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MOLECULAR STRUCTURE AND DYNAMICS IN MONOLAYERS OF LONG CHAIN ALKANES AND ALKYL–DERIVATIVES

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Abstract: Long chain alkanes ($C_{34}H_{70}$ and $C_{50}H_{102}$), a fatty acid ($C_{17}H_{35}COOH$) and an alkyl–substituted triiodobenzoate ($I_3H_2C_6COOC_{18}H_{37}$) have been adsorbed at the interface between organic solutions and the basal plane of graphite. *In–situ* scanning tunneling microscopy (STM) has been employed to investigate their structure and dynamics on the scale of 10 pm and 1 ms or longer. All adsorbates form two–dimensional polycrystals. The molecules tend to organize in lamellae with the extended alkyl chains oriented parallel to a lattice axis within the basal plane of graphite. The n–alkane chains pack in a lattice commensurate with the graphite lattice and the carbon skeleton planes approximately perpendicular to the substrate. Due to the additional space required by a carboxyl end group the alkyl lattice in the fatty acid is incommensurate with the substrate and the carbon skeleton planes lie approximately parallel to the surface. In the triiodobenzoate the headgroup takes the space of about two alkyl chains resulting in an interdigitated packing.

INTRODUCTION

Scanning tunneling microscopy (STM) [1–3] has been used *in–situ* at the solid–fluid interface to investigate structure and dynamics of long chain alkanes and alkyl–derivatives as described earlier [4–6]. Here we report in particular on the alkyl packing for different end group sizes, as well as on domain boundaries in alkanes and fatty acids. The STM has been home–built [7]. Imaging was performed at the internal interface between highly oriented pyrolytic graphite (HOPG) and concentrated but not saturated solutions of alkanes (tetratriacontane ($C_{34}H_{70}$) and pentacontane ($C_{50}H_{102}$)), a fatty acid (octadecanoic acid ($C_{17}H_{35}COOH$)) and an alkyl–substituted triiodobenzoate ($I_3H_2C_6COOC_{18}H_{37}$) dissolved in phenyloctane, as described before [6]. All images presented here were obtained at quasi–constant height in the variable current mode using Pt/Ir tips. No digital image processing has been performed. The average current was set to 1 nA and the tip–bias was around +1 V. These are tunneling conditions, under which, in general, the STM images show contributions of both substrate and adsorbate simultaneously [5]. However, the contrast also depends on the particular tip condition.

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RESULTS AND DISCUSSION

Fig. 1 shows a STM image obtained from a tetratriacontane ($C_{34}H_{70}$) monolayer. It exhibits a lamellar structure with the molecules oriented parallel to each other and approximately perpendicular to the lamella boundary. By comparison with STM images taken from the HOPG surface before adsorption, it can be concluded, that the molecular axes run parallel to a graphite lattice vector. The fact that there is no superstructure along the lamellae has been attributed to the commensurability of the adsorbate lattice with the substrate lattice [5]. The distance measured between adjacent molecules is 430 pm and corresponds to the repeat unit between second next carbon rows of the graphite substrate (426 pm) [5]. If the alkyl skeleton planes would be oriented parallel to the substrate as well as in registry with it, as has been proposed earlier for alkanes [8] as well as for another alkyl derivative [9], it would require a compression of the monolayer by more than 10% compared to the bulk structure. On the other hand, the separation between perpendicularly oriented carbon skeleton planes and second next carbon rows in graphite agree very well. Due to the relatively weak interaction between the alkyl chains and graphite we believe, therefore, that in alkane monolayers the carbon skeleton planes are oriented preferentially perpendicular to the graphite surface plane.

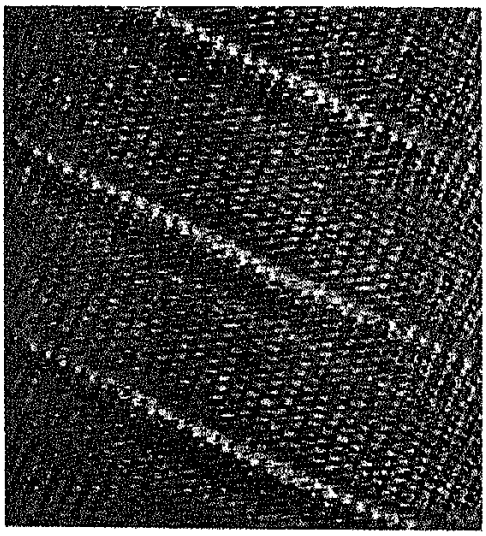

Fig. 1. STM image of a tetratriacontane ($C_{34}H_{70}$) monolayer within one domain. Image size: 12.5 nm x 13.3 nm.

