

# Detecting Molecular Chirality by Scanning Tunneling Microscopy

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## Introduction

A highly interesting but challenging goal in the field of single-molecule detection by scanning probe microscopy (SPM) is the direct observation of molecular chirality. In this regard, to our knowledge the direct detection of chirality at individual tetrahedral stereocenters in organic molecules has yet to be achieved. Aside from obvious intrinsic interest in such a feat, development of techniques for reliable establishment of absolute configuration by SPM has potential practical implications as well.

An excellent system for probe microscopy of relatively complex organic "small" molecules involves imaging of liquid crystals (LCs) on graphite.<sup>1</sup> This approach has a long history in the scanning tunneling microscopy (STM) field, and is currently an active research area. In the LC on graphite system a small droplet of LC sample melted into the isotropic phase is applied to a freshly cleaved (0001) surface of highly oriented pyrolytic graphite. The STM tip is engaged while the substrate is held at a temperature where the organic thin film is liquid crystalline. Scanning sometimes produces images which are interpreted as deriving from a monolayer of molecules strongly physisorbed to the surface in a two-dimensional (2-D) crystal. This 2-D crystal, while composed of molecules which form liquid crystal phases, is NOT liquid crystalline. The bulk LC overlayer is apparently not directly observed in the experiment.

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These images are thought to result from a combination of topographical and electronic factors producing intramolecular contrast in the STM experiment. Conventional wisdom holds that the 2-D crystals are usually heteroepitaxial with the graphite substrate, the packing mode being dominated by the well-known relatively strong interaction of the  $\alpha$  hydrogens of all-anti aliphatic chains with the graphite. Furthermore, it is thought that primarily due to electronic factors aromatic rings appear bright in the STM experiment while aliphatic chains appear dark. More specifically, when imaging is done in constant current mode the tip-surface separation required to maintain constant current is apparently larger when the tip is over aromatic moieties than when the tip is over aliphatic molecular fragments.

While many LCs are chiral, the vast majority of LC/STM studies have involved achiral materials, in particular simple alkyl- and alkoxybenzophenyls. Our own work focuses on chiral smectic (i.e., layered) ferroelectric liquid crystals (FLCs),<sup>2</sup> where we have been exploring STM as part of an approach for understanding the FLC/solid surface interactions responsible for FLC alignment. In the course of this work many chiral FLC systems have been studied by STM, affording images of chiral molecules and chiral 2-D crystals at molecular, and in some cases near atomic, resolution. A discussion of some highlights of this work, focusing on stereochemical issues, follows.

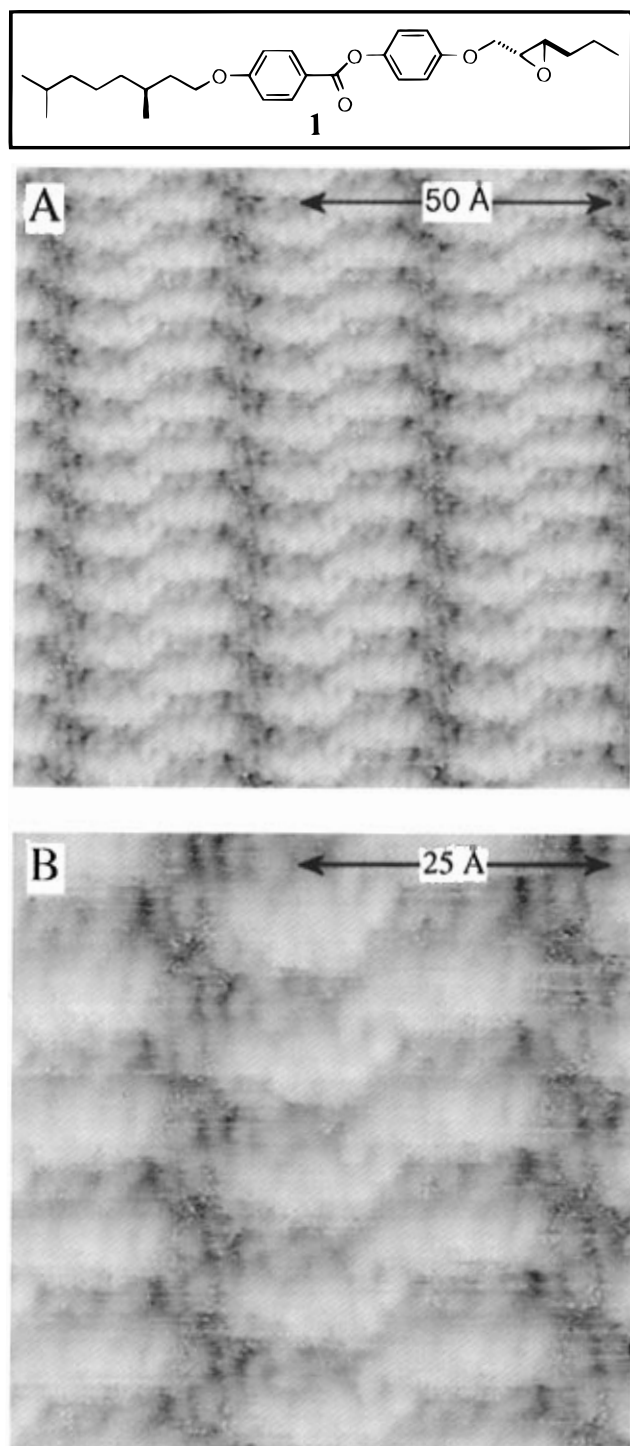
## Near Atomic Resolution Imaging of a Chiral Epoxide

