

## C-H...F Hydrogen Bonds as the Organising Force in F-substituted $\alpha$ -phenyl Cinnamic Acid Aggregates Studied by the Combination of FTIR Spectroscopy and Computations

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It has been found previously that short-range ordering prevails in  $\alpha$ -phenyl cinnamic acid (*E*- or *Z*-2,3-diphenyl propenoic acid) solutions (the organising force is strong O-H...O hydrogen bonds), while weak (aromatic)C-H...O hydrogen bonds are responsible for long-range ordering in the solid state [1]. If substituents are present in the molecules that are capable to act as hydrogen bond donors and acceptors (the oxygen of the methoxy group on the aromatic rings [2] or the fluorine in the CF<sub>3</sub> group in position 3 – substituting the olefinic hydrogen [3]), they take part in forming extended aggregates, but only in the solid state. In this contribution the scope is further extended, experimental and computational results concerning the aggregate-forming properties of *E*- $\alpha$ -phenyl cinnamic acid molecules having one or two fluorine substituents on the phenyl rings and in some cases methoxy substituent as well are communicated.

Six molecules have been synthesized and used for exploring all possible hydrogen bonding interactions in solution and the solid state too. They are the *E* isomers of 2-phenyl-3-(4'F-phenyl), 2-(4'F-phenyl)-3-(4'F-phenyl), 2-(2'methoxyphenyl)-3-(4'F-phenyl), 2-(4'methoxyphenyl)-3-(4'F-phenyl), 2-(4'F-phenyl)-3-(2'methoxyphenyl), 2-(4'F-phenyl)-3-(4'methoxyphenyl) propenoic acid molecules. In the experimental part of the work FTIR spectroscopy (BIORAD FTS 65/896 spectrophotometer, 4000–400 cm<sup>-1</sup> range) was the tool of structural investigation. For the solution-phase studies CCl<sub>4</sub> was chosen as the solvent and the 10<sup>-2</sup>-10<sup>-4</sup> mol/dm<sup>3</sup> concentration range was investigated. For measurements in the solid-state the KBr technique was applied. Molecular modelling was performed with semiempirical and *ab initio* codes included in the *HyperChem* package [4].

The combination of experimental and computational approaches proved to be powerful in exploring hydrogen bonding possibilities. It was found that large aggregates were formed, but again only in the solid state. They were kept together by hydrogen bonds. The major organising force was C-H...F hydrogen bonding. It connected the acid dimers (which were the basic unit of the hydrogen-bonded aggregates). All forms that could be envisaged were identified indeed. Beside the expected (aromatic)C-H...F hydrogen bonds, the scarcer (olefinic)C-H...F bonds also proved to be major structure-organising forces. When methoxy substituent was present even (aliphatic)C-H...F bonds could be identified. Although the various forms of the C-H...F interactions were crucial in forming extended structures even in these molecules, (aromatic)C-H...O and even (aliphatic)C-H...O hydrogen bonds contributed, too. Fluorine is so much involved in hydrogen bonding that a model with nine dimers kept together by (olefinic)C-H...F only could be built easily, forecasting that modelling even 3-dimensional structure is within reach.

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