Identification of the Conformation of Individual Molecules by Scanning Tunneling Microscopy

Hongbin Fang, Leanna C. Giancarlo, and George W. Flynn*

Department of Chemistry and Columbia Radiation Laboratory, Columbia University, New York, New York 10027

Received: March 29, 1999; In Final Form: May 1, 1999

In the gas phase the carboxyl group of an *n*-carboxylic acid molecule may adopt a number of different conformations. Upon adsorption on a solid surface, however, the carboxyl group usually assumes one of two possible configurations. Atomically resolved STM images show that the conformations of the carboxyl groups in 12-bromododecanoic acid and 2-bromohexadecanoic acid molecules differ when adsorbed at the liquid (phenyloctane)−solid (graphite) interface.

Introduction

The conformation of molecules is of great importance in the determination of chemical and physical properties. In polymers, chain conformation determines the degree of crystallinity. For example, in poly(ethylene terephthalate) (PET), the conformation of the $O-CH_2-CH_2-O$ part of the chain has been determined by two-dimensional NMR in different states. Crystalline PET was found to have a trans content of 100%, while amorphous PET has a trans content of 14%.[1] For organic monolayers of alkyl chains adsorbed on a silicon wafer, the electron transfer efficiency drops dramatically when the conformation of some of the molecules is transformed from all trans to gauche.[2] Recently, growing interest in the field of molecular electronics has created demand for better control of the structure of two-dimensional molecular assemblies. Long-chain hydrocarbons, which represent a class of molecules that form ordered structures on different substrates,[3−5] can serve as a model system for studying the effect of molecular structure on packing order. Although the self-assembly of such molecules has been extensively studied on a number of surfaces, there is almost no detailed analysis of the conformation of the functional groups in such molecules.[6]

Direct analysis of the conformation of individual molecules presents a very challenging experimental problem. Scanning probe microscopies (SPMs), and in particular scanning tunneling microscopy (STM), have proven to be very powerful tools in the real-space imaging of molecules. In some cases, the information obtained from STM images can be used to deduce the conformation of individual molecules. For example, when Cu tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (Cu-TBPP) adsorbs onto different substrates, the σ bond between the phenyl group and the porphyrin ring rotates thereby producing different conformers. STM images of Cu-TBPP on these surfaces reveal four bright lobes (corresponding to the TBP groups) which appear with different aspect ratios depending on the conformation.[7] In the studies presented here, two-dimensional self-assembled structures formed at the liquid−solid interface by 12-bromododecanoic acid and 2-bromohexadecanoic acid have been imaged by STM. The atomically resolved images allow us to identify the conformations of individual molecules directly. The carboxylic functional group is found to adopt different conformations in these two molecules upon adsorption on the same graphite substrate.

Experimental Section

The molecules studied here (12-bromododecanoic acid and 2-bromohexadecanoic acid) were obtained from Aldrich and used without further purification. 80 mg of either compound 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. Typical tunneling parameters used for imaging these molecules were 1.2−1.4 V (sample negative) for the bias voltage and 200−400 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 were acquired at constant current and display the relative topographic height as the tip is raster scanned across the sample. In these images, “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

In the gas phase, the carboxyl group of long-chain *n*-carboxylic acid molecules may rotate about the C−C σ bond. Simple ab initio calculations show that the energy barriers for rotation of the carboxyl group are 1.47 kcal/mol for normal carboxylic acids and 2.34 kcal/mol for α-bromo carboxylic acids.[8] When these same molecules adsorb on the surface of a solid substrate, they usually assume an all-trans conformation with the carbon skeleton parallel to the surface. To hydrogen bond to the next molecule, the end carboxyl group can only adopt one of two conformations, schematically shown in Figure 1. In Figure 1a, the alkyl tail is eclipsed by the hydroxyl group, while in Figure 1b, the alkyl tail is eclipsed by the carbonyl group. In these two conformations, the hydroxyl group has a

