

# Ordering of Adsorbed Organic Monolayers Confined in Molecule Corrals during Scanning Tunneling Microscopy Observation

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Since the first report of the imaging of organic molecules by scanning tunneling microscopy (STM) (Foster, J. S.; Frommer, J. E. *Nature* **1988**, 333, 542–545) questions have arisen about the physical interaction between the scanning tip and the adsorbed monolayer. How much this interaction affects the adsorbed monolayer, and whether the monolayer structure observed by STM is the same structure which is present in the absence of STM observation have been difficult questions to address, since the monolayer typically cannot be seen at high resolution except by STM. Many reports of tip-induced substrate damage have appeared, but here we report nondestructive tip-induced orientation of an adsorbed monolayer confined in molecule corrals and on graphite terraces. We believe this is the first evidence that in some cases the scanning action of the STM tip can act to *orient* an adsorbed monolayer. For adsorbed monolayers of octadecanol and octatriacontane, the structures observed by STM are *not* the same structures which are present in the absence of STM observation. The ordering action of the STM tip removes information about the initial appearance of the monolayer but may lead to better understanding of the physical interactions between the tip and adsorbed monolayers and between the adsorbed monolayers and the substrate.

## Introduction

The ordering of liquids at solid surfaces is of interest for applications such as lubrication, adhesion, wetting, and in alignment of liquid crystal displays. These systems have also been useful for elucidating a fundamental understanding of many important surface phenomena.<sup>1</sup> In cases where molecules self-assemble into two-dimensional crystals on flat conducting surfaces, scanning tunneling microscopy (STM) can be used to image the 2D adsorbed crystal at molecular or higher resolution.<sup>2,3</sup> However, the STM tip can interact strongly with the surface, making it unclear whether the adsorbate structure observed by STM is the same “intrinsic” structure that would be present in the absence of STM observation. Here we report STM observations of octadecanol and octatriacontane confined within “molecule corrals” on graphite where the scanning of the STM tip has a clear effect on the orientation of the adsorbed monolayer. The absence of this effect in other systems suggests that the STM can image some adsorbates without perturbing them.

It has been known for some time that heating graphite in air gives rise to circular etch pits one monolayer deep.<sup>4–6</sup> Previous work by this group used these etch pits to contain small ensembles of molecules for study, and hence the etch pits were termed “molecule corrals.”<sup>7</sup> These molecule corrals are extremely useful for observing many different domains of a monolayer, since the domains in each corral nucleate separately from each other and separately from domains on the surrounding terrace.

Previous results from this group<sup>8</sup> showed that monolayers of the liquid crystal 8CB (4'-octyl-4-cyanobiphenyl) on the terraces, which crystallize first, influence the orientation of monolayers which later form in the corrals, and the effect is strongest when the corrals are small. This result shows that domains of 8CB which are separated by a step on the graphite surface are still interacting in some manner. It seemed reasonable that this interaction was via some ordering of the bulk liquid near the

surface, probably related to the liquid crystalline order of 8CB at room temperature. To test this, we decided to perform a follow-up study by measuring the orientation in the molecule corrals of materials which are not liquid crystals, and octadecanol and octatriacontane were chosen for this purpose. Unlike 8CB, these molecules in the liquid or solution state are isotropic and have no long-range order. Short-range order (over a few molecule lengths) has been proposed for isotropic liquids, but recent studies of liquid alkanes<sup>9</sup> and alcohols<sup>10</sup> have shown no evidence for even very short-range order.

