Microscopic Origin of the Odd−Even Effect in Monolayer of Fatty Acids Formed on a Graphite Surface by Scanning Tunneling Microscopy

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Monolayers of saturated fatty acids with various chain lengths were adsorbed onto a graphite substrate, then studied using the scanning tunneling microscope (STM). The STM images indicate that in the direction parallel to the molecular axis the molecules form centrosymmetrical dimers via hydrogen bonds between the carboxyl groups. From the symmetry of the STM images, it was found that a unit cell of fatty acids with an even number of carbons is different from that of the odd-numbered series. These phenomena provide evidence for a basic mechanism of the odd−even effects in the arrangement of alkyl chains.

Introduction

As typical two-dimensional systems, the ordered arrays of organic molecules[1] such as *n*-alkanes,[2,3] *n*-alkanols,[3,4] and fatty acids[5−8] have been investigated using the scanning tunneling microscope (STM). These arrangements are affected by the lattice of a highly oriented pyrolytic graphite (HOPG) substrate. Alkyl chains of molecules with an all-trans conformation lie parallel to the graphite basal plane, and the direction of the long axis of the molecules is in accordance with the three main crystallographic axes of HOPG. The molecules form densely packed monolayers in which the alkyl chains of neighboring molecules lie parallel to each other. The molecular arrangements depend on the existence of functional groups, such as hydroxyl or carboxyl groups at the end of the alkyl chains. From STM images of these monolayers, we have concluded that the interaction between the alkyl chains is the dominant force for forming ordered structures of these molecules on HOPG.[6]

It is well-known that three-dimensional crystals of fatty acids with even and odd number of carbons exhibit individual polymorphic structures.[9] The even-numbered fatty acids crystallize in at least three forms, while the odd-numbered fatty acids crystallize in three different but related forms. Although the crystallization conditions from the melt or from different organic solvents give rise to different polymorphic structures, the different structures of crystals between even- and odd-numbered series follow the fundamental principles governing interactions between alkyl chains. If the dimension is reduced to two, the packing of the molecules is constrained to take two-dimensional structures. In fact, the monolayers of fatty acids adsorbed onto HOPG are composed of densely packed molecules forming a two-dimensional array, leaving the alkyl chains with no free space to move along the surface of HOPG. Therefore, it is plausible that the structure of the fatty acid monolayers on HOPG is influenced by the number of carbon atoms in the fatty acid molecule. To clarify the basic mechanism responsible for the arrangements of the even- and odd-numbered fatty acids on HOPG, we have obtained STM images with atomic resolution of these adsorbed films. Recently, we have obtained images

of arachidic acid molecules at the solid/liquid interface, e.g., at the internal interface between graphite and phenyloctane, with atomic resolution by STM.[5] In this paper, we present STM images obtained from monolayers of fatty acids with odd and even number of carbon atoms adsorbed at the graphite/phenyloctane interface. On the basis of these images, the microscopic origin of odd−even effects will be considered.

Experimental Section

Fatty acids with an even number of carbon atoms, such as myristic ($C_{13}H_{27}COOH$), palmitic ($C_{15}H_{31}COOH$), stearic ($C_{17}H_{35}COOH$), arachidic ($C_{19}H_{39}COOH$), and behenic acids ($C_{21}H_{43}COOH$), and those with an odd number of carbon atoms, such as heptadecanoic ($C_{16}H_{33}COOH$) and nonadecanoic acids ($C_{18}H_{37}COOH$), were purchased from Sigma Chemical Co. (St. Louis, MO). They were dissolved at concentrations near the saturation value in phenyloctane (Aldrich Chemical Co. Inc., Milwaukee, WI), and the solution was spread on HOPG. The STM images of fatty acids adsorbed onto HOPG were observed in constant-current mode at room temperature, using a Nanoscope II (Digital Instruments, Santa Barbara, CA). The tips used were mechanically sharpened Pt−Ir 80/20 wires. Typical operating conditions were 0.8 nA current and 1.3 V bias voltage (sample negative). For each image, we also obtained a reference image of HOPG under 0.1 V bias voltage at almost the same position on the sample. This was used to correct the size of the fatty acid molecule. All the STM images presented here were flattened by software. The STM images were obtained with different tips and samples to check for reproducibility and to ensure that the images were free from artifacts caused by the tip or the sample. As for obtaining near-atomic resolution good enough for the analysis of the details of raw STM images, our success rate is about five tips in a hundred.

