

Scanning Tunneling Microscopy Investigation of a Chirally Pure Molecule at the Liquid–Solid Interface: Unambiguous Topographic Markers

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Received: November 20, 2000

The self-assembly of mixtures of hexadecanoic acid with (*R*)-2-Br-hexadecanoic acid and hexadecanoic acid with (*S*)-2-Br-hexadecanoic acid have been investigated on graphite at the liquid–solid interface using scanning tunneling microscopy (STM). The STM study of a chirally pure species provides an unambiguous assignment of geometric configurations for various functional groups in these molecules. Specifically, the absolute conformation of the bromine atom in 2-Br-hexadecanoic acid has been determined to be pointing “up” away from the graphite surface. This assignment confirms an earlier conjecture that Br atoms appearing with high tunneling probability in STM images are conformationally in the up position. Furthermore, this geometric designation reinforces an explanation for the spontaneous separation of racemic 2-Br-hexadecanoic acid into enantiomerically pure domains as a process induced by energetically favorable conformations of 2-Br-hexadecanoic acid on a surface.

Introduction

Scanning tunneling microscopy (STM) has become a widely used tool for elucidating surface features and patterns. STM is an especially powerful technique because it allows surface structures to be mapped out on a molecule by molecule and even atom by atom basis. In addition to investigations of metal and semiconductor surfaces, STM's numerous applications include studies of molecules physisorbed and chemisorbed on surfaces both in UHV^{1–3} and at the liquid–solid interface under ambient conditions.^{4–6} However, the interpretation of STM images of weakly adsorbed molecules on substrates remains a difficult task because the tunneling mechanism through which topographs are obtained is quite complicated.

STM images do not represent true physical topographs but, more accurately, are a measure of the local density of states (LDOS) at the Fermi level of the sample surface at the position probed by the STM tip;⁷ the density of states is mapped by measuring the tunneling current (or tunneling probability). At any point on the surface, the tunneling current is a convolution of factors that include electronic coupling to the surface and the distance from tunneling tip to surface adatom or admolecule and its orientation. For topographs obtained in constant current mode (tunneling current held fixed, tip height varies), brighter regions correspond to a retraction of the STM tip and darker regions to a movement of the tip toward the surface. Thus, formally, “bright” regions correspond to topographical protrusions, while “dark” regions correspond to topographical depressions; however, these assignments are overly simplistic and may not reflect the true geometric orientation of atoms on the surface. The electronic coupling of an atom to the surface is expected to increase when the atom is nearer to the surface (a topographical depression), while the tunneling probability from tip to atom is also expected to increase when the atom is nearer to the tip (a topographical protrusion). Since both of these effects enhance the tunneling probability, it is not generally possible to assign a high tunneling current atom as a topographical protrusion. Constant height STM studies (tip height fixed, tunneling current

varies) provide information on the tunneling current at a given position on the surface, which is controlled by a similar convolution of electronic and geometric factors.

Due to the complicated factors that can affect tunneling probability, atoms in a physisorbed molecule that physically protrude from the surface can actually appear as depressions. Thus, Xe physisorbed on Ni appears as an expected topographical protrusion;⁸ however, acetylene on copper is observed as a dumbbell-shaped depression.⁹ Partially fluorinated long-chain carbon compounds physisorbed at the liquid–solid interface exhibit a counterintuitive topographical depression at the positions of the F atoms, despite the fact that they are closer to the tip than the H atoms, which in turn appear as topographical protrusions.¹⁰

Chemical marker groups have been used to simplify the interpretation of STM images for surfaces covered by physisorbed molecules. Marker groups are chemical functional groups contained within a molecular adsorbate that exhibit unusually high or low contrast in the STM topograph relative to the rest of the molecule. This unusual contrast can be used to locate particular functionalities within a given molecule. A number of physisorbed molecular systems that contain such markers have been successfully explored on graphite;^{11–17} however, the unusual image contrast arises from both topographic positioning and electronic coupling to the surface as discussed above, thereby limiting the usefulness of information provided by these chemical marker groups.