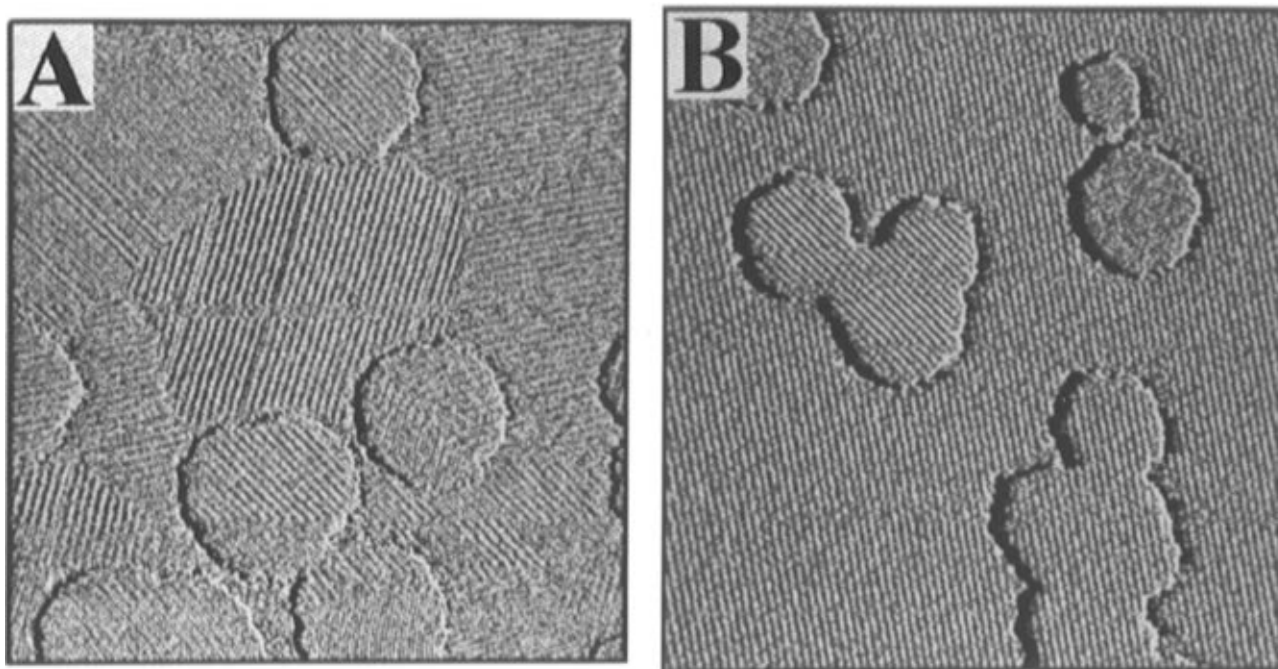
Because of the 3-fold symmetry of the highly oriented pyrolytic graphite (HOPG) and the epitaxial relationship of the adsorbed monolayer with the HOPG lattice, there are three possible energetically degenerate relative angles between molecular domains in corrals and domains on the terrace: 0°, +60°, and -60°. Aligned pairs of corral-terrace domains exhibit a relative angle of 0°, while misaligned pairs exhibit an angle of ±60°. For a purely statistical distribution, the corral domain would be aligned with the terrace domain in one out of every three observations and misaligned in two out of every three observations. Thus, for isotropic liquids we expected to see a flat distribution, independent of corral size, with one-third of the corrals showing the same alignment as the surrounding terrace, and the remaining two-thirds showing domains rotated by ±60°.

## Experimental Section

The STM used in these studies is custom built and has been described elsewhere.<sup>11</sup> All images were acquired while scanning with the tip penetrating through a thin layer of solution or neat liquid at room temperature using tips mechanically cut from Pt/Rh (90:10) or Pt/Ir (80:20) wire.

For this work we etched highly oriented pyrolytic graphite (HOPG) at 650 °C in air using a varying number of thermal “shocks” (1 min in the oven followed by 3 min out) followed by a variable etch time in the oven (generally between 3 and 20 min). In agreement with previously published results,<sup>4,5</sup> we found that increasing the number of thermal shocks increased

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**Figure 1.** Both images are  $1925 \text{ \AA} \times 1925 \text{ \AA}$ , collected in constant-height mode on etched HOPG. Image A shows a typical image of octadecanol. Note that all the corrals are ordered, and many domains are present ( $-0.60 \text{ V}$ ,  $140 \text{ pA}$ ). Image B shows a typical image of neat 8CB. Note that only one domain is present on the terrace, not all corrals were ordered at the time this image was acquired, and the ordered corrals contain only a single domain each ( $-0.57 \text{ V}$ ,  $170 \text{ pA}$ ).

the density of corrals, though not in a predictable way, and that the corral diameter increased linearly with etch time at a rate of about  $45 \text{ \AA}/\text{min}$ .

