

Packing of Br(CH₂)₁₀COOH and Br(CH₂)₁₁COOH on Graphite: An Odd–Even Length Effect Observed by Scanning Tunneling Microscopy

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Scanning tunneling microscopy (STM) has been used to study 11-bromoundecanoic acid, Br(CH₂)₁₀COOH, and 12-bromododecanoic acid, Br(CH₂)₁₁COOH, adsorbed on the basal plane of highly oriented pyrolytic graphite (HOPG) from phenyloctane solution. The STM tip is immersed in a drop of solution and images molecules at the liquid–solid interface. Atomically resolved images provide a clear picture of the conformation of these two molecules on the graphite surface. Although differing in structure by only a single methylene group, the 11-bromo and 12-bromo species exhibit very different packing structures at the liquid (phenyloctane solution)–solid (graphite) interface. A simple geometric effect is believed to be responsible for the observed packing differences.

Introduction

The molecular arrangement of adsorbates at the liquid–solid interface is very important in the study of wetting, lubrication, adhesion, adsorption, and the fabrication of future microelectronic devices. Long-chain hydrocarbon molecules represent a class of molecules that form self-ordered structures on different substrates.^{1,2} Subtle changes in molecular structure can significantly affect the packing order of such adsorbates and must be studied thoroughly to provide optimum control of the self-assembly process, a necessary prerequisite in the manufacture of many future miniature devices.

Scanning tunneling microscopy (STM) is a powerful tool for studying molecular ordering at the liquid–solid interface.³ Early STM studies of singly substituted long-chain alkane molecules at the solution–substrate interface have shown that different functional groups can have important effects on molecular ordering. For example, *n*-alkanes^{4–6} form lamellar structures on graphite with their molecular axis perpendicular to the lamellar boundary, 1-alcohols^{5–7} have a 60° angle between their molecular axes and the lamellar direction, 1-carboxylic acid molecules^{8,9} assume an interdigitating structure, and 1-bromo- and chloroalkanes¹⁰ take the same surface arrangement as the *n*-alkanes. Thus, the end groups of these molecules play a pivotal role in their packing pattern. Much less information is available for molecules having different functional groups on both ends; however, recent STM studies¹¹ have begun to explore thin-film arrangements arising from disubstituted hydrocarbons. Different alkanol halides have been found to form diverse packing structures on a graphite surface. 12-Bromo-1-dodecanol and 12-chloro-1-dodecanol form herringbone structures, while 12-iodo-1-dodecanol assumes a lamellar structure with molecules in the adjacent lamellae parallel to each other. For singly substituted molecules, the number of carbons in the chain has little, if any, consequence in determining the overall packing arrangement on the surface. However, in this STM study of doubly substituted 11-bromoundecanoic acid, Br(CH₂)₁₀COOH, and 12-bromododecanoic acid, Br(CH₂)₁₁COOH, we show that

chain length, in particular even and odd numbers of carbon atoms, can have a significant impact on thin film, interfacial ordering.

Experimental Section

11-Bromoundecanoic acid, Br(CH₂)₁₀COOH, and 12-bromododecanoic acid, Br(CH₂)₁₁COOH, were obtained from Aldrich and used without further purification. A 60 mg sample of these compounds was dissolved in 1 mL of 1-phenyloctane (Aldrich). A drop of solution was directly applied to the basal plane of a freshly cleaved piece of highly oriented pyrolytic graphite (HOPG, Advanced Ceramics Corp.). All the STM experiments were performed on a Nanoscope III (Digital Instruments) with mechanically cut Pt/Rh (87/13) wire tips (Omega) immersed in solution, and images were collected under ambient conditions at room temperature. Typical tunneling parameters used for imaging these molecules were 1.2–1.4 V (sample negative) for the bias voltage and 240–400 pA for the tunneling current. Different tips and samples were used to check for reproducibility and to ensure the absence of image artifacts caused by tip or sample. All of the images have been acquired at constant current and display the relative topographic height as the tip is raster scanned across the sample. Here, “bright” areas correspond to topographically higher regions, while “dark” areas reflect lower ones.

Molecular models were created with Biosym (InsightII, Molecular Simulations, Inc.) software running on a Silicon Graphics workstation.

Results and Discussion

Structure of 12-Bromododecanoic Acid on Graphite.