10.1021/jp991075w CCC: $18.00

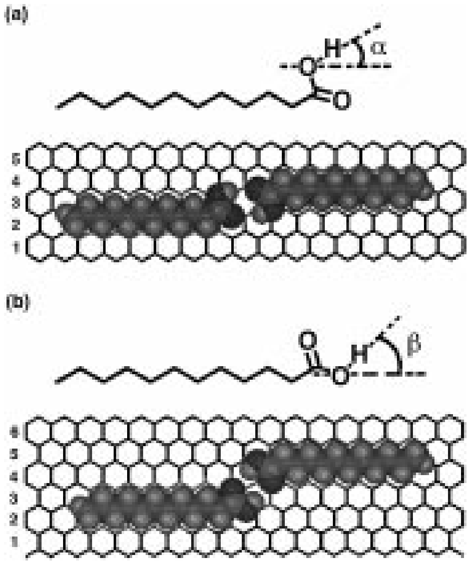

Figure 1. Schematic representation of the two conformations adopted by the −COOH group of *n*-carboxylic acids (*n*-dodecanoic acid is used as an example here) upon adsorption on a graphite surface. (a) The alkyl tail is eclipsed by the hydroxyl group. α is the angle between the hydroxyl group and the long molecular axis. Two *n*-dodecanoic acid molecules adopting this conformation are shown lying on top of a graphite lattice. (b) The alkyl tail is eclipsed by the carboxyl group. *β* is the angle between the hydroxyl group and the long molecular axis. Two *n*-dodecanoic acid molecules adopting this conformation are shown lying on top of a graphite lattice.

different orientation relative to the carbon skeleton. The angles between the hydroxyl group and the long molecular axis, defined as α and *β*, respectively in Figure 1a and b, are different for each of these two conformations. Assuming $\angle$CCC (the angle between carbons along the hydrocarbon backbone) equals 109.5°, $\angle\mathrm{CCO} = \angle\mathrm{OCO} = 120°$ and $\angle\mathrm{COH} = 109.5°$, α is calculated to be 24.75° and *β* to be 45.75°. When the next molecule lies down and forms a hydrogen bond with these two different conformers, each must come from a different angle to optimize interactions. Indeed, upon adsorption on the graphite surface, if the molecules assume the conformation shown in Figure 1a, neighboring molecules must offset in a direction perpendicular to its long molecular axis by half a molecular width. As can be seen in Figure 1a, the left molecule is aligned on top of the second and third rows of the graphite lattice, while the right one covers the third and fourth rows. If the molecules assume the conformation shown in Figure 1b, the neighboring molecules offset by a whole molecular width in order to satisfy hydrogen-bonding requirements. As can be seen in Figure 1b, if the left molecule takes the second and third rows of the graphite lattice, the right one must overlap the fourth and fifth rows.

When 12-bromododecanoic acid, $\mathrm{Br(CH_2)_{11}COOH}$, adsorbs on a graphite surface from phenyloctane solution, it forms the structure shown in the STM image of Figure 2a. A computer-generated molecular model of this structure is shown in Figure 2b for comparison. As has been shown in a previous study,[9] each individual parallelogram drawn on the image corresponds to one molecule lying flat on the graphite surface. Each molecule in Figure 2a is composed of three parts: a large bright head at one end, a dark trough at the other end, and a few little protrusions in between. The large bright spot is attributed to the location of the bromine atom along the chain, and the carboxyl group resides at the dark trough. The atomic resolution obtained in this image allows us to see the individual hydrogen atoms on the 11 methylene carbons (small protrusions in the image). In addition, each −COOH group is always next to another −COOH group forming a hydrogen bond. The angle between the direction of the hydrogen bond and the long molecular axis (labeled as $\alpha = \angle\mathrm{AOB}$ in the image, with the line OA running along the long molecular axis and the line OB running along the short edge of the dark trough formed by the carboxyl groups) is measured to be 25° ± 4°, which corresponds very well to $\alpha = 24.75°$ in Figure 1a. Also, the two molecules (marked by the two parallelograms in Figure 2a) connected by a hydrogen bond are offset by half a molecular width. In Figure 2b, the corresponding two molecules are also marked by two parallelograms. Comparison between the STM image shown in Figure 1a and the model shown in Figure 1b confirms the above observations.

When (*R*)/(*S*)-2-bromohexadecanoic acid, $\mathrm{CH_3(CH_2)_{13}CHBrCOOH}$, adsorbs on a graphite surface from phenyloctane solution, different domains are formed on the surface. These domains appear to be composed of single enantiomers.[10] Figure 2c is an STM image taken from one of the domains. A computer-generated molecular model is shown in Figure 2d for comparison. All the molecules in this figure correspond to R conformers.[10] Each parallelogram in the image marks one molecule lying flat on the surface adopting an all-trans conformation. The dark segment is ascribed to the position where two −COOH groups of neighboring molecules meet and hydrogen bond to each other. The large bright spot next to this dark segment marks the location of the bromine atom. The angle *β* formed by the line OD (which marks the orientation of the dark segment, and can be considered roughly as the direction of the hydrogen bond), and the line OC (which marks the long molecular axis) is measured to be 53° ± 5°, close to the value $\beta = 45.75°$ of Figure 1b. As can be seen with the help of the two parallelograms in Figure 2, c and d, the two molecules attached by the hydrogen bond are offset by a whole molecular width.