1-Octadecanol ( $\text{CH}_3(\text{CH}_2)_{17}\text{OH}$ ), octatriacontane ( $\text{CH}_3(\text{CH}_2)_{36}\text{CH}_3$ ), and 1-phenyloctane ( $\text{C}_6\text{H}_5(\text{CH}_2)_7\text{CH}_3$ ) were used as received from Fluka. Octatriacontane was studied as a saturated solution in phenyloctane. For octadecanol, two methods of sample preparation were used. "Solution" samples were made by placing a drop of a saturated solution of octadecanol in phenyloctane on etched HOPG at room temperature. "Melt" samples were made by melting a small amount of octadecanol onto the etched HOPG, covering with a drop of warm phenyloctane, and allowing the sample to cool slowly to room temperature. Both methods could be used on the same HOPG sample by washing with acetone between samples. After washing with acetone, no adsorbed molecules could be detected by STM. 8CB (Aldrich) was used as a thin layer of neat liquid. Unless noted, images were acquired in constant-height mode,  $-0.6 \text{ V}$  (tip positive),  $160 \text{ pA}$ , and were not processed except for least-squares plane subtraction to compensate for sample "tilt". STM images could not always be obtained at once, and voltage pulses (produced by briefly increasing the bias voltage by a factor of 10) were applied until the monolayer could be imaged.

## Results

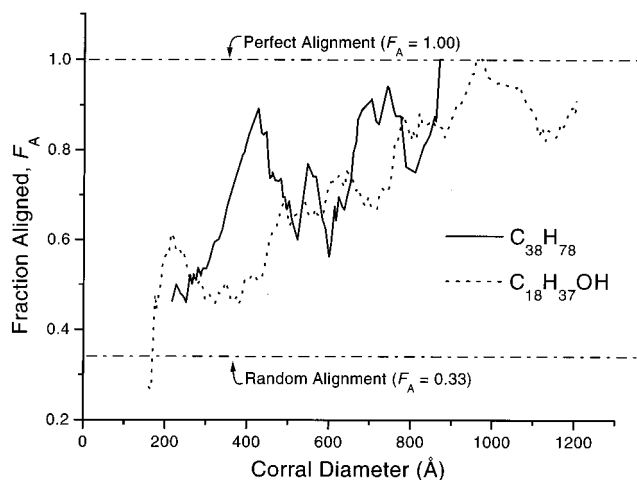
Several different HOPG samples were etched to give a range of corral sizes. A solution of octadecanol or octatriacontane was applied to each sample, images of the monolayer were obtained by STM, and the angle formed between domains inside corrals relative to domains outside corrals was measured using standard image analysis software. STM images of octadecanol or octatriacontane typically showed several domains, with each domain extending over a few hundred angstroms. Domains always showed rotations of  $0^\circ$  or  $\pm 60^\circ$  from one another, as seen in Figure 1A, reflecting the substrate symmetry. For octadecanol, no significant differences were observed between samples prepared from "solution" and from "melt". The organic monolayer and underlying HOPG could sometimes both be

observed at the same location by changing the bias voltage. Whenever this was done (for either material) the molecular long axis was found to be parallel to one of the three HOPG lattice vectors (i.e. the monolayers were epitaxial).

Data collection was made difficult by the presence of multiple domains, both within corrals and on the surrounding terrace, as can be seen in Figure 1A. This behavior is different from 8CB, which forms a small number of large domains on the terrace and forms only single domains within corrals, as seen in Figure 1B. Only corrals which contained a single domain and contacted only one domain on the surrounding terrace were counted in the analysis of domain alignment. Domain angles from 892 such corrals for octadecanol and 260 corrals for octatriacontane were measured, and the fraction aligned,  $F_A$ , was plotted in a histogram obtained by constant-width ( $100 \text{ \AA}$ ) moving window boxcar averaging. After averaging, any points which represented the average of fewer than 10 angle measurements were discarded.

