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## Organic Thin Films and Crystals

The atomic force microscope (AFM) has been used to record molecular structure on free-standing organic crystals and on Langmuir-Blodgett (LB) films. Crystals of tetracene and pyrene have been imaged with molecular resolution which allows the assignment of lattice parameters to the surface layer. The intermolecular spacings on the surface of tetracene correspond remarkably closely with those in the bulk. Pyrene however, shows a reconstruction of the surface. We also present images, with molecular resolution, of LB films of cadmium arachidate deposited on an amorphous silicate substrate. Despite the disorder in the substrate, the films display a periodic structure over large distances.

### Organic crystals

#### Tetracene

Tetracene is the four-ring analogue in the naphthalene-anthracene series of linear, fused benzene rings, *figure 1* [1]. Many different analytical methods have been used to investigate tetracene's bulk structure. With the inception of the field of scanning force microscopies [2], the low concentration of surface molecules no longer eludes analysis. Here, we present atomic force microscope measurements performed with Nanoscope II outfitted with a  $1 \mu\text{-scanner}$ . Cantilevers are V-shaped,  $200 \mu\text{m}$  long, and have integrated tips of  $\text{Si}_3\text{N}_4$  and spring constants of  $0.12 \text{ N/m}$  [3]. The images are recorded in the ambient atmosphere, at room temperature, and on freshly cleaved samples of single crystals as well as on sublimed films. Scanning is performed on the ab-cleavage plane, the characteristic cleavage plane in this class of molecules. In performing these AFM measurements, the typical applied force in the order of  $10 \text{ nN}$ . The application of higher forces has no apparent effect on the recorded images.

The tetracene crystal is triclinic with two molecules per unit cell (*figure 1*). These two translationally inequivalent molecules are designated I and II in *figure 1*. The crystallographic parameters are presented in *table I*, along with the corresponding intermolecular spacings detected by AFM on the crystal surface. From the comparison of bulk and surface values, it can be seen that the arrangement of molecules in the ab-plane of the surface corresponds very closely to that of the bulk [4].

TABLE I. - Crystallographic and AFM data of tetracene. Tetracene lattice parameters.

	AFM surface	Literature [7] bulk
a (Å)	8.0	7.915
b (Å)	6.3	6.065
c (Å)	-	13.445
$\alpha$ (°)	-	101.10
$\beta$ (°)	-	113.31
$\gamma$ (°)	85.5	85.91

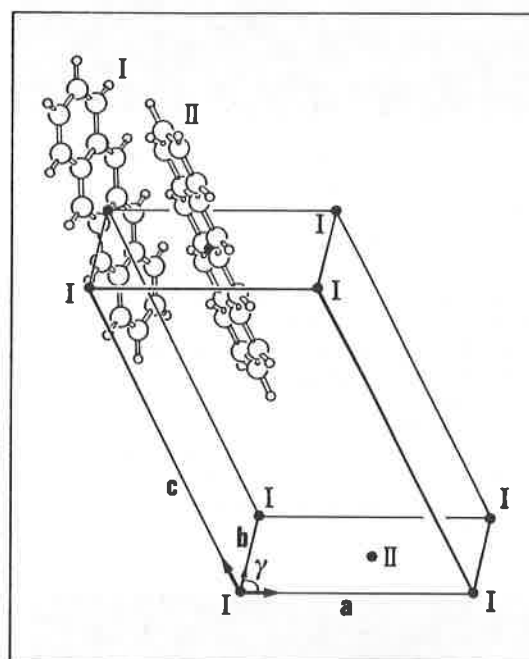


FIGURE 1. - The unit cell of crystalline tetracene in a perspective view. Representative molecules of type I and II are drawn in full to illustrate the orientations in the bulk.

In *figure 2* a superstructure of rows spaced  $8.0 \text{ \AA}$  can be discerned. This lattice, composed of rows of the inequivalent molecules, I and II, can be explained by the different orientation of II relative to I on the surface, as predicted by the bulk crystal structure.

The short axes of the molecules are not perfectly parallel to the ab-plane, presenting a slightly tilted edge to the surface. The combined effect of the different orientations of type I and type II molecules relative to each other, and their non-parallel orientations relative to the ab-plane, accounts for the periodicity of  $8.0 \text{ \AA}$  of the row structure.

#### Pyrene

Pyrene belongs to another more exotic lattice with two pairs of parallel adjacent molecules in a unit cell. Owing to such dimer structure of closely spaced parallel molecules pyrene crystals exhibit strong excimer fluorescence. The parallel molecules in a dimer have a separation distance of  $3.53 \text{ \AA}$ . Such configuration causes considerable overlap of  $\pi$  orbitals [5]. The crystal structure is similar to that of tetracene, except it is monoclinic.

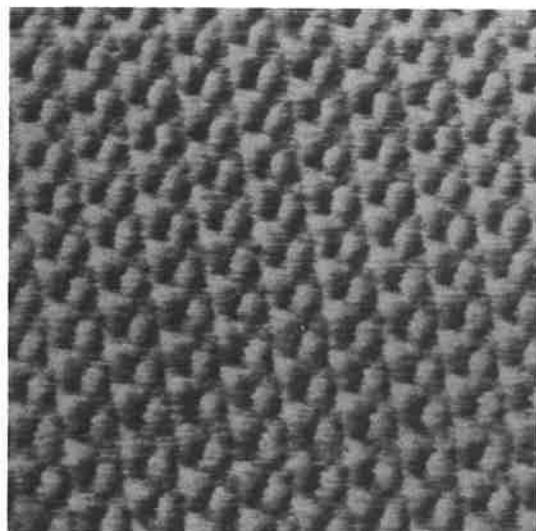


FIGURE 2. -  $10.0 \times 10.0 \text{ nm}^2$  AFM image of the tetracene ab-plane. The inequivalent molecules, I and II, create a superstructure of rows spaced  $8.0 \text{ \AA}$  apart. The magnified circle is of an area of about  $20 \text{ \AA}$  in diameter.

