

## Structures Formed by the Chiral Assembly of Racemic Mixtures of Enantiomers: Iodination Products of Elaidic and Oleic Acids

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The self-assembled monolayer structure of the products of elaidic acid iodination (the racemic mixture of 9,10-(9*S*,10*R*)-diiodooctadecanoic acid and 9,10-(9*R*,10*S*)-diiodooctadecanoic acid) and the products of oleic acid iodination (the racemic mixture of 9,10-(9*R*,10*R*)-diiodooctadecanoic acid and 9,10-(9*S*,10*S*)-diiodooctadecanoic acid) are studied by high-resolution scanning tunneling microscopy. For the iodination products of elaidic acid, the separation of enantiomers into distinct chiral domains during the formation of the 2-D crystal on the highly ordered pyrolytic graphite (HOPG) surface is not observed. Instead, within the diiodooctadecanoic acid SAM, each row of molecules is composed of opposite racemates. The two opposite racemates pack alternately inside a row, using different faces to adsorb on the surface. The unit cell is composed of a pair of opposite racemates, forming a heterochiral structure. For the iodination products of oleic acid, the racemic mixture is observed to exhibit quasi-phase separation during the formation of the 2-D crystal on the HOPG surface. Each row is composed of homochiral acid molecules, either the 9,10-(9*R*,10*R*)-diiodooctadecanoic acid (*R*) or the 9,10-(9*S*,10*S*)-diiodooctadecanoic acid (*S*). The *R* row and the *S* row pack alternately, with a unit cell composed of four molecules. Two of the molecules in the unit cell are the 9,10-(9*R*,10*R*)-diiodooctadecanoic acid (*R*) molecules; two are the 9,10-(9*S*,10*S*)-diiodooctadecanoic acid (*S*) molecules. In the unit cell, the two molecules that have the same chirality pack antiparallel inside the homochiral row, using different faces to adsorb on the surface. These results suggest that several different types of chiral assembly are possible. Enantiomers with opposite chirality exhibit many chiral assembly patterns, forming heterochiral structures on the surface in addition to separation to form macroscopic chiral domains. By using different conformations, similar enantiomers with opposite chirality will display many chiral assembly patterns to form heterochiral structures on the surface.

### I. Introduction

Chirality is an important phenomenon in nature because of its role in biosystems, optically active materials, and numerous applications in catalysis. Pasteur's studies of chiral structures and the separation of sodium ammonium tartrate crystals marked the beginning of stereochemistry<sup>1</sup> and the study of 3-D chirality. Although chirality is extensively studied in the 3-D world, studies of chirality are more limited in the 2-D world of surfaces. History suggests that studies of chiral structures and separation behaviors on the surface are key steps to the understanding of 2-D chiral phenomena.

Depositing a racemic mixture of chiral molecules on the surface is a way of forming a 2-D chiral structure and is a good subject for studies of chiral resolution.<sup>2–16</sup> Unlike enantio-pure crystals in 3 dimensions, 2-D chiral structures usually have sizes in the nanometer range, which makes diffraction methods unsuitable for determining their structures. Because the scanning tunneling microscope (STM) is an ideal tool to characterize nanometer-scale surface features at atomic resolution, the application of STM to the study of 2-D chiral phenomena has drawn considerable interest.<sup>9–16</sup>

Previous scanning tunneling microscopy studies of racemic mixtures of enantiomers on the HOPG surface have shown that some mixtures spontaneously separate into symmetric domains.<sup>2,3</sup> With the submolecular resolution of the STM, the

chiralities of the molecules have been directly identified in some studies.<sup>3</sup> These spontaneously separated SAMs are the 2-D analogues of what Pasteur observed in 1848.<sup>1</sup>

In nature, most racemic mixtures do not spontaneously resolve upon crystallization. Studies of the surface structures formed by cocrystallized racemates are very limited. This is because structures composed of opposite racemates usually lack chiral shapes. Previous study of the adsorption of the iodination products of oleyl alcohol, the diiodooctadecanol racemic mixture, revealed a novel chiral structure.<sup>5</sup> In this case, a “quasi-phase separation” was observed in this structure, with the *R*-type molecules forming one row and the *S*-type molecules forming the other neighboring row, with the two rows packing alternately.