Results and Discussion

Figures 1 and 2 show typical STM images of fatty acid molecules with even (behenic) and odd (nonadecanoic) number of carbon atoms adsorbed onto HOPG, respectively. Brightness in the images corresponds to the increase in local electrical conductance. It can be seen from Figures 1 and 2 that the fatty acid molecules are roughly composed of two parts: one is a

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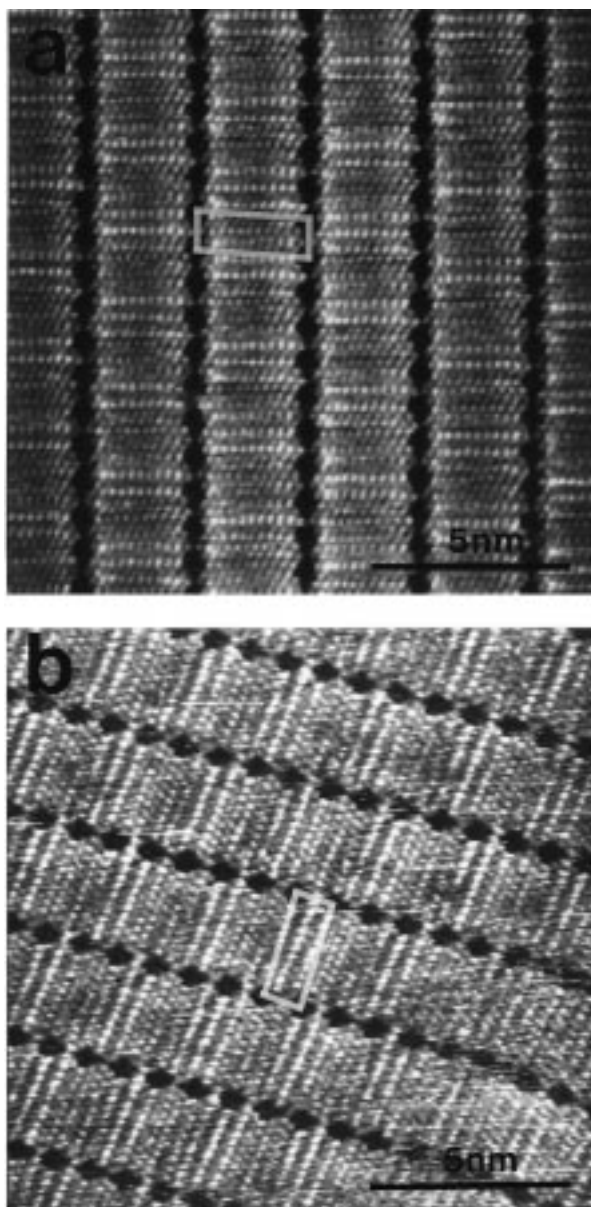
Figure 1. STM images of a monolayer of behenic acid molecules adsorbed onto a graphite substrate. The arrangement of molecules in part a is the mirror image of that observed in part b. A unit cell is represented by a box in parts a and b.

Figure 2. STM image of a monolayer of nonadecanoic acid molecules adsorbed onto a graphite substrate. A unit cell is represented by the box.

Figure 3. Length and width of fatty acid molecule adsorbed onto HOPG versus number of carbon atoms: (a) distance between the dark regions crossing over the band in STM images of fatty acids was plotted; (b) repeat distance of a pair of the straight rows in STM images was plotted. The experimental points are the average over 12−20 STM images obtained with 3−5 different tips. The error bars represent the standard deviation.

bright band and the other is the dark regions that lie between the two bright bands. STM images of the other fatty acids were essentially similar except for the width of the bright band, which increased systematically with the length of the alkyl chain.[5] We therefore interpret that the long axis of the molecule lies on HOPG and that the width of the bright bands corresponds to the length of alkyl chains of the fatty acids while the dark regions between the bands depict the carboxyl groups.