Instead of the expected random alignment over all corral sizes, plots for both octadecanol and octatriacontane showed values for the fraction of corrals containing domains aligned with the domains on the surrounding terrace ( $F_A$ ) to be approaching one-third (randomly oriented) only for small corral sizes but rising to nearly unity (non-random and therefore highly oriented) at larger corral sizes, as shown in the data plotted in Figure 2. This result would appear to imply an unphysical ordering force which is directly proportional to distance, having little effect at short range (i.e. for small corrals), but increasing at long range! However, such an interpretation is only valid if the monolayer domains observed are the same domains which originally formed as the monolayer crystallized—the intrinsic domains.

In fact, this is not the case, as evidenced by observations made during data collection. The STM used was equipped with the ability to scan samples using either  $x$  or  $y$  as the rapid-scan direction. Changing the rapid-scan direction typically had only a small effect on the appearance of the image, except when monolayers of octadecanol or octatriacontane were observed. With these molecules, the molecular rows were frequently



**Figure 2.** Histograms showing molecular row alignment vs corral size for octadecanol ( $N = 892$ ) and octatriacontane ( $N = 260$ ). Alignment is measured as the fraction of corrals which have domains aligned with the domain on the surrounding terrace ( $F_A$ ). Since there are two degenerate rotations ( $\pm 60^\circ$ ) an alignment fraction of 0.33 represents random alignment, while a fraction of 1.0 represents perfect alignment with the terrace.

observed to be perpendicular to the fast-scan direction used (or as close to perpendicular as allowed by the requirements of epitaxy with the HOPG surface). When the rapid-scan direction was changed from  $x$  to  $y$ , the molecular rows were often observed to reorient so as to again be nearly perpendicular to the rapid-scan direction, illustrated by the sequence of images shown in Figure 3 in which the rapid-scan direction used while obtaining each image is shown by an arrow. Changing the rapid-scan direction back to  $x$  often caused the rows to reorient again to their original orientation (though what had been one domain sometimes became several domains, or vice versa). On some occasions the rapid-scan direction could be changed between  $x$  and  $y$  many times with consistent results. Trace and retrace (scanning left-to-right and right-to-left, or top-to-bottom and bottom-to-top) images were nearly indistinguishable. The speed of reorientation varied, sometimes being nearly complete between scans (Figure 3B,C, corral and terrace) and other times requiring many scans (Figure 3D,E, corral). On some occasions no reorientation was seen when the rapid-scan direction was changed. On some other occasions a domain was observed to switch between two orientations multiple times while the rapid-scan direction was held constant (when this was seen, the two orientations were generally both  $\sim 60^\circ$  to the rapid-scan direction). The amount of reorientation was always  $\pm 60^\circ$  as required by epitaxy with the substrate. When one domain could be nearly at  $90^\circ$  to the rapid-scan direction, that domain usually dominated (Figure 3B,E, corral and terrace; D, terrace), but when two domains were both close to  $60^\circ$  from the rapid-scan direction, both domains were often seen (Figure 3C,F, corral and terrace).

Because of the large variation observed in the tendency of the monolayer to align with the scan direction, a separate experiment was performed to test the reproducibility of this effect. A saturated solution of 1-octadecanol in 1-phenyloctane was applied to a freshly cleaved HOPG surface (no etching) and scanned until the monolayer could be observed. Once the monolayer was seen, the scan area was changed to a "fresh" area of the sample a few micrometers away from the area initially scanned (to avoid any effects of scanning before the images were acquired), and two scans in  $x$  followed by two scans in  $y$  were taken (each scan about  $2000 \text{ Å} \times 2000 \text{ Å}$ ). The scans taken in  $y$  were then compared to the previous scans taken in  $x$  to see if the domains changed in response to the change in scan direction. The scanning tip was recut between

each set of four images, and data were collected from several different HOPG samples. Out of 41 sets of images taken with octadecanol, 19 sets showed noticeable change in domain alignment in response to the change in scan direction while 22 sets did not. The amount of reorientation varied from one small domain reorienting, to the entire imaged area reorienting. The speed of reorientation also varied, sometimes being complete in the first image after the scan direction was changed and sometimes only appearing in the second image. If more scans had been taken, reorientation would likely have been seen in a greater number of cases.

