



2D and 3D Crystalline Structure of a Wedge-Shaped Molecule

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Report:

Organic crystals and liquid crystals are the ultimate supermolecules assembled from individual molecules via weak intermolecular interactions.[1] Supramolecular crystal engineering, the design of such molecular materials, has emerged as one of the most appealing areas of chemical research in recent years for both fundamental and applied reasons.[2]

Wedge-shaped amphiphilic molecules containing a large hydrocarbon body and a small polar group at the tip provide powerful building blocks for the construction of supramolecular objects of cylindrical and spherical shapes.[3] Depending on the nature of the polar head, such compounds exhibit a wide variety of crystalline and liquid crystalline polymorphs, due to a subtle balance between the driving force for ordering of hydrophobic and hydrophilic parts of the molecule. Despite a large number of compounds studied so far, the detailed molecular packing in the crystalline as well as in the liquid crystalline states of these materials remains unclear. In this work, the structure of a new amphiphilic molecule with wedge-shaped

architecture, 3,4,5-tridodecyloxycinnamic acid in monolayer and in the bulk was analyzed (Fig. 1, top).

The self-assembly of the compound in 2D has been studied by scanning tunneling microscopy (STM).

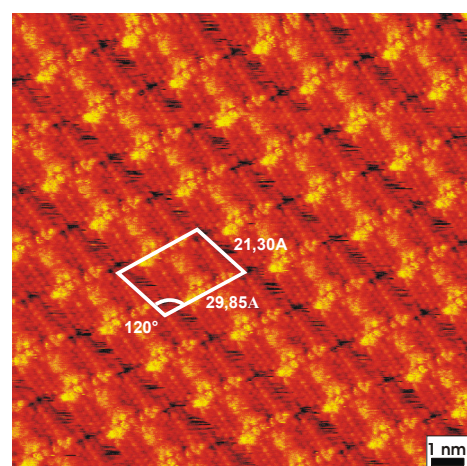
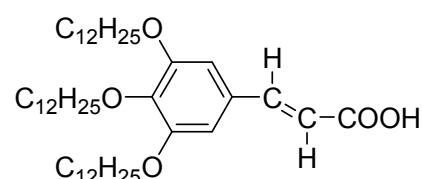


Fig.1: Chemical structure of the wedge-shaped molecule (top); STM micrograph of a monolayer adsorbed at the interface of graphite / trichlorobenzene (bottom).

A high-resolution STM image (Fig. 1, bottom) shows that the molecules form dimers. The 2D unit cell is oblique with the following parameters: $a=29.85 \text{ \AA}$, $b=21.30 \text{ \AA}$, and $\gamma=120^\circ$. The alkyl chains are located at different heights. Thus, for one molecule of the dimer the backbone plane of the middle alkyl

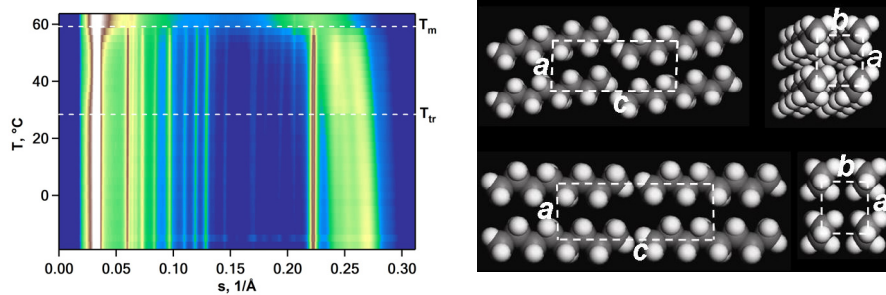


Fig.2 Left: Variable temperature WAXS corresponding to heating from $-20 \text{ }^\circ\text{C}$ to $60 \text{ }^\circ\text{C}$ with a rate of 2.5 K/min . Right: Packing of alkyl chains in the metastable crystalline phase ($25 \text{ }^\circ\text{C}$, upper panel) and in the stable crystalline state ($40 \text{ }^\circ\text{C}$, bottom panel).

chain is oriented perpendicular to the substrate whereas the other two are parallel to the substrate. The other molecule of the dimer has an opposite arrangement, i.e. the middle alkyl has the plane parallel to the HOPG and the two others – perpendicular. The structure of the bulk material was studied with WAXS experiments. After quenching the melt to 25°C , X-ray diffraction pattern reveals 100, 200, 300, 400 and 600 reflections, indicating the formation of a smectic liquid crystalline structure. The smectic layer thickness is measured to be 30.5 \AA , which indicates that a tilted smectic C (SmC) phase is formed. At $25 \text{ }^\circ\text{C}$ the compound undergoes a transition from SmC phase to a monoclinic crystal morphology: $a=32.62 \text{ \AA}$, $b=17.07 \text{ \AA}$, $c=4.05 \text{ \AA}$ (fiber axis) and $\gamma=112.8^\circ$, which takes approx. 7 min. Interestingly, that the **a**-parameter of the crystal lattice is close to the smectic distance. During heating from -20 to 60°C , the **a,b**-parameters of the main crystal lattice do not reveal significant changes (Figure 4). In contrast, the alkyl sub-lattice undergoes a transition at 28°C , which is indicated by the disappearance of peaks at 4.27 , 4.05 , 3.83 and 3.77 \AA and appearance of the meridional peak at 3.91 \AA . The resulting lattice parameters of this crystalline phase are the following: $a=32.52 \text{ \AA}$, $b=17.08 \text{ \AA}$, $c=3.91 \text{ \AA}$ and $\gamma=112.8^\circ$. These changes show that the main transformations occurs in the side-chains sub-lattice. In the low temperature crystalline phase, the alkyl chains form a triclinic sub-lattice, where **a**-axis is parallel to the fiber direction. The peak 101 (3.83 \AA) corresponding to the inter-chain distance is found to be at 72° with respect to the equator. At 28°C the triclinic sub-lattice transforms into an orthorhombic one where the alkyl chains are parallel to the **bc**-plane of the sub-lattice and **ab**-plane of the main lattice. Consequently, the inter-chain direction is parallel to the fiber direction and coincides with the **c**-parameter of the main crystal lattice. In conclusion, we have shown that the structure of the wedge-shaped molecule in 2D and 3D is similar. In contrast to primitive sub-lattice of the bulk structure, the alkyl chains on the substrate reveal alternative plane orientation.

References

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