

Keywords: pharmaceutical co-crystallization, hydrogen-bond propensity calculations, supramolecular chemistry

[1] Propensity calculations were carried out by a newer version of mercury software which is under development by CCDC. [2] P.T.A. Galek, L. Fabian, W.D.S. Motherwell, F.H. Allen, N. Feeder, *Acta Crystallogr., Sect. B* **2007**, B63, 768.

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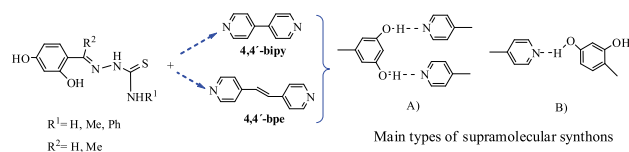
O-H...N Heterosynthons in co-crystals. Assemblies based on resorcinol derivatives

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Multicomponent molecular crystals usually referred to as co-crystals, have recently become into a focus since their potential applications in e.g. synthetic chemistry and pharmaceutical industry. The fact that a co-crystal is obtained reflects that is possible to analyse a few significant intermolecular interactions between chemically distinct components. Such idea leads directly to the concept of heterosynthons, which can describe as hydrogen bonded recognition unit between dissimilar molecules [1].

We have selected a series of pyridines (4,4'-bipyridine and trans-1,2-bis-(4-pyridyl)ethylene) with different derivatives of resorcinol (2,4-dihydroxybenzaldehyde and 2,4-dihydroxyacetophenone thiosemicarbazone) to explore the robustness of hydroxyl-pyridyl heterosynthons. Clearly, by choosing appropriate resorcinols as templates, a rational design of crystals can be achieved. We have used the graphics sets introduced by Etter for motifs generated from intermolecular hydrogen bonds in order to define a hydrogen-bond pattern [2].

The organizational consequences of hydrogen-bonds in the hydroxyl-pyridine heterosynthons in the presence of competitive hydrogen-bonding functional groups were elucidated. Co-crystallization produces discrete structures due to intermolecular hydrogen bonds between O-H...N orienting the pyridine molecules parallel to each other, and the pyridil rings are further stabilized by π - π interactions at a distance around 4Å. The ability of resorcinols derivatives to assemble pyridines yields also infinite 1D arrays. The stoichiometric of these co-crystals and the presence of any solvent in the crystallographic net are responsible for the polymorphs found.



[1] A. Mukherjee, G.R. Desiraju, *Chem. Commun.* **2011**, 47, 4090-4092. [2] M.C. Etter, *Acc.Chem.Res* **1990**, 23, 120-126.

Keywords: assembly, H-bridge, ayridine, lower cases

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Two in one: A fréchet-type dendron manifesting conformational duality

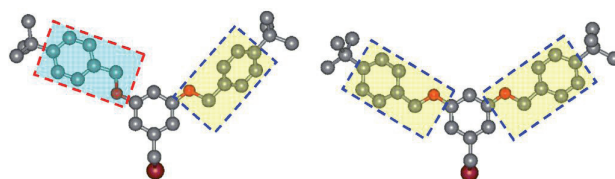
Lydia Brelot,^a Adrian-Mihail Stadler,^{bc} Corinne Bailly,^a ^a*Service de Radiocristallographie, Institut de Chimie de Strasbourg, France.* ^b*Institut de Science et d'Ingénierie Supramoléculaires, Université de Strasbourg, France.* ^c*Karlsruhe Institute of Technology (KIT), Forschungszentrum Karlsruhe (FZK), Institute for Nanotechnology (INT), (Germany)*. E-mail: brelot@unistra.fr

The molecular structure of a Fréchet-type dendron revealed two different conformers present in the same crystal. This case of conformational duality is described and a detailed analysis is carried out to understand this phenomenon.

The difference of conformation lies in the *m*-di(methyleneoxy)benzene motifs of the dendron, which are oriented in a different way. The low energy difference between the two types of conformation is discussed.

The solid state intermolecular interactions and the crystal packing are also investigated in order to rationalize this conformational duality. Indeed, the structure shows the presence of CH- π interactions between the molecules and generates a layered stacking with more or less coplanar molecules.

A comparative analysis is also done on other reported Fréchet-type dendritic structures existing in the Cambridge Structural Database (CSD) and showing conformational duality or diversity. This analysis shows that dendrimers and dendrons based on the *m*-di(methyleneoxy)benzene motif are flexible and this flexibility generates the formation of different conformers despite the existence of some preferred conformations [1].



[1] A.-M. Stadler, L. Brelot, *Crystal Growth & Design* **2010**, 10, 2285-2290.

Keywords: conformers, crystal engineering, dendrimer

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Inclusion compounds as secondary building units for supramolecular chemistry

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In last few years the field of coordination chemistry has seen a great rebirth due to the intense research concerning the synthesis, isolation and structural characterisation of Metal-Organic Frameworks (MOFs).

One strategy of synthesis concerns the use of rigid, chemically-stable, and usually large building blocks (the so-called Secondary Building Units – SBUs) to construct MOFs. This modular approach has been successfully employed to design remarkable structures [1]. Our research group has been actively working both in the preparation and study of coordination polymers and in crystalline phases of cyclodextrins (CDs) as remarkable examples of supramolecular host-guest systems for inclusion compounds. Recently, we introduced a new concept [2]: a CD-based SBU, by including 4,4'-biphenyldicarboxylate into β -CD, a bridging ligand capable of forming porous MOFs.

