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J.K. Spong, L.J. Lacombe, M. M. Dovek, J.E. Frommer, J.S. Foster. Imaging of liquid crystals with tunneling microscopy. *Journal de Physique*, 1989, 50 (15), pp.2139-2146. <10.1051/jphys:0198900500150213900>. <jpa-00211049>

**HAL Id: jpa-00211049**

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Submitted on 4 Feb 2008

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HAL Authorization

Classification

Physics Abstracts

61.30B — 61.30G — 64.70M

## Imaging of liquid crystals with tunneling microscopy

J. K. Spong <sup>(1)</sup>, L. J. LaComb Jr <sup>(2)</sup>, M. M. Dovek <sup>(2)</sup>, J. E. Frommer <sup>(1)</sup>  
and J. S. Foster <sup>(1)</sup>

<sup>(1)</sup> IBM Research Division, Almaden Research Center, San Jose, CA 95120, U.S.A.

<sup>(2)</sup> Department of Applied Physics, Stanford University, Stanford, CA 94305, U.S.A.

*(Reçu le 21 février 1989, accepté le 25 avril 1989)*

**Résumé.** — Nous avons utilisé un microscope à effet tunnel (STM) pour visualiser une grande variété de molécules de cristaux liquides organiques adsorbées sur un substrat en graphique. D'après les images, on voit que le STM a la résolution correspondant aux molécules individuelles et aux divers groupes fonctionnels à l'intérieur des molécules. La haute résolution permet l'observation directe de détails par encore connus ou qui étaient seulement déduits à partir d'expériences de rayons X, neutrons, dilatométrie, etc... Dans ce travail, nous analysons les images de plusieurs exemples de molécules de cristaux liquides, mesurons leurs arrangement et angles de liaisons. On en déduit que les phases de cristal liquide apparaissant à la frontière du substrat ont un degré d'ordre et une stabilité supérieure à ceux de la phase massive. Cette phase en surface reste intacte, même après un réchauffement de 10 à 15 °C au-dessus de la température de transition isotrope de la phase massive.

**Abstract.** — We have used the scanning tunneling microscope (STM) to image a wide variety of organic liquid crystal molecules adsorbed onto a graphite substrate. From the images it is apparent that the STM is resolving individual liquid crystal molecules, as well as the different functional groups within the molecules. The high resolution allows direct observation of features that were not previously known, or had to be inferred from X-ray diffraction, neutron scattering, dilatometry, and other means. In this work, we image four diverse examples of liquid crystal molecules, and measure their packing arrangement and internal bond angles. We find that liquid crystal phases occur at the substrate boundary which have a higher degree of order and stability than the corresponding bulk phase. This surface phase remains intact even when heated 10-15 °C above the bulk isotropic transition temperature.

### 1. Introduction.

The scanning tunneling microscope (STM) operates by bringing a sharp electrode (« tip ») into close proximity to a flat conducting sample. If the tip-to-sample separation is sufficiently small ( $< 10 \text{ \AA}$ ) electrons can tunnel across the gap to the opposite electrode. The magnitude of the tunneling current depends sharply on the work function of the electrodes, and on the distance between them. The tunneling current can therefore reveal material or topographic

changes with very high spatial resolution. Images of a surface can be made by scanning the tip over the sample and measuring either the magnitude of the tunneling current (constant height mode), or the amount by which the tip must be retracted in order to keep the tunneling current constant (constant current mode).

The STM is now an established tool for the study of ordered metal and semiconductor surfaces on an atomic scale [1, 2]. However, its applicability to organic samples has been uncertain because most organic materials are insulating and many do not form well-ordered solid phases. In this work, we demonstrate the ability of the STM to image a variety of organic molecules with near-atomic resolution [3, 4]. The molecules are liquid crystals, characterized by their ability to self-assemble into one- and two-dimensionally ordered liquid phases [5]. When applied to the surface of graphite, liquid crystal molecules form an orderly molecular monolayer over the substrate that can be imaged with the STM. The high resolution of the technique allows direct observation of features that were previously unknown, or had to be inferred from X-ray diffraction, neutron scattering, dilatometry, and other means.