The present study examines the structures formed by racemic mixtures of the iodination products of isomers of the related octadecenoic acids, oleic and elaidic acid. In this study of diiodooctadecanoic acid racemic mixture monolayers, the same quasi-phase separation has also been observed in the oleic acid iodination product monolayer domain except with a more complicated unit cell structure. In the case of oleic acid iodination product adsorption, molecules in the same row always have the same chirality, and through chiral assembly the domain formed by the racemic pair is still a chiral domain. In studies of chiral self-assembled monolayers formed by the adsorption of racemic mixtures on the surface, both spontaneous separation and quasi-phase separation have been observed.<sup>2,3,5</sup> Naturally these observations raise the question of whether a certain degree of

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separation is a universal behavior of the racemic mixture upon forming an ordered structure on the surface.

Elaidic acid (9*E*-octadecenoic acid) and its isomer oleic acid (9*Z*-octadecenoic acid) have been iodinated, and the self-assembled monolayers of iodination products formed upon adsorption on the HOPG surface have been examined here. In the case of oleic acid iodination product adsorption, the same quasi-phase separation as was observed for oleyl alcohol iodination products<sup>5</sup> has also been observed, except with a more complicated unit cell structure. In the case of elaidic acid iodination product adsorption, separation is not observed. The purpose of these studies is to develop an understanding of what chiral structures are formed in the deposition of self-assembled monolayers from chiral adsorbates.

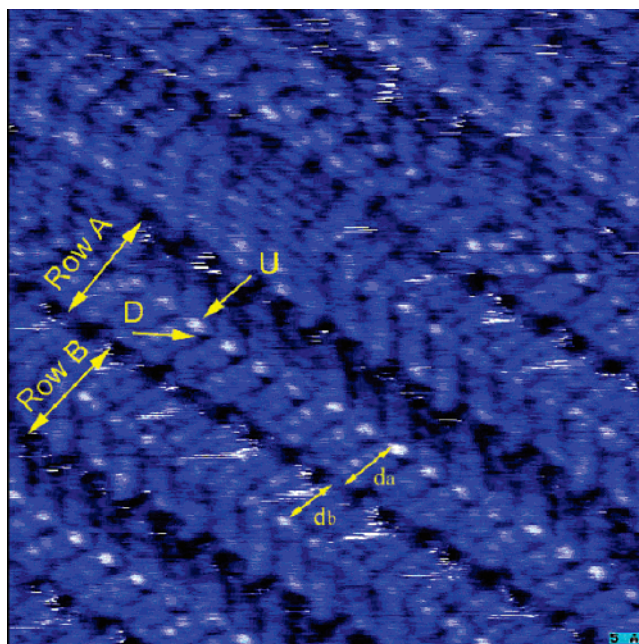
## II. Experiment

The STM used in these experiments is a laboratory-built ultrahigh-vacuum variable-temperature STM.<sup>17</sup> The tip is cut from 0.01-in.-diameter platinum iridium wire (Pt/Ir = 90/10) from Goodfellow. Samples are positively biased, and all scans were carried out under ambient condition at the liquid/solid interface. Oleic acid, elaidic acid, phenyloctane, and iodine were purchased from Sigma-Aldrich and used without further purification. HOPG (ZYA grade) is from Union Carbide. One drop of iodine-saturated CCl<sub>4</sub> solution is added to one milliliter of oleic or elaidic acid phenyloctane saturated solution. Halogenation of the central double bond in the oleic acid results in a solution that is a mixture of oleic acid, 9,10-(9*R*,10*R*)-diiodooctadecan-1-oic acid, 9,10-(9*S*,10*S*)-diiodooctadecan-1-oic acid, and CCl<sub>4</sub>. Halogenation of the central double bond in the elaidic acid results in a solution that is a mixture of elaidic acid, 9,10-(9*R*,10*S*)-diiodooctadecan-1-oic acid, 9,10-(9*S*,10*R*)-diiodooctadecan-1-oic acid, phenyloctane, and CCl<sub>4</sub>. The reaction mixtures were characterized by thin-layer chromatography and NMR. The chromatograms indicated the presence of an additional compound. The NMR confirmed the iodination reaction across the double bond, showing the characteristic multiplet due to the coupling of methylene protons to the adjacent iodine. A drop of either mixture was deposited on a newly cleaved surface of HOPG. Neither CCl<sub>4</sub> nor phenyloctane is observed to form any stable structures on the HOPG surface at room temperature. Hence the stable monolayer structures observed by STM are the structures of either the iodination products or the parent alkanolic acids.

