SCANNING TUNNELING MICROSCOPY STUDIES OF PHASE TRANSITIONS IN LIQUID CRYSTALS

Margarita Rivera Hernandez* and Mervyn J. Miles

H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL, United Kingdom

Abstract

The phase transitions of two different liquid crystal materials adsorbed on graphite were studied using scanning tunneling microscopy. From the dimensions, the periodicity and the symmetry of the observed structures at different temperatures, a strong relationship between the bulk phases and the adsorbed monolayer phases was found. In addition, this study shows that the transition temperatures of the adsorbed molecules in both transitions are the same as the transition temperatures in bulk.

Key Words: Scanning tunneling microscopy, liquid crystals, phase transitions, antiferroelectric, smectic, nematic, monolayer adsorption.

*Address for correspondence:
Margarita Rivera Hernandez
H.H. Wills Physics Laboratory
University of Bristol,
Tyndall Avenue
Bristol, BS8 1TL,
United Kingdom

Telephone Number: +44 (0)117 928 8707
FAX Number: +44 (0)117 925 5624
E-mail: phmr@siva.bris.ac.uk
or M.J.Miles@Bristol.ac.uk

Introduction

Investigations of the adsorption of organic molecules from solution onto graphite surfaces were underway before scanning tunneling microscopy was available (Everett and Findenegg, 1969). It was found that under appropriate conditions of temperature and solution concentration, the mass of alkane molecules adsorbed from solution was equivalent to that of a monolayer. Such monolayers adsorbed to the surface of highly-oriented pyrolytic graphite (HOPG) have been imaged by scanning tunneling microscopy (STM) (McGonigal et al., 1990). Predating this work, STM images of liquid-crystal molecules containing alkyl groups were reported. It was found by Frommer and coworkers (Foster and Frommer, 1988; Spong et al., 1989a,b) and by Smith et al. (1989) that under ambient conditions, adsorbed molecules of 4'-n-octyl-4-cyanobiphenyl (8CB) of the alkyl cyano-biphenyl family of molecules (mCB) formed ordered monolayers which could be imaged by STM on HOPG substrates. The degree of order was that of a 2 dimensional crystal rather than that of a liquid crystal. In the highest resolution images, it was possible to identify individual phenyl groups and the methylene repeat of the alkyl groups. The structure consisted of bright rows (phenyl groups) and less bright rows (alkyl groups), such that the molecules were arranged head-to-head, forming parallel bilayers in the plane of the substrate, a structure similar to, though more ordered than, the smectic, layered structure of the bulk. The adsorbed layer exhibited a repetitive jog in the structure along the rows, resulting in an eight-molecule unit cell for 8CB. Similar images were subsequently obtained by other groups in the field (McMaster et al., 1990, 1991; Mizutani et al., 1990; Nejoh, 1990; Shigeno et al., 1990; Shindo et al., 1990; Poulin and Kagan, 1991; for a review, see Frommer, 1992).

The adsorbed layer of 8CB on a molybdenum disulfide (MoS$_2$) substrate has been investigated extensively by Hara and coworkers beginning in 1990 (Hara et al., 1990). It was found that on this substrate, 8CB was arranged again in alternating bright and less bright rows, but that these rows had widths corresponding to a single molecule rather than the bilayer structure observed on HOPG. This structure, which the authors called a monolayer structure, consisted of neighbouring molecules, along the rows, pointing in opposite directions (the use of "monolayer" should not be confused

with the monolayer thickness of the adsorbed film). Energetically, this is an unfavourable molecule-molecule interaction, suggesting that the molecule-substrate interaction plays a more important role in MoS_2 than in HOPG, for which molecule-molecule interactions seem to be more important. Similar structures to those of 8CB on MoS_2 were observed for 7CB (which has only a nematic phase unlike 8CB, which has both a smectic and a nematic phase) on HOPG by Shigeno *et al.* (1990). These, and further studies by Hara and coworkers demonstrated that the monolayer structure can be associated with the nematic phase and the bilayer structure with the smectic phase (Iwakabe *et al.*, 1990, 1991, 1992, 1994). The relationship of the molecules to the HOPG and the MoS_2 lattices was investigated by Smith *et al.* (1992).

