

Influence of lauric Acid on the Adsorption of 12-Bromododecanoic Acid at the Liquid Solid Interface as Studied by STM

A. Cavanagh
Fort Lewis College, Durango, CO

K. Kannappan and G. Flynn
Columbia University, New York, NY

ABSTRACT

Physisorbed self assembled monolayers (SAM) of binary mixtures of dodecanoic and 12-bromododecanoic acids in phenyloctane have been studied via scanning tunneling microscopy (STM). Sub-molecular resolution STM images revealed significant differences in the packing structure and efficiency for the individual molecules. Atomic scale images of the mixtures with various mole ratios were obtained. Packing patterns and ratios of physisorption have been quantitatively measured for the various ratios of the co-solutes in solution.

Introduction

As traditional manufacturing techniques strive for ever smaller circuitry a ceiling is approached by what is capable within the realm of lithography. In order to follow Moore's law and continue the current trends in consumer electronics it is necessary to develop a novel means by which to surpass the current boundaries set forth by the limits of lithographic techniques. Self assembly use thermodynamics to stabilize a system in its lowest energy state. If these self assembled states can be applied to the technological problems set forth by the limits of lithography then this is perhaps the solution to the next generation of technology. In order to harness self assembly as a tool it is first necessary to develop an understanding of the fundamental intermolecular and surface adsorbate interactions. By examining self assembled surface structures with scanning tunneling microscopy (STM) images it is possible to observe the subtle effects caused by molecular differences.

Molecular electrons are bound within the wave functions of the molecules that encapsulates it. According to classical mechanics these electrons should not be able to escape because they do not have the energy necessary to overcome the potential barrier maintained by the molecule. In quantum mechanics however a small amount of the

electrons will ignore this barrier and tunnel from molecule. It is this quantum phenomenon upon which STM is based. When the metallic tip of the STM is brought within 10 angstroms of the surface there is enough of an overlap between the wave functions of both the molecule and the tip to allow tunneling. By applying a potential across the tunnel gap (tip to sample) it is possible to increase this tunneling phenomena into a quantifiable current. By scanning the tip over the x,y direction of the surface it is possible to measure this current at localized points, compiling that data provides the STM topograph.

Molecules were dissolved in a non-conducting solvent as not to induce faradic current. The solution was placed on a clean graphite surface. The lattice spacing in graphite is commensurate with the carbon-carbon spacing in the hydrocarbon tail of the molecule of interest. The distance, through space, between carbons bonded to a common carbon is 0.251 nm, an equivalent distance on the graphite lattice is 0.246 nm. This lattice match enhances the stability of the monolayer. Since all of the experiments are occurring at the liquid/solid (solvent/graphite) interface the adsorption of molecules is at equilibrium. By having a strong interaction between the molecule and the surface the equilibrium will lie on toward the adsorbed molecules. This stability is necessary to allow an atomically sharp, but nonetheless macroscopic, tip to scan the surface. In theory a single atom is at the point of the STM tip, it is between this tip and the adsorbed molecule that the tunneling or flow of electrons will occur.

Previous studies of monolayers at the liquid solid interface have shown that the effects of chirality¹, chain length² and functional groups³ have large effects on the packing and stability of monolayer formation. In the study by Yablon et al.¹ of mixtures of hexadecanoic acid and 2-bromohexadecanoic acid it was observed that hexadecanoic acid preferential adsorbed to the surface. This is of particular interest because hexadecanoic acid and 2-bromohexadecanoic acid form similar packing geometries as adsorbed monolayers. This is not the case in this study, lauric and 12-bromodecanoic acids have been characterized in previous works^{1,4} and show distinctly different packing structures.