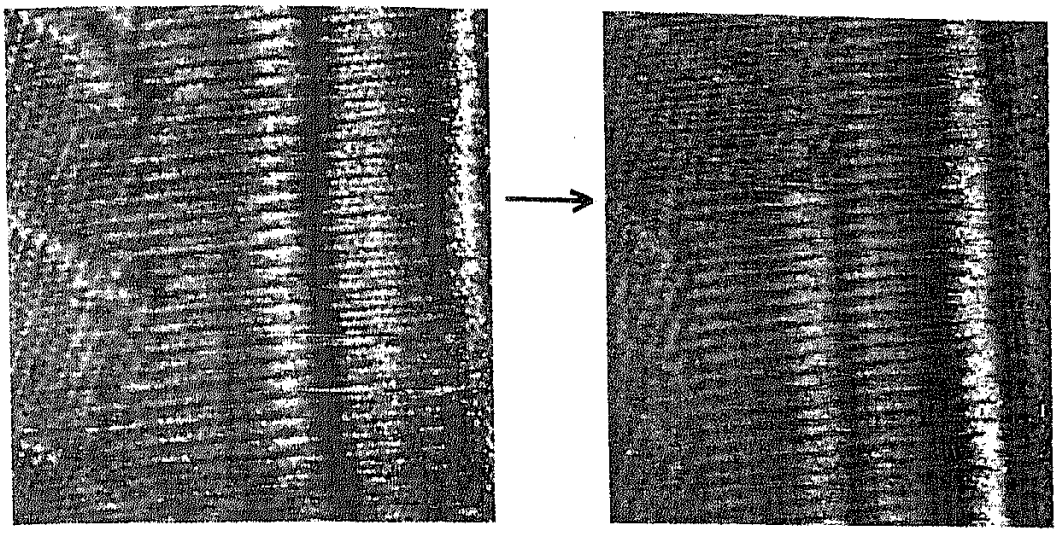

Fig. 2. STM images of tetratriacontane ($C_{34}H_{70}$) monolayers at a domain boundary, where due to the symmetry of adsorbate and substrate lattice a perfect and close packing is not possible. Accordingly, considerable dynamics can be observed. During the recording of image (b) from bottom to top the left domain grew on the expense of the right domain (the line scanned during the rearrangement is marked by an arrow). Image sizes: 12.5 nm x 13.3 nm.

Occasionally domain boundaries were found, where two perfectly ordered domains meet at an angle of 120° corresponding to the symmetry of the graphite substrate. At the domain boundary no close packing is possible with the consequence of high molecular mobility. Fig. 2(b) was imaged a few seconds after Fig. 2(a). While the tip was scanned from the bottom to the top, one lamella of the right domain dissolved, and the left domain immediately grew to fill the vacant site. The whole process took place within a few milliseconds while the tip was at the position marked by the arrow. Similar rearrangements have been found also in monolayers of didodecylbenzene [4] and octadecanol [5].

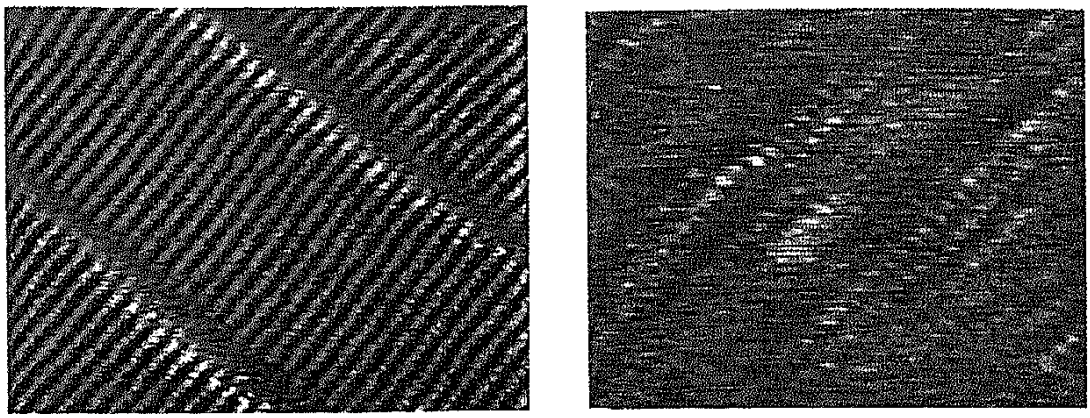

Fig. 3. STM images of pentacontane ($C_{50}H_{102}$) monolayers.
Image sizes: (a) 13.0 nm x 10.0 nm; (b) 8.3 nm x 6.6 nm.

