

## Chiral Pair Monolayer Adsorption of Iodine-Substituted Octadecanol Molecules on Graphite

Yuguang Cai and Steven L. Bernasek\*

Contribution from the Department of Chemistry, Princeton University,  
Princeton, New Jersey 08544

Received September 16, 2002; E-mail: sberna@princeton.edu

**Abstract:** High-resolution scanning tunneling microscopy has been used to examine the adsorbate structures formed when a racemic mixture of (9*R*,10*R*)-9,10-diiodooctadecan-1-ol and (9*S*,10*S*)-9,10-diiodooctadecan-1-ol is adsorbed at the basal plane of highly ordered pyrolytic graphite. The herringbone structure characteristic of the adsorption of long-chain molecules on graphite is observed. Close examination of the micrographs indicates a unique structure in which the chiral molecules adsorb in pairs, with one enantiomer filling half of the unit cell, and the other enantiomer filling the other half. Instead of forming separate chiral domains, as is sometimes observed when a racemic mixture adsorbs on an achiral surface, chiral pairs are formed and the pairs form an ordered monolayer, exposing opposite faces of the same molecule. An achiral racemic mixture is observed to form a chiral structure on an achiral surface in the regions of the surface examined here.

### I. Introduction

Physisorption from the liquid of long-chain alkane and substituted long-chain alkane molecules at the basal plane of highly oriented pyrolytic graphite (HOPG) has been intensively studied in recent years.<sup>1–16,18,19</sup> These adsorbed structures are important models that provide information relevant to molecular electronic devices, biological recognition chips, tribology, and corrosion inhibition systems. Scanning tunneling microscopy images provide a detailed view of these structures, where adsorbate/substrate and adsorbate/adsorbate interactions play a critical role in the formation of ordered structures. Too strong a substrate/adsorbate interaction makes it difficult to distinguish

adsorbate from substrate, while if the interaction is too weak, the molecules on the surface are too mobile to be imaged. The distance between 6-fold hollows of HOPG is 2.46 Å, and the distance between the hydrogens of the neighboring methylene units in the alkane chain is 2.53 Å. This good match between the substrate lattice and the organic molecule adsorbate dimension results in a significant barrier to molecule diffusion that makes an ideal system for STM study of the adsorbed molecule structure. Previous studies have shown that long-chain *n*-alkanes, alkanols, 1-alkanethiols, fatty acids, and ethers all form highly ordered structures when physisorbed on the HOPG surface.<sup>4,6,10,11</sup>

Certain chiral molecules have been observed to separate spontaneously during crystallization, as Louis Pasteur discovered in 1848 for sodium ammonium tartrate. Chiral organic molecules adsorbed on the HOPG surface are particularly interesting due to potential applications in biologically active chiral molecule recognition and separation, as well as in the design of chirally selective catalysts. Some chiral long-chain alkane derivatives form crystalline monolayers on the basal plane of HOPG. Different optical isomers have been observed to separate spontaneously, each forming a chiral domain on the HOPG surface. With the help of STM, these enantiomers have been identified either by the chiral shape of the domains<sup>16,17,20,21</sup> or, in the case of very high resolution images, by directly identifying the chiral center.<sup>18</sup> These molecules behave like two-dimensional crystals of sodium ammonium tartrate.<sup>17,18,20,21</sup> Most racemic mixtures do not spontaneously separate. Studies of racemic mixtures that are not observed to form separate chiral domains on adsorption or crystallization are still quite rare, partly due