## 2. Experimental procedures.

The liquid crystal molecules studied are all crystalline solid at room temperature. Samples are prepared for the STM by applying several milligrams of the bulk solid to the surface of freshly-cleaved, highly oriented pyrolytic graphite (HOPG) mounted on a microscope stage. The stage is then heated to the temperature at which the particular liquid crystal forms a smectic phase in the bulk [6]. Liquid crystal molecules from the droplet become physisorbed to the graphite in large, well-ordered molecular arrays. The molecules are thereby immobilized with respect to the surface without being chemically bonded.

The tunneling tip is immersed in the droplet and brought to within tunneling range (5-10 Å) of the surface by means of an electronic feedback circuit. Although the conducting surface is now covered by non-conducting liquid crystal molecules, tunneling can still take place because the insulating barrier is only one monolayer thick. Because tunneling takes place under a drop of the pure liquid, the system is relatively free from contaminants and need not be evacuated. Imaging is done in the constant current mode, with + 0.8 V bias on the tip, and drawing 0.2 nA of tunneling current. Scanning in the  $x$ -direction is performed at about 1 kHz, and in the  $y$ -direction at about 2 Hz, allowing the real-time images to be viewed on a television and stored on magnetic tape by a video cassette recorder. The data are thereafter lightly filtered and unit-cell averaged [7].

The images are taken in the constant current mode, and show the individual liquid crystal molecules appearing bright on a featureless dark background. Since these molecules are non-conducting and are not chemically bound to the surface, the contrast mechanism whereby they are imaged by the STM is not obvious. In a recent work, we have proposed that the mechanism for imaging physisorbed species on a conducting surface is by detecting changes in the work function of the surface due to the adsorption of a molecule [4]. A polarizable adsorbate can lower the surface work function, thereby enhancing the tunneling current. The adsorbate would therefore appear bright on a dark background. Because different parts of the molecule possess different polarizabilities, this mechanism can even allow the resolution of internal molecular structures. Generally, aromatic portions of the molecule appear brighter than the aliphatic portions, because they are more polarizable.

Typically, several hours elapse before liquid crystal molecules are visible on the graphite substrate. This is presumably the time required for the molecules to orient and assemble on the surface. During this time, graphite is apparent in the images, with the carbon atoms arranged in a close-packed hexagon and adjacent atoms separated by 2.46 Å [2]. Formation

of the monolayer can be induced, however, by applying a 4 V, 500 ns voltage pulse to the tip. The function of the voltage pulse is not entirely understood, but it appears to nucleate the liquid crystalline order or attach the molecular sheet to the graphite surface. After the molecules become visible, graphite can no longer be seen through the adsorbed organic layer.

### 3. Results.

Figure 1a shows the molecular structure of the liquid crystal 5-nonyl-2-n-nonyloxyphenylpyrimidine, commercially known as PYP 909. The molecule has an aromatic core (phenylpyrimidine) disubstituted with an alkyl and an alkoxy side chain. Figure 2 shows an STM image of these molecules adsorbed on the surface of graphite at 50 °C. The dimensions of the scan are  $43 \times 52 \text{ \AA}$ . Individual liquid crystal molecules appear in the image as bright features on a dark background, lying down on the surface and arranged in rows. The rows often lie parallel to