While for linear alkanes with 19 to 44 carbon atoms only highly ordered lamellar phases were observed, less ordered monolayers were frequently found for longer alkanes. Fig. 3 shows a monolayer of pentacontane ($C_{50}H_{102}$) of (a) well and (b) less well ordered areas. For entropic reasons the formation of monolayers with only orientational order appears favored for the longer alkanes. Due to the intermolecular interaction energy, which is not very specific with respect to relative molecular orientation, metastable defects can be trapped in the monolayer packing. The dynamics of defects on a timescale of milliseconds to seconds gives rise to a change of contrast of individual molecules. Similar molecular dynamics has been observed before within the highly ordered monolayers of dotriacontane, however at a much lower rate [4].

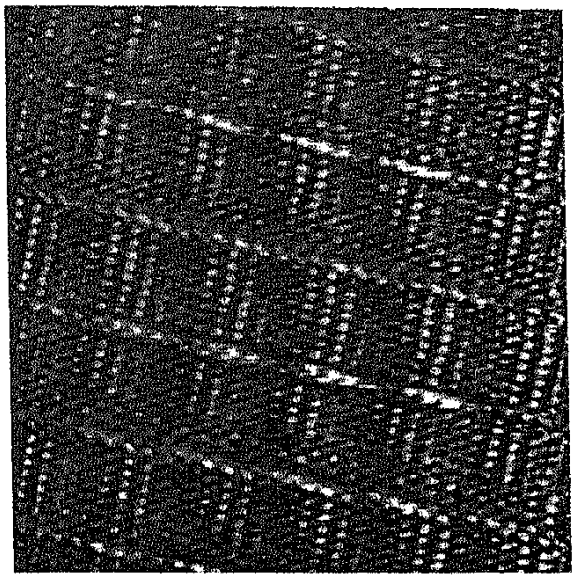

Fig. 4. STM images of an octadecanoic acid ($C_{17}H_{35}COOH$) monolayer. Image size: 16.4 nm x 15.5 nm.

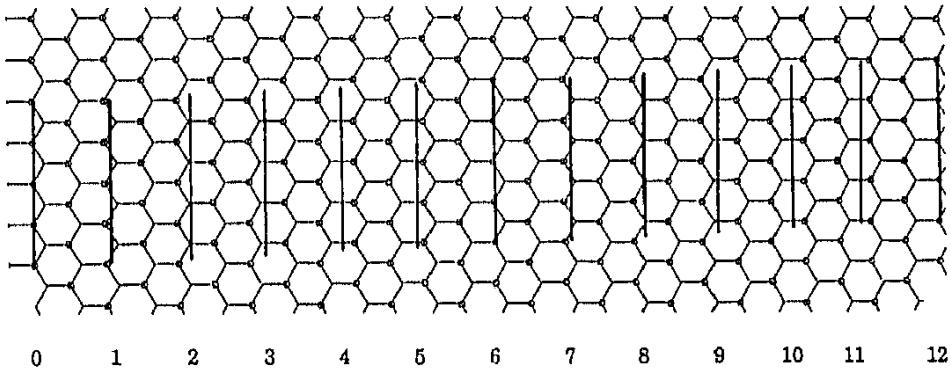

Fig. 5. Schematic displaying the misfit between adsorbate and substrate in the case of the fatty acid on HOPG.

Fig. 4 shows a STM image of a monolayer of octadecanoic acid on graphite. Like in the bulk phase the molecules form dimers giving rise to a double layer structure. Because of the bulkiness of the headgroups and their electrostatic repulsion the intermolecular distance is widened to about 480 pm. This leads to a monolayer structure incommensurate with the substrate. The lattices of the graphite and of the monolayer form a moiré pattern, which is clearly visible in the STM image. The molecular distance of 480 pm together with a slight offset of the molecules along their long axis results in equivalent positions for every sixth molecule as shown in Fig. 5.

From the intermolecular distance of 480 pm it can also be concluded that the planes through the carbon backbones of the alkyl chains run parallel to the graphite surface, in good agreement with the corresponding alkyl–alkyl–distance in the crystal structure of octadecane [8]. Also in the case of the octadecanoic acid monolayers domain boundaries were found. Fig. 6 shows a region, where domains of all three symmetry equivalent orientations meet.

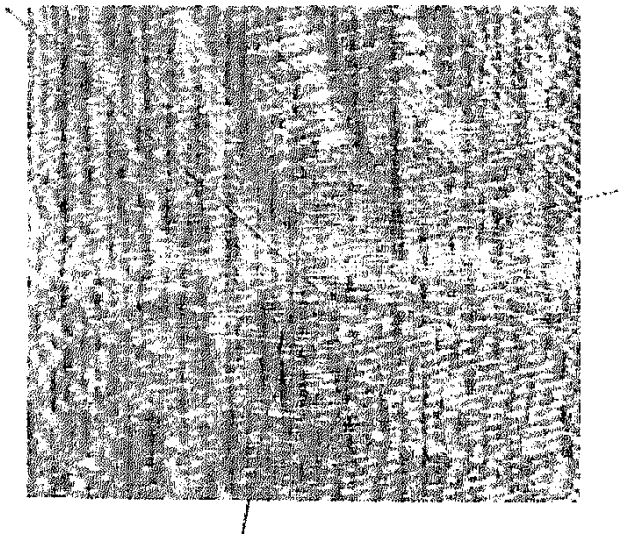

Fig. 6. STM images of an octadecanoic acid ($C_{18}H_{35}OOH$) monolayer at a triple point where the three possible domains meet.
Image size: 13.5 nm x 11.8 nm.