- (1) Spong, J. K.; et al. *Nature* **1989**, *338*, 137–139.
- (2) Smith, D. P. E.; Horber, H.; Gerber, C.; Binnig, G. *Science* **1989**, *245*, 43–45.
- (3) Smith, D. P. E. *J. Vac. Sci. Technol.* **1991**, *B9*, 2, 1119–1125.
- (4) Claypool, C. L.; et al. *J. Phys. Chem. B* **1997**, *101*, 5978–5995.
- (5) Lei, S.; Xu, B.; Wang, C.; Xu, Q.; Bai, C. *Jpn. J. Appl. Phys.* **2001**, *40*, 4273–4276.
- (6) Yin, S.; Wang, C.; Xu, Q.; Lei, S.; Bai, C. *Chem. Phys. Lett.* **2001**, *348*, 321–328.
- (7) Rabe, J. P.; Buchholtz, S. *Science* **1991**, *253*, 424–427.
- (8) Rabe, J. P.; Buchholtz, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 2, 189–191.
- (9) Yeo, Y. H.; McGonigal, G. C.; Thomson, D. J. *Langmuir* **1993**, *9*, 649–651.
- (10) McGonigal, G. C.; Yeo, Y. H.; Bernhardt, R. H.; Thomson, D. J. *J. Vac. Sci. Technol., B* **1991**, *9* (2), 1107–1110.
- (11) Nishino, T.; Buhlmann, P.; Ito, T.; Umezawa, Y. *Surf. Sci.* **2001**, *490*, 1579–584.
- (12) Lee, H. S.; Musselman, I. H. *Anal. Chem.* **2001**, *73*, 5532–5538.
- (13) Okawa, Y.; Aono, M. *Nature* **2001**, *409*, 683–684.
- (14) Hibino, M.; Sumi, A.; Hatta, I. *Jpn. J. Appl. Phys.* **1995**, *34*, 3354–3359.
- (15) Hibino, M.; Sumi, A.; Hatta, I. *Jpn. J. Appl. Phys.* **1995**, *34*, 1 No.2A 610–614.
- (16) Charra, F.; Cousty, J. *Phys. Rev. Lett.* **1998**, *80* (8), 1682–1685.
- (17) Stevens, F.; Dyer, D. J.; Walba, D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, No. 8 900–901.
- (18) Fang, H.; Giancarlo, L. C.; Flynn, G. W. *J. Phys. Chem. B* **1998**, *102*, 7311–7315.
- (19) Poulennec, C. L.; Cousty, J.; Xie, Z. X.; Mioskowski, M. *Surf. Sci.* **2000**, *448*, 93–100.

- (20) Eckhardt, C. J.; et al. *Nature* **1993**, *362*, 614–616.
- (21) Viswanathan, R.; Zasadzinski, J. A.; Schwartz, D. K. *Nature* **1994**, *368*, 440–443.

to the lack of very high resolution images which would allow direct identification of the chiral center of the molecule.<sup>19</sup> In this study, due to both the unique conformation of the molecules and the high-resolution images obtained, the chiral identity of the molecule is determined directly.

Depending on the structure of a monolayer, different aspects of the same molecule can be imaged. For example, in the case of the striped phase of self-assembled alkanethiol monolayers on Au(111), the molecule is imaged with the chain parallel to the substrate.<sup>22</sup> In the  $\sqrt{3} \times \sqrt{3}R30$  phase, in contrast, the alkanethiol is imaged with the chain standing up.<sup>23</sup> Relatively flat chiral molecules, with no mirror symmetry, can expose two different “faces”. When such molecules adsorb on a surface, usually only one face is exposed. The overall adsorption energy of the system will normally favor a specific molecular orientation upon adsorption.

Here the structure of a racemic mixture of (9*R*,10*R*)-9,10-diiodooctadecan-1-ol and (9*S*,10*S*)-9,10-diiodooctadecan-1-ol adsorbed on the (0001) plane of HOPG is reported. In this case the enantiomers do not form separate chiral domains. They instead form chiral pairs, and the pairs form an ordered monolayer, in which different faces of the same molecule are exposed and imaged.