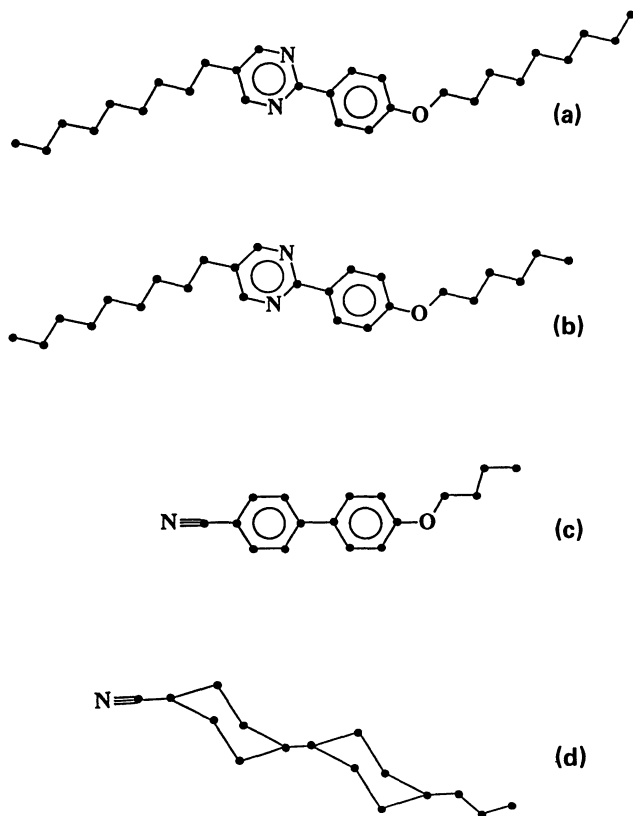


Fig. 1. — Ball-and-stick models of the molecular structure of the liquid crystal compounds studied. The solid dots represent carbon atoms ; oxygen and nitrogen locations are labelled O and N, respectively. a) 5-nonyl-2-n-nonyloxyphenylpyrimidine (PYP 909) : PYP 909 melts at 34 °C, undergoes a  $S_3$  to  $S_4$  transition at 61 °C, and becomes an isotropic liquid at 75 °C. b) 5-nonyl-2-n-hexyloxyphenylpyrimidine (PYP 906) : PYP 906 melts at 33 °C, undergoes a  $S_4$  to nematic transition at 71 °C, and becomes an isotropic liquid at 72 °C. c) 4-cyano-4'-n-butoxybiphenyl (M12 or 4OCB) : 4OCB has a crystalline to isotropic liquid transition temperature at 78 °C, and can be cooled into a  $S_A$  phase at 75.5 °C. d) 4-(4'-n-propylcyclohexyl)-cyanocyclohexane (CCH3) : CCH3 melts at 54 °C and clears at 80 °C. It also has a  $S_2$  to  $S_3$  at 44 °C, and  $S_3$  to  $S_4$  at 57 °C [6].

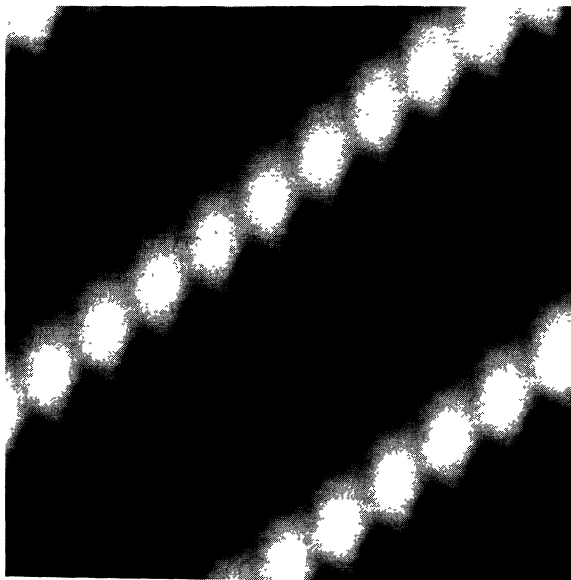


Fig. 2. — STM image of PYP 909 on graphite, taken at 50 °C. The scan dimensions are  $43 \times 52 \text{ \AA}$ . The graphite substrate, which is not visible through the monolayer of liquid crystal molecules, is a close-packed hexagonal array, with adjacent atoms separated by  $2.46 \text{ \AA}$  [2]. The rows of liquid crystal molecules often lie along one of the three principle axes of the graphite hexagon. The data in this image have been unit-cell averaged [8].