Figure 1a depicts an image of 12-bromododecanoic acid, Br(CH₂)₁₁COOH, collected at the interface between the phenyloctane solution and graphite. The black bar in the image corresponds to one molecule lying flat on the graphite surface. Each molecule in Figure 1a is composed of three parts: a large bright head, a dark trough, and a few little protrusions in between. We attribute the large “bright” spot to the location

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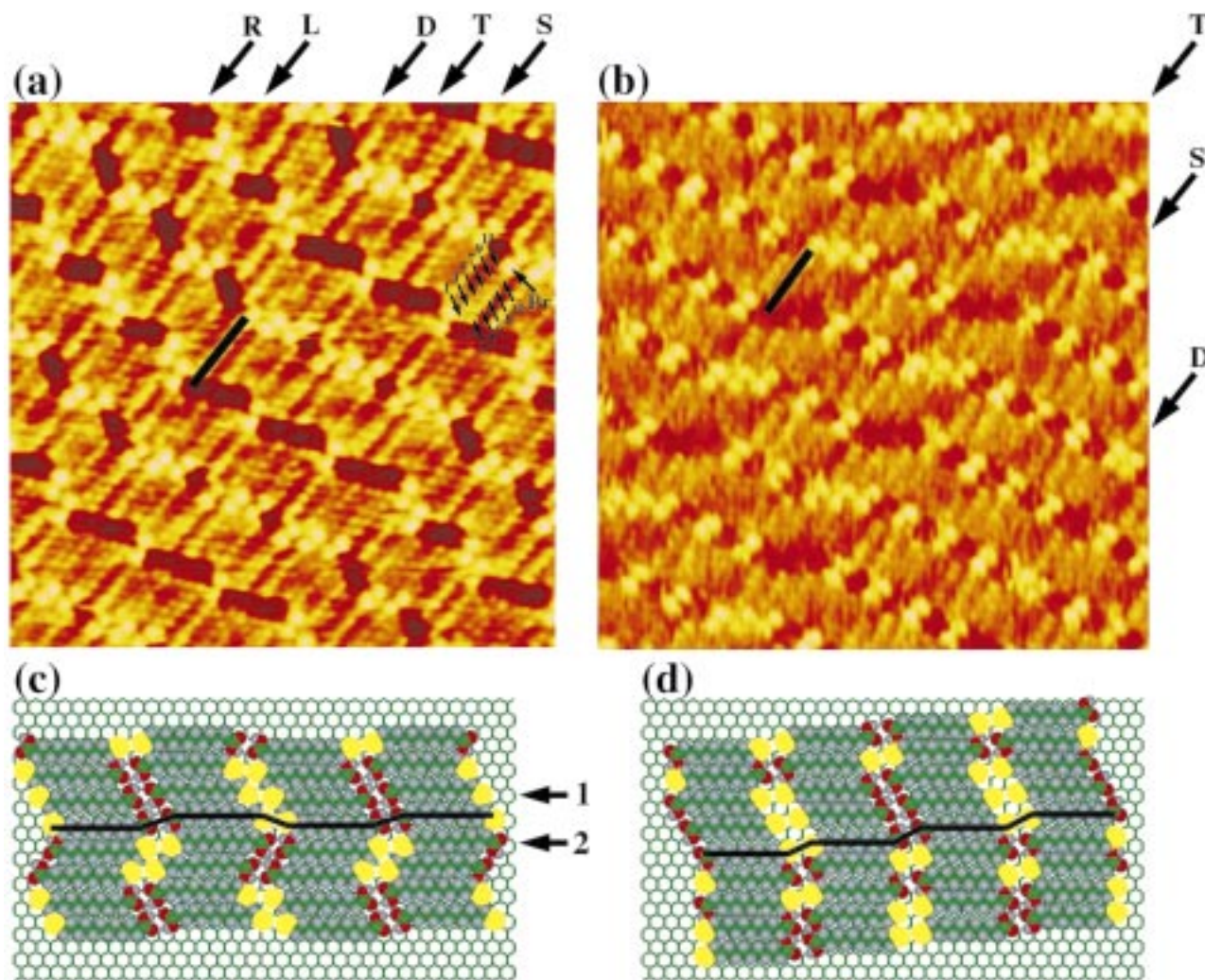