During the course of early work aimed at obtaining fast-switching FLCs for electrooptic applications, many chiral epoxy ether phenylbenzoates were prepared.<sup>3</sup> The Sharpless epoxide 4-[(*R,R*)-(2,3-epoxyhexyl)oxy]phenyl 4-[(*S*)-(3,7-dimethyloctyl)oxy]benzoate (compound **1**, Figure 1), possessing three tetrahedral stereocenters and stable LC phases close to room

(1) (a) Smith, D. P. E.; Hörber, H.; Gerber, C.; Binnig, G. *Science* **1989**, *245*, 43–45. (b) Smith, D. P. E.; Hoerber, J. K. H.; Binnig, G.; Nejjoh, H. *Nature (London)* **1990**, *344*, 641–644.

(2) Walba, D. M. In *Ferroelectric Liquid Crystals: A Unique State of Matter*, in *Advances in the Synthesis and Reactivity of Solids*; Mallouk, T. E., Ed.; JAI Press Ltd.: Greenwich, CT, 1991; Vol. 1, pp 173–235.

(3) Walba, D. M.; Vohra, R. T.; Clark, N. A.; Handschy, M. A.; Xue, J.; Parmar, D. S.; Lagerwall, S. T.; Skarp, K. *J. Am. Chem. Soc.* **1986**, *108*, 7424–7425.

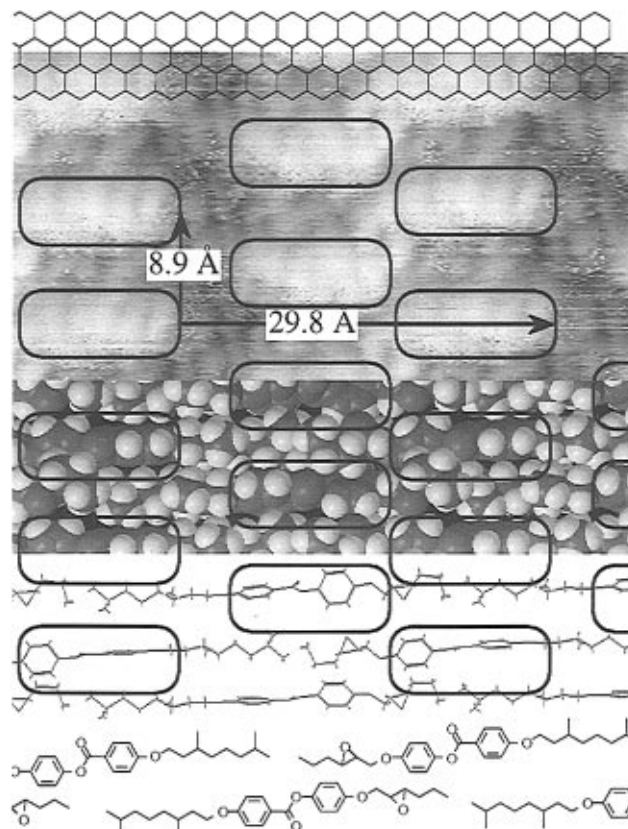


**Figure 1.** Structure of the FLC compound **1**, and two  $400 \times 400$  data point STM images of 2-D crystals grown from **1** on graphite. The scan size of the top image was 10 nm, and that for the bottom image was 5 nm.

temperature,<sup>4</sup> was chosen for investigation by STM specifically in order to attempt imaging of the chiral epoxide moiety. While obtaining molecular-resolution images of 2-D crystals grown from compound **1** on graphite was relatively rare, this material did provide one of the highest resolution imaging sessions reported to date for LC molecules.<sup>5</sup> Thus, of about 110 imaging sessions using samples of **1** or its enan-

(4) Liu, H. Y.; Huang, C. C.; Min, T.; Wand, M. D.; Walba, D. M.; Clark, N. A.; Bahr, C.; Heppke, G. *Phys. Rev. A* **1989**, *40*, 6759–6762.

(5) Walba, D. M.; Stevens, F.; Parks, D. C.; Clark, N. A.; Wand, M. D. *Science* **1995**, *267*, 1144–1147.



**Figure 2.** Proposed structure of the 2-D crystals shown in Figure 1. The figure shows, from bottom, structural formulas, framework and space-filling models, the STM image, and a fragment of graphite, all to scale according to the proposal.

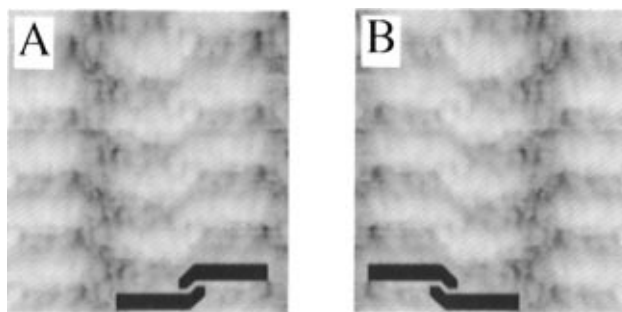
tiomer, only 37, or about one-third, of the sessions, produced images showing periodic structure on the 3 nm scale. What can subjectively be called molecular resolution was observed in 21 of these sessions, and clean near atomic resolution was observed in one session (a total of 17 images of extraordinary quality were collected during this session). We now think much of this variability is due to a reluctance on the part of compound **1** to form stable crystals (i.e., in the sessions where no images are obtained this is likely due to lack of robust 2-D crystals on the surface). Variability in the sessions producing molecular resolution seems most likely due to variability in tip structure.