one of the principle axes of the underlying graphite hexagonal array. The bright oval areas correspond to the phenylpyrimidine cores from which the dimmer, aliphatic side chains extend. The corrugation depth between the cores and side chains is about  $1 \text{ \AA}$ . The molecules are spaced about  $6 \text{ \AA}$  apart, and are tilted at an average angle of  $75^\circ$ . This average angle consists of a  $60^\circ$  tilt of the phenylpyrimidine core from the row normal, and a  $90$  and  $75^\circ$  tilt of the side chains with respect to the row normal. The two different bond angles are presumably due to the R-O-C bond on one side and the R-C bond on the other side of the core. We note that all the molecules line up parallel to each other, despite the fact that this molecule possesses a permanent dipole moment along its axis [8]. The row width of the liquid crystalline array is  $25 \text{ \AA}$ , approximately  $7 \text{ \AA}$  shorter than the molecular length, indicating that the molecules are slightly overlapped. This overlap is just discernible in the image. We estimate that the uncertainty in these measurements at about  $\pm 10 \%$ , due to the resolution of the image and the calibration of the instrument.

5-nonyl-2-n-hexoxyphenylpyrimidine (PYP 906), shown in figure 1b, is similar to PYP 909 except that the alkoxy side chain is only six carbon atoms long. The STM image of PYP 906 adsorbed on the graphite substrate is shown in figure 3. Although this molecule is nearly identical to PYP 909, it forms a significantly more complicated structure. Adjacent molecules appear to be rotated  $180^\circ$  about their long axis, giving rise to an alternating row (bilayer) structure. The molecules are spaced within the rows every  $6 \text{ \AA}$ , and the row width is about  $23 \text{ \AA}$ . Bond angles are equivalent to those given by PYP 909. The reason for the increased complexity and packing density is unclear. It may be a result of graphite periodicity being enforced on the molecular arrangement, or it may be a function of the (odd-even) asymmetry of the side chains of this particular liquid crystal molecule.

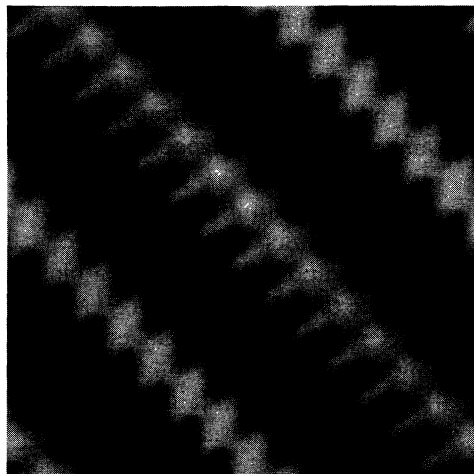


Fig. 3. — STM image of PYP 906 on graphite, taken at 50 °C. The scan dimensions are  $52 \times 52 \text{ \AA}$ .

The molecular structure of 4-cyano-4'-n-butoxybiphenyl, commercially known as M12 or 4OCB, is shown schematically in figure 1c. Cyanobiphenyl compounds are a major component in many liquid crystalline display devices. They are comprised of a biphenyl core, with a cyano « head » group, and an alkyl or alkoxy « tail » group. Much of their liquid crystalline behavior is determined by interactions between the very polar head groups of neighboring molecules. In fact, anomalous periodicities in the X-ray diffraction data of these compounds led to the proposal that many cyanobiphenyls form a bilayer in their liquid crystalline phases, by lying head-to-head and interdigitating their cyano head groups [9, 10]. The bilayer structure of the liquid crystal 4OCB is plainly confirmed in the STM image of these molecules on graphite, figure 4, taken at 80 °C. Rows of molecules are apparent in the