In the present study, STM is used to investigate a chirally pure molecule adsorbed onto a graphite substrate. An enantiomerically pure adsorbate provides a known absolute geometric configuration for a given functional group, thereby enhancing the interpretation of the STM images. Combining known topography with the presence of a chemical marker group helps to clarify the tunneling mechanism for the functional group in question. The bromine atom has been of particular interest in this regard, as it has been observed as both a bright^{12,18–20} and a dark marker group,²¹ depending on its position along a hydrocarbon chain. This observation has led to uncertainty

regarding the true geometric orientation of the bromine atom and the consequent impact of its position on the tunneling probability over the bromine atom.

In this work, the uncertainty about the geometric orientation of the bromine atom is removed by studying mixtures of (*R*)-2-Br-hexadecanoic acid with hexadecanoic acid and (*S*)-2-Br-hexadecanoic acid with hexadecanoic acid. The enantiomerically pure mixtures reveal that bromine atoms in an “up” orientation pointing away from the surface have a high tunneling probability and thus show up as “bright” spots in STM topographs. This verifies an earlier conjecture that the tunneling mechanism for the bromine atom in this molecule is dominated by geometric effects¹² and lends support to the hypothesis that the “up” configuration of the Br atom is more thermodynamically stable for molecules physisorbed at the liquid–solid interface. This hypothesis is fundamental to the proposed mechanism for the previously observed spontaneous segregation of racemic 2-Br-hexadecanoic acid on graphite.¹⁸

Experimental Section

A. Methods. All the studies described were performed under ambient conditions at room temperature using a Nanoscope III scanning tunneling microscope (Digital Instruments). The experiments were conducted at the liquid–solid interface by immersing an STM tip, mechanically cut from a 0.25 mm diameter platinum/rhodium (87/13) wire (Omega), into a droplet of solution. The small (10 μ L) droplet of solution is applied directly to the surface of a freshly cleaved piece of highly oriented pyrolytic graphite, HOPG (Advanced Ceramics, ZYB grade).

All of the images displayed were obtained in the constant current mode of operation whereby the height of the STM tip relative to the surface is monitored via an electronic feedback loop and adjusted in order to maintain a fixed tunneling current set by the user. A zeroth-order flattening procedure has been utilized to normalize the vertical offset produced in this operating mode. Typical tunneling parameters used in the experiments include a bias voltage of 1.5 V (sample negative) and a tunneling current of 250–400 pA. The resulting images display relative distances between the STM tip and the surface where “bright” corresponds to topographically higher areas on the surface and “dark” corresponds to topographically lower regions on the surface. The relative tunneling probability at any point on the surface is, as noted above, a convolution of the interface topography and the local density of states at the surface Fermi level, as modified by any electronic coupling between the surface and the adsorbed molecules.

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

B. Materials. Hexadecanoic acid ($\text{CH}_3(\text{CH}_2)_{13}\text{CH}_2\text{COOH}$) was procured from Aldrich and dissolved in 1-phenyloctane (Aldrich) to produce a saturated solution.

Synthesis of (*R*)-2-Br-Hexadecanoic acid ($\text{CH}_3(\text{CH}_2)_{13}\text{CHBrCOOH}$) and (*S*)-2-Br-Hexadecanoic acid. This synthesis has been described in detail elsewhere.²² It is a three-step process. (i) Commercially available racemic 2-bromohexadecanoic acid was reacted with (*R*)-(+)-1,1'-bi-2-naphthol to provide two diastereoisomeric esters, which were separated by medium pressure liquid chromatography. (ii) The two esters obtained were reduced to the corresponding optically pure 2-bromo-alcohols: (*R*)-(+)-2-bromo-1-hexadecanol and (*S*)-(–)-2-bromo-1-hexadecanol, respectively. The absolute configuration of the chiral center was assigned by comparing the optical rotation value

with literature data.²³ (iii) Oxidation of (*R*)-(+)-2-bromo-1-hexadecanol and (*S*)-(–)-2-bromo-1-hexadecanol afforded (*R*)-2-bromohexadecanoic acid and (*S*)-2-bromohexadecanoic acid, respectively. The enantiomeric excess of the synthesized acids was determined to be greater than 95% by using (1*R*,2*R*)-(+)-diphenylethane-1,2-diamine as an NMR chiral solvating agent.²⁴