All images were calibrated using the bare HOPG hexagonal lattice. STM images of the mixture solution were taken under various tunneling conditions ( $V_b = 0.3\text{--}1.2$  V, tunneling current =  $0.4\text{--}1.2$  nA). Several different tips and HOPG samples were used to ensure reproducibility. Images shown here were corrected by planar background subtraction, unfiltered unless specified.

## III. Results and Discussions

**A. Oleic Acid Iodination Products.** Pure oleic acid in phenyloctane solution is not observed to form any stable structures on the HOPG surface. The molecular structural similarity of the oleyl alcohol and oleic acid suggests that their iodination products might have similar SAM structures upon adsorption on HOPG. However, STM experiments show that this is not the case. Most long-chain carboxylic acid self-assembled monolayers on the HOPG surface pack in the same way: molecules self-assemble into parallel rows.<sup>18,19</sup> Inside each row, the molecule chain is perpendicular to the row boundary. The molecules pack antiparallel inside the row (i.e., side by side



**Figure 1.** Molecular resolution image of the 9,10-(9*S*,10*S*)- and 9,10-(9*R*,10*R*)-diiodooctadecanoic acid SAM. Scan area is  $91 \times 91$  Å<sup>2</sup>;  $V_b = 1$  V; tunneling current  $I_t = 0.7$  nA.

and head to tail). When a carboxylic acid headgroup meets another carboxylic acid headgroup from another molecule in the neighboring row, the two headgroups form a hexagonal ring by hydrogen bonding. The ring appears as a dark hole in the STM image. This straight-chain carboxylic acid SAM packing arrangement has two characteristics:

- (a) At both ends of a row of molecules, there are dark holes.
- (b) The distance between the dark holes along the row boundary direction corresponds to twice the molecule width ( $8.8$  Å in the long-chain carboxylic acid case).

Figure 1 is an STM image of the adsorbed 9,10-diiodooctadecanoic acid (oleic acid iodination products) 2-D crystal domain. As with most long-chain carboxylic acid SAMs on HOPG, the SAM is composed of rows of molecules. In this image, the two characteristics of these structures described above fit very well. The SAM is the typical structure of a carboxylic acid SAM.<sup>18,19</sup>

Details of the structure that differ from that of the ordinary carboxylic acid SAM are observed, however. First, the repeat unit of the SAM is composed of two rows. There are two types of rows, as labeled in the image, A and B. The rows pack alternately in an ABABAB pattern. Second, inside a row the molecules are bent at the center. The bending angle is  $120^\circ$ . The bending directions of row A and row B are opposite. Overall, the structure exhibits a chevron-shaped unit cell.

A modeling study using the AM1 semiempirical method<sup>20</sup> shows that if the two iodines adopt an "all-trans" configuration then the 9,10-diiodooctadecanoic acid molecule is bent and has the lowest energy in the gas phase. In row A of Figure 1, at the bending point, there is a bright protrusion and a small, dark depression, labeled in the Figure as U and D, respectively. The bright protrusion is assigned as the iodine atom pointing upward, and the dark depression, as the iodine atom pointing downward.<sup>10</sup> The observed molecule configuration in row A is exactly as the modeling predicts. Inside row A, except at the row boundary where the carboxylic acid headgroup and the methyl tailgroup pack alternately, all of the molecules look the same. The relative positions of the bright spot (U) and the dark spot (D) of each individual molecule are also the same. The 9,10-diiodooctadecanoic acid molecules also pack antiparallel, and