Direct interpretation of weakly adsorbed molecules characterized by STM remains a challenge. The tunneling mechanism for interactions between the tip, sample,

molecule and solvent are understood but extremely complex. First impressions of STM images show correlations with molecular structure, bond angles, lengths *et cetera*. Closer examination reveals subtleties that do not agree. A carboxylic dimer exhibits a characteristic dark spot where the two head groups interact through hydrogen bonding, this dark spot is related to height through the attached scale. At first glance this might seemingly state that the acid groups are not as far above the surface as the attached hydrocarbon tail, the reason for this is that the STM topographs are not in fact true topographs. To obtain a height image the tip move up and down as it raster scans the surface, the up and down motion is employed to maintain a constant tunneling current/probability. In the case of the carboxylic dimers it is not that dimer is somehow lower than the hydrocarbon tail, it is simply that the tip must move down lower to maintain the same tunneling current. In that regard this inquiry will focus not on the absolute meaning of the STM images, but on the details that may be observed about molecular packing and the ratios of brominated to non-brominated acids on the surface.

Experiment

Lauric and 12-bromododecanoic acids were obtained from the Aldrich Corporation and were used without further purification. Phenylloctane (Aldrich) solutions of the compounds were made for both pure molecule solutions as well as a variety of moles ratios. Solutions were allowed to equilibrate for at least 24 hours prior to scanning. ZYB grade highly ordered pyrolytic graphite (HOPG) (Advanced Ceramics) was freshly cleaved prior to the application of the 10 μ l aliquot. Tips were mechanically cut from 0.25 mm platinum/rhodium (87/13) wire (Omega Engineering). Tips were manually immersed into the droplet of solution until adhesion was observed between the solution and the tip. The final approach was completed by the STM computer controls. Images were obtained on a Digital Instruments Nanoscope III scanning tunneling microscope (STM) under ambient conditions. Room temperature was maintained between 56 $^{\circ}$ -59 $^{\circ}$ F, humidity was observed between 40%-60%.

Images were obtained in one of two scanning scenarios. In constant height mode the piezo tube was maintained at a constant voltage in the z direction and as such a constant height The tunneling current was measured as tip raster scanned in x and y plain

of the sample. The image produced is a topographic display of the tunneling current/probability, where light spots represent high tunneling current and dark spots represent low tunneling current. In constant current mode the height (z) of the tip was maintained with an electronic feedback loop to ensure a constant tunneling current. Height data was extrapolated from the potentials across the z direction of the piezo tube. The topographic image was a display of the height off the surface required to maintain a user defined tunneling current. A dark spots represents depression where the tip height was reduced to maintain current and light spots represent regions where the tip height was increased to maintain current. The majority of the images in this study were collected in constant height mode. Representative images were collected with a bias of 1-1.5 volts, sample negative. The typical setpoint for the tunneling current was 250-400 pA. All images underwent zero order flattening process.

Molecular models were made using software from Advanced Chemical Development Inc.

Results

Lauric Acid

Sub-molecular resolution images as well as low resolution images of large regions were obtained of lauric acid monolayers physisorbed at the liquid (phenyloctane) solid (HOPG) interface (SEE FIGURES 1&2). In both of these images it is possible to observe the long organized stripe pattern (lamellae) characteristic of the monolayer. Though occasional boundary regions were observed the lamellae formed extensive domains. The width of the lamellae on low resolution images (1.7 nm) corresponded to the molecular chain length on high resolution images (1.7 nm), these concur with the expected value for the chain length (~1.5 nm). In these images, collected in constant current mode, the dark spots represent the position of two carboxylic acid heads forming a dimer through hydrogen bonding. The wider/ lighter regions adjacent to these carboxylic dimers are the hydrocarbon tails on which it is possible to observe individual hydrogens. It was observed that the packing pattern for lauric acid was simply rows of molecules packed head to tail with dimerization occurring with adjacent rows offset by one molecule. While this molecule does not exhibit three dimensional stereo chemistry it does exhibit two

dimensional stereo chemistry, meaning that it is different than its mirror image when both molecules are fixed in a plane. Molecular models aided in determining what handedness the molecule assumed on the surface. It was apparent that for any domain all molecules assumed one of the two possible handednesses.