The experimental data are the same like those of tetracene. The measurements (cf. figure 3) show nearly a hexagonal structure of pyrene molecules. The crystallographic parameters of the dimers are presented in table II, along with the intermolecular spacings detected by AFM on the crystal surface. The density of the molecules remains consistent on the surface ; i.e. about  $35 \text{ \AA}^2/\text{molecule}$ . However, the orientations of the molecules to each other are quite different. Pyrene shows no dimer structure on the surface any more and the molecules form a hexagonal-like pattern with a periodicity of about  $6.0 \pm 0.3 \text{ \AA}$ .

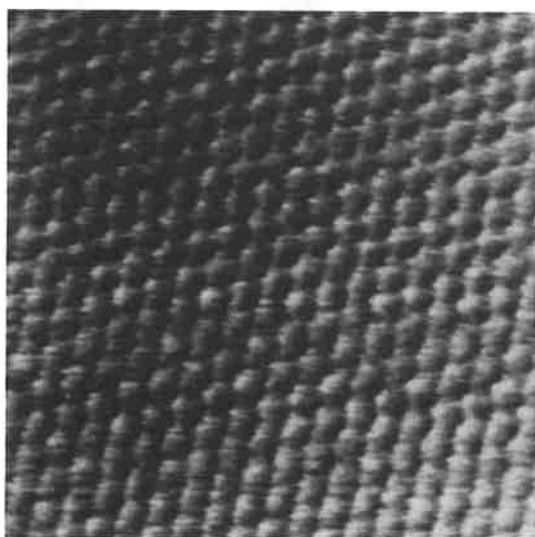


FIGURE 3. -  $10.0 \times 10.0 \text{ nm}^2$  AFM image of the pyrene ab-plane. The molecules form a hexagonal structure of  $6.0 \pm 0.3 \text{ \AA}^2$  periodicity. The surface shows no dimer structure.

TABLE II. - Crystallographic and AFM data of pyrene. Pyrene lattice parameters.

		AFM surface molecule	Literature [8] bulk dimer
a	( $\text{\AA}$ )	6.2	13.65
b	( $\text{\AA}$ )	6.0	9.26
c	( $\text{\AA}$ )	-	8.47
$\alpha$	( $^\circ$ )	-	90.0
$\beta$	( $^\circ$ )	-	100.28
$\gamma$	( $^\circ$ )	58.0	90.0

The experimental data of the LB layers and our microscope are described elsewhere [6]. In our studies we used a four-layer system of cadmium arachidate molecules deposited on an amorphous silicate substrate. Because of the substrate the film is hydrophobic. The AFM is operated at ambient pressure with repulsive forces on the order of  $10^{-8} \text{ N}$ . We used a  $\text{SiO}_2$  rectangular cantilever with a diamond tip and a spring constant of  $0.7 \text{ N/m}$ .

Figure 4 shows a  $5 \times 5 \text{ nm}^2$  image. The molecules are arranged regularly despite of the amorphous substrate. The intermolecular distances are  $5.0 \pm 0.3 \text{ \AA}$ . During the measurements we observed no damage to the film caused by the probing tip. However, at higher loadings, plastic deformation of the film has been observed.

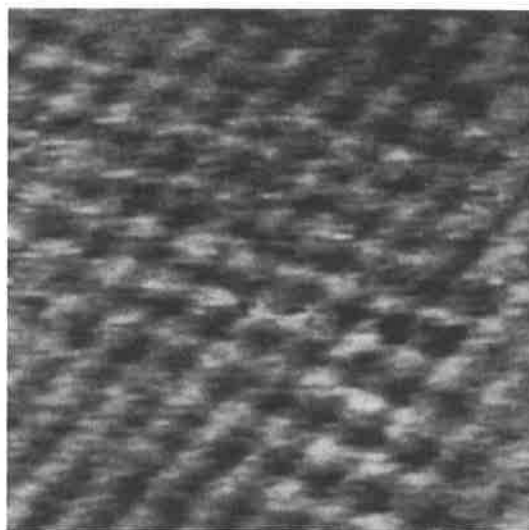


FIGURE 4. -  $5.0 \times 5.0 \text{ nm}^2$  AFM image of a four-layer cadmium arachidate film. The molecules show a periodic arrangement despite of the amorphous silicate substrate.

## Conclusion

In our studies, the atomic force microscope, operated under ambient conditions, has provided information on the arrangement of molecules on the surface of molecular crystals and LB-films. Tetracene and pyrene show different behavior on the surface. The surface of pyrene is reconstructed while the tetracene remains bulk-like. It is possible to imaging fragile LB-films by the AFM. The observed LB films develop long-range order on amorphous surfaces.

## Organic thin films

The ability to prepare thin films of amphiphilic molecules (Langmuir-Blodgett (LB) films) is valuable to many areas of research. In biology they provide models for ideal membranes. Also they are interesting for their tribological characteristics.

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