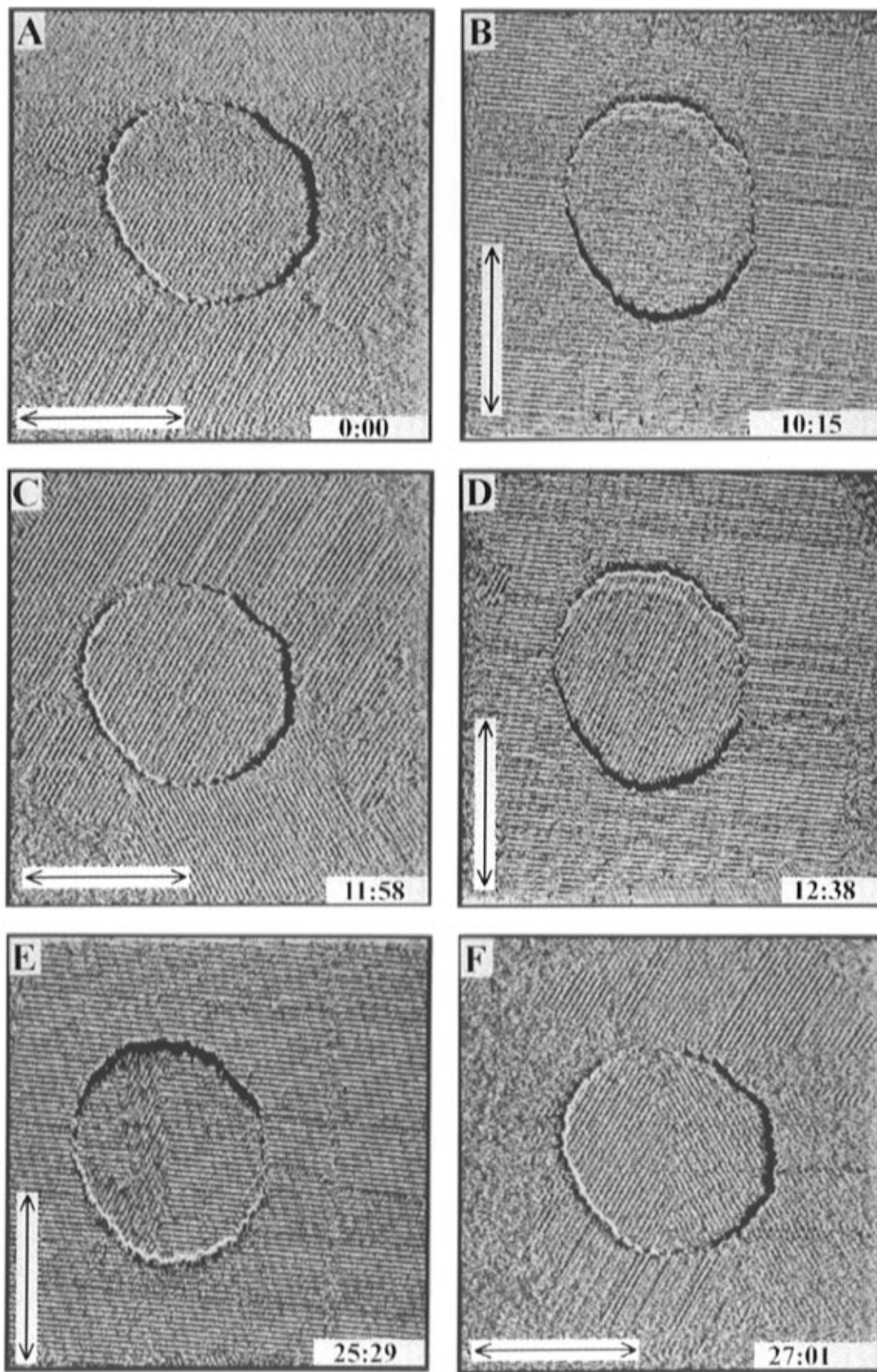
When a similar experiment was performed using 8CB, out of 40 sets of images taken, none showed any sign of changes in domain orientation. Although domain walls in 8CB have been observed to shift under the influence of scanning,<sup>12</sup> large-scale domain reorientations are not seen in 8CB. Thus the domains observed in 8CB probably do represent the "intrinsic" domains that formed when the 8CB monolayer first crystallized.

