

P.08.13.7*Acta Cryst.* (2005). A61, C340**The Crystal Structure of Tetraformylethane**

Dag Semmingsen^a, Torbjörn Gustafsson^b, Svein Nordenson^c,
^aHedmark College, Blæstad 2322 Ridabu, Norway. ^bDept. of
 Materials Chem., Box 538, Uppsala Univ., Sweden. ^cSINTEF IKT,
 Forskningsv. 1, P.O. Box 124, Blindern, 0314 Oslo, Norway. E-mail:
 dags@hihm.no

cis-enol arrangement in β -diketones has recently been investigated [1,2]. These compounds prefer the *cis* arrangement with an *intra*-molecular hydrogen bond. When the terminal groups become small, as in the β -dialdehydes, the *trans*-enol form becomes more stable, at least in the solid-state, where the molecules form chains of *inter*-molecular bonds. Tetraformylethane prefers the *trans*-enolic isomer in the solid state, s. g. **Fddd**. $\frac{1}{2} + \frac{1}{4}$ of a molecule constitutes the asymmetric unit. $\frac{2}{3}$ of the molecules crystallize in asymmetric *inter*-molecular hydrogen bonded chains. The pairs of chains formed by centres of inversion comprise an antiferroelectric arrangement of oppositely polarized molecules. Single and double bonds are clearly recognizable but the amount of conjugation is amazingly high. The remaining $\frac{1}{3}$ of the molecules form chains of molecules situated on the intersection of three twofold axes, rendering single and double bonds indistinguishable. These molecules are connected by *inter*-molecular hydrogen bonds across centres of inversion with hydrogen bond distances slightly shorter than that of their asymmetric counterpart. The crystal structure was originally solved in a cell with an *a*-axis $\frac{1}{3}$ of that in the present study (also in **Fddd**). Photographic and diffractometric studies revealed the tripling of the *a*-axis. We venture to call the strange arrangement found "frustrated antiferroelectric".

[1]Herbstein F., Iversen B.B., Larsen F.K., Madsen G.K.H. Reisner G.M., *Acta Cryst.*, 1999, **B55**, 767-787. [2] Lyssenko K.A., Lyubetsky D.V., Antipin M. Y., *Mendelev Comm. Electronic Version*, 2003, **Issue 2**, 1-3

Keywords: hydrogen bond, super structure, organic molecule**P.08.13.8***Acta Cryst.* (2005). A61, C340**Computing the Solid-state: Novel Plane-wave DFT Approaches to Hydrogen Bonding**

Chick C. Wilson^a, Derek S. Middlemiss^a, Carole A. Morrison^b,
^aDepartment of Chemistry, University of Glasgow, Glasgow G12
 8QQ. ^bSchool of Chemistry, University of Edinburgh, Edinburgh EH9
 3JJ, UK. E-mail: c.c.wilson@chem.gla.ac.uk

Hydrogen bonding is a critical link between crystallography and many physical, chemical and biological processes in condensed matter systems. Much of our recent work on hydrogen bonds has focused on multi-temperature and pressure X-ray and neutron diffraction, indicating often subtle behaviour of the hydrogen bonding present. Some of these effects challenge the limits of current experimental diffraction, and also our theories of hydrogen bond potentials.

As a complementary approach to this issue, we have been developing methods for studying hydrogen bonds in the solid state. These are based on the application of plane-wave (periodic) density functional theory calculations, which we have shown to be far superior in the study of a variety of hydrogen bonding systems. In addition we have developed advanced MD approaches to these calculations allowing us to examine computationally the temperature evolution of molecular structures in the solid state. This leads to a fuller understanding of the hydrogen bond potential and an improved description of structural evolution as observed in experiments.

These approaches will be illustrated by the results of a range of combined experimental and computational studies. Systems studied molecular complexes with short intermolecular hydrogen bonds, intramolecular hydrogen bonded structures, and dimeric systems containing subtle energy asymmetry leading to structural disorder.