## II. Experimental Section

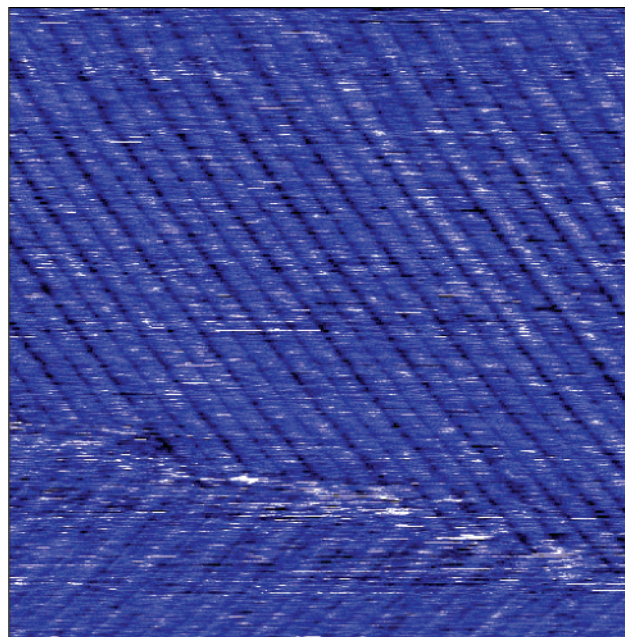
The scanning tunneling microscope used in these experiments is a laboratory-built ultrahigh vacuum variable-temperature microscope.<sup>24</sup> The microscope is mounted in an ultrahigh vacuum chamber on an eddy current damped suspension stage. A horizontally mounted single-tube scanner and tip are used for scanning. 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 conditions at the liquid/solid interface.

Oleyl alcohol and iodine were purchased from Sigma-Aldrich and used without further purification. HOPG is from Union Carbide, ZYA grade. One drop of iodine-saturated CCl<sub>4</sub> solution is added to 1 mL of oleyl alcohol. Halogenation of the central double bond in the oleyl alcohol results in a solution that is a mixture of oleyl alcohol, (9*R*,10*R*)-9,10-diiodooctadecan-1-ol, (9*S*,10*S*)-9,10-diiodooctadecan-1-ol, and CCl<sub>4</sub>. The composition of the solution following iodination was confirmed by <sup>1</sup>H NMR and mass spectrometry. One drop of the resulting solution is directly applied onto a newly cleaved HOPG surface, and this surface is imaged.

STM studies of pure oleyl alcohol and pure carbon tetrachloride applied to the HOPG surface were also performed. Neither oleyl alcohol nor carbon tetrachloride can be seen by STM to form stable ordered structures on HOPG. All images were calibrated using the bare HOPG hexagonal lattice. STM images of the mixture solution are taken under various tunneling conditions ( $V_b = 0.3\text{--}1.2$  V, tunneling current 0.4–1.2 nA). Several different tips and HOPG samples were used to ensure reproducibility.

## III. Results and Discussion

Figure 1 shows a large area image of the adsorbate structure. The most obvious feature in the image is the alternating bright and dark bands on the surface. As with alkanols adsorbed on HOPG,<sup>4,5,9,10</sup> the molecules form a herringbone structure.



**Figure 1.** A large area scan image of 9,10-diiodooctadecanol adsorbed on HOPG. The scan area is  $492 \times 492$  Å.  $V_b = 0.91$  V (sample positive), and the tunneling current  $I = 0.73$  nA. These are raw data except for background subtraction to correct the thermal drifting during the scan. The figure shows two domains, with different packing orientations on the HOPG surface.

Figure 2 is a higher resolution image of the same adsorbate structure.

The herringbone angle is  $124 \pm 2^\circ$ . The length of the molecule measured from the image is found to be  $22.5 \pm 0.3$  Å, which is very close to the length calculated from an extended model of the iodinated oleyl alcohol molecule (22.4 Å).<sup>22</sup> Structural features different from those seen with the parent alkanol can be identified. The “heights” of the neighboring rows of the diiodooctadecanols are different. The diiodooctadecanol rows form a high/low/high/low pattern as seen from the profile scan in Figure 2. At the center of each row, there is a dark trough. The dark troughs in the lower rows are darker than the troughs in the higher rows. In addition, for each row of diiodooctadecanol, the left half of the molecule is brighter (higher) than the right half.