Examples of images obtained from the highest resolution session are shown in Figures 1 and 2. Figure 1A shows a representative  $100 \times 100$  Å scan, while Figure 1B shows a  $50 \times 50$  Å scan. In our experience, obtaining intermolecular contrast at the latter scan size is extremely rare. The 2-D crystal is considered to be relatively flat; the observed image contrast is thought to be due to variations in tunneling efficiency through different parts of the molecules rather than topographical factors (see below). The image consists of bright columns separated by relatively dark regions. Within the columns clearly resolved individual bright features are organized in subcolumns. While the detail shown in this image was obtained only in the highest resolution session, the basic features of the image (bright columns and subcolumns) have been reproduced many times (scans of more representative resolution are shown below for the enantiomer of **1**).

Autocorrelation analysis of eight images obtained in the best session afforded a unit cell with axes measuring  $8.9 \pm 0.5$  and  $29.8 \pm 0.3$  Å at an angle of  $91^\circ \pm 3^\circ$ . These dimensions are consistent with graphite heteroepitaxy assuming a graphite lattice vector is oriented normal to the bright columns. On the basis of the LC STM conventional wisdom outlined above, a proposed interpretation of the observed image is presented in Figure 2. The image derives from a 2-D crystal strongly adsorbed at the LC/graphite interface. The molecules in the crystal are basically close-packed in the plane of the crystal, and the surface of the crystal is fairly flat; intramolecular contrast in tunneling efficiency is responsible for the observed image. The bright regions derive from the phenylbenzoate units in the 2-D crystal (outlined in Figure 2) while the dark regions are alkyl chains. More specifically, each bright region within a subcolumn is a single phenylbenzoate unit, the epoxide and alkyl tails extending horizontally on either side of the bright region. The bright columns are composed of molecule pairs rotated  $180^\circ$  about the axis normal to the surface and translated horizontally with respect to each other. Thus, phenylbenzoates within a subcolumn are oriented along their long axes in the same way, while the phenylbenzoates in the adjacent subcolumn within a bright column are rotated  $180^\circ$ . Relative to the graphite surface, all of the molecules in the crystal are oriented in the same way (i.e., all the molecules in the crystal are homomeric).

In order to test this basic structural motif, molecular modeling of a fragment of 2-D crystal on graphite was accomplished using a combination of molecular mechanics minimizations and dynamics using the Dreiding II force field in the POLYGRAF (Molecular Simulations, Inc.) molecular modeling program. While this force field does not provide good configurations for compound **1**, nor does it contain good intermolecular potentials for modeling the molecule/graphite interaction, the exercise does serve to show that the molecules can fit onto the graphite lattice as proposed. Space-filling and framework models of the calculated crystal structure are shown to scale with the STM image in Figure 2, with phenylbenzoate units outlined. Given at the bottom of the figure are structural formulas oriented according to the proposed structure and approximately to scale. Other possible 2-D crystal structures have also been examined computationally. In particular, a diastereomeric motif where each molecule in the crystal is rotated  $180^\circ$  about an axis passing through the geometrical center of the molecule and perpendicular to the surface also appears quite reasonable.<sup>5</sup> Experiments aimed at distinguishing between these possibilities are in progress.

While the details of electron tunneling in a system such as this are not well enough understood to state precisely the origins of the contrast observed in images, it seems likely that overlap of molecular orbitals of the adsorbate molecules with states in the graphite and the tip are involved.<sup>6</sup> Our current working hypothesis is that the graphite behaves like a uniform metal whose Fermi level is approximately halfway between the benzene HOMO and LUMO. When the surface is negative, overlap of unoccupied molecular orbitals (UMOs) on the molecules with the



**Figure 3.** Illustration that the images shown in Figure 1B are chiral in two dimensions. The image at left (A) shows a reduced version of the original 2-D crystal. On the right (B) is the same image reflected through a vertical plane normal to the page.

graphite-filled states increases the probability of finding an electron in the space between the surface and tip, thereby increasing the tunneling efficiency relative to vacuum. Overlap of unfilled states on the tip with occupied orbitals on the molecules may also enhance tunneling efficiency, though it seems reasonable that the molecules are closer to the graphite than to the tip during the experiment (especially when the tip is over a bright region), and thus perhaps the UMO overlap should be more important than occupied MO overlap in modulating the tunneling efficiency when the surface is negative.