Keywords: hydrogen bonds, ab initio periodical calculations, structural change**P.08.13.9***Acta Cryst.* (2005). A61, C340**Conformational and Database Study on the Intramolecular N-H \cdots π Interaction**

Carla Bazzicalupi^a, Paolo Dapporto^b, Sara Giachetti^a, ^aDepartment of
 Chemistry, University of Florence. ^bDepartment of Energy
 Engineering, University of Florence, Florence, Italy. E-mail:
 carla.bazzicalupi@unifi.it

In the last years, much work has been devoted to studying systems characterised by the so-called weak interactions. Between them, the N-H \cdots π interaction has been the subject of several theoretical [1], spectroscopic [2], and structural studies [3], and has been shown to take part in the folding of biological macromolecules [4], competing with the $\pi\cdots\pi$ stacking interactions. In particular, intramolecular X-H \cdots π bond has been found to influence the conformation of compounds containing both X-H and aromatic groups [5], [6].

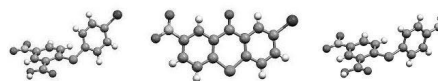
Considering that several organic compounds, functionalized by aminic and aromatic groups linked by an aliphatic chain, are the parent structure for a variety of biologically important compounds, like dopamine or adrenaline, and have therapeutic potential [7], [8], we have decided to carry out a structural study of the intramolecular N-H \cdots π interaction.

[1] a) Pletneva E.V., Laederach A.T., Fulton D.B., Kostic N.M., *J. Am. Chem. Soc.*, 2001, **123**, 6232; b) Basch H., Stevens W. J., *J. Mol. Struct.*, 1995, **338**, 303. [2] Piracha N. K., Ito F., Nakanaga T., *Chem. Phys.*, 2004, **297**, 133, and references therein. [3] Braga D., Grepioni, F., Tedesco E., *Organometallics*, 1998, **17**, 2669, and references therein. [4] a) Hunter C. A., *Chem. Soc. Rev.*, 1994, 101; b) Mitchell J. B., Nandi L., McDonald I. K., Thornton J. M., *J. Mol. Biol.*, 1994, **239**, 315. [5] Bazzicalupi C., Dapporto P., *Structural Chemistry*, 2004, **15**, 259. [6] Worth G. A., Wade R., *J. Phys. Chem.*, 1995, **99**, 17473.

Keywords: weak interactions, π -cloud, database study**P.08.13.10***Acta Cryst.* (2005). A61, C340**From Carboxylic Precursors to Thioxanthenes: Interplay of Hydrogen Bonds, Br \cdots Nitro, S \cdots Carbonyl and $\pi\cdots\pi$ Stacking Interactions**

Maria Teresa Duarte^a, M. Fátima M. Piedade^{a,c}, Cristina Jacob^a, M.
 Paula Robalo^{a,b}, M. Helena Garcia^{a,c}, ^aCQE, IST, Lisboa, Portugal. ^b
 DEQ, ISEL, Lisboa, Portugal. ^cDQB, FCUL, Lisboa, Portugal. E-
 mail: teresa.duarte@ist.utl.pt

Recently large effort has been set into the synthesis of helical molecular systems, such as sterically overcrowded alkenes. These can be used as photorefractive materials as they allow the presence of measurable dipolar and magnetic contributions to NLO effects[1]. The helical environment is due to the presence of bulky substituents causing sufficient hindrance between the upper and lower half of the alkene to enforce a helical distortion [2]. We present here the results obtained in the precursors and thioxanthene used as basic templates. A systematic study of the intra and inter hydrogen bonds and intermolecular interactions is presented, due to its relevance in the folding and packing of the molecules [3].



[1] Goovaerts E., et al, *Advanced Electronic and Photonic Materials and Devices*, 2001, Vol. 9, Academic Press. [2] Feringa B.L., et al., *Chem. Rev.*, 2000, **100**, 1789. [3] Glidewell C., et al, *Acta Cryst.*, 2005, **B61**, 227.

Keywords: hydrogen bond patterns, helical molecules, supramolecular assemblies**P.08.14.1***Acta Cryst.* (2005). A61, C340-C341**Structure Peculiarities of Polydisperse TiO₂ Particles with Metal-Modified Surface**

Tamara Bezrodna^a, Galyna Puchkovska^a, Valentyna Shymanovska^a,
 Anton Hauser^b, ^aInstitute of Physics NAS Ukraine, Kyiv, Ukraine.