12-Bromododecanoic acid

Images were obtained of 12-bromododecanoic acid physisorbed at the liquid/solid interface. Unlike the lauric acid monolayers which were readily imaged 12-bromododecanoic acid required a far more extensive study to obtain even a low resolution image (SEE FIGURE 3). Molecular lengths of approximately 1.6 nm were observed and concur with the expected value of ~ 1.5 nm. In this image, collected in height mode, the carboxylic groups are represented by dark regions (low tunneling current for a given height) while the bromines are represented by light regions (high tunneling current). In between these two marker groups the individual hydrogens of the hydrocarbon can be discerned. Acid pairs joined via hydrogen bonding at the carboxylic head were observed in a step like packing structure. Molecules were packed head to head in groups of two and three. Alternating back and forth between these two groups in a parallel/ antiparallel fashion the molecules packed in the following manner per column. Three molecules oriented in the same direction with respect to heads/tails, two molecules packed in the opposite direction, repeat. The adjacent columns packed tail to tail and head to head with this procession. Whereas in the non-brominated acid it was possible to distinguish individual carboxylic dimer pairs due to their separation by alternating chains it was not feasible in the case of the 12-bromo compound. This was due to the fact that the carboxylic dimers in the 12-bromododecanoic acid were adjacent to one another and therefore overlapped. Though these molecules are strikingly similar in structure, local packing as observed by STM showed extreme differences. The addition of a bromine atom to carbon twelve alters the monolayer formation, stability and packing. As with lauric acid this molecule exhibits two dimensional stereo chemistry. The integral difference is that the observed domains consisted of an orderly mixture of both handedness.

Mixtures

Images of a 95/5 mole ratio, lauric and 12-bromododecanoic respectively, have been collected (SEE FIGURE 4). In this mixture the lamellae formed in a similar fashion to the lamellae of pure lauric acid. This similarity is best characterized by the straight line type lamellae that are nearly perpendicular to the molecular axis. Preliminary studies of 95/5 mole ratio solution are elluding to a 90/10 surface ratio. This result requires further study as it is not what is to be expected. The initials studies of 12-bromodecanoic acid showed less surface stability as such there should be of the bromo compound on the surface. In other words the lauric acid should dominate the monolayer.

Myristic acid

Initially this study sought to make the same comparisons on a pair of 14 carbon acids as opposed to the aforementioned 12 carbon acids. As such great deal of instrument time was devoted to the collecting of STM images of myristic acid. This acid as with other even chain length acids, such acid lauric, forms highly ordered straight lamellae that are nearly perpendicular to the molecular axis (FIGURES 5,6&7)

Conclusion

It has been possible to examine 12-bromododecanoic acid and lauric acid as individual molecules in solution and as mixture of varying mole ratios via STM. It has be found that both molecules however structurally similar have different packing structures a liquid solid interface of an adsorbed monolayer. While it has not been fully studied it has been observed that low mole fractions of the bromo acid allow the monolayer to pack in the manner defined by the pure lauric acid. Studies are underway to resolve the issue of solution mole ratio versus surface mole ratio.

Acknowledgements

This work was supported by grants from the National Science Foundation in support of the Research Experience for Undergraduates program, jointly with funding

from the U.S. Department of Energy to Columbia University's Environmental Molecular Science Institute. The author would like to acknowledge Thomas Mueller and Ryan Pearman for their time and insight.

Reference and Notes

¹ Yablon, D.; Giancarlo, L.; Flynn, G. *J. Phys. Chem. B* **2000**, 104, 7627-7635.

² Yablon, D.; Wintgens, D.; Flynn, G. *J. Phys. Chem. B* **2002**, 106, 5470-5475.

³ Giancarlo, L.; Flynn, G. *Annu. Rev. Phys. Chem.* **1998**, 49, 297-336.

⁴ Fang, H.; Giancarlo, L.; Flynn, G. *J. Phys. Chem. B* **1998**, 102, 7421-7424.