Besides the mCB family, several other liquid-crystal molecules have been imaged by STM (e.g., Matsushige *et al.*, 1993; Taki and Matsushige, 1994; Walba *et al.*, 1995) including molecules exhibiting an antiferroelectric phase (Hara *et al.*, 1991; Jandt *et al.*, 1995). STM images of the structure of adsorbed layers from a mixture of liquid-crystal molecules have shown a rich variety of molecular arrangements (Sautière *et al.*, 1992; Iwakabe *et al.*, 1994; Stevens *et al.*, 1996).

The relevance of these STM studies to the behaviour of the liquid crystals in bulk or on surfaces other than graphite and molybdenum disulphide (MoS_2) must be considered. In liquid-crystals displays, where these molecules have their practical application, the surface is usually a rubbed polyimide (PI). So far, STM images of liquid-crystal molecules on this surface have not been achieved. However, STM studies showing liquid-crystal alignment on Langmuir-Blodgett films of PI have been reported (Fang *et al.*, 1992, 1993).

In order to investigate further the relationship between the bulk structure and the adsorbed monolayers as observed by STM, the structure of the adsorbed monolayers on graphite, in the presence of the bulk, during phase transitions of the bulk liquid crystal have been examined. Two transitions have been studied: (i) the smectic-nematic (first-order) transition occurring in 8CB (Fig. 1) at about 33.5°C in the bulk, and (ii) the anti-ferroelectric-ferroelectric (second-order) transition for the liquid-crystal molecule shown in Figure 1 and occurring in the bulk at about 43°C. This is a second-order transition.

Experimental Method and Materials

The 4-n-alkyl-4'-cyano-biphenyl (8CB) liquid-crystal-material is commercially available from Merck (Poole, UK) and was used without further purification (Fig. 1). The phases and the transition temperatures of this molecule are as follows:

Crystal $\rightarrow$ Smectic A $\rightarrow$ Nematic $\rightarrow$ Isotropic Liquid
      21.5°C   33.5°C   40.5°C

The antiferroelectric liquid crystal (AFELC) 1-propylheptyl 4'-
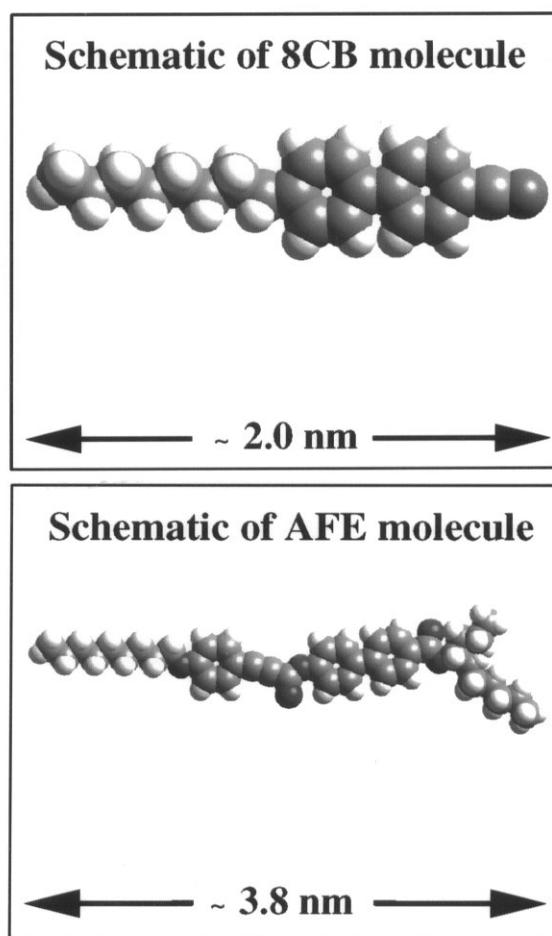

Figure 1. Molecular structure of the 4'-n-octyl-4-cyanobiphenyl (8CB) and the antiferroelectric liquid crystal {provided by DRA (Malvern, UK); produced by J. Goody and coworkers from the Chemistry Department, University of Hull, U.K.}.