As pointed out in our previous work,[5,6a] two adjacent rows in the bright band in Figure 1 are composed of a total of 21 bright spots. Similarly, STM images of stearic and arachidic acid molecules are found to have 17 and 19 bright spots, respectively. Since the number of carbon atoms in the alkyl chain of behenic acid molecules is 21, we can assign two adjacent rows composed of 21 bright spots to correspond to 21 CH_2 or CH_3 units found in the zigzag alkyl chain of a behenic acid molecule. The dark region between the bands thus corresponds to the part of two carboxyl groups in the head region (see Figure 4).
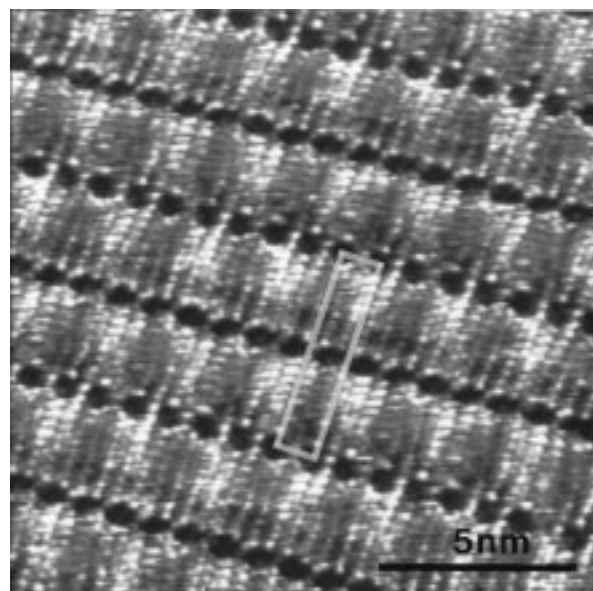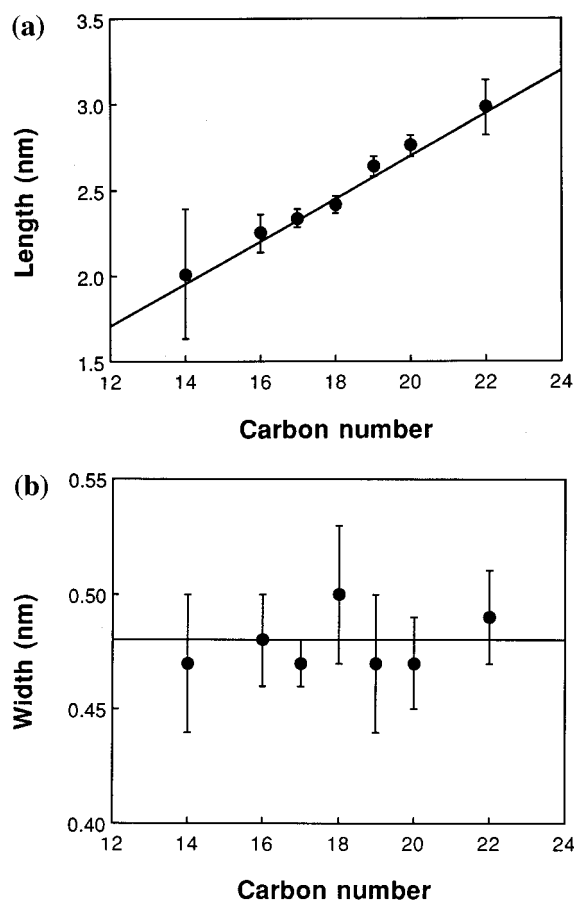
