

FA4-MS07-P01

Molecular Versus Crystal Properties in Optically Nonlinear 3-Dinitrobenzene. Grażyna Wójcik^a, Izabela Mossakowska^a, Robert Zaleśny^a, Wojciech Bartkowiak^a. ^a*Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, 50-370 Wrocław, Poland.*

E-mail: grazyna.m.wojcik@pwr.wroc.pl

An optically nonlinear material, 3-dinitrobenzene, has been studied experimentally (multi-temperature X-ray diffraction and the analysis of anisotropic displacements within the TLS approach [1]) and theoretically (the quantum chemical calculations of the electronic and vibrational contributions to the static first hyperpolarizability at different levels of theory [2]). The results of both studies corroborate and enable to conclude the importance of the out-of-plane vibrations of the nitro groups. The large amplitude torsional vibrations of two nitro groups are responsible for the largest thermal expansion along the crystallographic *c* axis. The calculations prove that these vibrations have a predominant contribution to the vibrational part of the molecular hyperpolarizability and that the vibrational part of β is much larger than its electronic counterpart. The vibrations of about 60 cm⁻¹ wave numbers have been as well observed in the lattice vibrations' range of Raman spectra. This suggests strong coupling between the torsional vibrations of the nitro groups of adjacent molecules along the crystallographic *c* axis realising a cooperative motion and the vibrational part of the nonlinear susceptibility of the 3-dinitrobenzene crystal. The molecular mechanical and electrical anharmonicity corrections to the vibrational hyperpolarizability are substantially larger than the harmonic terms and correspond to the direction of the largest thermal expansion along the polar *c* axis. Thus, the direction of the strongest anharmonic interactions in the crystal is in line with the direction of the molecular anharmonicity.

[1] Wójcik, G., Mossakowska, I., Holband, J. and Bartkowiak, W., *Acta Cryst.* **2002**, B58, 998. [2] Zaleśny, R., Wójcik, G., Mossakowska, I., Bartkowiak, W., Avramopoulos, A. and Papadopoulos, M. G., submitted to *Chem. Phys. Let.*

Keywords: nonlinear optical material; nitro group vibrations; quantum chemical calculations

FA4-MS07-P02

Charge Density Study of a Weak CH/π Interaction of Relevance in Enantioselective Catalysis. Fernando J. Lahoz^a, Pilar García-Orduña^a, Enrique Espinosa^b, Slimane Dahaiou^b, Pierre Fertey^c. ^a*Instituto de Ciencia de Materiales de Aragón, CSIC-UZ, Zaragoza, Spain.* ^b*CRM2, Université Henri Poincaré-CNRS, Nancy, France.* ^c*Synchrotron SOLEIL, Saint-Aubin, France.* E-mail: lahoz@unizar.es

Our work in the area of stereoselective organometallic catalysis has focused on the development and structural characterization of half-sandwich catalysts, based on late transition metal complexes, having the central metal as

a chiral centre. We have used new cationic complexes of general formula $[(\eta^n\text{-ring})M(L^1-L^2)^*L^3]^{n+}$ as chiral catalysts in enantioselective reactions. In these compounds, the metal belongs to group 8 or 9 (Ru, Os, Rh, Ir), the η^n -ring represents an arene molecule, the bidentate chiral chelate ligand L^1-L^2 * possesses C_1 or C_2 -symmetry, and L^3 represents a good leaving group, usually a solvent molecule. In particular, we have shown the ability of *R*-Prophos-Rh(III), phosphino-oxazoline-Rh(III), Ir(III), Ru(II), and Os(II) and pyridylimino-Ir(III), Rh(III), and Ru(II) complexes to act as catalysts for the Diels-Alder reaction between methacrolein and cyclopentadiene [1], or for the related 1,3-cycloaddition of α,β -unsaturated aldehydes and nitrones [2]. The accumulated information obtained along these previous works have made us clear that catalytic stereoselectivities -and more specially enantioselectivities- are very sensitive to feeble intra- or inter-molecular interactions occurring in the metal complex intermediates.