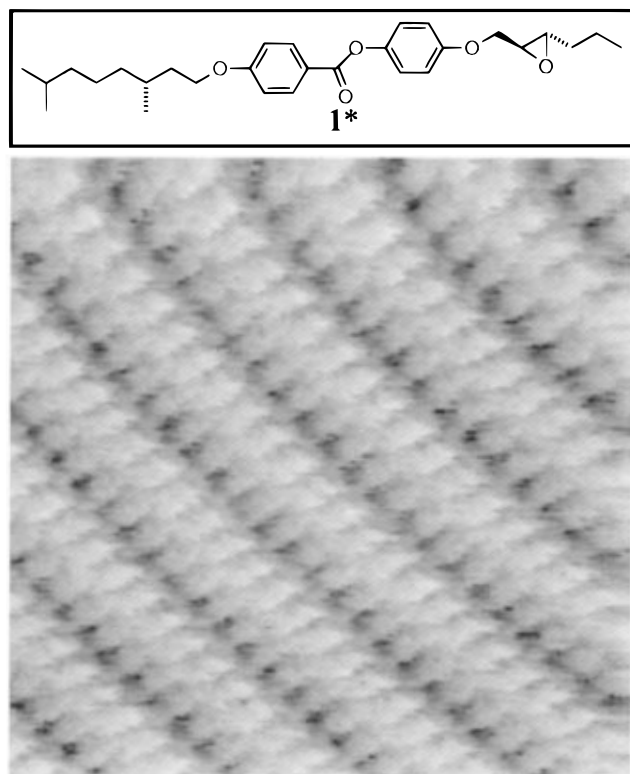
This overlap is enhanced when the local UMO levels are closer in energy to the graphite Fermi level, and is diminished when the UMOs are energetically farther from the graphite levels, thus accounting for the enhanced tunneling through aromatic rings relative to alkane tails. In the present case, analysis of the orbitals derived from the model crystal structure shown in Figure 2 suggests that a combination of HOMO and LUMO, a group of LUMOs, and a group of HOMOs all seem to explain the basic features of the observed images equally well.

### Chiral Images from Chiral Molecules

It is obvious from inspection of the high-resolution images of compound **1** shown in Figure 1 that they are chiral in two dimensions. That is, the 2-D image embedded in a plane cannot be superposed with its mirror image without removing the image from the plane. This is illustrated explicitly in Figure 3, where the image from Figure 1B is shown next to a version of the same image reflected through a vertical plane. It is not possible to superpose these images by rotation and translation in the plane of the page. More interestingly, according to our model the bright region deriving from each individual molecule is also chiral in two dimensions, with the "chiral part" corresponding spatially with the location of the chiral epoxide moiety! This is illustrated by the black objects shown in Figure 3, designed to capture the symmetry of the bright regions of the image as simply as possible. Note that each individual black object in the figure is chiral in two dimensions.

It seems reasonable that the chirality of the images obtained from compound **1** derives from the chirality of the molecules themselves. Since 2-D chirality in complex images is very easy to achieve, it might be argued that this observation is trivial (it might be argued that obtaining *achiral* images in 2-D is difficult). However, there is a simple test for whether

(6) Ou-Yang, H.; Marcus, R. A.; Källébring, B. *J. Chem. Phys.* **1994**, *100*, 7814–7824.

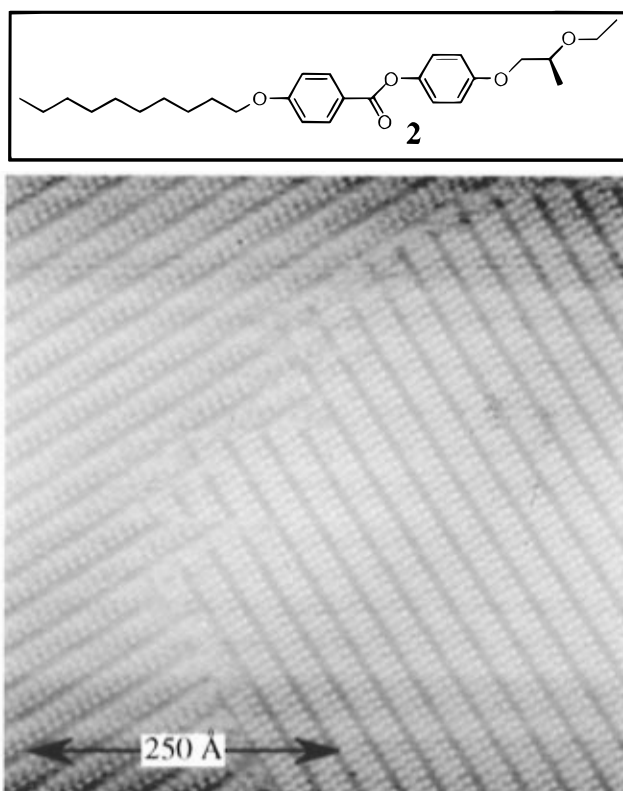


**Figure 4.** A representative molecular resolution image of **1\*** showing the same basic image features observable at higher resolution in Figure 1 for enantiomer **1**.

the chirality of the image derives directly from the chirality of the molecules, or from some imaging artifact or other effect; examine crystals deriving from the enantiomeric material, which should provide enantiomorphous (i.e., possessing nonsuperposable mirror-image morphology) images. In this regard many images of the enantiomer of compound **1** (designated **1\***) have been obtained, some at good molecular resolution.<sup>7</sup> One such image is shown in Figure 4. This image is representative of those typically obtained from scanning sessions with either **1** or **1\*** when molecular resolution has been achieved. And while the basic features of the image are the same as those obtained in the highest resolution session, the resolution is not high enough to allow determination of the handedness of the molecules. That is, images of **1\*** are not observably enantiomorphous with the high-resolution images of **1** shown in Figure 1. It is possible that the 2-D chirality of the images of Figure 1 is an artifact. It seems more likely, however, that in this particular system the chirality of the crystal is of such subtlety that very rare resolution is required to observe it.

