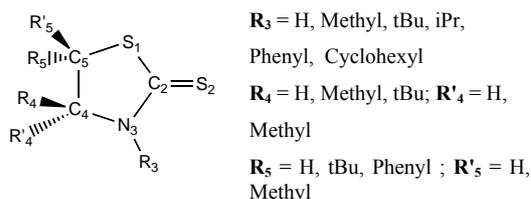


Keywords: Thiazolidine 2-thione, conformation, Heterocycle

In the prospect to study the heterocyclic thiazolidin-2-thione and its derivatives variously substituted (see figure below), our investigation in the solid state will be completed by *AMI* and *ab-initio* calculations.[5,6].

Both of the two theoretical methods leads us to preferential conformations and the comparison between the most stable molecular conformations of the different molecules investigated, helps us to estimate the "weight" of each effect in the real structure of the compound. Our interest has essentially been carried on the conformational behaviour of the heterocycle th-2-th studied and more exactly on the

Csp³-Csp³ part which is the soft part of cycle.



The detailed analysis of the conformations in the solid state [1,2,3,4] shows the flexibility of the heterocycle pentagonal form S1C2N3C4C5 and reveals a relationship between the flexibility of the cycle which is defined by the twisting angle S1C5C4N3 and the distance C4-C5. The quasi-planar and planar conformations are associated together with very short distances C4-C5 (up to 1.40 Å).

The study of the heterocycle by the semi-empirical methods [6] shows that the evolution towards the planar state entails a stabilization of the molecule by covering of *s* and *p* orbitals and particularly in part C4-C5.

At the end, it's possible to envisage that the combination of steric effects and electronic effects could lead to an efficient model in the treatment of the heterocyclic systems.

[1] J.Jaud, A.Laknifli et al, Z. Kristallogr., **210**, 311 (1994)

[2] A.Laknifli, M. Pierrot, F. Chanon et M. Chanon, Acta Cryst., **C51**, 2113-2116 (1995)

[3] A.Laknifli, M. Pierrot, F. Chanon et M. Chanon, Acta Cryst., **C51**, 2661-2665 (1995)

[4] A.Laknifli, M. Pierrot, F. Chanon et M. Chanon, Acta Cryst., **C52**, 2113-2116 (1995)

[5] F.Chanon, M.Rajzmann, M.Chanon, J.Metzger, G.Pouzard, Can.J.Chem., **58**,599 et 604 (1980).

[6] A.Haminei, DESA, Agadir, Morocco 2005.

MS16 P16

Coumarin 120 - crystallization experiments leading to a new type of polymorphism. Zofia Urbanczyk-Lipkowska, Dorota Niedziałek, *Institute of Organic Chemistry, Polish Academy of Sciences*. 01-224 Warsaw, Poland. E-mail: ocryst@icho.edu.pl

Keywords: coumarins, new polymorph, electronic structure

Coumarins are natural or synthetic compounds used as pharmaceuticals and herbicides. They exhibit fluorescent

properties (due to presence of benzopyrone moiety) and therefore, are used as high quantum yield laser dyes (e.g. coumarin 4, coumarin 120, etc). Their frequent use as a model compounds in photophysical studies prompted us to look for their polymorphs.

Crystallization experiments involved recrystallization from polar and non-polar solvents and their mixtures, co-crystallization with 5 % or equimolar amount of another coumarin derivative. We also investigated the influence of the crystallization solvent and additives on crystal habit. The transition behavior of the crystalline forms of coumarin 120, its melting point, and enthalpy were investigated by DSC, FTIR and X-ray crystallography.

These experiments allowed to obtain a new crystalline form of 7-amino-4-methyl-coumarin (coumarin 120) with unprecedented crystal structure, containing two types of molecules – nonpolar and polar. These crystals exhibit also a new type of polymorphism – where molecules of two different electronic structures co-exist in the same crystal. Both types of molecules are bound by the same hydrogen bonding pattern, similar to that found in first polymorph [1]. Although, polar molecules are bound slightly tighter (m.p. of a new form higher by 3 °C) during melting new polymorph transforms irreversibly into the first form. These studies confirm that fluorescence quenching observed for coumarin 120 [2] is due to the presence of equilibrium of various electronic structures in solution.

[1] Jasinski J.P., Wounderberg R.C., *Acta Cryst.* C50, 1994, 1954.

[2] López Arbeloa T., López Arbeloa F., José Tapa M., López Arbeloa I. *J. Phys. Chem.* 1993, 97, 4704.

MS21 P08

Crystal structure of the new titanium phosphate Na₃CaTi(PO₄)₃

S. Krimi^a, A. El Jazouli^b, A. Lachgar^c,

^aLPCMI, Faculté des Sciences Ain Chock, Casablanca, Maroc.

^bLCMS, Faculté des Sciences Ben M'Sik-UH2M, Casablanca, Maroc.

^cDepartment of Chemistry, Wake Forest University, Winston-Salem, North Carolina, USA.

Key Word : Titanium phosphate, Nasicon – type

Titanium phosphates are currently of interest for their chemical and physical properties as catalysts, non-linear materials and ionic conductors. In this context the new titanium phosphate Na₃CaTi(PO₄)₃ has been synthesized and structurally characterized. Single crystals were obtained by melting a mixture of Na₂CO₃, CaCO₃, TiO₂ and (NH₄)₂HPO₄ in stoichiometric proportion, at 900°C, followed by slow cooling (3°C/hr).

Na₃CaTi(PO₄)₃ crystallizes in the space group R32 with a = 8.985(1)Å, c = 21.920(3)Å, V = 1532.6(3)Å³, and Z = 6. The refinement factors are R₁ = 0.0365 and wR₂ = 0.0944. The structure of Na₃CaTi(PO₄)₃ belongs to the Nasicon-type family. It consists of a three dimensional network of PO₄ tetrahedra and AO₆ (A = Ti, Ca) octahedra sharing corners. A 2-2 ordered distribution of titanium and calcium occurs along the c axis giving rise to two different units [Ti₂(PO₄)₃] and [Ca₂(PO₄)₃]. Within this covalent framework exist two additional cationic sites usually labeled M1 and M2 where the sodium ions are located.