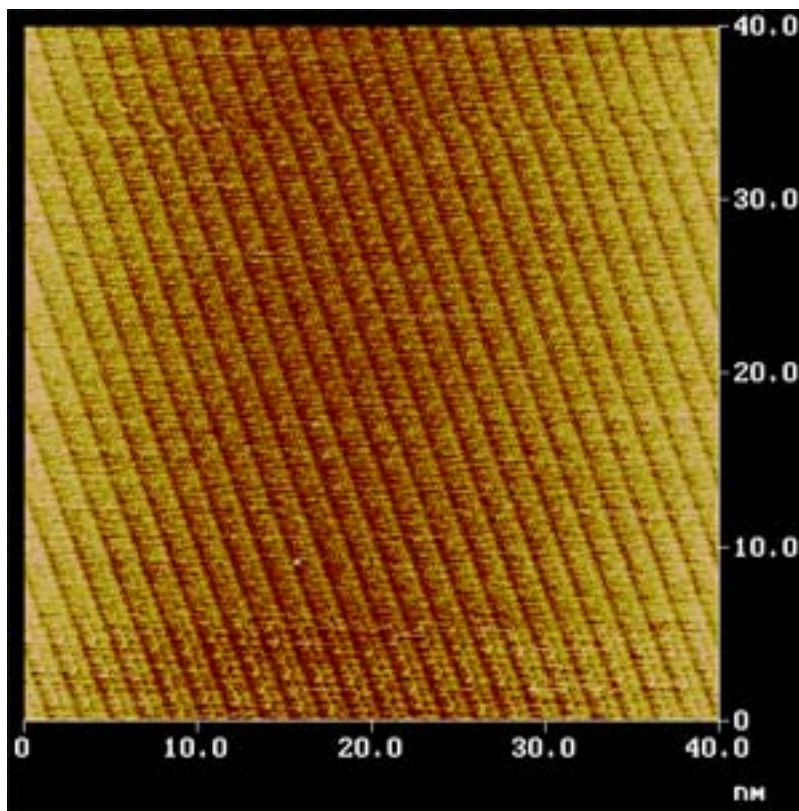


FIGURE #1: 40nm x 40nm dodecanoic acid. This image was collected in constant current mode. The thin dark lines represent rows of carboxylic dimer. The set point was 300 pA and the bias was 1.35 volts (sample negative).

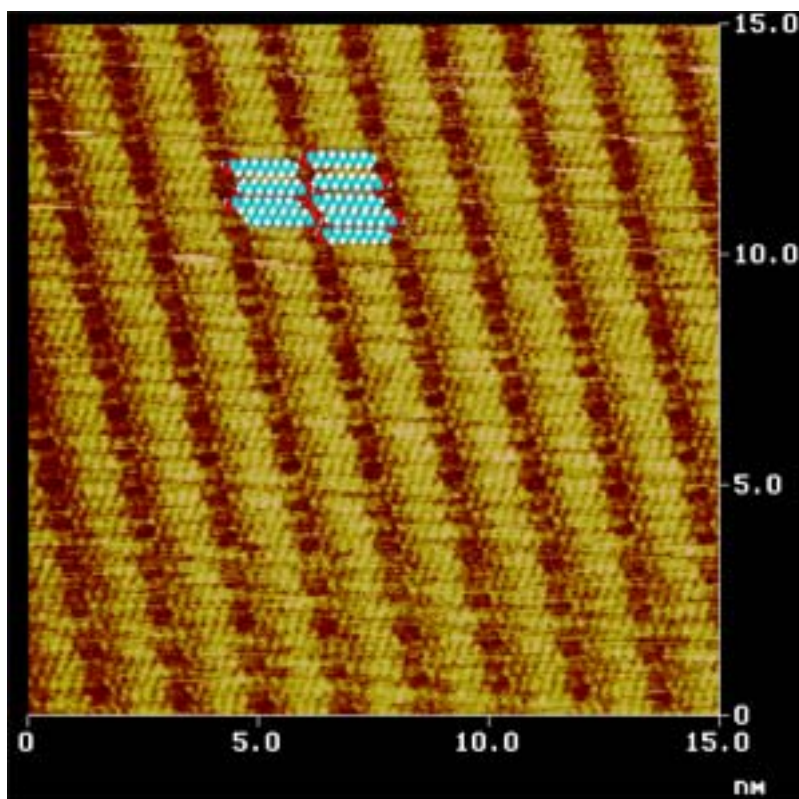


FIGURE #2: 15nm x 15nm dodecanoic acid. This image was collected in constant current mode. The dark lines represent rows of carboxylic dimer. In this image is possible to resolve bumps on the hydrocarbon chains (in between the dark line), these are individual hydrogens. Molecular models have been added to aid in the interpretation of molecular orientation. The set point was 300 pA and the bias was 1.35 volts (sample negative).