(4-n-nonyloxyphenylpropioloyloxy) biphenyl-4-carboxylate (Fig. 1) was supplied by DRA (Malvern, UK) and produced by J. Goodby and coworkers at the University of Hull, UK. It exhibits the following phase behaviour:

Crystal $\rightarrow$ Smectic C_A^* $\rightarrow$ Smectic A $\rightarrow$ Isotropic Liquid
      40.0°C   43.0°C   63.0°C

The STM samples were prepared by placing a small amount of liquid-crystal material on a freshly-cleaved surface of highly oriented pyrolytic graphite (HOPG, Advance Ceramics, Cleveland, OH) mounted on a heating stage. In order to prevent temperature fluctuations, the STM head was enclosed, and the STM room was isolated. The temperature
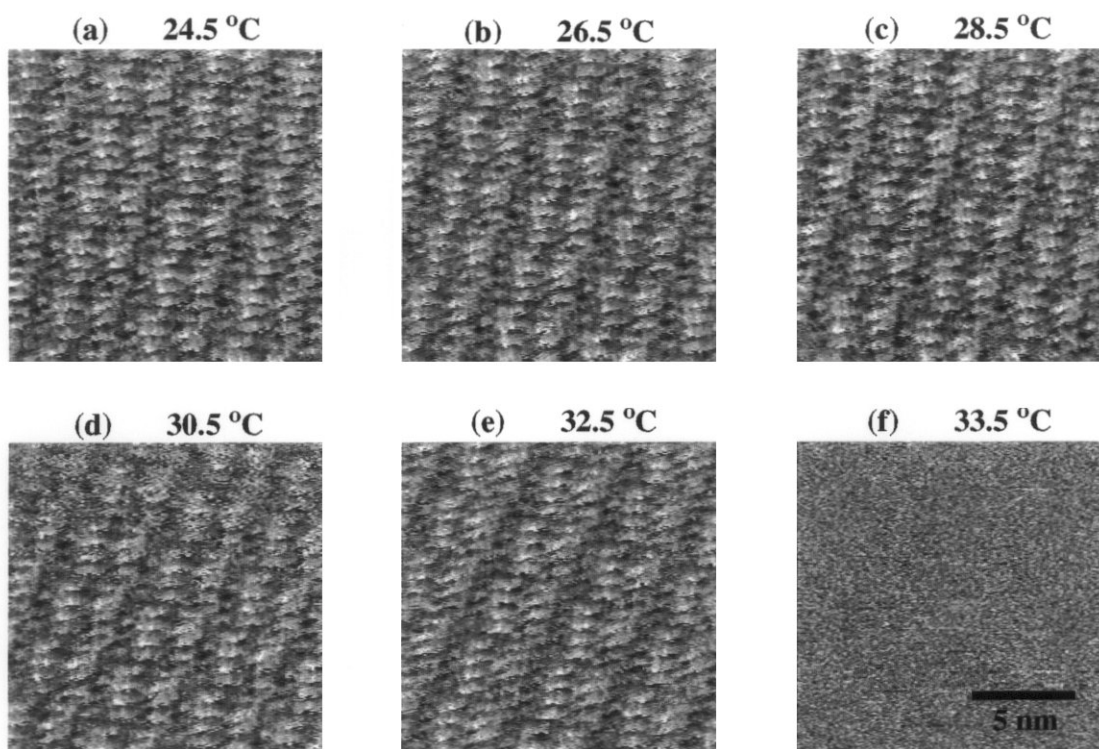
Figure 2. Scanning transmission micrographs of the molecular lattice of the 8CB at different temperatures. Images (**a**) to (**e**) show the typical double-row band structure of the Smectic phase. The noisy image (**f**) corresponds to the nematic phase. Scan parameters were 0.08 nA (aperture) and an accelerating voltage of 700 mV. The scan dimensions are 15 nm x 15 nm.

was measured using a thermocouple placed at the interface graphite-liquid crystal. With this configuration, changes in 0.1°C were easily detected. The sample was then heated up to temperatures at which it formed the isotropic phase. Once in the isotropic phase, the samples were allowed to cool down to the desired temperature. The experiments were carried out over a temperature range of 23°C to 50°C. The heating rate in both cases was approximately 0.1°C per minute.