STM images of fatty acids show that the distance between the dark regions across a band and the repeat distance of two adjacent rows in a band correspond to the length and the width
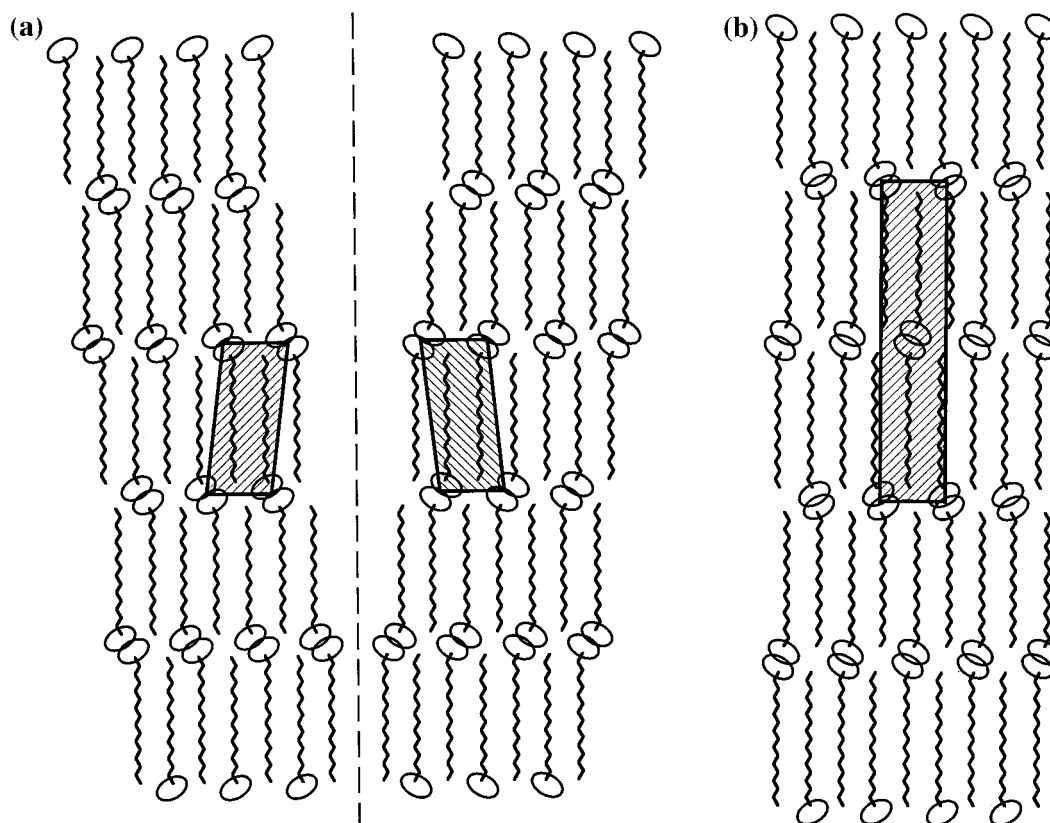
Figure 4. Schematic arrangement of fatty acid molecules. The mirror plane is indicated by the dashed line, and the right- and left-handed structures are shown. Part a shows the even-numbered series, where the number of carbon atoms is 16. The left- and right-handed structures correspond to the molecular arrangements in parts a and b of Figure 1, respectively. Part b shows the odd-numbered series, where the number of carbon atoms is 17. Each domain structure is composed of racemic mixtures of two opposite enantiomers. A unit cell is represented by a box in parts a and b.