In our recent work, we have obtained structural parameters that strongly support the presence of a weak CH/π interaction between the coordinated enal (methacrolein) and a phenyl group of the chiral bidentate ligand (*R*-Prophos). We considered that this interaction constrains the rotation of the enal group around the M-O single bond, making both faces of the methacrolein dissimilar for the second part of the Diels-Alder reaction. If our proposal is correct, these weak CH/π interactions could then be controlling the origin of the enantioselectivity, and its detailed characterization, in terms of the charge density distribution, should help us to rationalize the observed stereoselectivity[3]. We will present in this work the charge density results of the high resolution X-ray diffraction experiment carried out on $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{R-Prophos})(\text{methacrolein})](\text{SbF}_6)_2$ to characterize the CH/π interaction proposed on the basis of structural parameters (interatomic distances). Data has been taken at 100 K having $2\theta \leq 60^\circ$ at CRISTAL beamline in SOLEIL synchrotron source. The results will be presented in the context of other related structural and theoretical studies on CH/π interactions.

[1] Carmona D., Lamata M.P., Viguri F., Rodriguez R., Lahoz F.J., Dvoinovitch I.T., Oro L.A., *Dalton Trans.* **2008**, 3328; Carmona, D., Lamata M.P., Viguri F., Rodriguez R., Barba C., Lahoz F.J., Martín M.L., Oro L.A., Salvatella L., *Organometallics* **2007**, 26, 6493. [2] Carmona D., Lamata M.P., Viguri F., Rodriguez R., Lahoz F.J., Oro L.A., *Chem. Eur. J.* **2007**, 13, 9746. [3] Carmona D., Lamata M.P., Viguri F., Rodriguez R., Lahoz F.J., Dvoinovitch I.T., Oro L.A., *Adv. Synth. Catal.* **2007**, 349 1751; Carmona D., Lamata M.P., Viguri F., Rodriguez R., Oro L.A., Lahoz F.J., Balana A.I., Tejero T. Merino P. *J. Am. Chem. Soc.* **2005**, 127, 13386.

Keywords: charge density; stereoselective catalysis; weak interactions

FA4-MS07-P03

Synthesis and Structures of N,N-dialkyl-N'-(2-methylbenzoyl, 4-fluorobenzoyl) thiourea derivatives. Gulten Kavak^a, Gun Binzet^b, Nevzat Kulcu^b, Suheyyla Ozbey^c. ^a*Department of Physics, Faculty of Arts and Sciences, Dicle University,*

21280, Diyarbakır, Turkey. ^bDepartment of Chemistry, Faculty of Arts and Sciences, Mersin University, 33343, Mersin, Turkey. ^cDepartment of Physics Engineering, Hacettepe University, 06800 Beytepe, Ankara, Turkey.

E-mail: gulten.kavak@gmail.com

The structure and intra- and inter-molecular hydrogen bonding behavior of many *N,N*-dialkyl-benzoyl-*N'*-alkylthioureas have been thoroughly investigated [1-3]. There are many reasons for the interest in such molecules. Some derivatives are biologically active, such as antiviral, antibacterial [4], antifungal [5], antitumour [6], herbicidal and insecticidal [7]. *N,N*-dimethyl-*N'*-(2-methylbenzoyl) thiourea, (I), *N,N*-dibutyl-*N'*-(2-methylbenzoyl) thiourea, (II), *N,N*-dihexyl-*N'*-(2-methylbenzoyl) thiourea, (III), *N,N*-dimethyl-*N'*-(4-fluorobenzoyl) thiourea, (IV), *N,N*-diethyl-*N'*-(4-fluorobenzoyl) thiourea, (V) and *N,N*-dibutyl-*N'*-(4-fluorobenzoyl) thiourea, (VI), were synthesized and characterized by elemental analysis, FTIR, ¹H-NMR spectrometer and analyzed by single crystal X-ray diffraction. Compound I, IV, V and VI crystallize in the monoclinic system. Compound II crystallizes in the orthorhombic system. In these compounds, molecules form dimers through the strong intermolecular hydrogen bonds. Moreover, there are also different type of intra molecular interactions in the crystal structures, and therefore the molecules of all compounds pack differently.

[1] Arslan H., Flörke U., Külcü N., *Acta Cryst.*, **2003**, E59, o641. [2] Arslan H., Flörke U., Külcü N., *Journal of Chemical Crystallogr.*, **2003**, 33, 919-924. [3] Binzet, G., Flörke, U., Külcü, N. and Arslan, H., "cis-Bis[N-(2-chlorobenzoyl)-*N'*]-*N'*-diphenylthioureato] nickel(II) dichloromethane solvate", *Acta Crystallographica*, E59, m705-m706, **2003**. [4] Binzet G., Arslan H., Florke U., Kulu N., Duran N., "Journal of Coordination Chemistry", **2006**, 59 (12) 1395-1406. [5] Campa R., Criado J.J., Garcia E., Hermosa R.M., Jimenez-Sanchez A., Manzano J.L., Monte E., Rodriguez-Fernandez E., Sanz F., *J. Inorg. Biochem.*, **2002**, 89, 74-82. [6] Sacht C., Datt M.S., Otto S., Roodt A., *J. Chem. Soc., Dalton Trans.*, **2000**, 5, 727-733. [7] Xu X., Qian X., Li Z., Huang Q., Chen G., *J. Fluorine Chem.*, **2002**, 117, 63-66.