To help explain this fine structure, a model study using Spartan<sup>22</sup> was carried out. The distance between the two hydrogen atoms on the same side of the C9–C10 bond in octadecanol is seen to be 2.53 Å. The atomic radius of iodine is taken to be 1.4 Å in the Spartan code. When iodine is added across the double bond, the ends of the molecule must rotate a bit around the C9–C10 bond to provide space for the two bulky iodine atoms. Figure 3 shows models of (9*R*,10*R*)-9,10-diiodooctadecan-1-ol and (9*S*,10*S*)-9,10-diiodooctadecan-1-ol, built using Spartan and the PM3 semiempirical calculation method available in Spartan. While these structures may not be the lowest energy conformations of the molecule in the gas phase, on the basis of the molecular length derived from the STM image, this stretched conformation is reasonable for an adsorbed molecule. From these models, the angle of I–C9–C10–I is  $89^\circ$ , while this angle is  $65^\circ$  in the unsubstituted octadecanol. It is very clear that the two iodine atoms are on the same side of the backbone chain. The good match between the H–H distance on the alkane chain and the HOPG unit cell

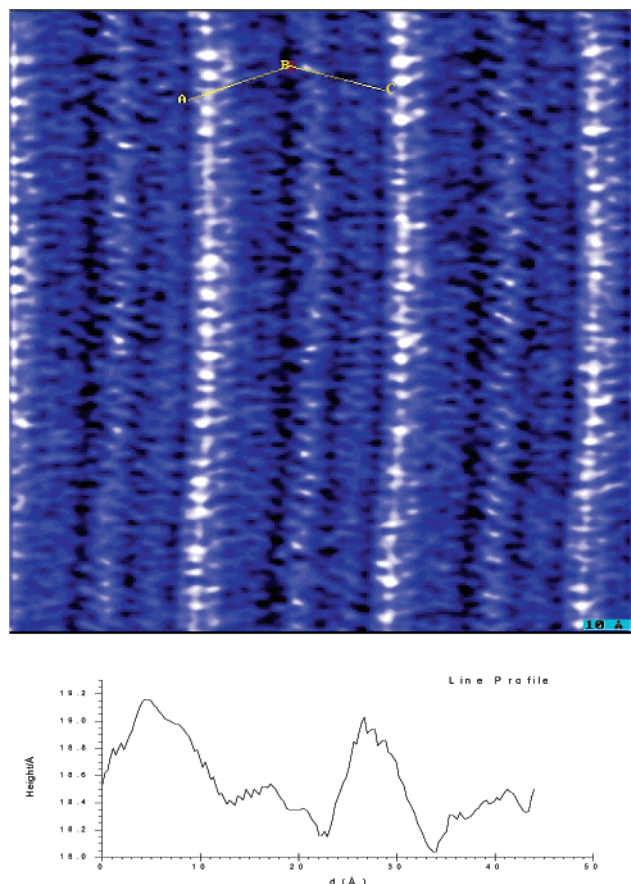
(22) Leung, T. Y. B.; Gerstenberg, M. C.; Lavrich, D. J.; Scoles, G.; Schreiber, F.; Poirier, G. E. *Langmuir* **2000**, *16*, 549–561.

(23) Poirier, G. E.; Tarlov, M. J.; Rushmeier, H. E. *Langmuir* **1994**, *10*, 3383–3386.