Following our interest in preparing new SBUs, we present the study of the inclusion compound β CD·PPNO, (PPNO = 4-phenylpyridine-*N*-oxide) which was prepared by treating stepwise an aqueous solution of β CD with PPNO at 60 °C. Two different phases were obtained: while phase II was obtained after 1 day of slow cooling to ambient temperature, phase I was obtained by slow evaporation of the solvent after several days. The two phases show diffraction patterns similar to models described in the review of Cairra [3], which correspond to specific crystal packings of the hosts, and were ultimately confirmed by single crystal X-ray diffraction. Phase I crystallises in the monoclinic *C2* space group while phase II crystallises in the triclinic *P1* space group. In phase I the cavities are aligned forming the so-called “channel packing”, and in phase II the host dimers form a supramolecular packing named “intermediary packing” in which the cavities are isolated from each other. In both structures the guests are included in to the CD cavities. We serendipitously discovered that samples of phase II readily transform by at least two ways into phase I, but never the opposite: i) the milling of crystals of phase II for about one minute produces a phase I powder; ii) crystals of phase II transform into crystals of phase I in a few days. This latter phenomenon was monitored by X-ray diffraction: a specific crystal was indexed as belonging to phase II and two days later it was indexed as the lower crystallinity phase I.

Two different phases of β CD·PPNO were readily prepared, with the remarkable ability of fast conversion of one into the other. The use of either phase as SBU model for the synthesis of MOFs is the following step of the present work.

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[1] C. Mellot-Draznieks, C. Serre, S. Surble, N. Audebrand and G. Férey, *J. Am. Chem. Soc.*, **2005**, *127*, 16273-16278 as example.[2] J.A. Fernandes, F.A. Almeida Paz, S.S. Braga, P.J.A. Ribeiro-Claro, J. Rocha, *New J. Chem.*, **2011**, DOI:10.1039/C0NJ00796J. [3] M.R. Cairra, *Rev. Roum. Chim.* **2001**, *46*, 371-386.

Keywords: cyclodextrins, secondary building units, metal-organic frameworks

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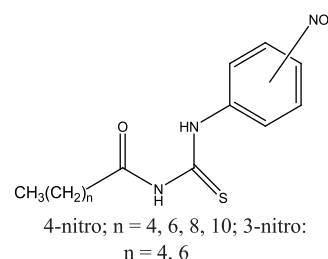
Crystal packing in a series of *N*-nitrophenylcarbomothioyl-alkylamides

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The structures of a number of 4- and 3-nitrophenyl

carbomothioylalkylamides will be reported and the effect on the crystal packing of varying the position of the nitro-substituent and the length of the alkyl chain will be examined. In each molecule intramolecular N—H...O contacts effect the molecular conformations. Centrosymmetric dimers resulting from N—H...S



hydrogen bonds dominate the crystal packing. These are augmented by a variety of C—H...O(S) contacts that vary with the substitution in the benzene ring and the length of the alkyl chain.

Keywords: packing, chains, carbomothioylalkylamides

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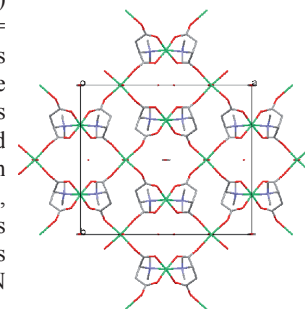
Solvothermal synthesis of metal organic framework structures in Zn- Cd- Ni-OAc -DMF system

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Synthesis and characterization of porous metal organic frameworks (MOFs) has prompted considerable interest because of the possibility for designing networks, where both pore size and physical/chemical properties can be manipulated by suitable selection of the basic components. Several synthetic pathways have been exploited for MOF construction. Significant interest has arisen in organic and coordination chemistry for the design and synthesis of novel coordination polymers with ligands generated in situ at relatively low temperatures.

In this work, we have chosen DMF as solvent in the solvothermal synthesis, of metal-organic framework compounds in the system Zn-Cd- Ni-OAc with different dicarboxylate acids. It is known that during solvothermal synthesis DMF decomposes to formate ions which are easily incorporated in MOF's [1], [2]. Thus we investigated the effect of the temperature variation of this decomposition on MOF structure generation.

The obtained MOFs are characterized by single-crystal X-ray diffraction, X-ray powder diffraction, TG analyses and IR spectroscopy analyses. Preliminary X-ray single crystal diffraction results show that at least two different types of structures may be produced in function of the temperature. The Zn- and Cd- structures crystallizes in the hexagonal R-3c, with respective parameters of $a = 8.1901(6)$, $c = 22.151(7)$ Å and $a = 8.5112(4)$, $c = 23.015(6)$ Å. The Ni- crystallizes in the monoclinic *C2/m* with $a = 14.1421(7)$, $b = 16.5006(4)$, $c = 6.7254(2)$ Å $\beta = 109.096(4)$. The Zn and Cd structures could be considered as isotypical. The difference in the unit cell parameters of Zn and Cd MOFs is explained by the difference of coordination capability of the cations. In contrast, even though Ni also coordinates octahedrally its structure consists of a mixture of Ni-O and Ni-O/N octahedra (Fig. 1).



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