The key point of the above observation is that the same functional group may adopt different conformations (rotated by 180°) in different molecules when adsorbed on a graphite surface in order to optimize adsorbate−adsorbate and adsorbate−substrate interactions. When such long-chain hydrocarbon molecules lie down on a graphite surface, they are always close packed, maximizing these interactions. There are a few specific interactions which appear to dominate in the packing of 12-bromododecanoic acid and 2-bromohexadecanoic acid molecules on the graphite surface. In a series of studies of bromine-substituted long-chain hydrocarbon molecules adsorbed on graphite, bromine atoms have been found to lie near other bromine atoms on an adjacent molecule, forming a pair that shows up in the STM image as a bright twin structure.[9−11] The origin of this strong attraction is currently under theoretical investigation. Hydrogen bonding constitutes another strong interaction between molecules with a bond energy on the order of 10 kcal/mol. When there is a −COOH group in an adsorbed molecule, the tendency to hydrogen bond to another molecule through this same group is a dominant force in determining adsorbate structure on the surface. The other strong force is adsorbate−substrate attraction. Previous studies have shown that, upon adsorption, *n*-alkane molecules are packed commensurate with a graphite lattice. The spacing between the hydrogen atoms on every other carbon (2.51 Å) matches the graphite lattice spacing (2.46 Å) very well, optimizing the interaction between the adsorbed hydrocarbon molecules and the graphite substrate. Experiments and calculations have shown that the heat of adsorption for *n*-alkanes on graphite is about 1.6−1.7 kcal/mol