## Discussion

Observing domains which reorient during STM observation means that the domains observed by STM at any time are not necessarily the same as the "intrinsic" domains which formed when the monolayer initially crystallized. Even the domains seen in the first scan of a region may have been reoriented by the tip. The observation that the STM tip influences the ordering and orientation of the molecules not only explains why the expected alignment behavior (random orientations at all corral sizes) was not observed, but also provides a reasonable explanation for the observed behavior (increasing alignment of corral-terrace domains at large corral sizes).

Inducing alignment between a domain in a corral and a domain on the surrounding terrace requires that the tip orient both the domain in the corral and the domain on the terrace. This does occur (Figure 3), but the two processes need not be controlled by the same factors. For example, it might seem reasonable that the ease of orienting domains in a corral would be related to corral size, while ease of orienting domains on a terrace would be related to corral density. We have some evidence that this is in fact the case. During the course of this study, 729 corrals on various samples were chosen with no particular systematic bias, and for each one the corral diameter and number of domains within the corral were measured. Assuming a constant rate of nucleation, the intrinsic number of domains per unit area should be constant, so the number of domains per corral would be expected to be proportional to the square of the corral diameter.<sup>7</sup> Figure 4 shows only a very small increase (from 1.0 to 1.8) in the average number of domains per corral over a 6-fold increase in corral diameter. This weak scaling is not caused by slow nucleation (which would tend to cause only a single domain to be observed over a range of corral sizes, as seen in 8CB) because even corrals smaller than  $400 \text{ Å}$  were often observed to contain multiple domains. The lack of a stronger area scaling suggests that domains in larger corrals are more easily oriented by the tip, which would tend to cause large corrals to contain only one domain and reduce the number of domains per corral from its intrinsic value to an artificially low value as the corral diameter is increased.

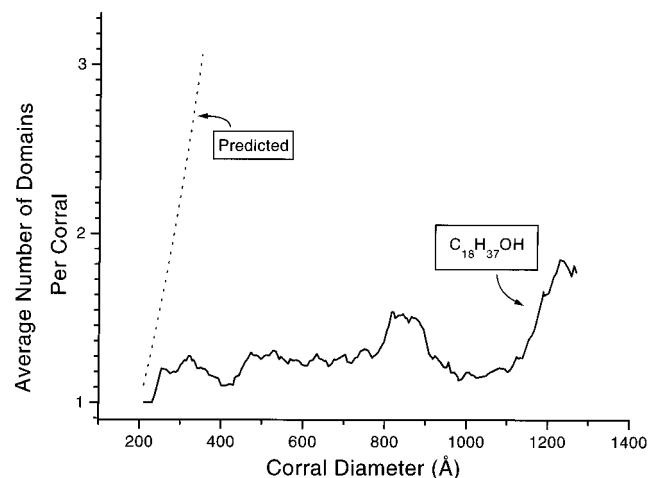
It is also reasonable to expect that the ease of reorientation of domains on the terrace would be related to the corral density. Previous work by this group<sup>12</sup> has shown that corrals can pin domain walls in 8CB on the terrace, and if a similar effect occurs with octadecanol and octatriacontane, then the more strongly the domain walls were pinned, the more strongly they would resist reorientation by the STM tip. Hence samples with a high corral density would be expected to show less reorientation of



**Figure 3.** Octadecanol on etched HOPG (each image  $2310 \text{ \AA} \times 2310 \text{ \AA}$ ,  $-0.64 \text{ V}$ ,  $160 \text{ pA}$ , constant height). Each image in this sequence was taken in the same location (elapsed time shown as minutes:seconds) while the rapid-scan direction was changed. The arrows on each image show the rapid-scan direction. Note that in images A–C the entire domain inside the corral orients the same way as the main domain on the terrace. In image D the terrace has switched, but the domain in the corral is unchanged from C. Image E shows the domain in the corral in the process of changing to align with the domain on the surrounding terrace. Finally in image F the scan direction was changed again and both terrace and corral domains switched, though different parts of the domain in the corral switched in different directions.

terrace domains, while samples with a low corral density would show greater reorientation of terrace domains.