#### Quasi-Enantiomorphous Images from a Single Enantiomer

STM study of films of the aliphatic ether-containing mesogen 4-[(*S*)-2-ethoxypropoxy]phenyl 4-(decyloxy)benzoate (**2**; Figure 5) on graphite afforded near atomic resolution images of two 2-D crystal domains which were observed to "anneal" on the minutes timescale.<sup>8</sup> One image from this session showing both



**Figure 5.** Annealing 2-D crystal domains grown from mesogen **2**.

domains is presented in Figure 5. Analysis of the basic features of this image shows the following. First, the image can be interpreted as showing two 2-D crystal domains with a "melted" domain wall separating them. Indeed, it is proposed that molecules exchanged locations during the acquisition of the image shown in Figure 5 (data taken on the up-scan). The image shows bright columns oriented at close to 90° in the two domains. On the basis of the measured sizes of the bright regions from images of **2**, it seems that the phenylbenzoate unit is bright while the rest of the molecule is dark, and further that the bright columns in both domains are again composed of pairs of molecules rotated by 180° and translated relative to each other.

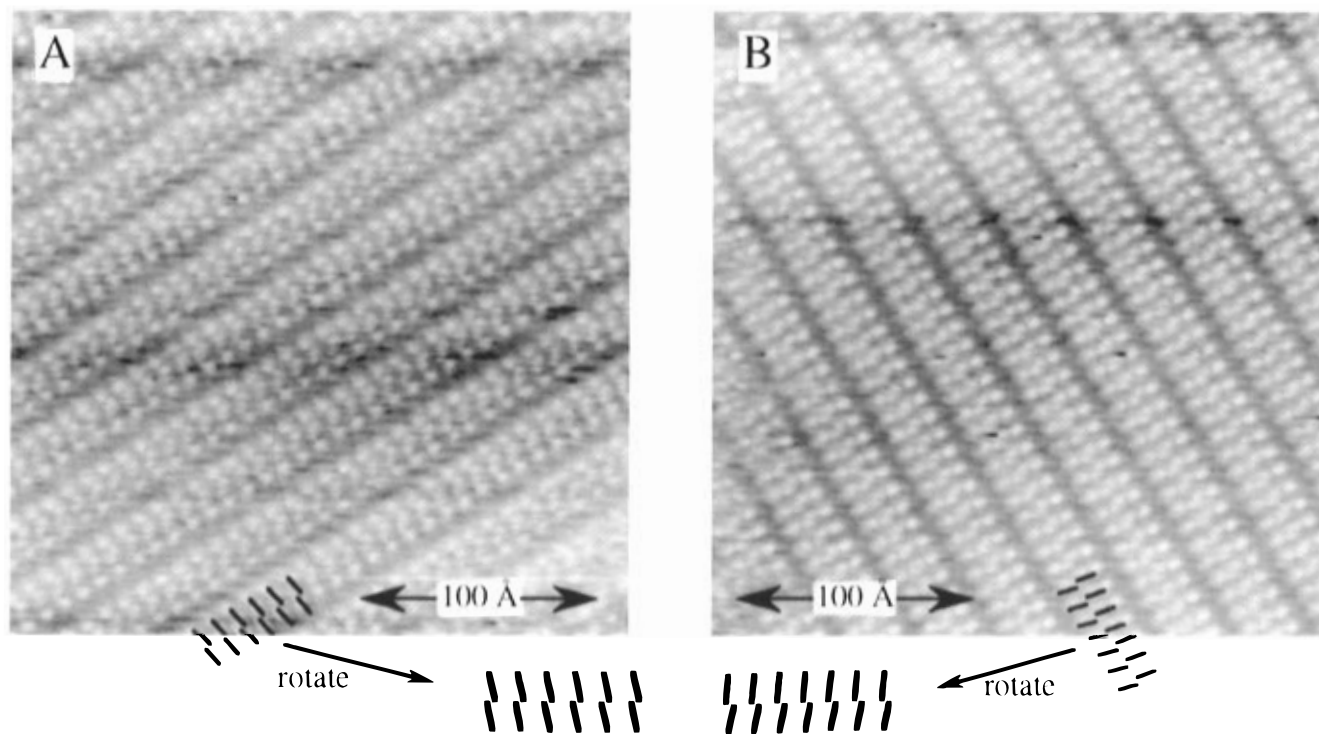
A more careful examination of these images, however, afforded a surprise: The seemingly isometric domains are in fact apparently heterochiral (i.e., chiral and of opposite handedness), as indicated in Figure 6. The images of the individual domains shown in Figure 6 were taken at higher resolution later in the session. As indicated in the figure, the domains are enantiomorphous not because the individual molecules appear chiral (in this case they do not), but due to the way the molecules are packed in the 2-D crystals.

This result seemed very surprising, since the two crystal domains cannot be truly enantiomeric because the molecules are present as only one enantiomer. Neither can the domains be homomeric (i.e., congruent), since homomeric structures could not produce truly enantiomorphous images (the enantiomorphous nature of the images could be an artifact). Thus, by symmetry the domains should in fact be diastereomeric.

The conclusion of this simple symmetry argument was proven independently by autocorrelation analysis

(7) Walba, D. M.; Stevens, F.; Dyer, D. *Enantiomer*, in press.

