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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.*

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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.

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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.

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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,*