Although an average value for corral density can be readily measured, the corrals are randomly distributed, so even on a



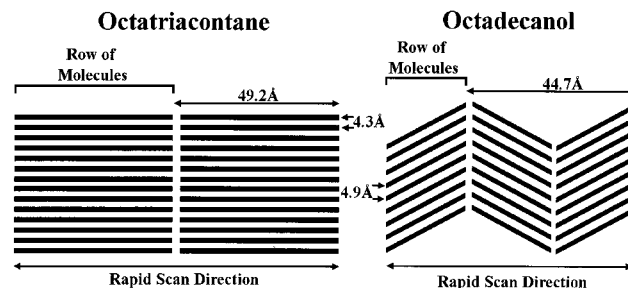
**Figure 4.** Plot showing the average number of domains per corral vs corral size for octadecanol. The solid line shows experimental data (100-Å constant-width moving window boxcar average). The dashed line shows expected values if the number of domains per unit area is constant and assuming that 200-Å diameter corrals contain only one domain.

fairly uniform sample, each corral may experience a different “local density” of nearby corrals. However, for most experiments there was, in general, an inverse correlation between corral size and corral density such that samples with small corrals generally had a fairly high corral density, while samples with large corrals generally had lower densities.

The above arguments fully explain the observed trend in ordering. Samples with small corrals usually have a high corral density, so domains both in corrals and on terraces would resist reorientation and better reflect the “intrinsic” random alignment. Samples with larger corrals usually have a lower corral density, so domains both in corrals and on terraces would be more easily reoriented by the tip and show a high degree of alignment.

When a corral contains an ordered monolayer that is rotated with respect to the monolayer on the surrounding terrace, the rotation can be in either direction, and we defined the rotation as  $+60^\circ$  if the corral domain was rotated clockwise from the terrace, and  $-60^\circ$  if the corral domain was rotated counter-clockwise from the terrace. Since the molecules and the alcohol and alkane monolayer structures are all achiral, the two possible rotations should be degenerate and occur in equal numbers. For octatriacontane, 78 rotated corrals were observed, with 31 oriented at  $+60^\circ$  and 47 oriented at  $-60^\circ$ . This is within the range of 27–51 corrals predicted for a random distribution (at a 99% confidence level).<sup>13</sup> However, for octadecanol, 330 rotated corrals were observed, with 202 oriented at  $+60^\circ$  and 128 oriented at  $-60^\circ$ . This is well outside the range of 141–189 corrals predicted for a random distribution (at a 99% confidence level). Although statistically significant, it seems very unlikely that this is a real effect, as it would imply a chiral effect arising from an achiral system. The data could be biased in some way related to the tip-induced ordering described above, but although this ordering could definitely bias a given image, some samples should be biased toward  $+60^\circ$  and others toward  $-60^\circ$ , so over the large number of samples observed the net effect should be negligible. This apparent preference for  $+60^\circ$  rotations suggests the existence of some additional bias in the data set which is still unexplained.

It is not entirely clear why the monolayer domains reorient as they do when scanned. For the alkane monolayer, the fact that the molecular rows (seen as bright bands in Figures 1 and 3) orient perpendicular to the rapid-scan direction can be rationalized by assuming a “combing” action by which the shear force of the scanning tip causes the molecular long axes to orient



**Figure 5.** Schematic showing structures of monolayers of octadecanol and octatriacontane on HOPG, showing the favored alignment relative to the rapid-scan direction (alignment relative to the rapid-scan direction is usually rotated somewhat from that shown, due to the constraints of epitaxy with substrate). For octatriacontane the molecules appear to align such that the molecular long axis is parallel to the rapid-scan direction. For octadecanol, the herringbone structure makes it impossible for all molecules to be parallel to the rapid-scan direction, but the alignment shown allows the average molecular long axis to be parallel to the rapid-scan direction. The unit cell values shown are those predicted for close-packed epitaxial monolayers. Experimental unit cell values were as follows. Octadecanol (25 measurements):  $44.3 \pm 4.7$  Å,  $4.7 \pm 0.4$  Å,  $89 \pm 12^\circ$ . Octatriacontane (32 measurements):  $45.5 \pm 4.0$  Å,  $4.1 \pm 0.2$  Å,  $90 \pm 8^\circ$ . Error bars are 1 standard deviation.

