

FA4-MS26-T01

Hydrogen Bond Motifs in Polymorphs and Cocrystals. László Fábián, Simon Lawrence, Humphrey Moynihan, Anita Maguire. *Department of Chemistry, University College Cork, Ireland.*
E-mail: l.fabian@ucc.ie

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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Keywords: Hydrogen Bonding, Polymorphism, Cocrystals

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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.*
E-mail: bartolomeo.civalleri@unito.it

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}.
^a*REC-008, Novosibirsk State University, Russia.*
^b*Institute of Inorganic Chemistry, Novosibirsk, Russia.*
^c*Institute of Geology & Mineralogy, Novosibirsk, Russia.* ^d*Institute of Solid State Chemistry, Novosibirsk, Russia.*
E-mail: vasilyminkov@yahoo.com

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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FA4-MS26-T04

Molecular ordering in C₇₀@CNT nanopeapods. B. Verberck^{a,b}, J. Cambedouzou^b, G. Vliegthart^c, G. Gommer^d, P. Launois^b. ^a*Departement Fysica, Universiteit Antwerpen, Belgium.* ^b*Laboratoire de Physique des Solides, Université Paris-Sud, France.* ^c*Institute for Advanced Simulation, Forschungszentrum Jülich, Germany.* ^d*Institut für Festkörperforschung, Forschungszentrum Jülich, Germany.*
E-mail: bart.verberck@ua.ac.be

The successful insertion of fullerene molecules in carbon nanotubes (CNTs) has opened a new direction in the field of one-dimensionally confined systems. Because of their ellipsoidal shape, C₇₀ molecules encapsulated in a CNT adopt lying, tilted, or standing orientations depending on the tube's radius. In addition to the molecule-tube interaction, intermolecular interactions determine the structural and dynamical properties of chains of C₇₀ molecules confined in a CNT. Recently, the effect of heating the C₇₀@CNT system—resulting in the coalescence of the molecules into an internal CNT—has been investigated in detail by means of X-ray diffraction [1]. A change in rotational behavior of the molecules prior to coalescence has been inferred from the X-ray diffractograms.

We present Monte Carlo simulations of C₇₀@CNT systems supporting the experimental results and providing insight into the molecular orientations and rotations for varying temperature. In particular, we observe the transition from lying to standing molecular orientations for increasing tube radius. Also, molecular flipping and a temperature-dependent rotational mobility are found. In addition, we address the question of translational motion of the molecules inside the nanotube and predict temperatures above which migration of molecules between adjacent clusters can take place.

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Probing intermolecular interactions in 2-chloro-4-nitrobenzoic acid and nicotinamide. Catharine Esterhuysen. *Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag XI, Matieland, Stellenbosch, 7602, South Africa.*
E-mail: ce@sun.ac.za

2-chloro-4-nitrobenzoic acid has been found to crystallise in two different polymorphs [1], as well as in a co-crystal with nicotinamide [2]. The intermolecular interactions involved in the two polymorphs have been analysed using Hirshfeld surfaces [3], however the significance of each of the

interactions with respect to the stabilisation that they provide to the crystal structures of the two polymorphs has not been studied. In this paper the different intermolecular interactions undergone by 2-chloro-4-nitrobenzoic acid and nicotinamide are investigated by comparing the results of density functional theory (DFT) calculations with experimental results interpreted through Hirshfeld fingerprint plots. Specific intermolecular interactions are indicated by structural features such as spikes within the Hirshfeld fingerprint plots. The positions of these spikes within the fingerprint plots can be correlated to the strength of the interactions calculated for pairs of molecules using DFT methods. A comparison of nicotinamide-containing crystal structures from literature [4] shows a clear correlation between interaction strength and spike position.

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