(*R*)-2-Br-hexadecanoic acid and (*S*)-2-Br-hexadecanoic acid were dissolved in phenyloctane to produce two separate solutions, the former with a 40 mg/ml concentration and the latter with a 34 mg/ml concentration. Each solution containing brominated molecules was subsequently combined with a solution of hexadecanoic acid (described above) to form two different mixtures: one mixture composed of hexadecanoic acid with *R*-2-Br-hexadecanoic acid and a second mixture composed of hexadecanoic acid with *S*-2-Br-hexadecanoic acid. The solutions were allowed to thermally equilibrate for approximately 24 h prior to scanning under the microscope. Several samples of each mixture (hexadecanoic acid with (*R*)-2-Br-hexadecanoic acid and hexadecanoic acid with (*S*)-2-Br-hexadecanoic acid) were prepared and studied to check for reproducibility of results.

Results

A. Mixture of Hexadecanoic Acid with (*R*)-2-Br-Hexadecanoic Acid. Mixtures of (*R*)-2-Br-hexadecanoic acid with hexadecanoic acid exhibit long-range order when physisorbed onto a graphite substrate. Multiple domains are formed extending in width from 30 to over 100 nm. Figure 1a shows a representative STM topograph of a 1:1 mixture by volume of hexadecanoic acid with (*R*)-2-Br-hexadecanoic acid imaged at the phenyloctane–graphite interface. One molecular length is marked by a thick blue bar. The length of a given molecule, 2.29 ± 0.1 nm, corresponds to the expected 2.24 nm length of either a hexadecanoic acid or an (*R*)-2-Br-hexadecanoic acid molecule configured in an all-trans conformation lying flat on the basal plane of graphite.

The self-assembly portrayed in Figure 1a is very similar to the 2D organization formed by mixtures of hexadecanoic acid with racemic 2-Br-hexadecanoic acid that has been described elsewhere.²⁵ Most of the molecules in the 2D surface structure are hexadecanoic acid molecules with 2-Br-hexadecanoic acid molecules interspersed sporadically throughout the domain. Hexadecanoic acid forms a template consisting of a 90° angle between the lamellar and molecular axes. The troughs in the STM image (Figure 1a) consist mainly of dark, topographically depressed spots that signify a pair of hydrogen-bonding carboxyl groups.^{15,26} These dark spots in the troughs are sporadically dotted with bright regions. The bright (high tunneling probability) markers have been attributed in both experimental^{12,18–20} and theoretical studies^{19,27} to the bromine functional group when it appears at a nonterminal position along the hydrocarbon chain or at a terminal position in the gauche conformation. The geometric configuration of the bromine atom in this study is discussed in detail below. The chemical groups bromine (bright) and COOH (dark) provide convenient markers to differentiate hexadecanoic acid from 2-bromohexadecanoic acid in the STM constant current topograph.

The relative orientation of the bromine functional group to the carboxyl group is consistent throughout the topograph; black bars have been placed over the carboxyl/bromine orientation to highlight this configuration. The assignment of a bromine atom to a particular carboxyl group is achieved by carefully comparing distances between the bromine atom and neighboring carboxyl groups within a given trough. This assignment is