Figure 1. (a) STM image of 12-bromododecanoic acid ($\text{Br}(\text{CH}_2)_{11}\text{COOH}$) in phenyloctane on graphite. One molecular length is indicated by a black bar. Numbers 1–11 refer to the positions of 11 hydrogen atoms on the 11 methylene carbons of a single molecule, and Br refers to the position of the Br atom. Capital letters S, D, and T point to the strips of single-, double-, and triple-twin structures, respectively. Capital letters R and L point respectively to the positions where the lower twin in a double or triple twin shifts right or left relative to the twin lying above it. The image size is $12 \times 12 \text{ nm}^2$, and the imaging parameters are 1.4 V (sample negative) and 300 pA. (b) STM image of 11-bromoundecanoic acid ($\text{Br}(\text{CH}_2)_{10}\text{COOH}$) in phenyloctane on graphite. One molecular length is indicated by a black bar. Capital letters S, D, and T point to the strips of single-, double-, and triple-twin structures, respectively. The image size is $12 \times 12 \text{ nm}^2$, and the imaging parameters are 1.4 V (sample negative) and 300 pA. (c) Top view of a computer-generated model of a 12-bromododecanoic acid film on a graphite substrate. Yellow represents bromine atoms, green represents carbon atoms, gray represents hydrogen atoms, and red represents oxygen atoms. The black lines outline the alternate “up-and-down” profile formed when the twin structures are assumed by 12-bromododecanoic acid on graphite. Numbers 1 and 2 refer to two configurations in which the molecules shift right (1) or left (2) relative to the row above (see Figure 2a). (d) Top view of a computer-generated model of an 11-bromoundecanoic acid film on a graphite substrate. The black lines outline the staircase-like profile formed when twin structures are assumed by 11-bromoundecanoic acid on graphite.

of the bromine atom along the chain based upon a comparison to early work in this laboratory.¹⁰ This puts the carboxyl group at the dark position, in agreement with other studies of carboxylic acids adsorbed on graphite.^{8,9} Previous STM investigations of long-chain *n*-carboxylic acids have shown that these molecules lie down on graphite with the carboxyl end groups oriented facing each other in order to facilitate hydrogen bonding. These studies also show that the carboxyl end group appears with “darker” contrast compared to the rest of the hydrocarbon chain. Atomic resolution has been achieved in the image displayed in Figure 1a. There are 11 small protrusions visible on some molecules, which have been numbered 1–11 in the image. Previous experimental and theoretical studies of *n*-alkanes have assigned the small spots in such STM images to the positions of those hydrogen atoms of the adsorbed hydrocarbon molecules that protrude farthest out of the molec-

ular plane.¹² In a similar manner we attribute the 11 spots observed here to the hydrogen atoms on the 11 methylene carbons.

One striking feature of this image is the occurrence of large twin “bright” spots, signifying greater tunneling probability at this point in the molecular chain. A given “Br bright spot”, marked as Br in the image, always appears next to another Br on the surface, forming “twin” structures in which a molecule lies down on the surface head to head with its neighbor. This is consistent with our previous studies of 1-bromoalkanes,¹⁰ which indicate that these molecules prefer to assume a head to head configuration on a graphite surface. These twin structures are arranged by themselves (single, marked as S in the image), in pairs (double, marked as D in the image), or in threes (triple, marked as T in the image). These twin structures extend laterally and order in a direction parallel to their long molecular

axes; however, there is no long-range ordering in the direction perpendicular to the long molecular axis. The molecular model deduced from this image is shown in Figure 1c.

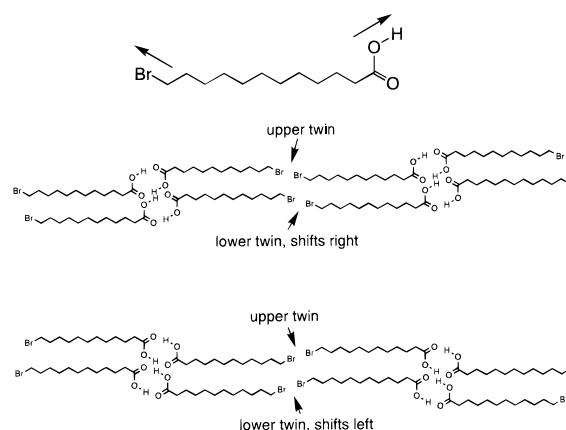
There is also a Moiré pattern formed in the STM topographs, which gives a contrast variation with a period of four molecules in a direction perpendicular to the long molecular axis. Previous studies^{5,8,9} have shown similar Moiré patterns for *n*-carboxylic acids adsorbed on graphite. For instance, in the direction perpendicular to their long molecular axes, arachidic acid (C₁₉H₃₉COOH) and stearic acid (C₁₇H₃₅COOH) molecules form superstructures with periods of four and five molecules, respectively.⁸ This results partially from the bulkiness of the carboxyl end groups. In order for adjacent carboxyl groups to lie down flat and hydrogen bond to each other, neighboring molecules are pushed slightly away from each other and no longer match with the graphite lattice. After a few molecular rows, the carboxylic acid molecules come back into registry with the lattice again. In the present case, to hydrogen bond with the next molecule and maintain the twin structure for the bromine end groups, molecules not only form a Moiré pattern on the graphite surface but also rotate 180° about an axis normal to the surface to achieve a stronger interaction and form a more stable interfacial film. Thus, as a result of the interplay between the competing adsorbate–adsorbate and adsorbate–substrate interactions, 12-bromododecanoic acid forms somewhat irregular patterns compared to the regular lamellar structure assumed by both singly substituted and unsubstituted *n*-alkanes.

