

## FA4-MS26-P02

**Deuterium disturbs – influence of deuterium on the aggregation of pyridine-N-oxides**

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Hydrogen/Deuterium (H/D)-exchange, the smallest possible modification of a molecule, is generally seen as a non-dominating parameter as far as the crystal structures or physical properties of the molecule are concerned.

Only some rare examples of observable isotope effect of deuterated compounds are known. For example, H/D-exchange can be purposefully used to improve such physical properties as ferroelectricity or dielectric constant of some inorganic materials [1]. Recent investigations of pyridine showed the existence of a further low-temperature crystallographic phase for perdeuteropyridine in contrast to the non-deuterated pyridine [2].

This background encourage us to investigate how the partial deuteration of pyridine-N-oxides influence the aggregation of the molecules in solid state?

In previous studies, we have shown that the substitution pattern on the benzene backbone of iodo-substituted benzonitriles and nitrobenzenes have an influence on the formation of the packing motifs in corresponding crystal structures [3]. Furthermore, our X-ray crystallographic studies of low melting fluorinated pyridines indicate the replacement of hydrogen by fluorine leads to significant changes in the molecular aggregation in solid-state [4].

Continuing our investigations on aggregation of substituted aromatic molecules in the solid state, herein, we report the crystallization behaviour of several deuterated pyridine-N-oxides. The crystal packing of pyridine-N-oxides were found to be very sensitive to H/D-exchange [5]. Using a carefully controlled *in situ* crystallization technique, we were able to characterize crystallographically two isotopomorphic low-temperature and high-temperature phases. The results are verified by DSC measurements.

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**Keywords:** deuteration effect, deuteropyridine-N-oxides, isotopomorphs

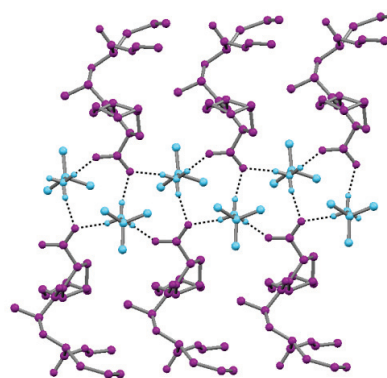
## FA4-MS26-P03

**Alternative crystal forms of the antihypertensive**

**Perindopril Erbumine.** Vânia André<sup>a</sup>, M. Teresa Duarte<sup>a</sup>, Luís Cunha-Silva<sup>b</sup>, Pedro Paulo Santos<sup>a</sup>  
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Besides the antihypertensive effect, perindopril also possess other properties, such as vasculoprotective and antithrombotic effects that can play a favorable role in terms of cardiovascular morbidity [1]. Perindopril erbumine is known to exist in different polymorphic forms. Perindopril is orally administered in the form of tablets containing its salts (1:1) with erbumine (tert-butylamine) or L-arginine. These pharmaceutical salts involve the transfer of a proton between the API and the coformer. New forms of these salts can have improved pharmaceutical properties and they often rely on different intermolecular hydrogen bonds between the active pharmaceutical ingredient and other components (coformers) with well-defined stoichiometries [2]. Forms alpha, beta and gamma were reproduced using different synthetic methods and some of them were for the first time characterized by single crystal X-Ray diffraction. Furthermore, a new hydrated form as also been disclosed and fully characterized. Tests have shown that this form is quite stable and its dissolution profile is very similar to the commercially available form.



[1] M. Remko, *European Journal of Medicinal Chemistry*. 2009, 44, 101-108. [2] V. André, D. Braga, F. Grepioni, M. T. Duarte, *Crystal Growth and Design*, 2009, 9, 5108-5116.

**Keywords:** pharmacologically important molecules structures, polymorphism, hydrates

## FA4-MS26-P04

**Hydrogen bond interaction energies of selected n-alkyldiammonium halide salts.**

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Studies of the halide salts of short-chain n-alkyldiamines form the basis of our research of these materials since they have important applications [1 – 2]. The compounds investigated in this work consist of materials that have the general chemical formula  $C_nH_{2n} \cdot 2(NH_3^+) \cdot 2X^-$ , with  $X = Cl^-; Br^-; \text{ and } I^-$  where we focus specifically on salts of compounds where  $n = 2, 3, 4$  and  $6$ . They form interesting packing motifs and have extensive, complex three-dimensional hydrogen bonding networks [3].