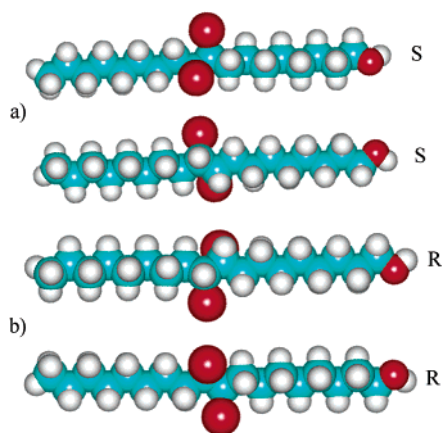
(24) Cai, Y., Ph.D. Dissertation, Princeton University, Princeton, NJ, 2002.

(25) Spartan for Silicon Graphics V5.0.1, Wavefunction, Inc., Irvine, CA 92612.





**Figure 2.** Higher resolution image of 9,10-diiodooctadecanol on HOPG. The scan size is  $135 \times 135 \text{ \AA}$ .  $V_b = 0.99 \text{ V}$ , and the tunneling current  $I = 1.03 \text{ nA}$ . The image is low pass filtered to remove noise. The angle between each pair is  $124 \pm 2^\circ$ . The length of the molecule measured from this image is  $22.46 \pm 0.2 \text{ \AA}$ . The line profile (A–B–C) is along the axis of one molecule pair.



**Figure 3.** Models of (a) (9*S*,10*S*)-9,10-diiodooctadecan-1-ol and (b) (9*R*,10*R*)-9,10-diiodooctadecan-1-ol, showing different faces of the two molecules.

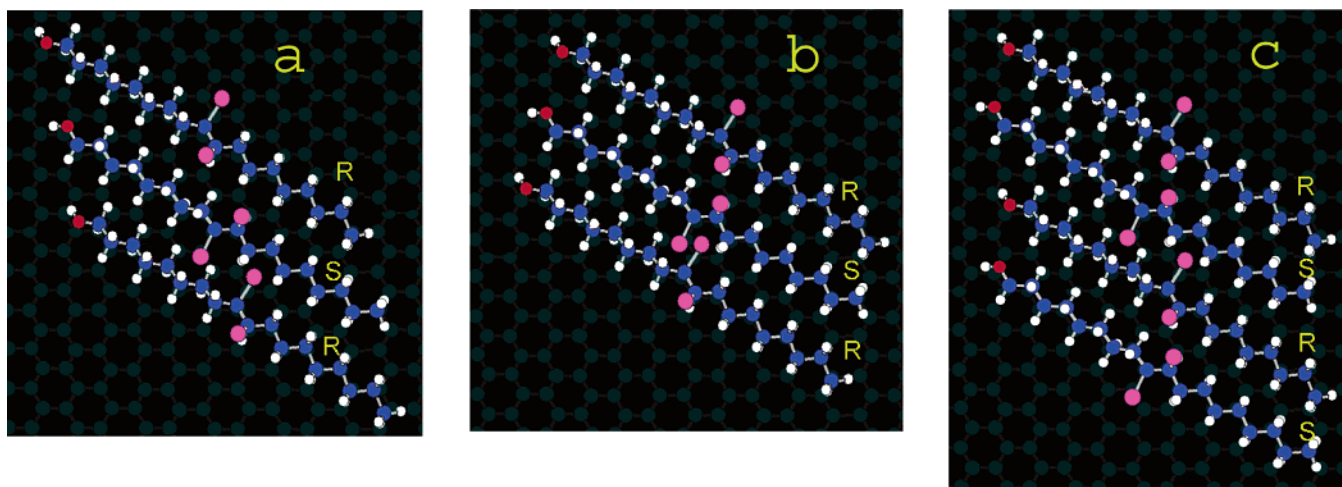
distance leads to well-ordered adsorption of long alkane chain molecules on the HOPG basal plane. For diiodooctadecan-1-ol, the zigzag of the hydrocarbon backbone chain must adsorb parallel to the HOPG basal plane. In this case, the two iodine atoms have only two possible positions: facing up, above the alkane chain, and facing down, buried underneath the alkane chain. Rotating the molecules  $180^\circ$  around the molecular axis converts one orientation into the other.