Before the first scan, the sample was left to stabilise for 20 minutes. Once the temperature was stable, the alignment of the molecules remained the same during scanning for several hours. No obvious thermal effects were observed on the tunneling process as the temperature was increased.

The scanning tunneling microscope used was a commercial instrument supplied by W.A. Technology/Oxford Instruments (Cambridge, UK). Specimens were imaged in the constant-current mode using tungsten tips electrochemically etched in 1 M KOH. Tunneling conditions used were typically 0.01 to 0.2 nA and 600 to 1100 mV for current and accelerating voltage, respectively. All images were normalised and plane fitted.

Results and Discussion

Figure 2 shows a sequence of pictures of the 8CB sample at different temperatures. Images (a) to (e) show the typical double-row (bilayer) band structure of the smectic phase. The periodicity of the bands is 3.7 nm. At higher magnification, details of the phenyl groups and the alkyl chains can be observed in agreement with previous reports.

From this set of images, no change in the packing structure of the molecules is observed as the temperature increases from 24.5°C to 32.5°C. However, at 33.5°C, the ordered structure disappeared. For high resolution, the STM requires immobilisation of molecules on the time scale of the scan, that is, tens of seconds. As the image (f) does not show any regular structure, it suggests that at this temperature, the mobility of the molecules increased. Because of the lack of positional order, we can infer that it has undergone a transition to a more mobile phase. The image contains more noise than that expected for simply a HOPG surface, each pixel of the image being a time average of molecular motion between the tip and substrate during data collection time for that point.
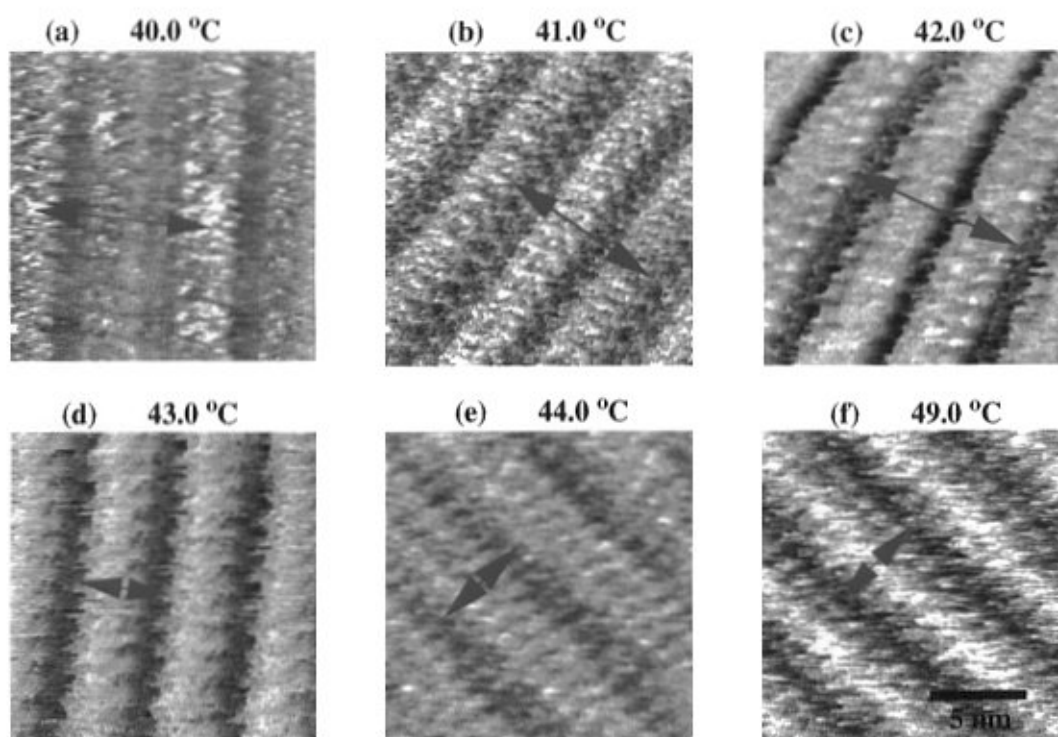
Figure 3. Scanning transmission micrographs of the AFELC sample at different temperatures. Images (**a**) to (**c**) correspond to the smectic C_A^*. The smectic A phase is present on images (**d**) to (**f**). The arrows indicate the periodicity of the bands at each temperature. Scan dimensions are 15 nm x 15 nm.