Structure of 11-Bromoundecanoic Acid on Graphite.

Figure 1b displays an image of 11-bromoundecanoic acid, Br-(CH₂)₁₀COOH, adsorbed at the phenyloctane solution–graphite interface. The black bar in the image corresponds to one molecule lying flat on the surface. Like 12-bromododecanoic acid, each single molecule in the STM image is composed of three parts: a large “bright” spot, Br, a carboxyl group lying in the “dark” trough, and a few small protrusions between these features. This molecule does not have long-range ordering in a direction perpendicular to its long molecular axis but instead forms twin structures similar to those observed for 12-bromododecanoic acid. The images are dominated by two kinds of twin structures: the single twin (marked as S in the image) and triple twins (marked as T in the image). There are very few double twins (marked as D in the image), which are sparsely distributed. The single twin part of the image is very similar to the structure assumed by *n*-carboxylic acid^{8,9} except that a bromine atom is simply stuck to the other end of the molecule. These single twin structures are separated by strips of triple twins. (In larger scale images, which are not shown here, these single- and triple-twin structures are found on the surface in equal proportion.) The triple-twin part of the image looks very much like that of 12-bromododecanoic acid. The submolecular resolution obtained in this image allows almost every other protruding hydrogen atom on the methylene carbons to be observed for each molecule.

Comparison between 11-Bromoundecanoic Acid and 12-Bromododecanoic Acid. There are some features common to both 11-bromoundecanoic acid and 12-bromododecanoic acid molecules adsorbed on the graphite basal plane. Both are ordered in a direction parallel to, but lack long-range order in a direction perpendicular to, their long molecular axes. Both adopt head to head (–Br Br–) configurations and form twin structures. However, 12-bromododecanoic acid is arranged in single, double, and triple twins, each of which has a similar population on the surface, while 11-bromoundecanoic acid mainly adopts single and triple twins. There are very few double

a) 12-Bromododecanoic acid



b) 11-Bromoundecanoic acid

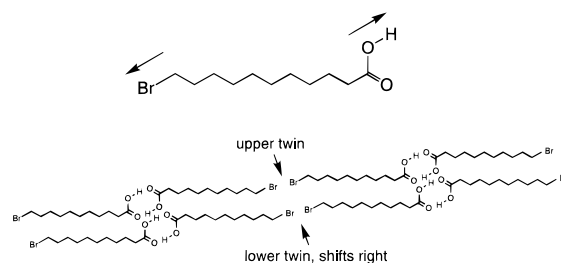
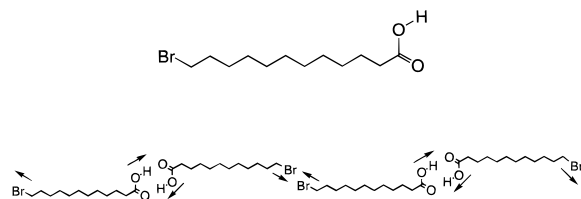


Figure 2. (a) Structure of 12-bromododecanoic acid molecule in the all-trans conformation. The bromine group and the hydroxyl group are on the same side of the long molecular axis, as depicted by the arrows. Two groups of molecules have been arranged to show the situation in which the lower twin shifts right or left relative to the upper twin. (b) Structure of 11-bromoundecanoic acid molecule in the all-trans conformation. The bromine group and the hydroxyl group are on different sides of the long molecular axis, as depicted by the arrows. A group of molecules have been arranged to show the situation in which the lower twin only shifts right relative to the upper twin.

twins on the surface for the 11-bromo species. These two images are typical reproducible topographs taken with these two molecules. The image resolution for 12-bromododecanoic acid was always found to be sharper than that for 11-bromoundecanoic acid, suggesting that the 11-carbon moiety is less stable on the surface than the 12-carbon one and ruling out a tip artifact. The difference between the melting points of these two molecules, i.e., 48–51 °C for 11-bromoundecanoic acid and 52–55 °C for 12-bromododecanoic acid, is consistent with this suggestion, as is the increased molecular length of the 12-species.