^bInstitut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Halle/S, Germany. E-mail: bezrod@iop.kiev.ua

Nowadays polydisperse titanium dioxide (TiO₂) is one of the most popular investigated object among metal oxides due to its wide applications.

TiO₂ materials of a high chemical purity, as-prepared and modified by metal cations (Fe³⁺, Co²⁺, Cu²⁺), have been investigated by the X-ray diffraction, X-ray fluorescence and AFM methods. All TiO₂ powders have a fine-dispersated anatase structure and consist of grown together nanocrystallites of ~ 8 – 17 nm. TiO₂ particles, usually ranging from 100 to 600 nm, show the ability to form large agglomerates, up to 2 μm in size. Contrary to pure anatase, metal-modified TiO₂ particles possess a positive charge on their surface and can be lifted away by the AFM tip from the substrate surface during the scanning. The strength of interactions between the AFM silicon tip and TiO₂ powders is different for each sample. In particular, the AFM tip removes Fe/A300 particles up to 250 nm in diameter, Co/A300 – 180 nm, Cu/A300 – 120 nm. The possible interaction mechanisms between different TiO₂ particles and the silicon tip are discussed. The electrostatic force has been found to play an essential role in the sample – tip interaction processes, and its value depends on the type of metal cation used.

Keywords: structural analysis, AFM, inorganic oxides

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Structural Conditionality of Physical Properties in Nb or Sb Doped KTP Crystals

Olga Alekseeva^a, Natalia Sorokina^a, Igor Verin^a, Valentina Voronkova^b, Vladimir Yanovskii^b, ^aInstitute of Crystallography RAS, ^bMoscow State University, Russia. E-mail: olalex@ns.crys.ras.ru

KTiOPO₄ (KTP) crystals and their solid solutions attract researchers attention by nonlinear optical characteristics. High ionic conductivity and ferroelectric phase transition of these crystals are also of great interest. All of these properties are susceptible to the changing of the crystals composition and can be regulated within certain limits by means of isomorphic replacements. Two series of KTP single crystals (sp.gr. Pna2₁) doped with Nb and Sb were grown. Features of physical properties and atomic structure of five crystals doped with Nb and three crystals doped with Sb were studied. For single crystals K_{1-x}Ti_{1-x}Nb_xOPO₄ (KTP:Nb) и K_{1-x}Ti_{1-x}Sb_xOPO₄ (KTP:Sb) the maximal x values are 0.11 and 0.23 correspondingly. New additional positions of K cations and a lot of potassium vacancies were found in the structure of KTP:Nb and KTP:Sb crystals. X-ray structural study of K_{0.93}Ti_{0.93}Nb_{0.07}OPO₄ crystal at 30K was done in order to localize safely the additional K positions with low occupancy. Results of this structural study confirmed the model received at room temperature and allowed establishing of presence of the potassium positions removal along c axis, which depends on temperature. Decreasing of the temperature of ferroelectric phase transition and strengthening of relaxation effect in the doped crystals are concerned with displacement and splitting of potassium positions. Disorder in the potassium sub-lattice leads to the increase of conductivity.

Keywords: structure physical property relationships, superionic conductivity, nonlinear optical materials

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Lanthanides Stereochemistry in the Structure of Oxygen Containing Compounds

Anna V. Vologzhanina, Denis V. Pushkin, Department of inorganic chemistry, Samara State University, Samara, Russia. E-mail: vologzhanina@mail.ru

The crystallographic analysis of 3476 compounds containing 4044 coordination polyhedrons LnO_n (Ln = La – Lu) has been carried out (data have been taken from [1] and [2]). Coordination numbers (CN) of all atoms, coordinates of missing hydrogen atoms and characteristics of Voronoi-Dirichlet polyhedrons (VDP) of Ln atoms have been calculated by means of program complex TOPOS [3]. It

was found out that CN(Ln) changes from 3 to 12, growth of CN is accompanied by increase of r(Ln-O) but VDP volume (V_{VDP}) of Ln atom depends only on Ln nature and its oxidation state. In our opinion this fact may be an evidence of a viewpoint in which complexing atom should be described as soft (that is able for deformation) sphere with a volume equal to V_{VDP} (radius of the sphere is R_{SD}). It was established that R_{SD}(Ln³⁺) meanings reduce from La to Lu. Decrease of oxidation state of Ln atom is corresponded by growth of their VDP volumes on 1 – 4 Å³. It was shown that the VDP characteristics may be used for determination of oxidation state of Ln atoms in crystal structure, description and analysis of nonvalent (for example agostic Ln...H-C) interactions and bonds between two metal atoms.

