

Castro,^c João D. B. Ribeiro,^b Teresa M. R. Maria,^b João Canotilho,^c M. Ermelinda S. Eusébio,^b ^aCEMDRX, Physics Department, University of Coimbra, P-3004-516 Coimbra, (Portugal). ^bDepartment of Chemistry, University of Coimbra, P-3004-535 Coimbra, (Portugal). ^cFaculty of Pharmacy, University of Coimbra, P-3000-548, (Portugal) E-mail: xelo@teor.fis.uc.pt

In the last decade, the synthesis of pharmaceutical co-crystals has emerged as an innovative strategy to successfully improve biopharmaceutical quality. Co-crystals are made up of two or more molecular neutral species linked by non-covalent bonds [1]. In this work the structure of a new equimolar co-crystal of (S)-naproxen, a nonsteroidal anti-inflammatory drug, and isonicotinamide is reported.

Single crystals were prepared by crystallization from 1:2.8 naproxen:isonicotinamide ethanolic solution at 2 °C. The pure crystals melt at $T_{\text{fus}} = 125$ °C.

In the new co-crystal structure the homosynthon amide...amide between two isonicotinamide molecules is retained, as in isonicotinamide polymorph I [2], and acid...N_{aromatic} and amide...acid heterosynthons link naproxen to isonicotinamide.

[1] N. Blagden, M. de Matas, P.T. Gavan, P. York, *Advanced Drug Delivery Reviews* **2007**, 59, 617-630. [2] C.B. Aakeröy, A.M. Beatty, B.A. Helfrich, M. Nieuwenhuyzen, *Crystal Growth & Design* **2003**, 3, 159-165.

Keywords: co-crystal, NSAID, isonicotinamide

MS53.P30

Acta Cryst. (2011) **A67**, C570

Growth and Characterization of p-CADHP and p-CAHS Single Crystals

Amani Direm, Wahiba Falek, Zina Boutobba, et Nourredine Benali-Cherif, *Laboratoire des Structures, Propriétés et Interactions Inter Atomiques (LASPI2A). Institut des Sciences Exactes, Technologie et Informatique. Centre Universitaire "Abbes Laghrour", Khenchela 40000, (Algérie).* E-mail: Amani_Direm@yahoo.fr

Hybrid materials including dihydrogenmonophosphate and bisulfate anions have received increasing attention [1, 2] owing to their interesting ferroelastic [3], NLO [4], phase transitions properties [5] and their potential application in pharmaceutical industry [6].

In order to contribute to the systematic investigation of the hydrogen bonding in those compounds, we have synthesized two new hybrid materials : p-Carboxyanilinium dihydrogenphosphate [7], p-CADHP and p-Carboxyanilinium hydrogensulfate [8], p-CAHS.

The packing of both compounds show alternating anionic (H_2PO_4^- or HSO_4^-) and cationic ($\text{COOH-C}_6\text{H}_4\text{-NH}_3^+$) moieties which are linked together by a three-dimensional hydrogen bonding network. In order to study different interactions between hydrogen bonds present in our compounds, we have applied the graph theory [9]. The graph set analysis of hydrogen-bond patterns present in our compounds gives rise to binary graph sets involving rings R and infinite chains C.

[1] M.T. Averbuch-Pouchot, A. Durif, J.C. Guitel, *Acta Cryst.* **1988**, C44, 99-102. [2] N. Benali-Cherif, F. Allouche, A. Direm, L. Boukli-H-Benmenni, K. Soudani, *Acta Cryst.* **2007**, E63, 2643-2645. [3] J. Fábry, V. Petricek, I. Cisarova, J. Kroupa, *Acta Cryst.* **1997**, B53, 272-279. [4] J. Pécaut, Y. Le Fur, R. Masse, *Acta Cryst.* **1993**, B49, 535-541. [5] N.L. Speziali, G. Chapuis, *Acta Cryst.* **1991**, B47, 757-766. [6] J.R. Rubin, P. Swaminathan, M. Sundaralingam, *Acta Cryst.* **1992**, C48, 379-382. [7] N. Benali-Cherif, A. Direm, F. Allouche, S. Soudani, *Acta Cryst.* **2007**, E63, 2272-2274. [8] N. Benali-Cherif, A. Direm, F. Allouche, L. Boukli-H-Benmenni, S. Soudani, *Acta Cryst.* **2007**, E63, 2054-2056. [9] J. Bernstein, R.E. Davis, L. Shimoni, N.-L. Chang, *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 1555-1573. [10] L.J. Farrugia, *J. Appl. Cryst.* **1999**, 32, 837-838.

Keywords: hybrid compounds, single crystals, hydrogen bonds.