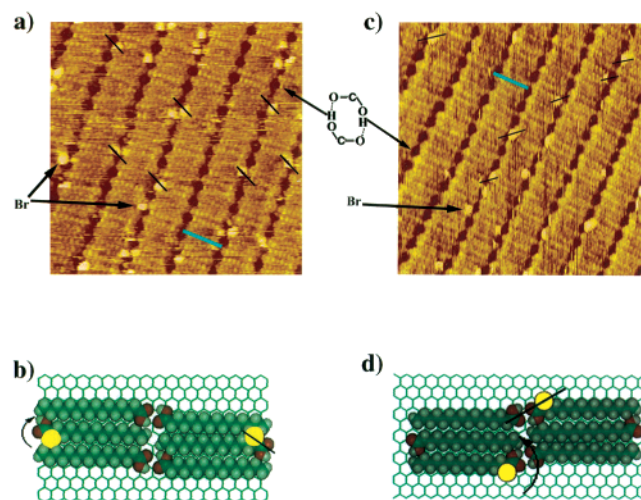


Figure 1. (a and b) Domains of hexadecanoic acid interspersed with (*R*)-2-Br-hexadecanoic acid. A 15 nm × 15 nm STM image taken at 300 pA and 1.5 V (sample negative) is shown in panel a, where a solid blue bar represents one molecular length of either 2-Br-hexadecanoic acid or hexadecanoic acid. The bromine atom (bright marker) lies in a fixed orientation to the carboxyl functional group (dark marker) throughout the topograph. This configuration is highlighted by superimposed black lines and shows all the bromines lying either above and to the left or below and to the right of the carboxyl group. A top view of a model of this domain is shown in panel b. The black line superimposed on one of the bromine/carboxyl combinations mimics the arrangement found in the STM image (a). An arrow marking the clockwise direction of the bromine–carboxyl–alkyl chain orientation with the hydrogen pointing “down” classifies the brominated molecules as the *R* conformer. (c and d) Domains of hexadecanoic acid interspersed with (*S*)-2-Br-hexadecanoic acid. An 18 nm × 18 nm STM constant current topograph taken at 300 pA and 1.5 V (sample negative) is shown in panel c, where a blue bar depicts one molecular length. A top view of a model of the domain from panel c is shown in panel d. The black lines in panels c and d superimposed on the bromine/COOH orientation show an organization that is the mirror image of that present in panels a and b. An arrow marking the counterclockwise direction of the bromine–carboxyl–alkyl chain orientation with the hydrogen pointing “down” classifies the brominated molecules as the *S* conformer.

further facilitated by taking advantage of the interdigitation patterning of the hexadecanoic acid molecules that separates neighboring carboxyl groups. When this procedure is followed, over 90% of the time the bromine atom (bright spot) is found to be closest (directly adjacent) to only one carboxyl group (dark region). In Figure 1a, all the bromines are either above and to the left or below and to the right of the carboxyl group. Figure 1b provides a molecular model based on a typical region of the self-assembled monolayer. The orientation of the carboxyl group with the accompanying bromine is accordingly reflected in the model.

B. Mixtures of Hexadecanoic Acid with (*S*)-2-Br-Hexadecanoic Acid. Mixtures of (*S*)-2-Br-hexadecanoic acid with hexadecanoic acid also exhibit long-range order when physisorbed onto a graphite substrate. Multiple domains are formed extending in width from 30 to over 100 nm. Figure 1c shows a representative STM topograph of a 3:1 mixture by volume of hexadecanoic acid with (*S*)-2-Br-hexadecanoic acid imaged at the phenyloctane-graphite interface. One molecular length is marked by a thick blue bar. The length of a given molecule, 2.18 ± 0.1 nm, corresponds well to the expected 2.24 nm length of either a hexadecanoic acid or an (*S*)-2-Br-hexadecanoic acid molecule configured in an all-trans conformation lying flat on the graphite surface.