of fatty acid molecules on HOPG, respectively. Parts a and b of Figure 3 show the plots of the length and the width versus the number of carbon atoms in the fatty acids, respectively. Figure 3a shows that the length of fatty acids on HOPG can be described by

$$\text{length of fatty acid on HOPG} =$$
$$\left[\frac{1}{2}(\text{no. of carbon atoms in fatty acid chain}) +\right.$$
$$\left.\frac{1}{2}(\text{no. of oxygens in carboxyl group})\right] \times 0.246 \text{ nm}$$

Here, 0.246 nm is the distance between the second-nearest-neighbor carbon atoms of a graphite lattice. The result obtained for behenic acid here is consistent with that found previously.[5b,8] This indicates that the arrangement of self-assembled fatty acid molecules on HOPG depends on the graphite lattice. As seen in Figure 3b, the width of the fatty acid on HOPG is constant regardless of the number of carbon atoms. This supports the notion that the molecules form densely packed monolayers on HOPG.

It is worth noting that for the even-numbered series, the arrangement of the dark regions in Figure 1a is similar to that in Figure 1b, but Figure 1a is the mirror image of Figure 1b. This indicates the appearance of domains having two distinct arrangements of the molecules in the monolayer of behenic acid molecules on HOPG. However, we did not obtained mirror images for the odd-numbered series. When the dark regions are shifted by every other molecular unit in the direction of the long axis, they are superimposed upon the other dark regions, as seen in Figure 2.

The above facts indicate that the molecular arrangements depend on the carbon number as shown schematically in Figure 4. For the even-numbered series, the mirror plane is indicated by the dashed line, and the right- and left-handed structures are shown. An alkyl chain and a carboxyl group are drawn by a zigzag chain and an open circle, respectively. All alkyl chains are in the trans conformation. As seen in Figure 4a, two fatty acid molecules are linked through hydrogen bonds between carboxyl groups; i.e., the molecules on HOPG form centrosymmetrical dimers via the hydrogen bonds. The dimer shifts by the length of a molecule in the direction of the long axis between neighboring dimers. It is worth pointing out that fatty acid molecules are generally achiral molecules in three dimensions but behave like chiral molecules in two dimensions because of the asymmetry of the carboxyl group. Thus, the dimers have two opposite enantiomers on HOPG, since there are two positions for the carboxyl group on the surface. For even-numbered fatty acids, the monolayer consists of two kinds of domains and each domain structure contains one type of enantiomer. As a result, even-numbered fatty acid molecules, which are achiral molecules, split spontaneously into the two distinct arrangements with chiral dimers having opposite handedness on HOPG. The arrangement of odd-numbered fatty acid molecules in Figure 4b is almost similar to that of the even-numbered series. However, this structure has a racemic mixture composed of two types of enantiomorphic dimers. Therefore, the unit cell is constructed by 2×2 molecules in a direction parallel to and also perpendicular to the molecular axis.

The difference in the arrangements between the odd- and even-numbered series becomes obvious as seen from the images in Figures 1 and 2. It should be noted that the atomic

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arrangements near the methyl ends and the carboxyl groups are essentially the same in both the odd- and even-numbered series as illustrated in Figure 4. Nevertheless, although these local arrangements in densely packed dimers of fatty acids are on the surface of HOPG, the overall dimer arrangements are different between the odd- and even-numbered series of fatty acids. The additional carbon in the odd-numbered series causes a change in the position of the carboxyl group relative to that found in the even series. This causes a difference in the unit cell arrangement in the odd- and even-numbered series of fatty acid. In the odd-numbered series a unit cell is composed of four fatty acid molecules, but in the even-numbered series a unit cell is composed of two fatty acid molecules. Although the local arrangements are essentially the same in both the odd- and even-numbered series, the arrangements of the hydrogen-bonded carboxyl groups are different layer by layer in the lamellar periods ruled by the molecular length. In the odd-numbered series the arrangements of the hydrogen-bonded carboxyl groups are equivalent over the two-dimensional structure, but the arrangements of the hydrogen-bonded carboxyl groups in the even-numbered series are enantiomorphic layer by layer. The above facts give rise to a difference in cohesion energy and may contribute to the odd−even effects in the melting temperature among the fatty acids. As a next step, we will study the relationship between differences in structure and differences in physical properties, which might be applied to the consideration of the odd−even effects in the three-dimensional crystals of fatty acids.

Conclusion

We have obtained atomic resolution STM images of fatty acid molecules at the graphite/phenyloctane interface. On the basis of these high-resolution images, we find that the arrangements of saturated fatty acid molecules adsorbed onto HOPG depend on the number of carbon atoms in the fatty acid chain and that there is a distinct difference between the arrangements found in the odd- and even-numbered series. Monolayers of fatty acids with an even number of carbon atoms consist of two kinds of molecular arrangements that are mirror images of each other, while those with an odd number of carbon atoms only exhibit one type of arrangement consisting of a racemic mixture of two dimer types that are opposite enantiomers in two dimensions. These phenomena are due to the effect of the number of carbon atoms in the alkyl chains, and the odd−even effect takes place as a result of the short-range interactions between the alkyl chains. This information is important for an understanding of not only processes such as two-dimensional arrangement of self-assembled molecules but also the basic mechanism in the formation of three-dimensional arrangements of fatty acids.

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