parallel to the rapid-scan direction. Since alkanes form structures with the molecules packed into rows in which the long axes of the molecules are oriented normal to the rows,<sup>3</sup> aligning the molecules parallel to the rapid-scan direction would cause the rows to form perpendicular to the rapid-scan direction, as was observed and as shown schematically in the left half of Figure 5. However, alcohols on graphite at room temperature form herringbone structures with the molecules tilted at  $\sim 60^\circ$  to the row direction and with alternate rows tilted in opposite directions.<sup>3</sup> For this structure, there is no way to orient the domains such that all the molecular long axes are parallel to the scan direction. An orientation as shown schematically in the right half Figure 5 is as close as can be obtained. Although rotation can make molecules in one type of row more closely parallel to the scan direction, it would necessarily make the molecules in the other type of row less parallel at the same time.

The fact that both alkane and alcohol monolayers reorient under the influence of the scanning tip, while 8CB does not, indicates that the net intermolecular forces in both the alkane and alcohol monolayers result in a weaker attraction than the net intermolecular forces in monolayers of 8CB, even though 8CB monolayers contain a considerable amount of internal strain.<sup>14</sup> This is not surprising in the case of the alkane, since alkane monolayers are held together by relatively weak van der Waals forces. However, in the alcohol monolayers each pair of rows is held together by a “zipperlike” arrangement of hydrogen bonds and thus might be expected to have a larger barrier to reorientation.

8CB, octadecanol, and octatriacontane all readily form ordered monolayers on graphite that can be easily observed by STM. However, the behavior of these monolayers varies greatly. Not only do octadecanol and octatriacontane reorient under influence of the scanning tip but they also form a large number of small domains while 8CB tends to form a few large monodomains (Figure 1). Domains of 8CB nucleate slowly, and corrals below 600 Å are rarely seen to be filled with an ordered monolayer at room temperature; larger corrals only order over many minutes or hours.<sup>7</sup> Also, even large corrals contain only one monolayer domain of 8CB. In contrast, with both octadecanol and octatriacontane, corrals smaller than 200 Å are observed to form an ordered monolayer within a few minutes (usually as soon as images can be obtained) and corrals

containing two or more domains are frequently seen. The large domains seen in 8CB indicate that domain growth is rapid compared to the nucleation rate, while the fact that ordered monolayers of 8CB form only slowly in small corrals indicates that the nucleation rate is slow. For octadecanol and octatriacontane, the growth rate and nucleation rate appear to be similar, as shown by the large numbers of domains observed. Observation of ordered alcohol and alkane monolayers in small corrals indicates a nucleation rate significantly faster than that of 8CB. Thus, we find that monolayers of 8CB on HOPG form with a slow nucleation rate and a relatively rapid growth rate, while monolayers of octadecanol and octatriacontane form with rapid nucleation rates and relatively slow or similar growth rates. A more quantitative measure of domain growth rates for octadecanol and octatriacontane could not be achieved at room temperature, since domain formation was typically complete by the time images could be obtained.

### Conclusions

These results present strong evidence that in the case of two organic molecules (octadecanol and octatriacontane) the scanning action of the STM tip orients the molecules, so the "intrinsic" molecular arrangement could not be observed, except in limiting form when the HOPG substrate had a high density of small corrals. The intrinsic structures of octadecanol and octatriacontane appeared to show the expected random orientations between domains in corrals and domains on the surrounding terraces. This implies that the presence of a domain on one side of a HOPG step has no effect on the growth of a domain on the other side of the step. That is, the bulk solution does not carry any information about orientation across the step. This is consistent with a lack of even short-range order in the solution, in contrast to the liquid crystal 8CB which has been

shown to carry orientation information across HOPG steps.<sup>8</sup> This difference between octadecanol or octatriacontane solution and 8CB shows that the ordering and orientation of an adsorbed monolayer are affected by the nature of the bulk material covering the monolayer.

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