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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.

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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.
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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.

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Keywords: molecular dipole; crystal packing; crystal symmetry

FA4-MS07-P05

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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

arenes/perfluoroarenes co-crystals. The second question is: Can the weak influence of secondary interactions of fluorine substituents on the crystal packing be amplified through the increase in the number of fluorine atoms?

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Keywords: crystal engineering; fluoropyridines; fluoroarenes; co-crystals

FA4-MS07-P06

Fruitful and Fruitless Resolution of *N*-(nitrobenzoyl)-DL-Alanine by Brucine. Agata Białońska^a, Zbigniew Ciunik^a. ^a*Faculty of Chemistry, University of Wrocław, 14. F. Curie-Joliot, 50-383 Wrocław, Poland.*

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Brucine is one of the most frequently used resolving agents for resolution of racemic acids [1]. It seems to be highly selective for a given enantiomer, and reveals a low selectivity for various compounds. Both these features allow using brucine to the separation of a wide spectrum of racemic acids (CSD version 5.29 (November 2007)) [2]. Among other, brucine is suitable resolving agent for racemic resolution of *N*-(4-nitrobenzoyl)-DL-alanine, forming crystals of brucinium *N*-(4-nitrobenzoyl)-D-alaninate methanol disolvate (first fraction) (**1a**) and brucinium *N*-(4-nitrobenzoyl)-L-alaninate 7.25-hydrate (**1b**). However, during racemic resolution of *N*-(3-nitrobenzoyl)-DL-alanine, a solid solution of brucinium *N*-(3-nitrobenzoyl)-(DL)-alaninate ?-solvate was obtained (**2**).

Solid solution of brucinium *N*-(3-nitrobenzoyl)-(DL)-alaninate ?-solvate (**2**) and crystals of particular brucinium diastereomeric salts, one containing *N*-(3-nitrobenzoyl)-D- (**2a**) and other containing *N*-(3-nitrobenzoyl)-L-alaninate anions (**2b**) are quasi-isomorphous in relation to each other. In **2**, **2a** and **2b**, brucinium cations form common corrugated monolayer sheets. Similar corrugated layers are also observed in **1a**. In **1b**, another brucinium self-assembly is observed. In all the cases, cations and anions are linked by ionic N-H⁺...O⁻ hydrogen bonds. In **1a**, amide O atom of brucinium cations is involved in hydrogen bond, in which solvent molecules are its donor. In **1b**, **2**, **2a** and **2b** solvent molecules reveal a disorder. Comparison of the above structures shows that capability to formation of well-defined hydrogen bonds pattern between resolved compound, resolving agent and solvent molecules belongs to the main factors, which differentiate properties of the diastereomeric salts and influence on a sequence of their crystallization (**1a** and **1b**). Similar capabilities to formation of well-defined hydrogen bonds patterns are reflected in quasi-isomorphous crystals of **2a** and **2b**, as well as in the solid solution (**2**).

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Keywords: resolution of racemic compounds; diastereomeric salts; solid solutions