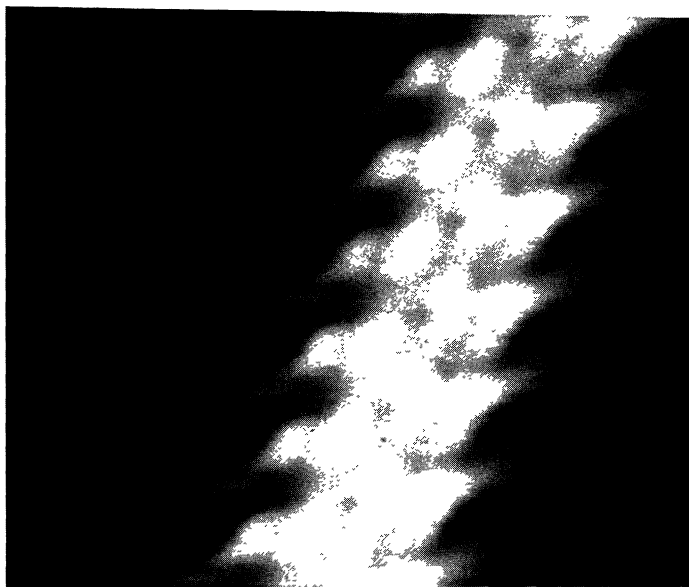


Fig. 4. — STM image of 4OCB on graphite, taken at 80 °C. The scan dimensions are  $30 \times 30 \text{ \AA}$ .

figure, however the row width, 24 Å, is much greater than the molecular length, about 17 Å. Within the row, adjacent molecules are spaced by 5 Å, and lie head-to-head with, and interdigitated with a set of opposing molecules. As was the case with PYP 909, the biphenyl head groups appear brighter than the aliphatic tail groups, and the corrugation depth is about 1 Å. The cores are tilted at an angle of 70° with respect to the row normal, and the tail groups are tilted by 40°.

The last example, shown schematically in figure 1d, is 4-(4'-n-propylcyclohexyl)-cyano-cyclohexane (CCH3). This molecule differs from the previous two in that it contains no oxygen or aromatic structures. It is composed instead, of a bicyclohexane core with a cyano head group and a short C<sub>3</sub>H<sub>7</sub> aliphatic tail. Figure 5 is an STM image of this material taken at 70 °C. It can be seen that this molecule also forms a bilayer, presumably due to its cyano head group. The intermolecular distance is 6 Å, and the bilayer width is 26 Å. The molecules are tilted 60° from the row normal. The hydrocarbon tail of this molecule is so short that it is no longer being resolved, and consequently no internal bond angle can be measured. Previously published values are available for this molecule, and give the molecular length as 16.5 Å and the molecular spacing as 5.7 Å [11]. This reference also gives the row spacing for the smectic B phase as 27.3 Å, confirming that the molecules form a bilayered phase in the bulk. This STM image of CCH3 has poorer resolution than the previous two, which we feel is a function of the molecule being imaged rather than the imaging conditions. We include it in order to demonstrate that no particular moiety is necessary to image these molecules ; it is only necessary that they be immobilized in a liquid crystalline matrix.

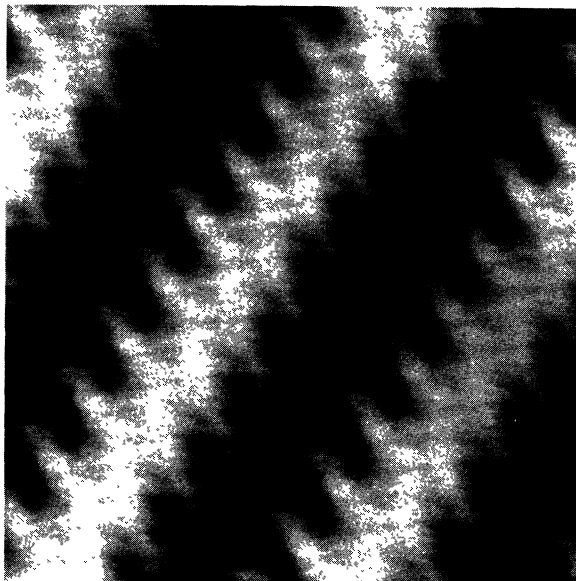


Fig. 5. — STM image of CCH3 on graphite, taken at 70 °C. The scan dimensions are 52 × 52 Å.