From the bulk phase diagram, we can associate this more mobile phase with the nematic phase in bulk. Also, a comparison of the transition temperature of the monolayer adsorbed on graphite with the transition temperature in bulk reveals that both occur around 33.5°C. These results show that for the 8CB molecule, the transition temperature of the interface molecular lattice is approximately the same as the bulk transition temperature. The fact that the layer at the interface undergoes a smectic-to-nematic-like transition is consistent with the observations of Iwakabe and Hara (1995), who found that the sequence of the phases found for the surface layer was the same as the sequences of the phases in the bulk. It is interesting to note that after the sample had undergone the transition into the nematic phase, and the temperature was decreased to 32.5°C and then to 30.5°C, the original smectic-like image did not return immediately. This may be due to the need for nucleation of this phase on the basal graphite lattice.

We also investigated an antiferroelectric-to-ferro-electric transition. Figure 3 presents a sequence of transmission electron micrographs of the AFELC at different temperatures. The images are composed of bright bands separated by dark regions. At 40°C, the bright bands present two different intensities arranged in an alternating way. Images at 41°C and 42°C present two different dark regions. Each one of them has a particular dimension and certain characteristic features within. The arrangement of these dark bands form an alternating pattern on the images. For these three temperatures, the identity period from the centre of one band to the next one with the same characteristics was found to be 6.9 nm. For temperatures between 43°C and 50°C, the image consists of one bright band followed of one dark band. The characteristics of the bands are the same for each region. At high magnification, some molecular details can be seen at 44°C. In this case, the orientation of the molecule appears perpendicular to the band direction. The periodicity of these bands was 3.8 nm. It is clear from the difference in the periodicity and characteristics of the bands that a change in the molecular packing occurred between 42°C and 43°C. From the alternation in brightness and the characteristics of the bands at the lower temperature, a packing structure similar to the smectic C antiferroelectric phase (Sm C_A^*) is indicated. In this phase, molecules with permanent electric dipoles aligned in adjacent

rows "pair" in opposite directions, forming a zigzag structure to cancel the dipole interaction. On the other hand, the molecular orientation at high temperatures suggests a structure similar to the smectic A phase where the molecules align parallel to each other perpendicular to the direction of the band. Again, a comparison of the phases and transition temperature between the adsorbed molecular lattice and the bulk suggests that the phases are not only similar in nature but also occur at a similar temperature.

The difference in the orientation of the bands for the AFELC material in Figure 3 can be understood in terms of drifting between domains in the sample as a result of thermal expansion or domains growing during heating.

The STM has produced images of different structures for the adsorbed monolayer depending on the temperature. The structures have similarities with the structures of the less ordered bulk phases of the materials for the same temperature. Transitions in the surface monolayer structures occur at similar temperatures to the bulk transitions for both types of transition in the two liquid crystal materials. This is different to the case of the alkanes adsorbed from solution where the ordered, adsorbed layer coexists with the bulk solution of random-coil molecules above it. The bulk and the surface-adsorbed layer are in different phases. It is likely that the alkyl groups of the liquid-crystal molecules are involved in the adsorption of these molecules to the graphite substrate. However, this ordered adsorbed layer appears to undergo the same type of transitions as the bulk.

Conclusions

The phase transitions of liquid-crystal molecules adsorbed on graphite were followed as a function of temperature. From observations on the images at different temperatures, a strong correlation between the bulk and the adsorbed monolayer phase diagram can be inferred. It is clear in each case, that not only are the characteristics of the phases are the same, but the transition temperatures are similar. This suggests that the information on the nature of the bulk somehow is propagated to the adsorbed layer.

Acknowledgements

References

Everett DH, Findenegg GH (1969) Nature **223**: 52.

Fang JY, Lu ZH, Ming GW, Ai ZM, Wei Y, Stroeve P (1992) Anchoring structure of liquid-crystal monolayers on polyimide Langmuir-Blodgett films observed by scanning tunneling microscopy. Phys Rev A **46**: 4963-4965.