This suggests an explanation for the high/low/high/low height modulation of the neighboring rows of the diiodooctadecanols. If the two iodine atoms are buried under the alkane chain, the diiodooctadecanol molecule will be a “high” molecule; if the two iodine atoms are facing up, above the alkane chain, the diiodooctadecanol will be a “low” molecule. In Figure 2, row A is a row of high molecules packed together, and the neighboring row B is a row of low molecules packed together. This packing model can be verified by examining the depth of the center trough in each row. Since the iodine atoms are at the center of the 9,10-diiodooctadecanol molecule, it is natural to assign the center trough as the positions of these marker atoms.<sup>18</sup> In the high row, the iodine atoms are blocked by alkane chains, while in the low row, the iodine atoms are exposed. Exposed iodine atoms appear darker than the alkane chain blocked iodine atoms in the high rows. The high/low/high/low height modulation of the neighboring rows suggests that two opposite faces of the same molecule are being imaged.

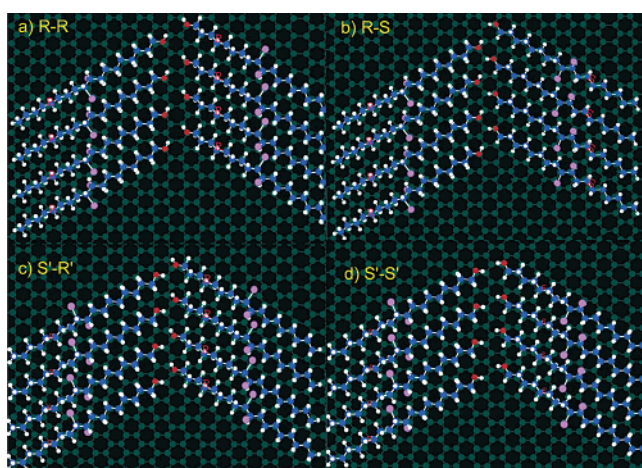
The model calculated using PM3 suggests that the dihedral angle of I1–C9–C10–I2 is  $89^\circ$  instead of the  $63^\circ$  dihedral angle of H–C9–C10–H. As a result of this rotation, half of the molecular backbone is twisted with respect to the other half. The hydrogen atoms on one half move to a higher position, making half of the molecule brighter (higher) than the other half.

Careful examination of Figure 2 provides further interesting information. The racemic mixture of (9*S*,10*S*)-9,10-diiodooctadecan-1-ol (*S*) and (9*R*,10*R*)-9,10-diiodooctadecan-1-ol (*R*) has been imaged. Long-chain 1-alkanols adsorbed on HOPG form a herringbone structure. Between the rows, the alkanol molecules are packed head to head, with the OH groups close enough to form strong hydrogen bonds. Within each row, the long chain of the molecule is packed side by side. In monolayers of long-chain alkanols on HOPG, the angle between the molecular axis and the trough (row boundary) is  $90^\circ$ . In the case of long-chain alkanols, the angle between the molecular axis and the trough (row boundary) is around  $62^\circ$ , and two neighboring chains thus form a  $124^\circ$  angle. This structure is governed by the requirements of hydrogen bonding.<sup>6</sup> Since the angle between the molecular axis and the trough is  $62^\circ$ , inside the row, each alkanol molecule can only shift one methylene unit ( $2.53 \text{ \AA}$ ) while packing.