The main difference between these two molecules when adsorbed on the graphite basal plane is the relative position of adjacent twins. For 12-bromododecanoic acid, the lower twins of the double- or triple-twin structures shift either right or left (marked as R and L, respectively, in Figure 1a) relative to the twin pairs lying above. For 11-bromoundecanoic acid, however, the lower twins of triple-twin structures only shift right relative to the one above, as can be seen in Figure 1b. This difference is also schematically shown in Figure 2a,b and is believed to arise from the presence of an odd or even number of carbons in the molecules. When these molecules adsorb onto the graphite basal plane with an all-trans conformation, the relative orientations of the bromine group and the hydroxyl group are different for each molecule. Figure 2a,b shows the structures of these two molecules with an all-trans conformation. In Figure 2a, the bromine and hydroxyl group of 12-bromode-

a) 12-Bromododecanoic acid



b) 11-Bromoundecanoic acid

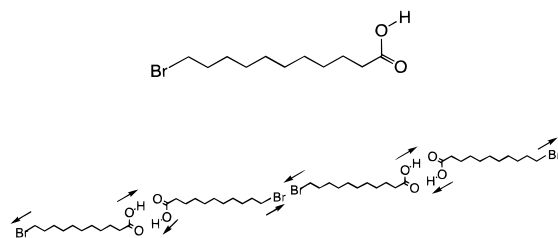


Figure 3. (a) Structure of 12-bromododecanoic acid molecule in the all-trans conformation. Four molecules have been arranged to show the “up-and-down” profile described in the text. (b) Structure of 11-bromoundecanoic acid molecule in the all-trans conformation. Four molecules have been arranged to show the staircase-like profile described in the text.

canoic acid are on the same side of its long molecular axis, as indicated by the arrows next to these groups, while in Figure 2b, the bromine and hydroxyl group of 11-bromoundecanoic acid are on different sides of its long molecular axis, as depicted by the arrows next to these groups. Figure 1c,d shows molecular models of 12-bromododecanoic acid and 11-bromoundecanoic acid on the graphite surface deduced from their STM images. They do not represent any specific area on the surface; however, the models do include most of the important features observed for these two molecules on graphite. In Figure 1c, the bromine and hydroxyl group of 12-bromododecanoic acid are always on the same side of its long molecular axis. When a twin structure is formed on the graphite surface, 12-bromododecanoic acid gives an alternate “up-and-down” profile in a direction parallel to the molecular axes, as depicted by the black lines in Figure 1c and schematically represented in Figure 3a. The next row of molecules can then assume two different configurations (numbered 1 and 2 in Figure 1c), in which the molecules can shift either right (1) or left (2).

In Figure 1d the bromine and hydroxyl group of 11-bromoundecanoic acid must be on different sides of its long molecular axis when in the all-trans conformation. When a twin

structure is formed on the graphite surface, 11-bromoundecanoic acid yields a staircase-like profile, as can be seen in Figure 1d and schematically displayed in Figure 3b. The next row of molecules can only orient in one configuration, which is exactly the same as that of the one above it, resulting in a shift to the right. If a molecule in this row were to assume the other configuration, in which the lower twins shift left relative to the ones above, a staircase-like molecular profile running in the other direction would result, i.e., stairs going down from left to right. When two domains such as this with different configurations are put together, a gap results between them, presumably making the film unstable on the surface and leading to the domination of one staircase structure over the other.

Conclusion

The disubstituted long-chain hydrocarbon molecules 11-bromoundecanoic acid and 12-bromododecanoic acid adsorbed at the phenyloctane solution–graphite interface have been imaged by STM with atomic resolution. The absolute conformations of these molecules have been determined unambiguously. Both molecules adopt structures different from their monosubstituted counterparts. The packing structure of these molecules on the surface has been found to be significantly affected by whether the hydrocarbon chain has an odd or even number of carbon atoms. A simple geometric effect and molecular model have been used to explain the source of this difference.

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