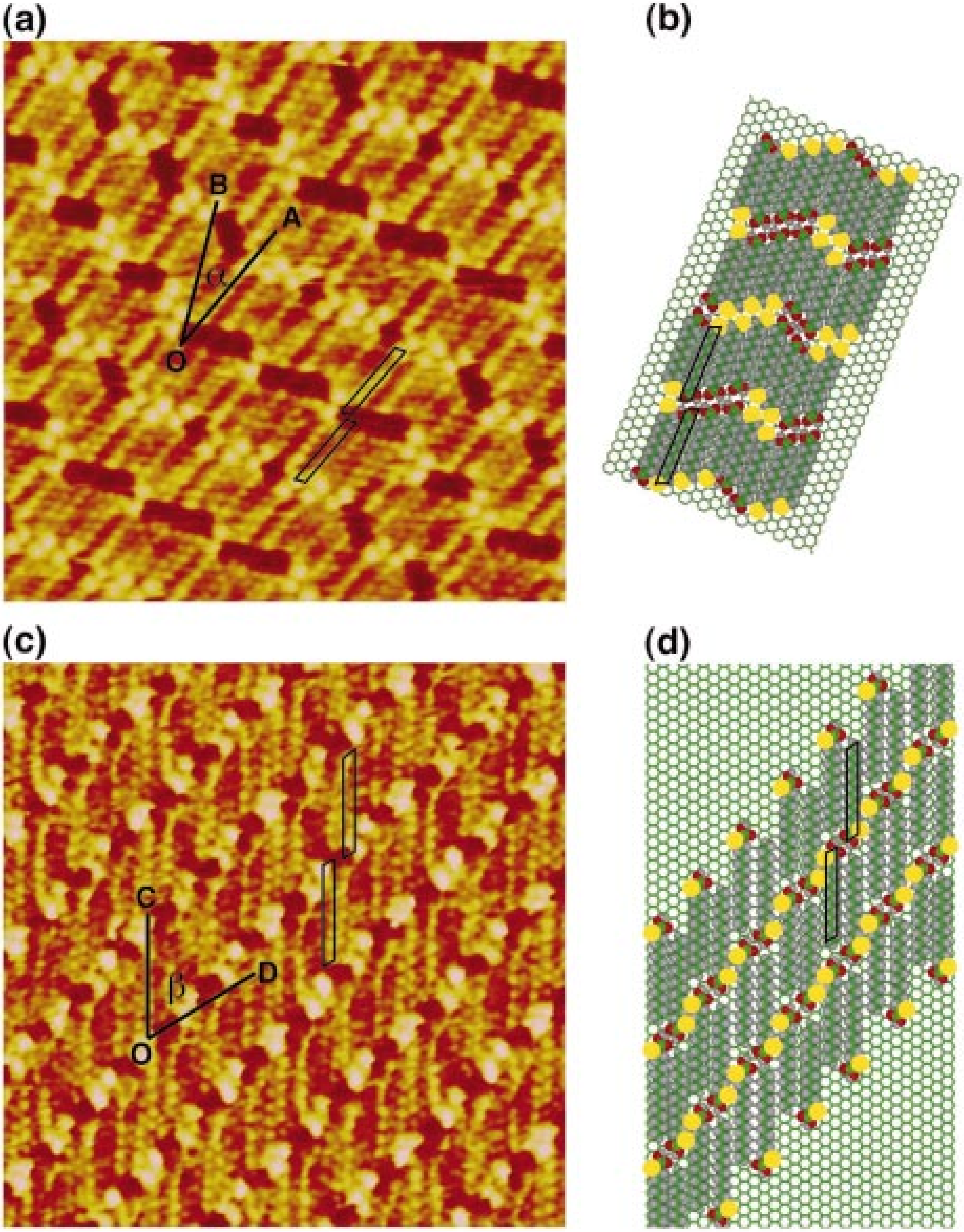

Figure 2. (a) A 12 × 12 nm^2 STM constant current image of 12-bromododecanoic acid at the interface of a phenyloctane solution and the basal plane of graphite. Two parallelograms outline two molecules hydrogen bonded through their carboxyl group, which are offset by half a molecular width. The angle $\alpha = \angle$AOB is that between the direction of the hydrogen bond (OB) and the long molecular axis (OA). (b) 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 two parallelograms indicate two molecules hydrogen bonded through their $-$COOH groups. (c) A 12 × 12 nm^2 STM constant current image of (*R*)-2-bromohexadecanoic acid at the interface of a phenyloctane solution and the basal plane of graphite. Two parallelograms outline two molecules hydrogen bonded through their $-$COOH groups, which are offset by a whole molecular width. The angle $\beta = \angle$COD is that between the direction of the hydrogen bond (OD) and the long molecular axis (OC). (d) Top view of a computer-generated model of an (*R*)-2-bromohexadecanoic acid film on a graphite substrate. The colors have the same meaning as those in (b).

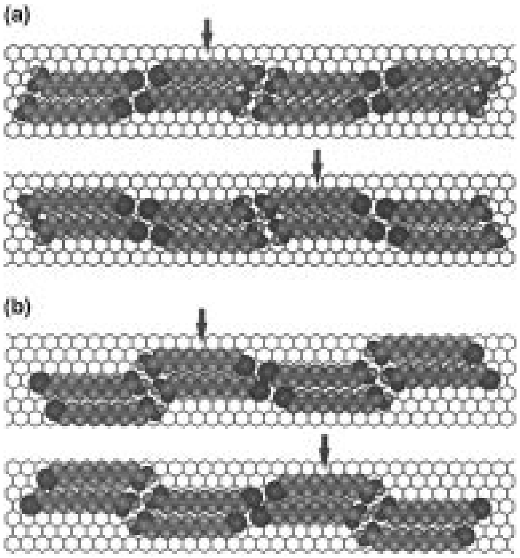

Figure 3. (a) Schematic representation of molecular structures on a graphite surface if 12-bromododecanoic acid molecules assume the conformation shown in Figure 1a. In this case a "symmetric" structure is formed, in which molecules on both sides of those marked by the arrow are offset by half a molecular width. When the molecular structures shown in the upper and lower panels are brought together, a close-packed structure is formed. (b) Schematic representation of molecular structures on a graphite surface if 12-bromododecanoic acid molecules assume the conformation shown in Figure 1b. In this case an "asymmetric" structure is formed, in which molecules on one side are offset by half a molecular width, while those on the other side are offset by a whole molecular width. When the molecular structures shown in the upper and lower panels are brought together, some energetically unfavorable vacancies will be formed on the surface.

per methylene unit.[12,13] Molecules adsorbing onto a graphite surface sample all different packing structures and assume the configuration that minimizes free energy.