Fang JY, Lu ZH, Wei Y (1993) Investigation of alignment mechanism of polyimide Langmuir-Blodgett films on liquid crystal. Mol Cryst Liq Cryst **225**: 107-111.

Foster JS, Frommer JE (1988) Imaging of liquid crystals using a tunneling microscope. Nature **333**: 542-545.

Frommer J (1992) Scanning tunneling microscopy and atomic force microscopy in organic chemistry. Angew Chem Int Ed Engl **31**: 1298-1328.

Hara M, Iwakabe Y, Tochigi K, Sasabe H, Garito AF, Yamada A (1990) Anchoring structure of smectic liquid-crystal layers on MoS2 observed by scanning tunneling microscopy. Nature **344**: 228-230.

Hara M, Umemoto T, Takezoe H, Garito AF, Sasabe H (1991) Novel quadruple zigzag structure of antiferro-electric liquid crystal molecules observed by scanning tunneling microscopy. Jap J Appl Phys (Part 2) **30**: L2052-L2054.

Iwakabe Y, Hara M (1995) Anchoring phase transition and bulk phase sequence of liquid crystals studied by scanning tunneling microscopy. Mol Cryst Liq Cryst **267**: 129.

Iwakabe Y, Hara M, Kondo K, Tochigi K, Muhoh A, Garito AF, Sasabe H, Yamada A (1990) Two types of anchoring structure in smectic liquid-crystal molecules. Jap J Appl Phys (Part 2) **29**: L2243-L2246.

Iwakabe Y, Hara M, Kondo K, Tochigi K, Muhoh A, Yamada A, Garito AF, Sasabe H (1991) Correlation between bulk orderings and anchoring structures of liquid crystals studied by scanning tunneling microscopy. Jap J Appl Phys (Part 1) **30**: 2542-2546.

Iwakabe Y, Hara M, Kondo K, Ohhara S, Muhoh A, Sasabe H (1992) Anchoring structure of binary mixtures of liquid crystals studied by scanning tunneling microscopy. Jap J Appl Phys (Part 2) **31**: L1771-L1774.

Iwakabe Y, Kondo K, Ohhara S, Muhoh A, Hara M, Sasabe H, (1994) Anchoring phase of liquid crystal mixtures studied by scanning tunneling microscopy. Langmuir **10**: 3201-3206.

Jandt KD, Tixier S, Towler MJ, Blackmore JM, Miles MJ (1995) Observation of phase transitions in an anti-ferroelectric liquid crystal investigated by scanning tunneling microscopy. J Appl Phys **77**: 122-126.

Matsushige K, Taki S, Okabe H, Takebayashi Y, Hayashi K, Yoshida Y, Horiuchi T, Hara K, Takehara K, Isomura K, Taniguchi H (1993) Scanning tunneling microscope observation of a polar liquid crystal and its computer simulation. Jap J Appl Phys (Part 1) **32**: 1716-1721.

McGonigal GC, Bernhardt RH, Thomson DJ (1990) Imaging alkane layers at the liquid graphite interface with the scanning tunneling microscope. Appl Phys Lett **57**: 28-30.

McMaster TJ, Carr H, Miles MJ, Cairns P, Morris VJ (1990) Adsorption of liquid crystals imaged using scanning tunneling microscopy. J Vac Sci Technol **8**: 672-674.

McMaster TJ, Carr H, Miles MJ, Cairns P, Morris VJ (1991) Scanning tunneling microscopy images of the surface ordering of the liquid crystal 4-n-octyl-4'-cyanobiphenyl. Liquid Crystals **9**: 11-18.

Mizutani W, Shigeno M, Ono M, Kajimura K (1990) Voltage-dependent scanning tunneling microscopy images of liquid crystals on graphite. Appl Phys Lett **56**: 1874-1976.

Nejoh H (1990) Visible mechanism of liquid crystals on graphite under scanning tunneling microscopy. Appl Phys Lett **57**: 2907-2090.

Poulin JC, Kagan HB (1991) Simultaneous observation of a liquid crystal, 8CB, and of its substrate by scanning tunneling microscopy. C R Acad Sci Ser II **313**: 1533-1538.

Sautière L, Day S, Miles MJ (1992) Smectic structures in a 2-component liquid-crystal mixture. Ultra-microscopy **42**: 1054-1058.