Keywords: crystal and molecular structure; crystal structure analysis; inter and intramolecular interactions

FA4-MS07-P04

The Influence of Molecular Dipoles on Crystal Packing of Triacylmethanes. Vladimir Stilinović^a, Branko Kaitner^a. ^aDepartment of Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia. E-mail: vstilinovic@chem.pmf.hr

Over recent years there has been a growing interest in the use of dipole-dipole interactions in crystal engineering.[1] However the exact limits of the influence of molecular dipole interactions on the solid state organization are far from clear. On the one hand, it is hard not to recognize the importance of local electrostatic interactions in crystal structures of many molecular solids comprising polar molecules. On the other hand, dipolar interactions contribute only slightly to the overall packing energy.[2] Some attention was also

given to the connection between molecular dipole magnitude and the centrosymmetry in molecular crystals, with conclusions varying from denying existence of any connection [3] whatsoever, to demonstrating unequivocal preference of molecules with large dipole moments to pack in centrosymmetrical structures.[4]

For the subject of our study of dipole interactions in molecular crystals we chose triacylmethanes. Triacylmethanes are acyclical 1,3,3'-triketones i. e. triketones with three acyl groups bonded to the same methyne carbon. Their central triketone group is of approximate C₃ symmetry rendering the molecule highly polar. 26 such compounds were synthesized and their crystal structures determined. In all these structures dipolar interactions almost entirely determine the molecular aggregation in one dimension. The molecules pack in columns so that their dipole moments are collinear (or quasi-collinear) and aligned in a head to tail manner. Further packing of molecular rows does not appear to be much influenced by molecular dipoles. If molecules can participate in C—H•••O or C—H•••π hydrogen bonding it often leads to formation of centrosymmetric dimers which are stacked to form double columns in which molecules are placed as described above.

A relatively large fraction of triacylmethanes (9 out of 26) was found to crystallize in polar space groups. It does not appear to be any significant correlation between the dipole magnitude and centrosymmetry. There is however a correlation between centrosymmetry and the ability of molecules to form weak hydrogen bonds; of all triacylmethanes crystallizing in polar space groups only one displays significant C—H•••O contacts. It therefore appears that in triacylmethanes hydrogen bonding has a greater influence on the crystal symmetry than the dipole interactions.

[1] R. Paulini, K. Müller, F. Diederich, *Angew.Chem.Int.Ed.* **2005**, 44, 1788; [2] A. Gavezzotti, *J.Phys.Chem.*, **1990**, 94, 4319; [3] J. K. Whitesell, R. E. Davis, L. L. Saunders, R. J. Wilson, J. P. Feagins, *J.Am.Chem.Soc.*, **1991**, 113, 3267; [4] A. Day, G. R. Desiraju, *C. Chemm.Commun*, **2005**, 2486.

Keywords: molecular dipole; crystal packing; crystal symmetry

FA4-MS07-P05

The Influence of Fluorine Substitution on Crystal Packing of Arenes. Vera Vasylyeva^a, Klaus Merz^a, ^aDepartment of Inorganic Chemistry I, Ruhr-University Bochum, Bochum, Germany.

E-mail: vira.vasylyeva@rub.de, klaus.merz@rub.de

Fluorine is a unique element. The question about the nature of the C-F•••H hydrogen bond is discussed controversially. Well known is the influence of fluorine on the electronic structure of aromatic backbones and therefore on the entire molecules. On the other hand, fluorine forms only weak intermolecular interactions and seems to have no influence on the crystal packing. Pauling's definition of the hydrogen bond would imply that fluorine, as the most electronegative atom, should be a stronger hydrogen-bond acceptor than oxygen and nitrogen. But the C-F group, the so-called "organic fluorine", does not form hydrogen bonds commensurate with electronegativity considerations in contrast to the C-O and C-N groups. We pose two questions: How can the influence of fluorine on molecule structure be useful for crystal engineering? In our studies the distinct differences in crystal packing between fluorinated and non-fluorinated arenes were established by X-ray analysis of