(8) Parks, D. C.; Clark, N. A.; Walba, D. M.; Beale, P. D. *Phys. Rev. Lett.* **1993**, *70*, 607.



**Figure 6.** Higher resolution scans of the domains shown in Figure 5. The enantiomorphous nature of the two domains is illustrated by the black rods superimposed on the figure.

of images of the two domains. This analysis showed that quantitatively the domains are very different. The domain labeled B in Figure 6 is shown to be a true 2-D crystal, with columns of molecules arranged in perfect rows. The domain labeled A in Figure 6, however, shows a novel structure where perfect 1-D crystalline columns are arranged in a "stacking-disordered" phase. In this quasi-crystalline domain adjacent columns are "slipped" relative to each other, and take up one of three possible positions. The distance of the slip is equal to one graphite lattice spacing, suggesting the 1-D crystals are all heteroepitaxial, and the slipping occurs along the graphite lattice. Using this assumption, the direction of the slip allows establishment of the orientation of the underlying graphite.

Analysis of the unit cell dimensions and angle, assuming the graphite is oriented as suggested above, and assuming heteroepitaxy, has provided a reasonable model for the structure of these two domains. The key point here is that the diastereomeric nature of the domains is fully consistent with the apparent heterochirality of the images, suggesting that the latter is not an artifact, but rather a result of the chirality of the actual 2-D crystals.

### Enantiomorphous Images from Enantiomers

From the standpoint of detection of 2-D crystal stereochemistry and its relationship to molecular structure, the direct and reliable observation of enantiomorphous images from enantiomers is an interesting goal in the tradition of Pasteur. As mentioned above, unfortunately this goal has so far proven unachievable in the chiral epoxide system due to the subtle nature of the 2-D chirality of the image. STM experiments with the enantiomers of the smectic mesogens 4''-[(1-methylheptyl)oxy]-3''-nitro-4'-biphe-

nyl-4-(5-*trans*-decenyloxy)benzoate (**S**-**3** and **R**-**3** (Figure 7), however, have recently afforded, for the first time to our knowledge, reproducibly enantiomorphous images from enantiomers.<sup>9</sup>

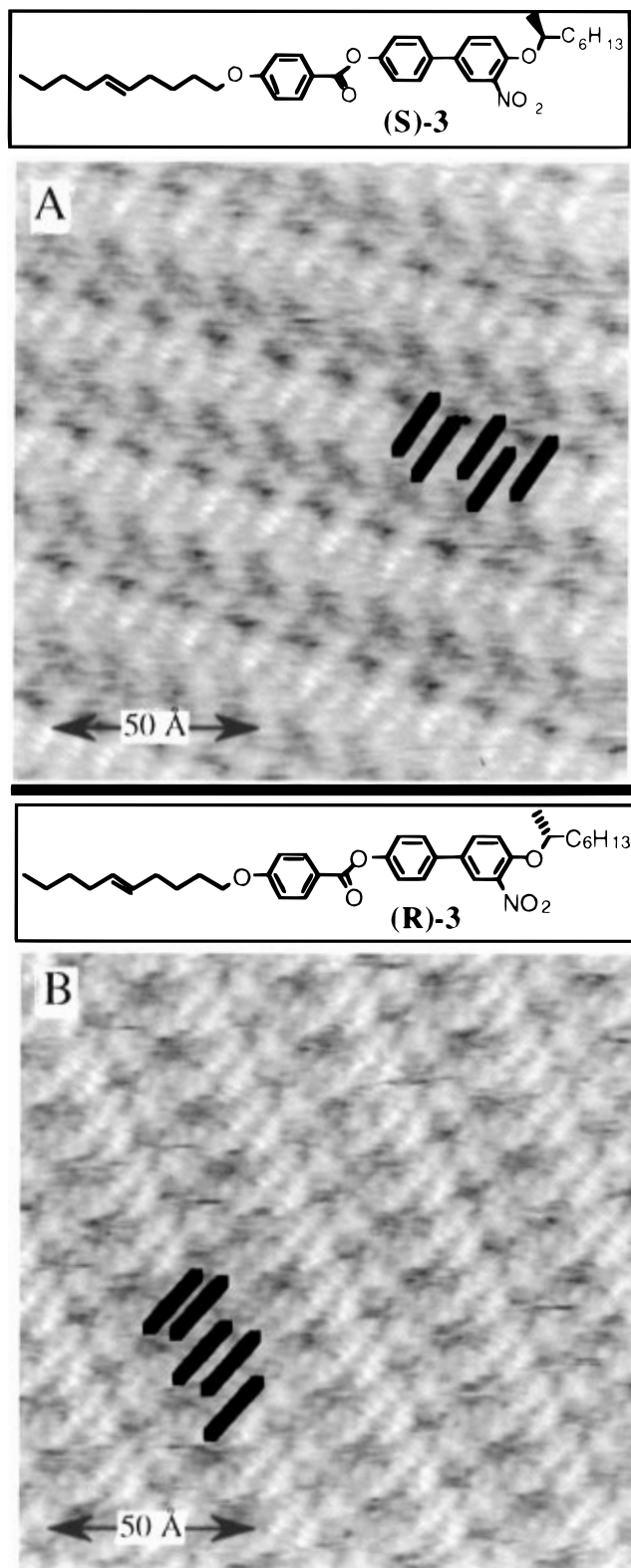
From the perspective of FLC STM, these materials are especially interesting for many reasons. Most importantly, during the course of this work it was discovered that many mesogens in this series produce 2-D crystals on graphite with extraordinary facility, with molecular resolution images obtained in virtually every session. This provided an ideal system for establishing the link between chirality of the 2-D crystal image and chirality of the molecules.

