

Mixtures of γ -oryzanol and β -sitosterol can form transparent organogels in edible oils. This process is a nice example of molecular self-assembly, where γ -oryzanol and β -sitosterol molecules form very well-defined supramolecular entities.

Small-angle X-ray scattering (SAXS) was used to elucidate the microstructure of the building blocks of these organogels in sunflower oil [3]. The measurements were performed at the high-brilliance ID2 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, allowing collection of SAXS data in the range $0.06 < q/\text{nm}^{-1} < 4.5$. Differential Scanning Calorimetry (DSC) was used to study the dissolution, melting and crystallisation behaviour of these systems during a heating-cooling-heating cycle.

It was found that the γ -oryzanol + β -sitosterol system forms tubules with a diameter of 7.2 ± 0.1 nm and a wall thickness of 0.8 ± 0.2 nm. Tubules prepared with γ -oryzanol-rich structurant show the least bundle formation, and can be supercooled during formation most easily. The tubes vanish at the melting point of the gel, in agreement with the loss of structuring capacity as observed in earlier experiments.

Moreover, a number of alternative sterols (e.g. stigmasterol, cholesterol, cholestanol) can replace β -sitosterol in the tubules. The diameter of the tubules for these systems varies between 7.2 and 8.0 nm, the wall thickness between 0.6 and 1.1 nm. The microstructure of the sterol(esters) in emulsions differs from that in pure oil.

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Keywords: organogels, self-assembly, small-angle X-ray scattering

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Synthesis and Structural Resolution of C₁₄H₁₃N₃S·H₂O, a new Thiosemicarbazone. Eva Fernández-Zapico^a, Rafael Mendoza-Meroño^a, Laura Menéndez-Taboada^a and Santiago García-Granda^a
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Thiosemicarbazones, a class of compounds possessing a wide spectrum of potential medicinal applications, have been studied for their antitumoral, antiviral, antibacterial, antimalarial, antifungal, anti-inflammatory and anti-HIV activities [1]. These properties are thought to arise from the metal-chelating ability of these ligands. In almost all cases, the ligands are bidentate and bind to the metal through the S and hydrazinic N atoms, although there are examples of them acting as monodentate ligands binding only through sulphur [2]. The synthesis, crystal structure and electron density topological properties for title compound C₁₄H₁₃N₃S·H₂O are reported here.

The thiosemicarbazone adopts an E conformation with a trans configuration observed about the C=N bond. The dihedral angle between benzene ring and the thiosemicarbazone moiety is $4.67(1)^\circ$, this value suggests that are nearly coplanar, due to the delocalized π -electrons in the benzaldehyde

thiosemicarbazone fragment.

The water molecules are involved in an extensive intermolecular N—H...O hydrogen bonds and O—H...S interactions, which link the molecules into chains extended along b axis. Sulphur atom is also involved in N—H...S intermolecular interactions, favouring the crystal packing in the ac plane. An intramolecular N—H...N hydrogen bond contributes to stabilize the molecular conformation. The intermolecular distance value between centroids of the planar rings in the b axis direction (6.350 Å), does not suggests π -stacking interactions between parallel molecules.

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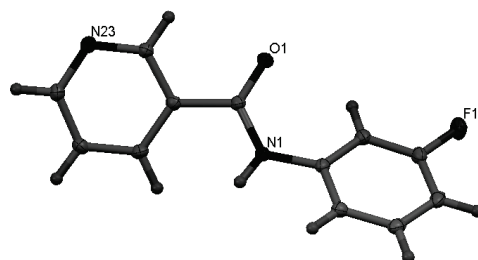
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Keywords: Thiosemicarbazones, Synthesis, Structural Determination, Electron Density Topology

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Structural and systematic studies of a 3x3 isomer grid of nine N-(fluorophenyl)-pyridinecarboxamides
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Nine N_{xx}F isomers (x = 4-, 3- or 2-N/F substitution) were investigated and compared to determine factors underpinning (a) the roles of the F/N atom substituents on molecular conformation and overall supramolecular aggregation, (b) competition between intermolecular amide...amide (in N_{pp}F) or intra-/intermolecular amide...pyridine hydrogen bond formation and (c) general structural and physico-chemical properties and trends.



Crystal structure analyses of the nine N_{xx}F isomers reveal different primary interactions as N—H...N or N—H...O=C. N_{pm}F and N_{po}F are isomorphous and the latter is also disordered. Conformational analysis of the N_{xx}F molecular conformations from DFT calculations differ from the crystal structure results for several isomers and highlighting the cooperative effects of intra-/intermolecular interactions in the solid state.