#### 4. Discussion.

The STM images of the three molecules have some common features that merit closer attention. In each case, molecules in one row are registered with adjacent molecules in the next row, resulting in two-dimensional order. In a bulk smectic phase, no registration

between the smectic layers occurs ; lack of order in this dimension is responsible for the liquid properties of smectic phases. The rows of molecules are also extremely orderly, and often lie along a principle axis of the underlying graphite lattice. The observed molecular orientations are repeated without defect or interruption for thousands of angstroms, the range of motion of the STM tip.

Furthermore, although each of the materials studied has several distinct bulk liquid crystalline phases in the temperature range 30-85 °C [6], no phase transitions were observed when heating the samples through this range. In fact, the molecular arrangements maintained their structure even at temperatures 10-15 °C above their bulk isotropic transition temperatures. At these temperatures, the liquid crystalline order can be perturbed by the presence of the STM tip. This effect is demonstrated in figures 6a-c. Figure 6a is an STM image of PYP 906, taken at 85 °C, 13° above the bulk isotropic transition temperature for this material. At these elevated temperatures, the image quality is poor, but the molecular rows are still apparent. In figure 6b, the tip is brought closer to the sample by increasing the tunneling current to 0.4 nÅ. As a result, molecular layer is disrupted and eventually destroyed (Fig. 6c).

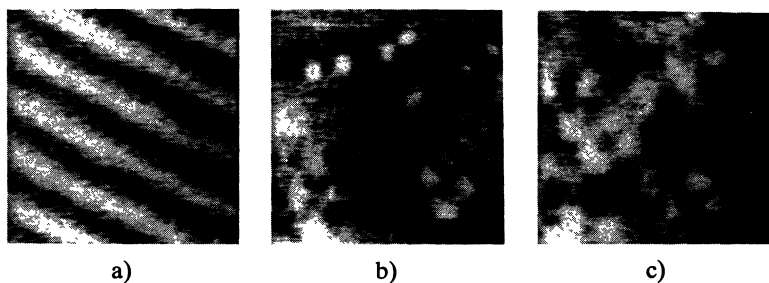


Fig. 6. — a) STM image of PYP 906 at 85 °C. b) and c) These images are taken seconds apart, and show the disruption of the liquid crystalline order that takes place when the STM tip is brought closer to the sample.

This process can be repeated by moving the tip laterally to a fresh spot on the surface where the liquid crystalline order is intact. When the tip is advanced toward the sample, the molecular array is again disrupted. Destruction of the liquid crystalline order by the STM tip, operating at these parameters, was only observed at temperatures well above the bulk isotropic transition temperature of each material.

These observations suggest a significant physisorption energy of the molecules to the graphite substrate. This substrate-adsorbate interaction results in a tightly bound surface layer with a higher degree of order than the corresponding bulk phase. Such highly ordered surface phases have been postulated to explain unexpected features in the X-ray reflection data of similar liquid crystal molecules [12]. The particular molecular arrangements observed here may be specific to the graphite substrate ; to date, efforts to image these materials on other surfaces, including gold, amorphous carbon, indium tin oxide (ITO) and polycrystalline graphite, have been unsuccessful.

## 5. Summary and conclusions.

Liquid crystal molecules deposited on a graphite substrate are demonstrated as an organic adsorbate system which can be imaged by the STM with near-atomic resolution. We have investigated the packing arrangements and surface interactions for four types of liquid crystal

molecules. In each case, a substantial substrate-adsorbate interaction results in the formation of a highly-ordered phase at the graphite surface. This phase is qualitatively different from the bulk phases of the materials, in terms of molecular packing, absence of phase transitions and elevated isotropic transition temperature.

Techniques described here are immediately applicable to a wide variety of liquid crystalline molecules commonly available. Their ability to form very large, highly-ordered assemblies over the graphite substrate make them useful in the study of two-dimensionally ordered systems, phase transitions, mixtures, and other phenomena on a molecular scale.

### Acknowledgments.

The authors gratefully acknowledge helpful discussions with F. Allen, E. Barrall, H. A. Mizes and C. F. Quate.

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