
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.

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


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 \([\eta^1\text{-ring}]M(L_{\text{1}}-L_{n}\text{*)L}_{\text{1}}\text{)}^+\) as chiral catalysts in enantioselective reactions. In these compounds, the metal belongs to group 8 or 9 (Ru, Os, Rh, Ir), the \(\eta^1\text{-}

Keywords: charge density; stereoselective catalysis; weak interactions
The structure and intra- and inter-molecular hydrogen bonding behavior of many \(N,N\text{-dialkyl-benzoyl-N'}\text{-alkylthioureas}\) 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 \([7]\). \(N,N\text{-dimethyl-N'}\text{-}(2\text{-methylbenzoyl})\text{thiourea},(1),N,N\text{-dibutyl-N'}\text{-}(2\text{-methylbenzoyl})\text{thiourea},(II),N,N\text{-dihexyl-N'}\text{-}(2\text{-methylbenzoyl})\text{thiourea},(III),N,N\text{-dimethyl-N'}\text{-}(4\text{-fluorobenzoyl})\text{thiourea},(IV),N,N\text{-diethyl-N'}\text{-}(4\text{-fluorobenzoyl})\text{thiourea},(V)\) and \(N,N\text{- dibutyl-N'}\text{-}(4\text{-fluorobenzoyl})\text{thiourea}(VI)\), were synthesized and characterized by elemental analysis, FTIR, \(\text{H-NMR}\) spectrometer and analyzed by single crystal X-ray diffraction. Compound I, IV 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.


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

\textbf{FA4-MS07-P04}

**The Influence of Molecular Dipoles on Crystal Packing of Triacylmethanes, Vladimir Stilinović\(^a\), Branko Kaitnner\(^a\). \textit{Department 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 acyclic 1,3,3’-triketones i.e. triketones with three acyl groups bonded to the same methylene carbon. Their central triketo 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 hydrogen bond 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.


**Keywords:** molecular dipole; crystal packing; crystal symmetry

\textbf{FA4-MS07-P05}

**The Influence of Fluorosubstitution on crystal packing of amines, Vera Vasylyeva\(^a\), Klaus Merz\(^a\). \textit{Department 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 then 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 amines were established by X-ray analysis of