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PRELIMINARY COMMUNICATION

Scanning tunnelling microscopic study of the interfacial order in a ferroelectric liquid crystal

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We present scanning tunnelling microscopy images of a ferroelectric liquid crystal in its chiral smectic C phase. These images show evidence of pronounced interaction between the adjacent lateral dipoles located near the chiral centres of neighbouring molecules. The two dimensional structure at the graphite–liquid crystal interface is found to be highly ordered. Features of this crystal-like order are the pronounced dimer arrangement within a layer and a kinked conformation in which the aromatic core is tilted with respect to the chains. The core axis is tilted at 30° with respect to the layer normal in the plane of the interface. This tilt is very similar to the tilt angle of the bulk material.

Understanding the mechanism responsible for the alignment of the rod-like molecules of liquid crystals on a solid substrate is of considerable importance. Not only will this enhance the fundamental understanding of the surface interactions for liquid crystals but it is also crucial for the performance of display devices. Scanning tunnelling microscopy (STM) permits the direct observation of the interfacial structure with molecular resolution.

There have been several STM studies of liquid crystals on graphite and molybdenum disulphide substrates [1–9]. In particular, Iwakabe *et al.* [9] have recently investigated the interfacial order of a series of *n*-alkylcyanobiphenyls (7CB–12CB) on MoS_2. For liquid crystals exhibiting a bulk nematic phase at room temperature (7CB–9CB), they observed a pronounced positional order at the MoS_2/liquid crystal interface, a feature of this interfacial order being the strong interdigitation reminiscent of that observed for the bulk. Similarly, for liquid crystals exhibiting a bulk smectic A phase at room temperature (10CB and 12CB), they observed a two dimensional structure at the MoS_2/liquid crystal interface which is similar to the bilayer packing seen in the bulk smectic A phase of the same materials. The substrate itself was also found to play a role in the surface order of these liquid crystals. For example, different surface structures have been observed for 8CB on graphite and on MoS_2[6–8]. While 8CB forms a fully interdigitated monolayer type

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structure on MoS_2, it has been observed to form both a monolayer and a bilayer structure on the surface of graphite. In addition, commensurate ordering of the aliphatic chains with the lattice vectors of both graphite and MoS_2 has been observed. This commensurate ordering is also seen with long chain alkanes on graphite [10].

Obviously it is important to consider carefully the contribution of the substrate to the interfacial ordering. The surface structure involves a balance between the forces driving the bulk order, such as dipole interaction and molecular shape, and the forces which arise during interaction of the liquid crystal molecules with the substrate. Careful analysis, however, can tell us which inter- and intra-molecular forces are the strongest at the liquid crystal/substrate interface. This, in turn, may lead to a better understanding of which forces lead to order in the bulk structure.

In this paper, we present an STM image of a ferroelectric liquid crystal in its chiral smectic C phase. The image shows distinct two dimensional order. Features of this surface structure include a pronounced dimer arrangement of the liquid crystal molecules in a kinked conformation and a tilt angle of the core with respect to the layer normal which is quantitatively similar to that seen for the bulk chiral smectic C phase. We investigate a possible correlation between the observed surface structure and the bulk ordering.

The liquid crystal studied is 4-((2-ethoxy)propyloxy)phenyl 4-decyloxybenzoate or W7 [11] which exhibits smectic A, chiral smectic C, and chiral smectic G phases. The W7 molecule consists of three sections, as shown in figure 1. The long and short alkyl chains create non-polar regions at both ends of the molecule. The short alkyl chain also contains the molecule's chiral centre which gives rise to the ferroelectric behaviour [12]. The aromatic core contains the phenyl benzoate moiety. The major contribution to the central transverse dipole originates from the carbonyl group. Smaller transverse dipoles arise from the ether linkages in the alkyl chains. Although the resulting dipole along the long molecular axis is small this should lead to a near neighbour antiparallel

