	Supramolecular Chirality of a Wedge-Shaped Molecule	Experiment number: MA-435
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Report:

The influence of molecular structure on supramolecular organization is a key question in modern science.[1] A very interesting challenge is to understand the origin of supramolecular chirality, i.e. formation of supramolecular non-covalent assemblies in a non-symmetrical arrangement, especially from optically inactive substances. Wedge-shaped amphiphilic molecules provide powerful building blocks for the construction of supramolecular objects of cylindrical or spherical shapes.[2] It has been demonstrated that such kind of molecules are capable of inducing helical superstructures. However, till now the influence of the molecular shape on the supramolecular chirality was not discussed, so the origin of the helical structure for wedge-shaped amphiphilic molecules is still unclear. In the present project we perform structure analysis of a wedge-shaped molecule 3,4,5-tridodecyloxycinnamic acid (Figure 1, top).

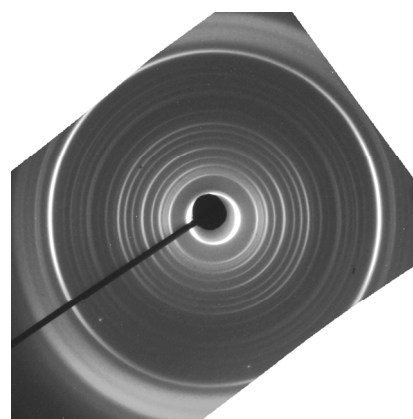
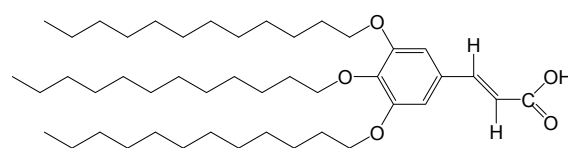


Fig.1: Schematic representation of studied molecule (**Top**), 2D .X-ray diffraction pattern of a fiber sample extruded from the quenched to 25 °C melt (fiber direction is vertical) (**Bottom**)

We used thermal X-ray diffraction technique to study the structures and thermal stability of the compound. It was found that after quenching of the melt to 25°C, X-ray diffraction pattern revealed 100, 200, 300, 400, 600

reflections, indicating the formation of a smectic liquid crystalline structure. During annealing at room temperature for 7 minutes the mesophase transforms into a crystal structure. In the smectic phase the material was extruded to obtain a fiber. WAXS pattern of the fiber shows an oriented structure, which can be ascribed to a monoclinic lattice with lattice parameters $a=30.41 \text{ \AA}$, $b=17.09 \text{ \AA}$, $c=4.05 \text{ \AA}$ and $\gamma=81.7^\circ$ (Figure 1, bottom). Then the fiber was cooled to -20°C , and thermal X-ray diffraction measurement was then carried out (Figure 2, top). During heating from -20 to 60°C , there is no significant change in the main crystal lattice in the ab -plane (Figure 2, top). In contrast, sub-lattice of alkyl chains undergoes a transition at 28°C , which is indicated by the disappearance of peaks at 4.05 , 4.27 and 3.77 \AA and shift of peak at 3.86 \AA to the meridian, which leads to the decrease of c -parameter of the main lattice to 3.91 \AA . We suppose that at room temperature the crystalline phase is metastable. The alkyl chains form a triclinic sub-lattice with the alkyls are inclined for 18° in respect to the ab -plane of the main lattice. Such sub-lattice is similar to the crystal lattice of n -octane. [3] At 28°C the triclinic sub-lattice transforms into orthorhombic one. In the orthorhombic unit cell the chains are parallel to the **ab**-plane. Based on the X-ray diffraction data, the molecular packing model for the crystalline structure was proposed (Figure 2, bottom). For the dense packing of the alkyl chains, it is necessary that they are not located in the same plane. We can see that the two alkyls at 3,5 positions of the benzene ring are in the same plane, while the one at 4 position is not. The molecule with such a conformation is chiral because of the lack of a plane of symmetry. The chiral conformers of the same handness form dimers through hydrogen bonding. The dimers are then packed together to build a chiral crystalline lattice. The change of the handness of the chiral conformer causes the handness conversion of the chiral crystalline lattice.

In conclusion, in this work we performed careful structural analysis of a wedge-shaped molecule. It has clearly been demonstrated that the dense packing of the alkyl chains of wedge-shaped molecules led to the formation of a non-planar chiral conformation. Following chiral selectivity the chiral conformers form enantiopure crystalline domains.

References:

1. J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH: Weinheim, **1995**.
2. V. Percec, J. Heck, G. Johansson, D. Tomazos, G. Ungar, *Macromol. Symp.* **1994**, 77, 237-265
3. H. Mathisen, N. Norman, and B. F. Pedersen, *Acta Chem. Scand.* **1967**, 21, 9.

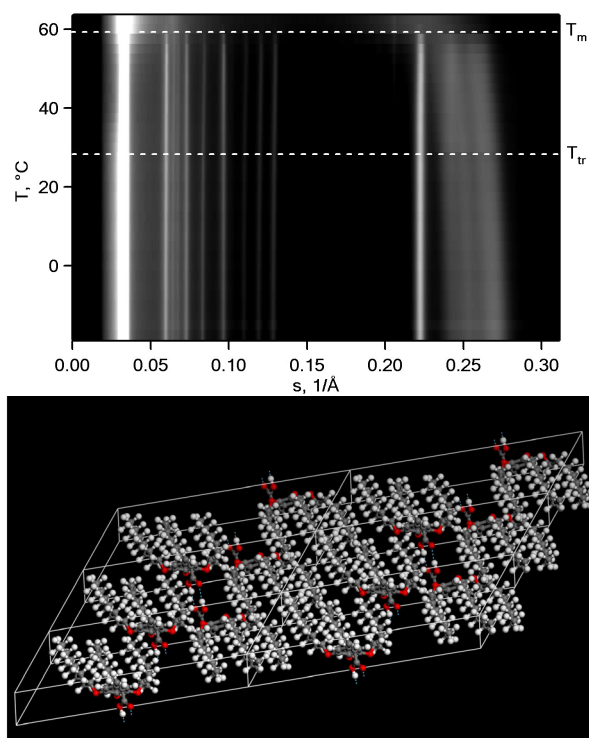


Fig.2: X-ray pattern of the fiber during heating -20 - 60°C (**Top**), dashed lines indicate transition and melting temperatures, respectively; Molecular packing of the molecule in the stable crystalline morphology (**Bottom**)