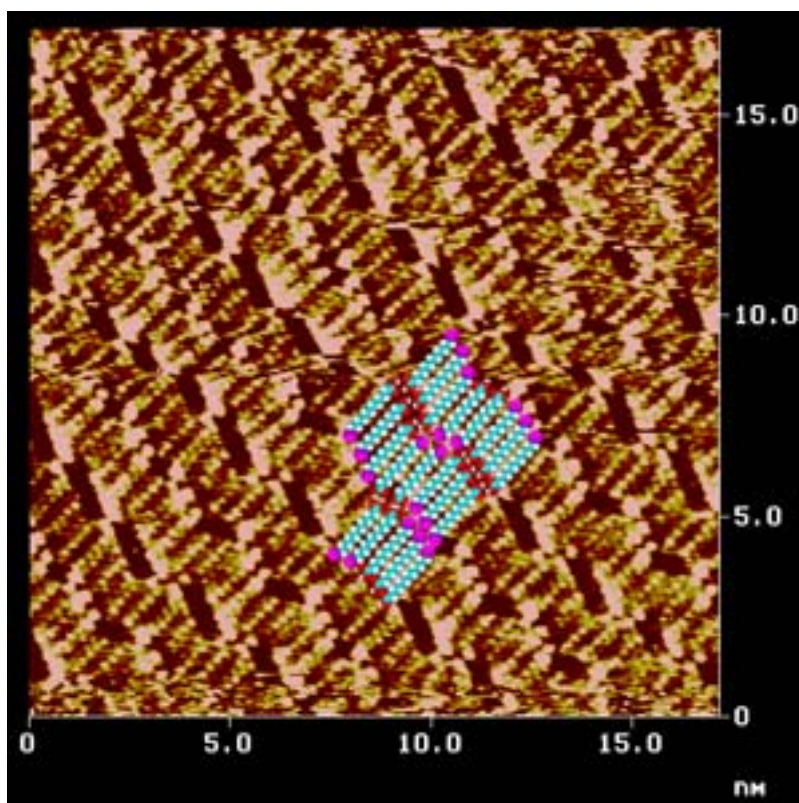


FIGURE #3: ~17nm x 17nm 12-bromododecanoic acid. This image was collected in constant height mode. The dark parallelograms represent a region where three carboxylic dimers overlap. The pink spots are the bromine atoms on carbon #12. Molecular models have been added to aid in the interpretation of molecular orientation. The set point was 300 pA and the bias was 1.4 volts (sample negative).