As a result of our previous work carried out on these materials [3,4], we have established that the packing of these materials in the crystal structure is stabilized by the hydrogen bonding networks. Since these networks are so extensive and complex, the intermolecular interaction energies have become an added point of interest to our research. This current work focuses on DFT theoretical calculations of the hydrogen bond interaction

energies of the halide salts; optimization of their geometrical parameters; the prediction of their thermochemical properties, and the resulting comparison to the experimental energy values and optimized parameters obtained from their structures determined by single-crystal X-ray diffraction. Similar work has been carried out on 1,6-hexanediamine hybrid semiconductors to predict their optical and electric properties [5].

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**Keywords:** *n*-alkylammonium halide salts, single-crystal X-ray diffraction, DFT calculations

#### FA4-MS26-P05

**Structural study of amine and amino acid salts consisting nitrate anions.** Nouredine BENALICHERIF, *Laboratoire des Structures, Propriétés et Interactions Inter Atomiques, Institut des Sciences et Technologie. Centre Universitaire Abbes Laghrour Khenchela 40000, Algeria.*

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Amine and amino acids salts are interesting for NLO applications. Their importance is due to the fact that all the amino acids have chiral symmetry and several compounds crystallize in noncentro-symmetric space groups [1].

Thus, salts of amine and amino acids with different organic/inorganic acids have been explored.

Several new complexes incorporating natural amino acids and nitrate anions have been recently crystallized [2] and their structural, optical [3], thermal properties and structural phase transitions [4] have been investigated.

In this present work, which is part of project of searching for potential new hybrid compounds obtained by the addition of amino acids with nitric acid, we will discuss crystalline structures of new salts rich in hydrogen bonding, based on nitrate anions, amine and amino acids, published by our research team during the last ten years.

All materials of this type are characterized by the presence of strong N–H...O and O–H...O hydrogen bonds connecting anionic and cationic entities together which participate in the stability and cohesion of crystal structures.

In these compounds Intramolecular bond lengths in nitrate anions depend closely to 3D intermolecular interactions.

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**Keywords:** amino acids, hydrogen bonds, hybrid compounds, x-ray diffraction

#### FA4-MS26-P06

**Asymmetrically Substituted Distyrylbenzenes and Their Polar Crystal Structures.** Frank Blockhuys, Roeland De Borger, Alain Collas, Christophe M.L. Vande Velde, *Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Belgium*  
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Oligomeric organic semiconductors possess a number of intrinsic advantages over their polymeric counterparts as well as over inorganic (CMOS) materials, the most important being the straightforward molecular tunability and the fact that they can be obtained as crystalline solids [1,2]. Indeed, the supramolecular structure of these materials becomes important when they are applied in optical devices [3,4] or various types of sensors [5,6]. More so, when applications are envisaged which require a polar bulk, such as non-linear optical (NLO) or switchable memory devices, avoiding the anti-parallel orientation of the molecular dipoles in the crystal is of supreme importance. Twelve asymmetric donor-acceptor distyrylbenzenes with either one nitrile group or one, two or three nitro groups as electron acceptors, and one, two or three methoxy groups as electron donors were prepared. The electronic structures of the new materials were studied using peak potentials obtained from cyclic voltammetry, UV/Vis data and molecular dipole moments obtained from quantum chemical calculations. The supramolecular structures of five of these compounds were studied using single-crystal X-ray diffraction to monitor the influence of the positions of donor and acceptor groups on the organisation of the molecules in the solid state, and three polar crystal structures have been identified in which the molecular dipoles do *not* organize themselves in a centrosymmetric lattice. Analysis of the solid-state structures in function of the substitution pattern of the DSB scaffold leads to the conclusion that, in general, the oligomers organise themselves in a head-to-tail fashion and generate CH...O networks involving mainly the different methoxy groups. Preliminary results on the NLO properties of these new materials are also presented.

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**Keywords:** organic semiconductors, crystal packing, polar crystals

#### FA4-MS26-P07

**Ionic and Neutral Forms of Ibuprofen within a Co-crystal.** Petra Bombicz<sup>a</sup>, Péter Molnár<sup>b</sup>, Edit Székely<sup>b</sup>, Béla Simándi<sup>b</sup>, *<sup>a</sup>Institute of Structural Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Hungary <sup>b</sup>Department of Chemical and Environmental Process Engineering, Budapest University of Technology and Economics, Hungary*