It was found that not only alkane derivatives with small and simple functionalities like carboxyl groups form monolayers on graphite but also numerous complex compounds with long alkyl substituents [10]. Fig. 7(a) gives an example showing a monolayer of octadecyl–2,3,5–triiodobenzoate. A structure of alternating lamellae containing the alkyl groups and the triiodobenzoate headgroups, respectively, is clearly resolved. From the width of the headgroup region (about 2 nm) it can be concluded that in each lamella two rows of headgroups are running parallel. Since the width of the alkyl part amounts to 2.3 nm the alkyl sidechains from adjacent lamellae must interdigitate to give an equal number of headgroups and sidechains in the monolayer. Fig. 7(b) shows the resulting model with an angle of about 75° between the alkyl chains and the lamellae boundaries as also observed experimentally (Fig. 7(b)). Again the carbon skeleton planes of the alkyl chains are oriented parallel to the

graphite substrate leading to an incommensurate structure and a corresponding superstructure along the lamellae in the STM images. This makes it difficult to identify the individual headgroups. Within the headgroup region numerous iodine–iodine contacts occur. This is in good agreement with a statistical analysis of crystal structures by Desideraju et al. [11], who showed that the formation of iodine–iodine contacts is energetically favorable for iodoorganic compounds. The nature of this iodine–iodine interaction, however, is not well understood.

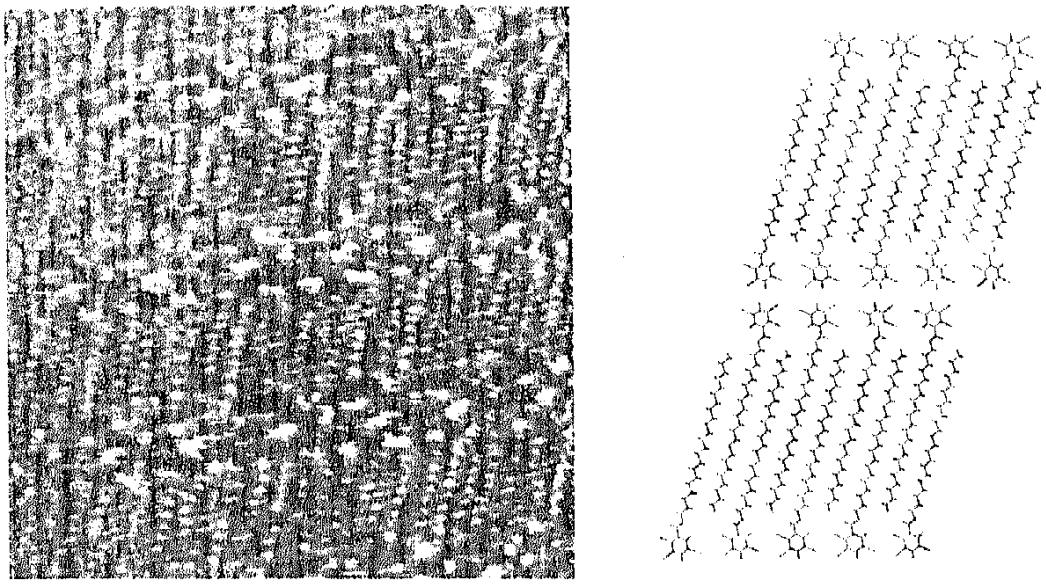

Fig. 7. (a) STM image and (b) model of a octadecyltriiodobenzoate ($H_{37}C_{18}OCOC_6H_2I_3$) monolayer.

To conclude we have shown that numerous compounds containing long alkyl chains form crystalline monolayers at the interface between organic solutions and the basal plane of graphite. The alkyl chains have always been oriented parallel to a lattice axis within the basal graphite plane. The carbon skeleton planes are oriented perpendicular or parallel to the substrate, depending on the size of the headgroups. The consequence is a commensurate or incommensurate packing of the alkyls with respect to the substrate, respectively. If the cross section of the headgroups becomes considerably larger than of the sidechains an interdigitated structure is formed, as demonstrated in the case of the triiodobenzoate. Considerable disorder as well as molecular dynamics on the time scale of milliseconds and longer is observed in particular within domains of the longest alkane ($C_{50}C_{102}$) investigated so far, as well as at alkane and fatty acid domain boundaries.

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