The structure formed by this mixture on the surface is similar to that described above for mixtures of hexadecanoic acid with

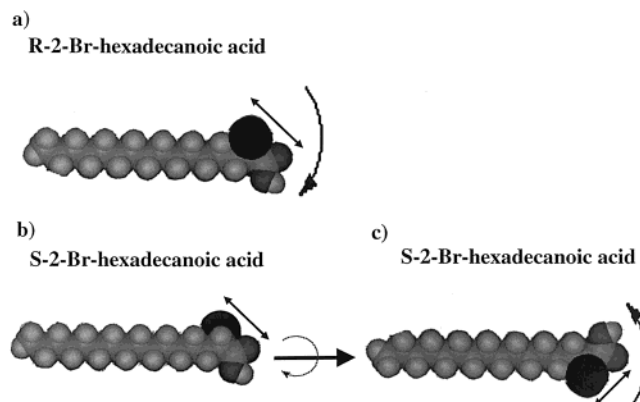


Figure 2. (a) Top view of a model of (*R*)-2-Br-hexadecanoic acid with the bromine atom colored in black and pointing “up” away from the plane of the paper (or surface). The straight arrow shows the bromine atom above and to the left of the COOH group. (b) Top view of a model of (*S*)-2-Br-hexadecanoic acid with the bromine atom colored in black where the bromine points “down” into the plane of the paper (or surface). The straight arrow indicates the Br atom is above and to the left of the carboxyl group. This molecule has been rotated in panel c, where now the bromine is pointing “up” away from the plane of the paper. In this orientation, the mirror image property of the Br/COOH combinations in (*S*)-2-Br-hexadecanoic acid (c) and (*R*)-2-Br-hexadecanoic acid (a) is more readily apparent.

(*R*)-2-Br-hexadecanoic acid except for the orientation of the bromine atom with respect to the carboxyl group. In Figure 1c, the bromine/carboxyl configuration is consistent throughout the domain and has been highlighted by black bars. This functional group orientation is the mirror image of the bromine/carboxyl conformation present in mixtures of hexadecanoic acid with (*R*)-2-Br-hexadecanoic acid (Figure 1a). In Figure 1c, all the bromines are above and to the right or below and to the left of the carboxyl group. Figure 1d presents a molecular model of this mixed self-assembly, preserving the carboxyl/bromine orientation found in the corresponding STM image (Figure 1c).

Discussion

Topographic information about the orientation of the bromine atom can be directly correlated with the STM image features in Figure 1a,c. The unambiguous assignment of a “bright” bromine pointing “up” away from the graphite surface is made with the use of a chirally pure molecule such as (*R*)-2-Br-hexadecanoic acid or (*S*)-2-Br-hexadecanoic acid. (*R*)-2-Br-hexadecanoic acid yields a clockwise orientation of the bromine–carboxyl–alkyl chain according to the Cahn–Ingold–Prelog sequence rules²⁸ (in this case, the lightest atom, hydrogen, points toward the back or “down” toward the graphite substrate). The α position in 2-Br-hexadecanoic acid has two hydrogens that can be replaced by a bromine. Figure 2a shows one such substitution that yields (*R*)-2-Br-hexadecanoic acid. Using the same molecule from Figure 2a but substituting the other hydrogen by a bromine yields the configuration shown in Figure 2b, where the bromine is now oriented “down” toward the graphite surface. The molecule from Figure 2b has been rotated in Figure 2c, where the Br/COOH configuration can be clearly seen to be the mirror image of that in Figure 2a. Figure 2b,c shows a molecule with a counterclockwise orientation of the bromine–carboxyl–alkyl chain (with the hydrogen pointed toward the surface), yielding (*S*)-2-Br-hexadecanoic acid.

The three functional groups critical to the absolute identification of chiral configurations are identifiable in the STM image from Figure 1a.^{18,25} The carboxyl group is signified by the dark red circular regions in the topograph.^{15,26} The bromine atom is

marked by the bright spot in the image, similar to other bromines at a nonterminal position along the hydrocarbon chain, or in a gauche orientation at the end of the chain.^{12,18–20} The position of the bromine directly indicates the location of the remainder of the alkyl chain since the bromine atom is located α to the carboxylic acid group. For instance, if the bromine lies to the left of the carboxylic acid group, the alkyl chain also lies to the left of this end group, as is the case for the molecules in Figure 1a.