Thus, imaging experiments with (**S**-**3** and with (**R**-**3** were undertaken. As shown in Figure 7A, (**S**-**3** forms a 2-D crystal with bright columns composed of individual bright regions of the correct length to derive from the biphenylbenzoate aromatic unit. In the figure five of these bright regions are marked with black rods. Again it appears that the molecules are arranged in pairs, with the two molecules of each pair rotated about their short axis by 180° relative to each other. Neither the nitro group nor the double bonds are discernible. Unit cell analysis of many molecular resolution images shows that the unit cell for this 2-D crystal is achiral (the angle being 90° ± 2°).<sup>10</sup> However, the image is clearly chiral in two dimensions, as the biphenylbenzoates appear tilted clockwise with respect to the column normal by about 30°.

Since the chirality of this crystal is easily observed without requiring unusual resolution, this system seemed well suited for a search for enantiomorphous images from enantiomers. This proved to be the case. Taking image variability into account, the images

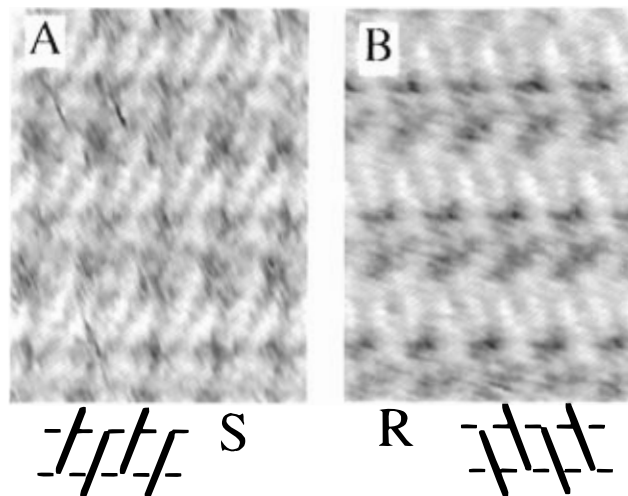
(9) Stevens, F.; Dyer, D. J.; Walba, D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 900–901.

(10) Stevens, F.; Walba, D. M.; Dyer, D. J. *Langmuir* **1996**, *12*, 436–440.



**Figure 7.** Molecular resolution images of enantiomers of biphenylbenzoate **3**.

obtained from (**R**)-**3** appear isometric to those obtained from (**S**)-**3**. One such image is shown in Figure 7B. While the images are similar to those obtained from (**S**)-**3**, the biphenylbenzoates are tilted counterclockwise in the images from the (**R**) enantiomer. This point is illustrated more clearly in Figure 8, where images from (**R**)-**3** and (**S**)-**3** are shown rotated such that the bright columns are horizontal (the column normal is vertical) and the biphenylbenzoate units are



**Figure 8.** Illustration of the heterochiral nature of the images from Figure 7. Image A is a portion of the image from Figure 7A, rotated such that the columns are horizontal. Image B shows a similarly oriented view of the image from Figure 7B.

rotated counterclockwise and clockwise from the column normal, respectively.

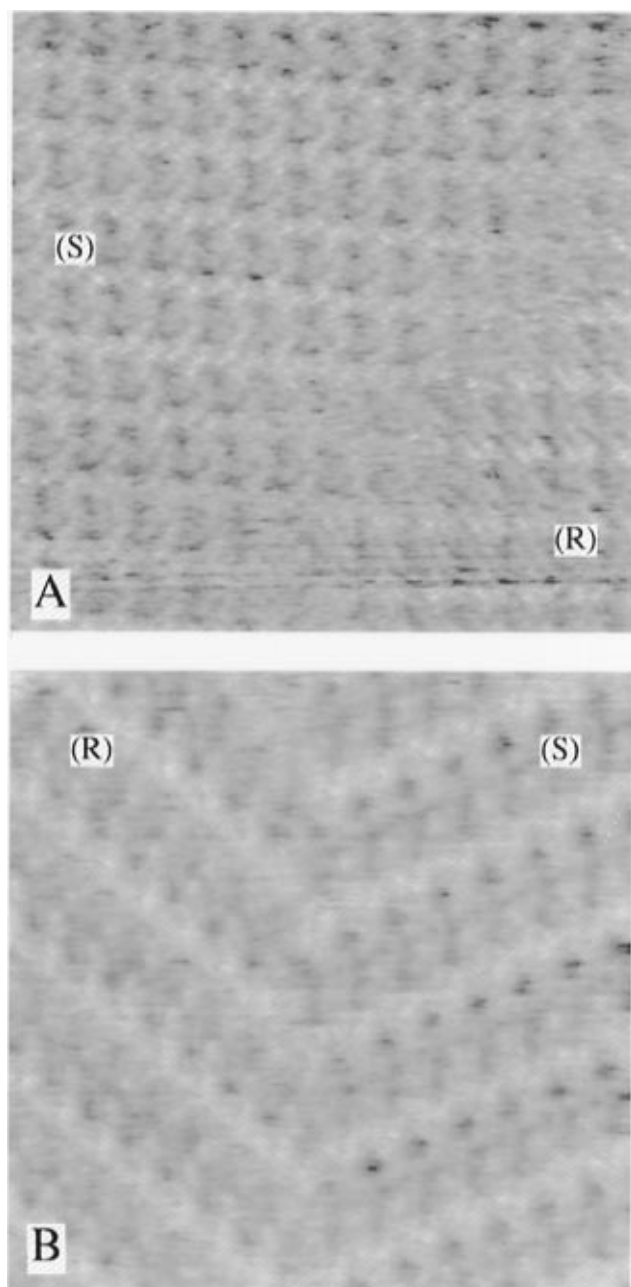
These observations proved highly reproducible. In all cases where monolayer chirality could be resolved, the handedness of the images was coupled to the configuration of the molecules. In nine separate sessions, (**S**)-**3** gave monolayer crystals providing images with clearly distinguishable chirality six times (the other three sessions produced images of such poor resolution that the chirality of the images could not be determined), while in six separate sessions (**R**)-**3** gave discernible chirality in each session (hundreds of images were observed in these sessions, and in no case was observable clockwise chirality associated with (**R**)-**3** or counterclockwise chirality associated with (**S**)-**3**). Thus, it can be stated with a high degree of certainty that molecular chirality is being transferred to a chiral supermolecular packing mode, which in turn gives rise to chiral images by STM. It can also be seen that the absolute configuration of a sample of this material can be established by STM, albeit empirically, by direct observation of several individual molecules packed in the 2-D crystal.