In Figure 2, it is seen that, in each row, the angle between the molecular axis and the trough (row boundary) is about  $62^\circ$ , and the angle between the hydrogen-bonded pair is around  $124^\circ$ , which is the same as in the 1-alkanol case. In row A of Figure 2 the row is entirely composed of high-type molecules, and in row B, the row is entirely composed of low-type molecules. Figure 4 shows the packing conditions within a row of these molecules. If within the row the molecules are a mixture of *R* and *S* types, only *RR* (or *SS*) packed side by side could satisfy the single methylene unit shift (the angle of  $60^\circ$  between the molecular axis and the trough) and maintain the correct registry with the graphite lattice. From the STM image it is clear that all molecules within a row are either all high (two iodine atoms facing down) or all low (two iodine atoms facing up) molecules. If *R* and *S* packed side by side, they could not form a  $60^\circ$  angle between the molecular axis and trough as indicated in the model structures of Figure 4. On the basis of the above analysis, each



**Figure 4.** Models of molecule registry with the HOPG lattice.



**Figure 5.** Four possible pairing arrangements for the adsorption of the *R* and *S* 9,10-diiodooctadecanol molecules.

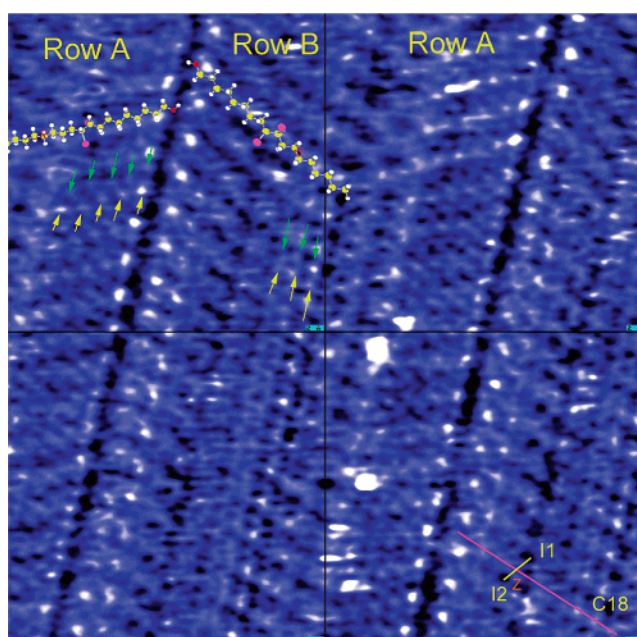
row must be composed of one type of optical isomer, either *R* or *S*, but cannot be composed of both.

To keep registry with the HOPG, if the molecules packed side by side are identical, each chain can shift only an integer multiple of the HOPG lattice length (2.46 Å). If *R* and *S* molecules pack side by side, only a half-integer multiple of the unit lattice shift is possible. (a) 3/2 unit lattice shift, *R* next to *S*. The angle is 49°. (b) 1/2 unit lattice shift, *R* next to *S*. The angle is 74°. (c) Alternating 1/2 and 3/2 unit lattice shift, *R* next to *S*. The angle is 60°, but the oxygen row is zigzag.

A line profile across several rows could identify the position of the OH group, since in the line profile the groove where two oxygen atoms from adjacent molecules meet must be deeper than where two methyl groups meet. After the OH position is located in Figure 2, it can be seen that, in the high row, the C18 side is higher; in the low row, the C1 side is higher.

This implies only four possible structural combinations, as illustrated in Figure 5:

- (a) high-type *R*, C18 part high- and low-type *R*, C1 part high (*RR*),
- (b) high-type *R*, C18 part high- and low-type *S*, C1 part high (*RS*),
- (c) high-type *S*, C18 part high- and low-type *R*, C1 part high (*S'R'*),



**Figure 6.** Very high resolution image of 9,10-diiodooctadecanol adsorbed on HOPG. The scan area is  $76 \times 76$  Å,  $V_b = 0.31$  V, and the tunneling current  $I = 1.0$  nA.

(d) high-type *S*, C18 part high- and low-type *S*, C1 part high (*S'S'*).

