, Elena Boldyreva^{a,d}.
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Structure-property investigation of crystalline amino acids is an important challenge since interactions between individual molecular fragments or even structural domains in the structure can simulate interactions in more complicated biological systems such as proteins and peptides. Besides crystalline amino acids are applied as drugs, as piezoelectric and nonlinear optical materials. Therefore understanding a crystal structure response to variation in temperature and pressure is significant in such applications.

Cysteine is a remarkable amino acid because its side-chain residue contains a sulfhydryl group involved in formation of additional hydrogen bonds (S-H...S or S-H...O). The presence of these very weak bonds in structure allows cysteine to take a peculiar place between hydrophobic (no contribution of side-chains to H-bonds) and hydrophilic amino acids (with that contribution). As a result of feebleness of such hydrogen bonds the side-chain residue can change its conformation quite easily on variation in temperature and more rather on increasing pressure.

In the present report we discuss an evolution of chiral and racemic cysteine crystal structures on cooling and on increasing pressure followed by X-ray crystallography and Raman spectroscopy. A special discussion is related to a comparison of the low temperature phase [1] and recently characterized new high-pressure polymorphic modifications of DL-cysteine [2], [3].

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