### Evidence for Formation of a 2-D Conglomerate

Growth of 2-D crystals on graphite from racemic **3** could give three possible results. First, racemic crystals (or even several different racemic structures), diastereomeric with the enantiomerically pure crystals shown in Figures 7 and 8, could result. Second, the material could spontaneously resolve into domains identical to those obtained from the enantiomerically pure material—2-D conglomerate formation. Finally, both of the above could be observed.

In fact, examination of many images from several sessions suggests that polymorphism does not occur with racemic **3**, and furthermore provides strong evidence for the formation of a 2-D conglomerate. The great majority of images obtained from racemic **3** were indistinguishable from those obtained from (**R**)- or (**S**)-**3**, with the important exception that half the images showed clockwise tilt and half showed counterclockwise tilt. In three imaging sessions, in a total of about





**Figure 9.** 2-D crystal domains grown from racemic **3**.

ten images, 2-D crystal domains separated by well-defined domain walls were observed within the STM field. While none of the images showing these domain walls were of the quality of the best images from either racemate or enantiomerically pure material, the heterochiral nature of the domains is clearly observable in several of these images.

Thus, in Figure 9A, a  $200 \text{ \AA} \times 200 \text{ \AA}$  scan of racemic **3** shows two domains separated by a relatively wide disordered domain wall. In this case the columns within the domains are approximately parallel, such that the biphenylbenzoate units must make a  $60^\circ$  angle with respect to each other. It is proposed that the latter causes the formation of a wide domain wall. In Figure 9B ( $200 \text{ \AA} \times 200 \text{ \AA}$ ) the bright rods are almost parallel, and the columns come together at about a  $112^\circ$  angle, with a very narrow domain wall separating the heterochiral domains.

Quantitative analysis of the best images from racemic **3** show that the images deriving from these crystals are indistinguishable (i.e., have identical unit cell dimensions and image morphology) from those derived from enantiomerically pure samples of **3**. It is possible that the enantiomorphous crystals grown from racemate are in fact racemic and diastereomeric with those from enantiomerically pure material, but are indistinguishable from the enantiomerically pure crystals by STM. This would require that (*R*) and (*S*) molecules within a putative racemic crystal be diastereomerically related, but could certainly occur. The much more likely interpretation, however, is that racemic **3** does form a 2-D conglomerate on graphite. While recently other evidence for the formation of 2-D conglomerates, by either scanning probe microscopy or grazing incidence X-ray diffraction, has been reported, we feel the results obtained with compound **3** present the strongest evidence to date for a 2-D conglomerate. Interestingly, since the unit cell is achiral, grazing incidence X-ray studies would not reveal the chiral nature of crystals deriving from either enantiomerically pure or racemic **3**.

## Conclusions

From this work it is clear that many chiral FLC materials form crystalline monolayers on graphite. Furthermore, in the course of these studies many interesting manifestations of molecular chirality have been observed directly at the molecular level.

While the goal of direct observation of molecular configuration at tetrahedral stereocenters by STM has not been attained, three cases of interesting manifestations of molecular chirality have been described. In one case, images attributed to individual molecules are seen to be chiral in 2-D. Unfortunately, unusually high resolution is required to observe the molecular chirality in this case, and enantiomorphous images from the enantiomeric molecules were not obtained. In a second system, enantiomerically pure molecules produced domains which appeared to be enantiomorphous. A simple symmetry argument shows these domains must be diastereomeric, and this was easily proved by quantitative analysis of the images. Finally, enantiomorphous domains from enantiomers were successfully obtained with good reproducibility in a third system. In this case, the images of individual molecules are achiral, but the crystal packing motif creates an STM image which is chiral in two dimensions. The racemate of this material forms a 2-D crystal structure indistinguishable from that of the pure enantiomers (but of both chiralities, of course), affording good evidence, but not absolute proof, that the material forms a 2-D conglomerate on graphite.

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