[1] *Inorganic crystal structure database, Release 2002/1*, FIZ Karlsruhe & NIST Gaithersburg, 2002. [2] *Cambridge structural database system, Version 5/25*, Cambridge Crystallographic Data Centre, 2003. [3] Blatov V.A., Shevchenko A.P., Serezhkin V.N., *J. Appl. Cryst.*, 1999, **32**, 377.

Keywords: lanthanides, computational analysis of crystallographic data, Voronoi-Dirichlet polyhedron

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Counteranion Effect on Macrocyclic Complex Materials

Diego Venegas-Yazigi^a, Verónica Paredes^a, Ricardo Baggio^b, Octavio Peña^c, Evgenia Spodine^a, ^aCIMAT, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile. ^bCNEA, Buenos Aires, Argentina. ^cUMR6511 CNRS Université de Rennes 1, Rennes, France. E-mail: dvy@ciq.uchile.cl

Dinuclear copper (II) macrocyclic complexes derived from the condensation of 4-methyl-2,6-diformylphenol with 1,3-diamine-2-propanol, with different counteranions, [Cu₂LCl₂]-2H₂O **1**; {[Cu₂L(μ₂-acetate)](acetate) **2a** [Cu₂L(acetate)₂(H₂O)₂] **2b** }·6H₂O; [Cu₂L(H₂O)₂](SO₄H)-2H₂O **3**, have been prepared. **1** and **3** crystallize in the triclinic P $\bar{1}$ (#2) space group with a=7.7223(16), b=9.3901(19), c=10.167(2) Å; α=73.377(3)β=85.768(4), γ=65.766(3) °; V=643.4(2) Å³; Z=1 and a=7.727(5), b=8.663(4), c=11.753(4) Å; α=82.199(6)β=85.519(10), γ=75.830(11) °; V=754.8(7) Å³; Z=1 respectively. **2a**, **2b** co-crystallize in the orthorhombic crystal system, Pnma(#62) space group with a=15.1671(11), b=27.4366(19), c=15.9786(11) Å; V=6649.2(8) Å³; Z=4. The copper (II) ions present a square base pyramidal geometry in three of the reported complexes, with axially coordinated halogens **1**, a syn-syn acetate ligand **2b** and water molecules **3**. Compound **2a** can be described as having a distorted octahedral environment, with aqua and acetate oxygens in the apices. Compound **2b** which co-crystallized with **2a**, presents a folded structure of the macrocyclic ligand due to the presence of the bridging acetate molecule. Strong antiferromagnetic exchange is observed in all complexes. The correlation between magnetic properties and structure will be discussed.

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Keywords: copper, macrocycles, magnetic materials

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Hybrid Organo-inorganic Materials of the VPO System

Evgenia Spodine^a, Svetlana Ushak^a, Jean-Yves Pivan^b, Eric Le Fur^b, Octavio Peña^b, ^aCIMAT, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile. ^bUMR 6511 CNRS Université de Rennes-1, Rennes France. E-mail: espodine@ciq.uchile.cl

One of the methods to obtain materials based on the VPO system is to incorporate organic molecules that modify the oxide structure. The organic species can be introduced as simple cationic species which act as charge compensating agents, or as the ligand of a transition metal complex species. Here we report the synthesis of [Cu₂L₂(VO₂)(HPO₄)₂NO₃]_n where L=bipy (**1**), phen (**2**) and the corresponding magneto-structural characterization. (**1**) and (**2**) crystallize in the P-1 space group with a=10.5927(13), b=12.0359(15), c=12.1655(15) Å; α=107.090(2), β=110.399(2), γ=93.876(2)°; V=1364.3(3) Å³; Z=2 for (**1**) and a=7.936(5), b=12.122(5), c=16.066(5) Å; α=107.216(5), β=94.496(5), γ=100.390(5)°;