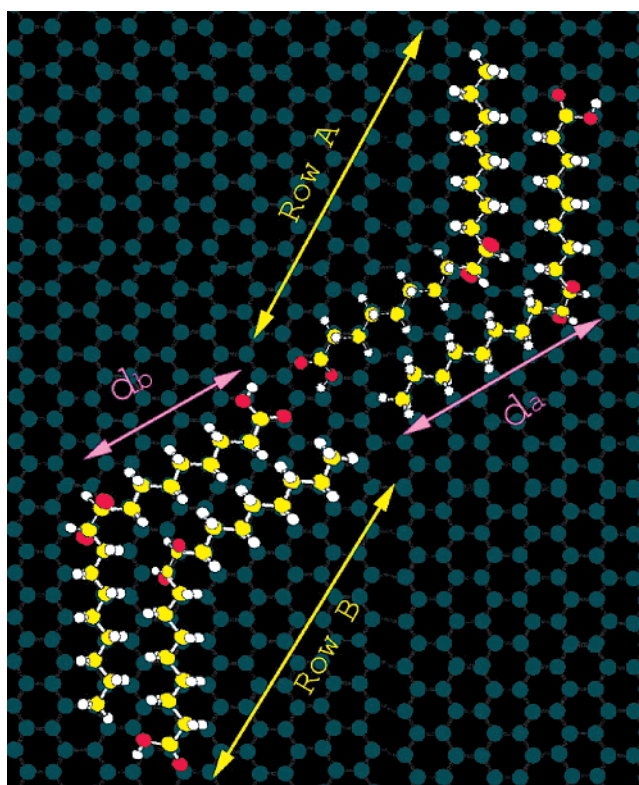
all molecules inside a row bend in the same direction. The only possible packing structure that satisfies all three of these requirements is that the row is composed of only one enantiomer that has the all-trans conformation at the C9–C10 bond. Specifically, as indicated in Figure 1, because in row A the downward iodine atoms are always on the lower left side of the upward iodine atom, molecules in this row are directly identified as 9,10-(9*R*,10*R*)-diiodooctadecanoic acid.

Row B has a shape different from that of row A. As discussed above, all three structural requirements also describe row B, so the same conclusion is also correct for row B. That is, the row is composed of only one enantiomer that has the all-trans conformation at the C9–C10 bond. The relative position of the dark spot (iodine pointing downward) with respect to the bright spot (iodine pointing upward) in row B is critical to the identification of the chirality of row B. If the dark spot is on the upper side of the bright spot in row B, then row B would also be composed of 9,10-(9*R*,10*R*)-diiodooctadecanoic acid molecules. In this case, rows A and B would be centrosymmetric, and the entire domain would be a homochiral domain. If the dark spot is on the lower side of the bright spot, then row B would then be composed of 9,10-(9*S*,10*S*)-diiodooctadecanoic acid molecules, and the domain would be heterochiral. Unfortunately, only the bright spot in row B is clear; the dark spot is less visible in the image. Because the position of the dark spot in row B is uncertain, direct identification of the chirality is not possible.

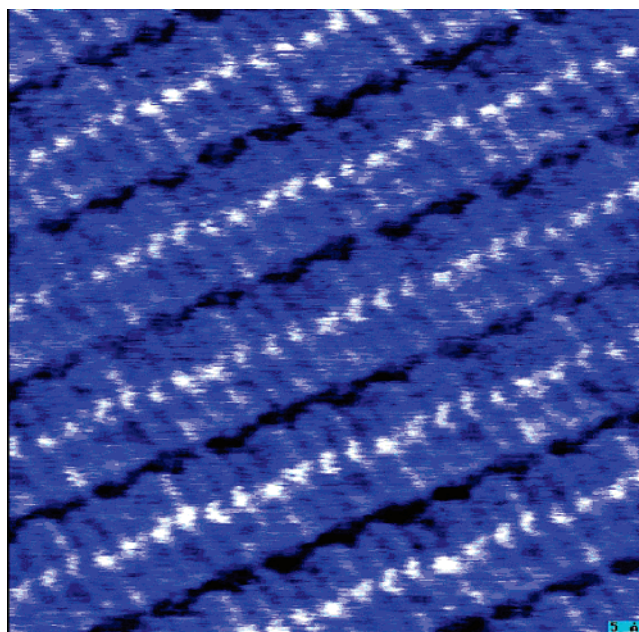
Deciphering the chirality by counting the number of hydrogen pairs along the row boundary direction, as was done in the diiodooctadecanol case,<sup>5</sup> is also difficult. In the observed conformation, the two iodine atoms are in an all-trans position, one upward and one downward. One hydrogen atom would be in the shadow of the iodine. It is not clear whether this hydrogen would appear as a protrusion or a depression or would not appear at all. To determine the identity of the molecules in row B, we measured the distances from the upward iodine atom (bright spot) to the row boundary in both rows A and B. These distances are labeled in Figure 1 as  $d_a$  and  $d_b$ . A modeling study shows that in the 9,10-(9*R*,10*R*)-diiodooctadecanoic acid molecule there are 10 carbon atoms from the molecular terminus to the upward iodine, which corresponds to 4.5 methylene units (2.5 Å). However, in the 9,10-(9*S*,10*S*)-diiodooctadecanoic acid molecule there are nine carbon atoms from the molecular terminus to the upward iodine, corresponding to four methylene units (2.5 Å). Hence if the molecules in row B are also 9,10-(9*R*,10*R*)-diiodooctadecanoic acid molecules, then the ratio  $d_a/d_b$  would be  $4.5/4.5 = 1$ ; if the molecules in row B are (9*S*,10*S*)-diiodooctadecanoic acid molecules, then the ratio  $d_a/d_b$  would be  $4.5/4 = 1.125$ . The measured ratio of these lengths is  $d_a/d_b = 1.13 \pm 0.04$ , which clearly indicates that row B is composed of 9,10-(9*S*,10*S*)-diiodooctadecanoic acid molecules.