Figure 6 is a very high resolution image of this adsorbate structure. Several points can be noted from this image:

- (1) The higher half of a row has only molecular resolution; i.e., only the overall alkane chain is visible. The lower half of the row shows submolecular resolution; i.e., the individual atoms inside the chain can also be seen.
- (2) In the high row (row A), along the oxygen trough direction, in the lower part there are five pairs of small raised features. In the low row (row B), along the oxygen trough direction, in the lower part, only three pairs of small raised features are visible.
- (3) In the low row (row B), in the center of the molecule, the central dark band now appears as a set of discrete dark spots. Each chain has two spots, one on each side.

These observed features fit very well with structural model b (*RS*) proposed above. Since the diiodooctadecan-1-ol twists



at the center, the lower part of the molecule still has a good match with the underlying graphite lattice. In the high part, the chain twists, and the good match no longer exists. The high part of the molecule has a weaker interaction with the HOPG substrate, which leads to poorer resolution compared with the lower part. The pairs of small features indicated by arrows in Figure 6 are the hydrogen atoms on the alkane chain.<sup>4,18</sup> Comparing the four possible conformations shown in Figure 5, along the oxygen trough direction, only structure b has five pairs of hydrogen atoms in the high row and three pairs of hydrogen atoms in the low row as noted in Figure 6.

The structure of the central dark band further supports this conclusion. The dark spots are iodine atoms. A line can be drawn across the alkane chain, connecting the two iodine atoms. The crossing point of this line and the diiodooctadecan-1-ol molecular axis is noted as Z in Figure 6. The iodine atom above the molecular chain is labeled as I1, and the iodine atom below the alkane chain as I2. Comparing the packing models in Figure 5, it is easy to see that if the molecules in the low row are *R* type, the angle C18–Z–I1 is greater than 90°; if they are *S* type, C18–Z–I1 is an acute angle. In Figure 6 it is very clear that this angle is an acute angle.

On the basis of the above analysis, the high row (row A) is directly identified as (9*R*,10*R*)-9,10-diiiodooctadecan-1-ol (iodines up) and the lower row (row B) as (9*S*,10*S*)-9,10-diiiodooctadecan-1-ol (iodines down). Interestingly, because of the HOPG substrate, although (9*R*,10*R*)-9,10-diiiodooctadecan-1-ol in the high row and (9*S*,10*S*)-9,10-diiiodooctadecan-1-ol in the low row are enantiomers in solution, on the surface the mirror image of the *R* type is not superimposable on the *S* type, and vice versa. The entire domain formed by alternating chirally

pure *R* rows and *S* rows is also a chiral structure. This means that an achiral racemic mixture is observed to form a chiral structure on an achiral surface in the regions examined here.

#### IV. Conclusion

An ordered monolayer formed from a racemic mixture of (9*R*,10*R*)-9,10-diiiodooctadecan-1-ol and (9*S*,10*S*)-9,10-diiiodooctadecan-1-ol on an HOPG substrate is imaged by STM. This ordered monolayer exhibits a periodic surface height modulation within the monolayer. Analysis of the STM images shows that the molecules are found to pack in alternately high and low rows. Due to the unique molecular geometry, opposite faces of the molecule are imaged. High-resolution STM images show that the high/low rows correspond to different optical isomers. The enantiomers spontaneously separate into different rows, and inside each row, chirally pure molecules assemble together. This quasi phase separation appears to be unique in the 2-dimensional world, and apparently does not have any three-dimensional analogue. Such a structure is in contrast to the more common instance of chiral molecules that separate spontaneously into pure chiral domains at a surface. The overall structure formed by these alternating chirally pure *R* rows and *S* rows is also a chiral structure; i.e., an achiral racemic mixture is observed to form a chiral structure on an achiral surface in the regions of the surface examined here.

**Acknowledgment.** This work was partially supported by the Chemistry Division of the National Science Foundation. We acknowledge stimulating discussions of this work with Professors R. A. Pascal and G. Scoles of this department.

JA0285619