MS53.P31

Acta Cryst. (2011) **A67**, C570

Crystal structure of Cytosinium-hydrogen maleate-cytosine

Wahiba Falek, Amani Direm, Zina Boutobba, et Nourredine Benali-Cherif, *Laboratoire des Structures, Propriétés et Interactions Inter Atomiques (LASPI2A). Institut des Sciences Exactes, Technologie et Informatique. Centre Universitaire "Abbes Laghrour", Khenchela 40000, (Algérie).* E-mail: falek_wahiba@yahoo.fr

The pyrimidine base, Cytosine, leads to the nucleoside cytidine and its corresponding nucleotide: cytidine 5'-monophosphate. It may be found in very small quantities as a post-modified form, 5-methylcytosine, in certain nucleic acids such as in tuberculinic acid. More recently, 5-fluoro-cytosine (5-FC) has been used as a prodrug in suicide gene therapy of cancer with the crystal structure of bacterial cytosine deaminase (bcd).

The crystal structures of cytosine [1] and cytosine monohydrate were determined many years ago. Many inorganic cytosinium salts have been previously synthesized: chloride [2], nitrate [3] and dihydrogenphosphate [4,5].

Cytosinium salts of organic acids are also common, the structures of a number of these including trichloroacetate, Cytosinium 3,5-dinitrosalicylate [6] and hydrogen maleate [7] have been recently reported.

[1] D.L. Barker, R.E. Marsh, *Acta Cryst.* **1964**, 17, 1581-1587. [2] N.S. Mandel, *Acta Cryst.* **1977**, B33, 1079-1082. [3] A. Cherouana, K. Bouchouit, L. Bendjeddou, N. Benali-Cherif, *Acta Cryst.* **2003**, E59, o983-o985. [4] M. Jasko 'lski, *Acta Cryst.* **1989**, C45, 85-89. [5] M. Bagieu-Beucher, *Acta Cryst.* **1990**, C46, 238-240. [6] G. Smith, U.D. Wermuth, P.C. Healy, *Acta Cryst.* **2005**, E61, o746-o748. [7] T. Balasubramanian, P.T. Muthiah, W. T. Robinson, *Bull. Chem. Soc. Jpn.* **1996**, 69, 2919-2922.

Keywords: transfer of protons, single-crystal X-ray study, hydrogen bonds.

MS53.P32

Acta Cryst. (2011) **A67**, C570-C571

Crystal structure and hydrogen graph motifs in Anilinium hydrogensulfate

Zina Boutobba, Amani Direm, Wahiba Falek et Nourredine Benali-Cherif, *Laboratoire des Structures, Propriétés et Interactions Inter Atomiques (LASPI2A). Institut des Sciences et Techniques. Centre Universitaire "Abbes Laghrour", Khenchela 40000, (Algérie).* E-mail: zinab.zina@hotmail.fr

Hydrogen bonding is one of the most versatile noncovalent forces in supramolecular chemistry and crystal engineering [1]. Therefore, in the past decades assessment of discrete hydrogen bonding patterns had received great attention [2] because of its widespread occurrence in biological systems.

The aim of this paper is to discuss hydrogen patterns assuring the connection between anilinium and hydrogensulfate entities and to establish their different graph-set motifs [3]. Bis (anilinium hydrogensulfate) is one of the hybrid compounds, rich in H-bonds [4-5], which could have potential importance in constructing sophisticated assemblies from discrete ionic or molecular building blocks due to the strength and the directionality of hydrogen bonds [6].

Recently, similar structures containing anilinium cations have

been reported. Among examples, can be named the following ones: anilinium nitrate [7], anilinium hydrogenphosphite and anilinium hydrogenoxalate [8]. This structure may be described as formed by alternating sheets of cations and anions which are held together with four five centered N-H...O bonds to form $C_4^4(10) C_4^4(10)$ infinite chains running through the c direction. Moreover, strong O-H...O hydrogen bonds observed between bisulfate anions generate $C_2^2(8)$ chains in the a axis direction. The infinite chains resulting from anion-anion and anion-cation interactions can be described as zigzag layers parallel (ac) plans. The crossing of these chains builds up different rings with $R_3^3(10)$ and $R_5^4(16)$ graph set motifs [9].

[1] S.C. Zimmerman, P.S. Corbin, *Struct. Bond.* **2000**, *96*, 63–94. [2] G.R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, 507. New York: Oxford University Press. **1999**. [3] J. Bernstein, R.E. Davis, L. Shimoni, N.-L. Chang, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1555–1573. [4] N. Benali-Cherif, H. Boussekine, Z. Boutobba, N. Dadda, *Acta Cryst.* **2009**, *E65*, o2744. [5] N. Benali-Cherif, W. Falek, A. Direm, *Acta Cryst.* **2009**, *E65*, o3058–o3059. [6] K. Jayaraman, A Choudhury C.N.R. Rao, *Solid State Sci.* **2002**, *4*, 413–422. [7] M. Rademeyer, *Acta Cryst.* **2004**, *E60*, o958–o960. [8] J.A. Paixao, A. Matos Beja, Ramos, M. Silva, J. Martin-Gil, *Acta Cryst.* **2000**, *C56*, 1132–1135. [9] M.C. Etter, J.C. MacDonald, J. Bernstein, *Acta Cryst.* **1990**, *B46*, 256–262.