Figure 2 is the unit cell of the proposed packing structure of this diiodooctadecanoic acid SAM. Each unit cell is composed of two 9,10-(9*S*,10*S*)-diiodooctadecanoic acid and two 9,10-(9*R*,10*R*)-diiodooctadecanoic acid molecules.

**B. Elaidic Acid Iodination Products.** As previous research has shown,<sup>18,19</sup> the elaidic acid in phenyloctane solution by itself forms a stable SAM on the HOPG surface. The SAM is composed of rows of elaidic acid. Inside each row, the molecule chain is perpendicular to the row boundary. The elaidic acid molecules pack antiparallel (i.e., side by side and head to tail) as is common for long-chain alkanolic acid structures. In the STM image, the central double bond appears as a bright band, and the size of the band is roughly the width of the molecular



**Figure 2.** Unit cell of derived packing structure of the 9,10-(9*S*,10*S*)- and 9,10-(9*R*,10*R*)-diiodooctadecanoic acid SAM.

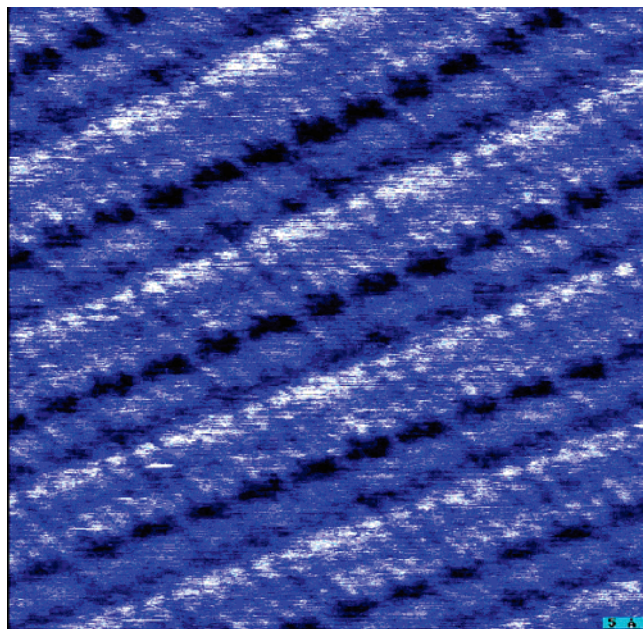


**Figure 3.** High-resolution image of the structure of the elaidic acid SAM. Scan area is  $90 \times 90 \text{ Å}^2$ ;  $V_b = 0.87 \text{ V}$ ; tunneling current  $I_t = 0.91 \text{ nA}$ .

chain. The band makes a  $60^\circ$  angle with respect to the molecular chain. Because of this angle, the two segments of the molecule on either side of the double bond are not in the same straight line. Figure 3 shows a high-resolution image of the elaidic acid SAM obtained in this work. The zigzag shape of the elaidic acid molecule is very clear in this image.

When elaidic acid and the racemic 9,10-diiodooctadecanoic acid mixture co-deposit on the HOPG surface, not only the elaidic acid SAM is found but also a new SAM structure is





**Figure 4.** STM image of the 9,10-(9S,10R)- and 9,10-(9R,10S)-diiodooctadecanoic acid SAM. Scan area is  $79 \times 79 \text{ \AA}^2$ ;  $V_b = 0.71 \text{ V}$ , tunneling current  $I_t = 0.82 \text{ nA}$ .

observed. Over 30 scans were taken on different HOPG samples, and only 1 new type of SAM other than the elaidic acid structure<sup>18,19</sup> was observed. Figure 4 shows an STM image of this new SAM. From this image, features different from those of the elaidic acid SAM could be identified:

(a) There is a dark line beside the bright center band in each row, but this is not observed in the elaidic acid structure.