Apparently, when the −COOH group of 12-bromododecanoic acid molecules adopts the conformation shown in Figure 1a, the energetically favorable close-packed structure shown in the STM image of Figure 2a is formed, satisfying all the interactions mentioned above without leaving energetically unfavorable voids in the monolayer film. This structure is also schematically depicted in Figure 3a. In the upper panel, the molecules on both sides of those marked by the arrow are offset perpendicular to the molecular axis by half a molecular width (one row on the graphite lattice). In the lower panel, which depicts the structure adopted when a pair of molecules having the conformation shown in Figure 1a shifts to the right of the upper one,[9] molecules on both sides of those marked by the arrow are offset by half a molecular width as well. When these two "symmetric" structures are brought together as observed in the STM image shown in Figure 2a, they form a close-packed structure represented by the molecular model of Figure 2b. Essentially, the structures in the upper and lower panels of Figure 3a fit together like pieces of a puzzle with no voids, because the offset in both cases corresponds to just one row on the graphite lattice.

If the carboxyl group were to assume the other conformation (shown in Figure 1b) rotated by 180°, as depicted in Figure 3b, an asymmetric structure is formed on the graphite surface. Essentially, the structures in the upper and lower panels of Figure 3b, when joined together like pieces in a puzzle, leave an energetically unfavorable void on the graphite lattice.

Figure 4. Schematic representation of molecular structures on a graphite surface if (*R*)-2-bromohexadecanoic acid molecules assume the conformation shown in Figure 1a. An energetically unfavorable vacancy is formed on the surface between the top and bottom molecules.

For 2-bromohexadecanoic acid, if the −COOH group assumes the conformation shown in Figure 1b, molecules form the energetically favorable close-packed structure shown in the STM image of Figure 2c. Simple ab initio calculations also suggest that in the gas phase this configuration is favored over that of Figure 1a by about 1.6 kcal/mol.[8] If the −COOH group were to assume the conformation of Figure 1a, some energetically unfavorable vacancies would also be formed on the surface corresponding to one empty row on the graphite lattice between the top and bottom molecules shown in Figure 4. Thus, the dominance of a given −COOH group conformation observed by STM is the result of a complex interplay among different adsorbate−adsorbate and adsorbate−substrate interactions.

Summary

We believe this study marks the first time that the same functional group, namely the −COOH group, has been directly observed by STM to adopt different conformations in different molecules when adsorbed onto the same substrate. Here, 12-bromododecanoic acid molecules self-assemble on graphite such that the molecule adopts a 25° angle between the direction of the hydrogen bond and the hydrocarbon backbone. In contrast, 2-bromohexadecanoic acid molecules orient with a 53° angle between the hydrogen bond direction and the long molecular axis when physisorbed on the same graphite substrate.

Acknowledgment. Support by the National Science Foundation (DMR-94-24296 and CHE-97-27205) and by the Joint Services Electronics Program (U.S. Army, Navy, and Air Force; DAAG55-97-1-0166) is gratefully acknowledged.

References and Notes

(1) Schmidt-Rohr, K.; Hu, W.; Zumbulyadis, N. *Science* **1998**, *280*, 714.

(2) Haran, A.; Waldeck, D. H.; Naaman, R.; Moons, E.; Cahen, D. *Science* **1994**, *263*, 948.

(3) Frommer, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1298.

(4) Cyr, D. M.; Venkataraman, B.; Flynn, G. W. *Chem. Mater.* **1996**, *8*, 1600.

(5) Giancarlo, L. C.; Flynn, G. W. *Annu. Rev. Phys. Chem.* **1998**, *49*, 297.

(6) Rabe, J. P.; Buchholz, S.; Askadskaya, L. *Synth. Met.* **1993**, *54*, 339.

(7) Jung, T. A.; Schlittler, R. R.; Gimzewski, J. K. *Nature* **1997**, *386*, 696.

(8) The calculations are carried out using Spartan program on n-hexanoic acid and 2-bromohexanoic acid.

(9) Fang, H.; Giancarlo, L. C.; Flynn, G. W. *J. Phys. Chem. B* **1998**, *102*, 7421.

(10) Fang, H.; Giancarlo, L. C.; Flynn, G. W. *J. Phys. Chem. B* **1998**, *102*, 7311.

(11) Cyr, D. M.; Venkataraman, B.; Flynn, G. W.; Black, A.; Whitesides, G. M. *J. Phys. Chem.* **1996**, *100*, 13747.

(12) Groszek, A. J. *Nature* **1964**, *204*, 680.

(13) Hentschke, R.; Schürmann, B. L.; Rabe, J. P. *J. Chem. Phys.* **1992**, *96*, 6213.