Keywords: graph theory, hybrid compounds, hydrogen bonds.

MS53.P33

Acta Cryst. (2011) **A67**, C571

Thiadiazolo[2,3-a](py) as an oxidative cyclization of (py)carbamothioyl by Cu^{2+}

Forogh Adhami, Farzaneh Simyari, Maryam Ehsani, *Department of Chemistry, Shahr-ray Branch, IAU, Tehran (Iran)*. E-mail: fadhami@gmail.com

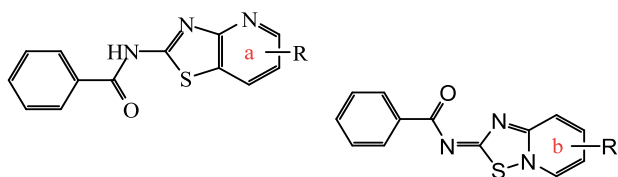
Some compounds are worth from different aspects. The existences of specific functional groups cause unique properties for them. Reaction of benzoyl chloride, potassium thiocyanate with 2-aminopyridine and 2-aminopicoline in one pot produces carbamothioyl benzamide derivatives. These compounds possess various sites to react with numerous reactants.

When 2-aminopyridine was used in above reaction, N-(pyridine-2-ylcarbamothioyl) benzamide was formed. This compound and the other synthesized derivatives were characterized by CHN, IR-, 1H NMR- and ^{13}C NMR spectroscopies. Also their crystal structures were determined.

The reaction of 2-aminopyridine and 2-aminopicoline with $Cu(II)$ salts resulted in oxidative cyclization. There are two possibilities of oxidative cyclization and two different structures (**a** & **b**) for these compounds. The products were characterized CHN, IR-, 1H NMR- and ^{13}C NMR spectroscopies.

The obtained crystals and x-ray single crystal diffraction confirmed the structure **b** is correct. The structure **b** of different derivatives is able to act as anti cancers.

Increasing of the anti cancer property of these products will be researched by changes and replacement of various groups and functions in both of aromatic rings.



Keywords: oxidative cyclization, thiadiazolo[2,3-a]pyridine

MS53.P34

Acta Cryst. (2011) **A67**, C571

mosquito® Crystal: fast, reliable automation of Protein Crystallization drop set-up

Joby Jenkins, David Smith, Chloe Carter, Wendy Gaisford, *TTP Labtech Ltd, UK*. E-mail: Joby.jenkins@ttplabtech.com

Automation of protein crystallography screening has contributed significantly to the rapid progress of crystallography based structural biology. Automation allows samples to be screened using smaller volumes of both protein and screen solutions, reducing costs and saving valuable protein. Additional benefits include increased throughput and accuracy.

One of the challenges to automating this process is the necessity to accurately pipette solutions of varying viscosities. Another challenge is that of drop positioning. The low volume drops have to be placed extremely accurately in order that protein and screen drops coalesce and are not distorted by the edge of the crystallization plates' subwell.

The ability of mosquito® Crystal to address these issues and to automate both micro batch and vapour diffusion methods of protein crystallography (sitting drop, hanging drop) without instrument configuration change offers ultimate flexibility for the crystallography laboratory.

Keywords: Screening-1, Pipetting-2, Mosquito-3

MS54.P01

Acta Cryst. (2011) **A67**, C571–C572

Ion substitution in tourmaline with chromophore elements growing in hydrothermal conditions

O.S. Vereshchagin, I.V. Rozhdestvenskaya, O.V. Frank-Kamenetskaya,^a T.V. Setkova, Yu.B. Shapovalov,^b ^a*Saint-Petersburg State University, Saint-Petersburg, (Russia)*. ^b*Institute of Experimental Mineralogy RAS, Chernogolovka, (Russia)*. E-mail: oleg-vereschagin@yandex.ru

Unique physical properties of tourmaline crystals (pyroelectric, piezoelectric) and possibility of their use in jewelry makes the growing of synthetic tourmalines a topic of the most immediate interest. Our work is devoted to the crystal chemistry of synthetic tourmalines doped by transition metal (3d) elements (Ni, Cr, Co, Fe, Cu) which are identified as coloring agents (table 1).

Table 1. Characteristic of growing tourmalines.

Smp	Color	3d-elements cont., wt. %	Unit cell parameters, Å		R_F
			a	c	
1	green	NiO-7.4 FeO-5.3	15.897(5)	7.145(2)	0.038
2	green	NiO-13.4 Cr_2O_3 -10.2 FeO-0.3	15.945(5)	7.208(2)	0.051
3	pink	CoO-14.4	15.753(8)	7.053(3)	0.057
4	blue	CuO-8.4	15.840(4)	7.091(1)	0.041