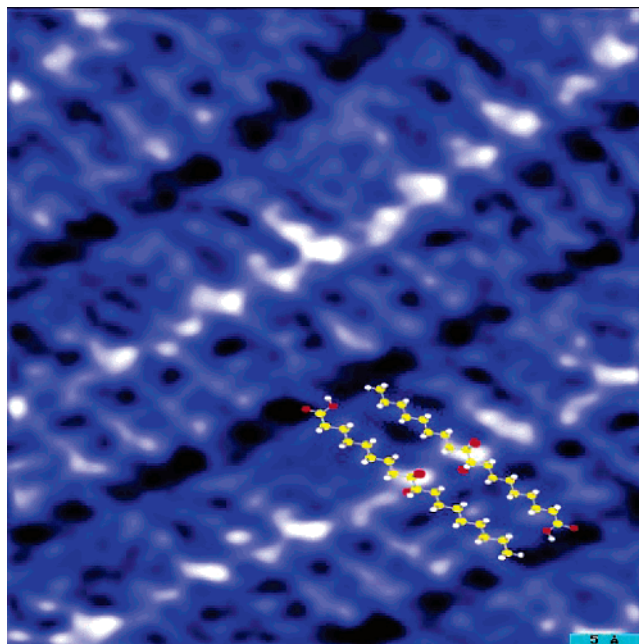
(b) Each chain is straight, but in the elaidic acid SAM, molecules have a zigzag shape due to the double bond.

The solution applied to HOPG is a mixture of elaidic acid and (9,10)-diiodooctadecanoic acid (elaidic acid iodination products), hence the new SAM must be the 9,10-diiodooctadecanoic acid (elaidic acid iodination products) SAM.

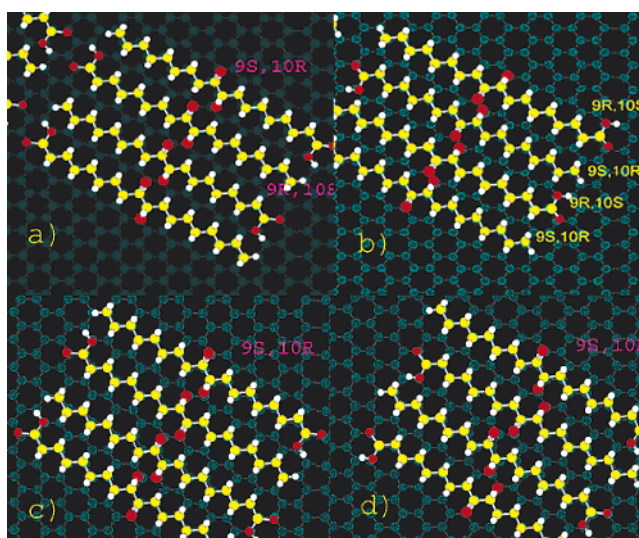
In Figure 4, on both sides of a row, there are also dark holes. The distance between the nearest holes corresponds to the width of two molecular chains. This feature is the same as in the elaidic acid SAM. The hole is the hexagonal ring formed by hydrogen bonding between two adjacent carboxylic acid groups. This structure of the diiodooctadecanoic acid (elaidic acid iodination products) SAM suggests that the acid molecules also pack in a side-by-side and head-to-tail pattern inside a row, as with the unsubstituted elaidic acid.

Figure 5 is a high-resolution STM image of the diiodooctadecanoic acid (elaidic acid iodination products) SAM. In this image, the bright and dark lines inside a row become discrete bright and dark spots. The bright spots are always on the alkane chain; the dark spots are always on the same side of the bright spot and always between the chains. The distance between the bright spots is one alkane chain width ( $4.8 \text{ \AA}$ ), which is also the distance between the dark spots.

By assigning the bright spot as the iodine atom pointing upward and the dark spot as the iodine pointing downward,<sup>10</sup> several packing models for the diiodooctadecanoic acid are constructed (Figure 6). To satisfy the observed facts—(1) antiparallel packing and (2) the  $4.8\text{-\AA}$  periodicity of the iodine atoms at the molecular center—packing models as shown in Figure 6c and d are ruled out because the periodicity of the bright/dark spots is doubled in these structures. The (9R,10S)-diiodooctadecanoic acid molecule must pack next to