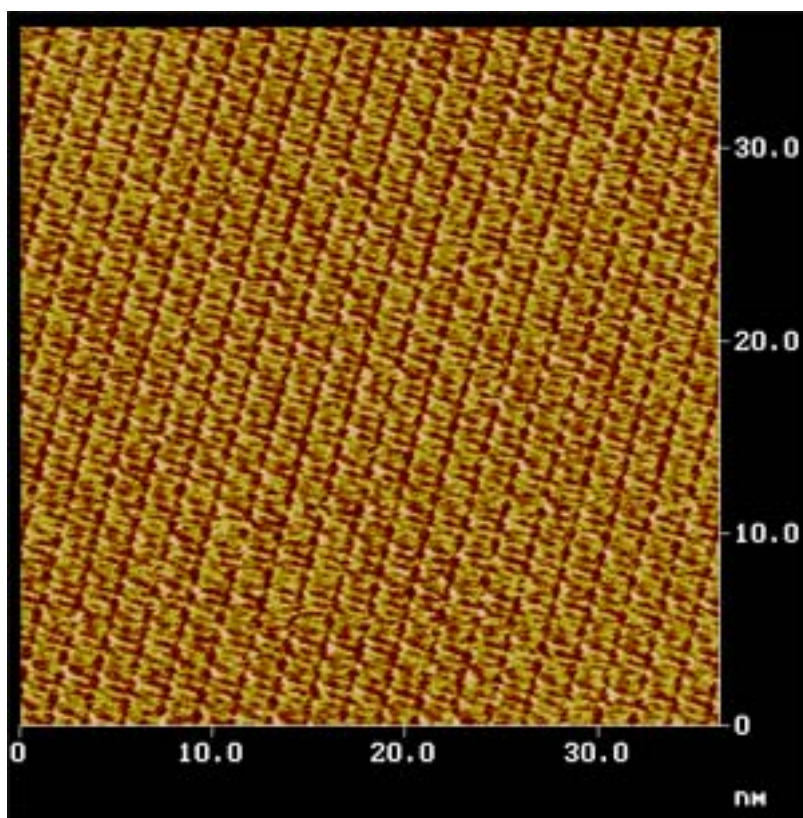


FIGURE #4: ~35nm x 35nm 95% dodecanoic acid & 5% 12-bromododecanoic acid. This image was collected in constant height mode. The dark spots represent carboxylic dimers. The pink spots are the bromine atoms on carbon #12. The set point was 300 pA and the bias was 1.4 volts (sample negative).

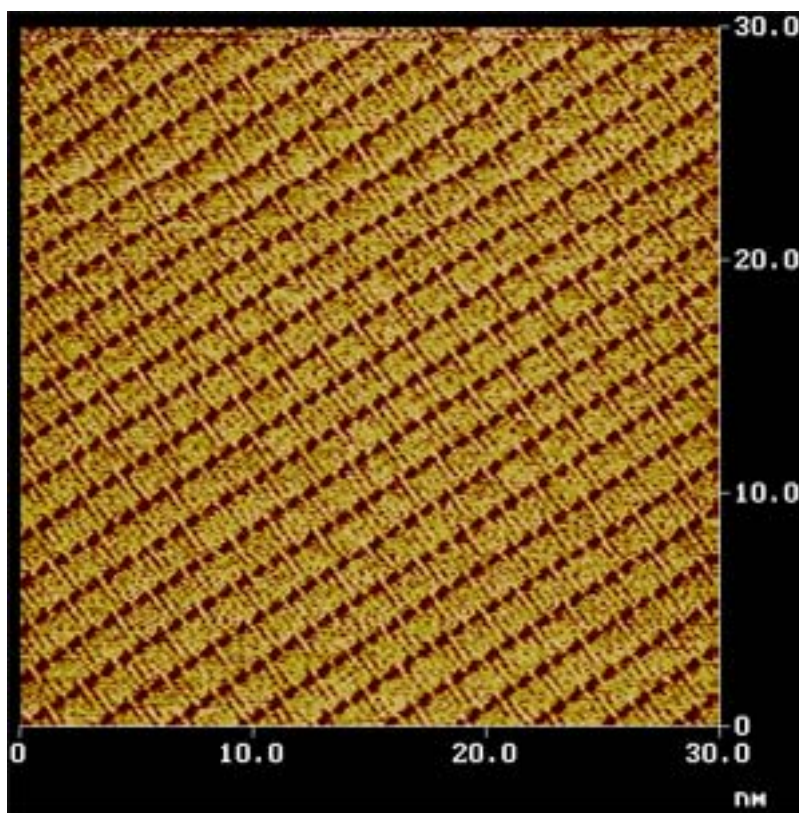


FIGURE #5: 30nm x 30nm myristic acid. This image was collected in constant current mode. The thin dark lines represent rows of carboxylic dimer. While it may be difficult to view individual hydrogen atom in this image it is clearly possible to observe individual hydrocarbon chains stemming from the carboxylic acid dimers. The set point was 300 pA and the bias was 1.5 volts (sample negative).