Shigeno M, Mizutani W, Suginoya M, Ohmi M, Kajimura K, Ono M, (1990) Observation of liquid crystals on graphite by scanning tunneling microscopy. Jap J Appl Phys (Part 2) **29**: L119-L122.

Shindo H, Kaise M, Kawabata Y, Nishihara C, Nozoye H, Yoshio K (1990) Surface structures of a ferro-electric liquid crystal on graphite observed by scanning tunneling microscopy. J Chem Soc - Chem Comm **23**: 760-762.

Smith DE, Hörber JH, Gerber C, Binnig G (1989) Smectic liquid-crystal monolayers on graphite observed by scanning tunneling microscopy. Science **245**: 43-45.

Smith DE, Heckl WM, Klagges HA (1992) Ordering of alkylcyanobiphenyl molecules at MoS2 and graphite surfaces studied by tunneling microscopy. Surface Science **278**: 166-174.

Spong J, LaComb L, Dovek M, Frommer J, Foster J (1989a) Imaging of liquid crystals with tunneling microscopy. J Phys **50**: 2139-2146.

Spong JK, Mizes HA, LaComb LJ, Dovek MM, Frommer JE, Foster JS (1989b) Contrast mechanism for resolving organic molecules with tunneling microscopy. Nature **338**: 137-139.

Stevens F, Dyer DJ, Walba DM (1996) Formation of 2-dimensional mixed crystals on graphite observed by scanning tunneling microscopy. Langmuir **12**: 436-440.

Taki S, Matsushige K (1994) Scanning tunneling microscope observations of aggregation structures in polar organic molecules. Jap J Appl Phys (Part 1) **33**: 3715-3719.

Walba DM, Stevens F, Parks DC, Clark NA, Wand MD (1995) Near-atomic resolution imaging of ferro-electric liquid-crystal molecules on graphite by STM. Science **267**: 1144-1147.

Discussion with Reviewers

K. Matsushige: Does the fact that the phase transition point of the sample is the same as that in the bulk suggest that the intermolecular interaction is the governing factor for the phase transition process, and the interaction between the adsorbed molecules and graphite substrate is rather weak?

Authors: Yes, we believe that in the case of complex molecules like the 8CB and the antiferroelectric one, the molecule-molecule interaction plays the important role in the transition process when graphite is used as a substrate. In fact, we found a different behavior for the transition temperature when a substrate other than graphite is used in the experiment.

H.J.K. Hörber: The result that the transition temperatures are very similar for the adsorbed layers on the surface compared to the bulk is really astonishing considering the behaviour of alkanes, where the bulk and the adsorbed layer coexist in different phases. In this context, I do not understand one of the statements at the end of the section **Results and Discussion**, namely, that the alkyl groups are involved in the adsorption of the liquid crystal molecules. Is this a stronger interaction than that of the alkane part? If this is true, I would have difficulty justifying why molecules interacting more strongly with the surface show no influence in the phase transitions, while molecules interacting more weakly show a strong influence.

Authors: The phenyl groups will, of course, also play a role in the adsorption of the molecules to the HOPG substrate. However, the observations might be misunderstood if the intermolecular interaction is increased by the phenyl groups, which cannot be the case for alkanes.

Reviewer III: It was noted in the paper that the recovery of the smectic phase in the 8CB did not occur immediately upon cooling down through the transition temperature. How long did it take? Was any induction/nucleation period observed when heating up through the transition temperature?

Authors: In order to recover the smectic phase on cooling down once the sample was in the isotropic phase, it was necessary to wait more than half an hour. We did not observe any induction/nucleation during heating.

J. Frommer: A brief "ruler" comparison of images (a) and (e) of Figure 1 appears to indicate a less close packing in (e) than in (a), at least in the direction parallel to the row direction. Please check this, since it is concluded that there is no change.

Authors: The orientation of the 8CB molecules, as we mentioned, remains the same during the heating process in the smectic A phase. The difference in the density of the packing structure can be understood in terms of the mobility of the molecules. As the temperature increases, the system approaches the isotropic phase, and the thermal excitation of

the molecules increases, causing less close packing. We found
a decrease of 4% in the number of molecules per unit area
between images (a) and (e).