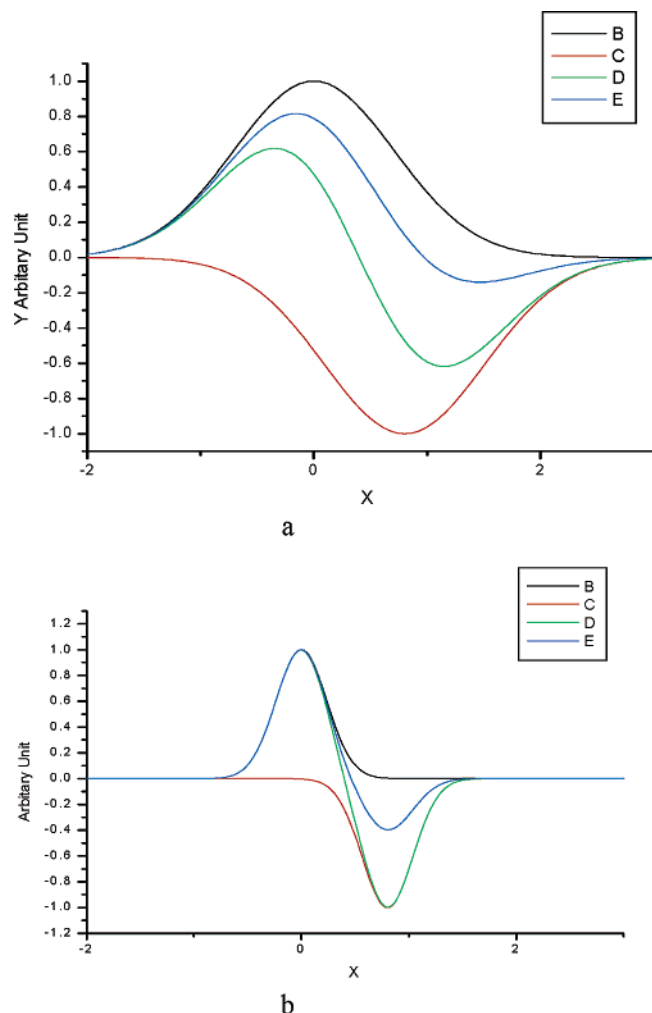
**Figure 5.** High-resolution STM image of 9,10-(9S,10R)- and 9,10-(9R,10S)-diiodooctadecanoic acid SAM with packing model overlaid on the image. Scan area is  $44 \times 44 \text{ \AA}^2$ ;  $V_b = 0.33 \text{ V}$ ; tunneling current  $I_t = 1.22 \text{ nA}$ . The image is low-pass filtered to remove noise and provide a better visual effect.



**Figure 6.** Packing models. (a and b) Symmetric structures formed by such heterochiral pairs, corresponding to the observed image of Figure 5. At this time, STM resolution is not good enough to distinguish the two structures. (c and d) If the homochiral molecules pack together in an antiparallel way, then the periodicity of the bright/dark spots is doubled.

a (9S,10R)-diiodooctadecanoic acid molecule, side by side inside a row. Parts a and b of Figure 6 show the only two possible derived packing structures that satisfy the above observed facts. The unit cell is composed of a pair of enantiomers of (9R,10S)- and (9S,10R)-diiodooctadecanoic acid molecules packed together in an antiparallel way. Although the pair is composed of enantiomers, it is still a chiral structure on the surface. Parts a and b of Figure 6 show the possible symmetric structures formed by such a heterochiral pair. At this time, the STM resolution is not sufficient to distinguish the two structures.

By carefully examining the position of the iodine atoms, we see that the bright spot is in the center of the molecular row,



**Figure 7.** Explanation of the observed iodine positions. These curves are simulations that illustrate the peak-shifting effect. (a) Simulation of the peak-shifting effect. The mathematical expressions are the following. B:  $y_1 = e^{-x^2}$ ; C:  $y_2 = e^{-(x-M)^2}$ , where  $M$  is a constant; D:  $y_3 = y_1 + y_2$ ; E:  $y_4 = y_1 + 0.4y_2$ . (b) Simulation of peaking-shifting effect of a sharp tip. For a very sharp tip, the topographical peaks are also sharp; the overall convolution result of the bump and dip will not affect the position of the bump and dip.