Organic synthesis results²² provide a priori knowledge of the identity of the chiral brominated conformer in Figure 1a as (*R*)-2-Br-hexadecanoic acid, which in turn reveals the topographic orientation of the bromine atom (bright marker) to be pointing “up” away from the graphite substrate (Figure 2a). In the STM image of Figure 1a, the bromines are either above and to the left or below and to the right of the COOH group. The only two possible orientations for these brominated molecules are those shown by the models in Figure 2a (where a bromine directed “up” away from the surface is above and to the left of the carboxyl group, indicated by a straight arrow) and Figure 2b (where a bromine directed “down” into the surface is above and to the left of the carboxyl group, indicated by a straight arrow). If the bright marker in the STM topograph of Figure 1a were identified as a bromine atom directed “down” into the substrate (Figure 2b), this orientation would incorrectly yield classification of the brominated molecules in Figure 1a as (*S*)-2-Br-hexadecanoic acid. Therefore, the bright spot must indicate a bromine directed “up” away from the surface, as depicted in Figure 2a, to correctly identify the brominated molecules in Figure 1a as (*R*)-2-Br-hexadecanoic acid. A similar approach can be taken with the STM image of (*S*)-2-Br-hexadecanoic acid (Figure 1c) that necessarily dictates the bromine must again be oriented in the “up” position (Figure 2c) to correctly yield the identity of the brominated molecules in the STM topograph as (*S*)-2-Br-hexadecanoic acid. Because the configuration where the bromine protrudes up toward the tip yields high tunneling probability, the high tunneling current over this atom must be dominated by geometric factors.

The conformation of bromine in the “up” position pointing away from the substrate has been hypothesized as a relatively more stable energetic configuration.^{18,19,25} The self-assembly configuration with a bromine pointing “down” toward the surface tilts the rest of the molecule away from the substrate. This, in turn, reduces the attractive interactions between the surface and the hydrogen atoms in the adsorbed molecule along the whole length of 2-Br-hexadecanoic acid, resulting in an overall energetically unstable conformation on the surface. Eventually, such conformations of 2-Br-hexadecanoic acid with the bromine pointing “down” into the surface must result in the 2-bromohexadecanoic acid molecules desorbing back into solution in favor of molecules having the more stable “Br up” configuration. It is precisely for this reason that racemic 2-Br-hexadecanoic acid spontaneously segregates into chirally pure domains;¹⁸ in order for *R*-2-Br-hexadecanoic acid and *S*-2-Br-hexadecanoic acid to mix on the surface within one domain, the energetically unfavorable conformation of 2-Br-hexadecanoic acid with a Br pointing “down” would be necessary.

Conclusion

The self-assembly of a mixture of hexadecanoic acid with (*R*)-2-Br-hexadecanoic acid and (*S*)-2-Br-hexadecanoic acid at the liquid–solid interface has been investigated with STM. Topographic information has been directly extracted from the STM images. The bromine atom in 2-Br-hexadecanoic acid that

appears “bright” or with high tunneling probability in STM topographs has been unambiguously identified as being in the “up” configuration, directed away from the graphite surface. This geometric orientation is consistent with previous work suggesting that the “up” conformation is more energetically favorable.^{25,29} Further, the tunneling mechanism for these substituted hydrocarbons has been shown to be dominated by geometric factors as previously proposed.¹²

Acknowledgment. The authors would like to express their gratitude to Prof. Koji Nakanishi and Dr. Nina Berova for stimulating discussions, advice, and the use of their chiral synthesis facilities. This work was supported by grants from the National Science Foundation (CHE-97-27205), jointly by the National Science Foundation and the U.S. Department of Energy through a grant to the Environmental Molecular Sciences Institute at Columbia University (NSF CHE-98-10367), and in part by the Columbia Materials Research Science and Engineering Center (DMR-98-09687). D.K. acknowledges support from the Columbia College Rabi Scholars Program.

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