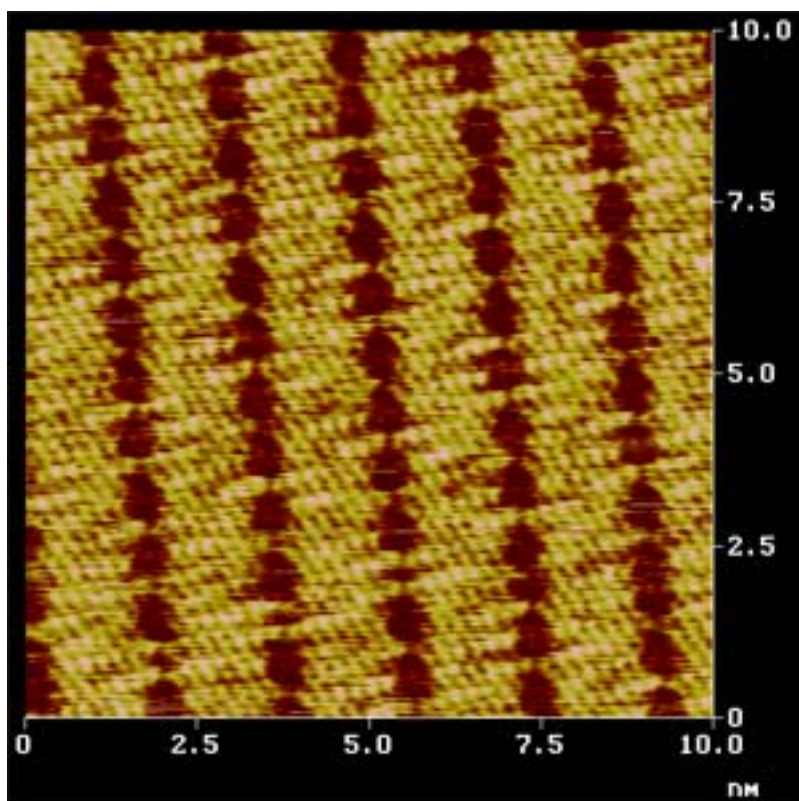


FIGURE #6: 10nm x 10nm myristic acid. This image was collected in constant current mode. The large dark spots represent carboxylic dimers. Individual hydrogen atoms are clearly visible in this image. The set point was 300 pA and the bias was 1.35 volts (sample negative).

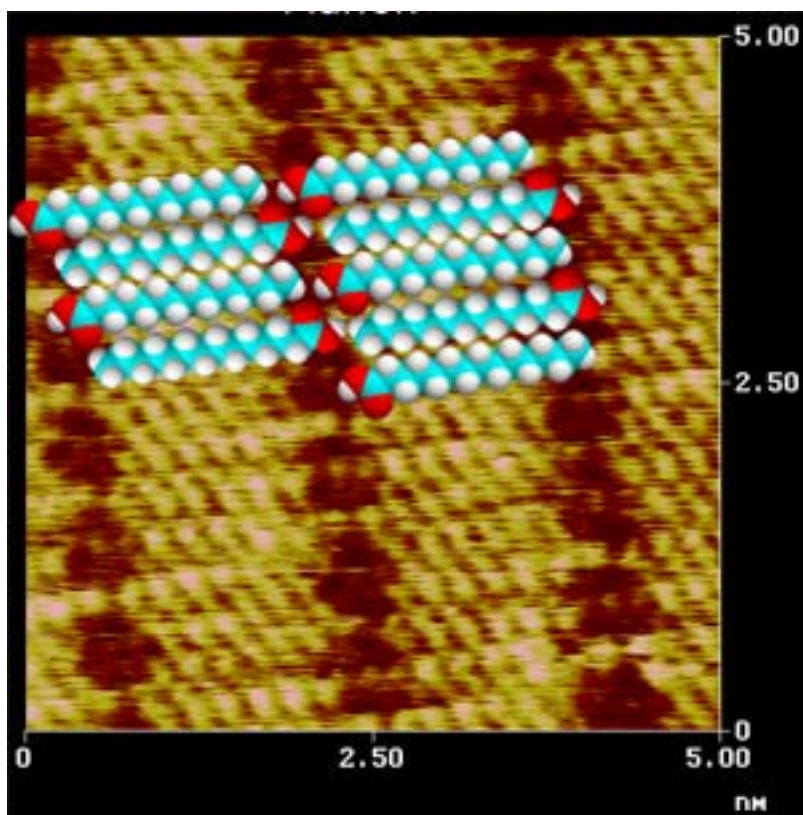


FIGURE #7: 10nm x 10nm myristic acid. This image was collected in constant current mode. The large dark spots represent carboxylic dimers. Individual hydrogen atoms are clearly visible in this image. Molecular models have been added to aid in the interpretation of molecular orientation. The set point was 300 pA and the bias was 1.35 volts (sample negative).