which is the same position as in the model, but the dark spot is off-center. To explain the odd position of the dark holes, it must be understood that in STM images the topography information is actually the convolution of the tip and the true surface feature. A spike may look like a broad bump if the image is acquired with a tip of large radius. In Figure 7, simple Gaussian curves are used to simulate the observed bump and dip in the STM image corresponding to the two iodine atoms. Because the two iodine atoms on the molecule are pointing up and down respectively, the upward iodine should give a broadened protrusion (curve B in Figure 7); the downward iodine should give a broadened depression (curve C in Figure 7) in the STM image. The centers of the protrusion and the depression should be the positions of the two iodine atoms, which do not overlap. The overall STM image is the summation of these features. As a result, the highest point of the protrusion and lowest point of the depression should move symmetrically away if their actual height and depth are equal (curve D, the overall summation of curves B and C in Figure 7a). In this case, the observed brightest and darkest spots are actually not the true position of the upward and downward iodine atoms. Considering that the iodine pointing downward is actually buried under the alkane chain,

the depth of the depression will be smaller than the height of the protrusion. Thus, the convolution would suggest that the highest point is nearly stationary, whereas the lowest point moves away from the center. (In curve E of Figure 7a, the depth of the depressed feature is set to 40% of the height of the protrusion.) This is what is observed in the STM image. This illusion is caused by the large radius of the STM tip. If the tip is very sharp, then the overall convolution of the protrusion and depression would not distort their true positions. A set of sharper Gaussian curves can be used to simulate this. In Figure 7b, the definitions of the curves are the same as in Figure 7a, except the curves have a sharper shape. After summation, curve E indicates that the highest and the lowest positions in curve E are almost the same as in curves B and C. Hence the observed off-center position of the dark line inside the row is caused by imaging with a larger STM tip radius.

#### IV. Conclusions

The SAM structures of the iodination products of oleic and elaidic acids are discussed here. The racemic pair formed by the iodination of oleic acid (9,10-(9*R*,10*R*)-diiodooctadecanoic acid and 9,10-(9*S*,10*S*)-diiodooctadecanoic acid) is observed to exhibit quasi-phase separation during the formation of the 2-D crystal on the HOPG surface. Each row is composed of homochiral acid molecules, either the 9,10-(9*R*,10*R*)-diiodooctadecanoic acid (*R*) molecule or the 9,10-(9*S*,10*S*)-diiodooctadecanoic acid (*S*) molecule. The *R* and *S* rows pack alternately. From this aspect, the racemic diiodooctadecanoic acid SAM is similar to the diiodooctadecanol SAM resulting from the iodination of oleyl alcohol.<sup>5</sup>

In this racemic diiodooctadecanoic acid SAM, each unit cell is composed of four molecules. Two are the 9,10-(9*R*,10*R*)-diiodooctadecanoic acid (*R*) molecules; two are the 9,10-(9*S*,10*S*)-diiodooctadecanoic acid (*S*) molecules. The two molecules that have the same chirality do not have the same position in the unit cell. They pack antiparallel inside the homochiral row. These two molecules use different faces to adsorb on the surface. Comparing the unit cell structure of the racemic diiodooctadecanoic acid SAM and diiodooctadecanol SAM,<sup>5</sup> it is suggested that by using different conformations, enantiomers with opposite chirality might exhibit many chiral assembly patterns to form a heterochiral structure. By using different faces to adsorb on the surface, the four acid molecules in the unit cell form a heterochiral assembly. Thus an achiral racemic mixture can still form a chiral structure on the surface.

The SAM formed upon adsorption of elaidic acid iodination products on HOPG is also a chiral structure. This structure is different from the oleyl alcohol and oleic acid iodination product SAMs, however. Separation of the racemic mixture does not occur. Rather, the unit cell is composed of a heterochiral pair, and the pair is packed inside the same row. This structure indicates that the separation process of the racemic mixture is not universal. Upon forming well-ordered structures on the surface, the racemic mixtures might undergo total spontaneous separation or quasi-phase separation and chiral pairing, or they may not separate at all.

Overall the SAM structures of the iodination products of oleyl alcohol, oleic acid, and elaidic acid adsorbed on HOPG show that through the chiral assembly (usually using different faces of the molecule to adsorb on the surface) the racemic mixture can still form chiral domains. As an example, in the elaidic acid iodination products SAM, the achiral shape of a domain does not guarantee the achirality of the structure.

For the iodination products of elaidic acid, the molecules can use different faces to adsorb on the surface. For other molecules,

there may be more than two conformations available to adsorb on the surface. Chiral molecules with multiple adsorption conformations may form an adsorbate structure using any of these adsorption conformations with similar adsorption energies. The combinations of these conformations in a unit cell may result in many possible chiral structures. This indicates the potential diversity of chiral structures in the 2-D world.

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