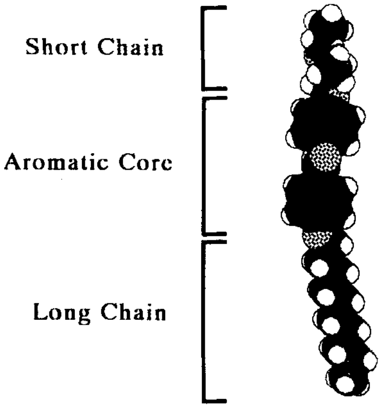

Figure 1. The structure of the W7 molecule. The conformation shown, with coplanar phenyl rings and the carbonyl bond extending perpendicular to that plane, is one of two lowest energy conformations obtained by MNDO calculations. In the second minimum energy conformation (not shown here) one of the phenyl rings is rotated by 90° so as to be perpendicular to the surface. The coplanar conformation may be favoured by increased interaction with the substrate. These geometry optimizations were carried out on various initial conformations of an isolated W7 molecule.

correlation of the longitudinal dipoles. Samples were prepared by placing a drop of W7 dissolved in chloroform upon freshly cleaved, highly oriented pyrolytic graphite. Following evaporation of the solvent, the sample was heated to the isotropic phase (50°C) and then allowed to cool slowly to room temperature at which the bulk compound has a chiral smectic C phase. Graphite was chosen as the substrate in order to exploit the unique alkyl chain–graphite interaction (i.e. the close match between the graphite lattice spacing and the spacing between alternate alkyl carbons allows the chains to close pack as they would in the bulk) [10]. Scans were taken at room temperature (22°C) using a STM built at the Naval Research Laboratory. Images were collected in constant current mode with a tunnelling current of 0·1 to 1·0 nA and a tip bias of +0·8 to +1·0 V.

The STM image of W7 on graphite is shown in figure 2(*a*) and a model of the proposed packing structure is shown in figure 2 (*b*). The brightness of each pixel in the image corresponds to the displacement of the tunnelling tip away from the surface during scanning. The bright to dark corrugation corresponds to a height variation of approximately 0·1 nm. Data processing included Fourier filtering and a correction to account for sample tilt. The image is filtered by identifying the strongest peak in the power spectrum and removing all peaks in both the real and imaginery parts with intensities less than 0·01 per cent of the strongest peak. The inverse transform was then calculated.

The STM image reveals a well-ordered, two dimensional structure extending over hundreds of nanometers. The bright band in the STM image has been assigned as the location of the aromatic cores of two opposing molecules. The individual phenyl rings are resolved within this bright band although atomic detail is not seen. The dark bands are assigned to the location of the long alkyl chains. We believe that the long alkyl chains lie along the graphite lattice vector and are extended in an all-*trans* configuration as they are in the crystalline form. This has been observed previously with other alkyl containing liquid crystals and long chain alkanes [1–10]. The width of the bilayer, 5 nm or 1·6 times the molecular length, requires the chains to be fully interdigitated. Little intermolecular interaction between phenyl groups is expected since the cores of neighbouring molecules are separated by 1 nm, the distance required to close pack three alkyl tails. Bond angle considerations require the alkyl chains to form an angle of about 105° with the aromatic core as can be seen in figure 2. From the diameter of the phenyl rings, measured in the cross-sectional profile, both rings must lie almost flat upon the graphite surface. Based on steric considerations and the fact that the large transverse dipole originating at the carbonyl group might be expected to align with the external field of the STM, the carbonyl group is most likely oriented perpendicular to the surface.

To examine the conformation of the aromatic core, the minimum energy conformation for an isolated W7 molecule was calculated using the MNDO program (minimum neglect of differentiating overlap) [13]. The conformation in which both phenyl rings lie within the same plane with the carbonyl bond perpendicular to that plane, was found to be a minimum energy conformation. The configuration is shown in figure 1. This coplanar configuration of the aromatic core agrees well with the observed STM images and indicates that the conformation of the core is not significantly perturbed by the substrate or neighbouring molecules.

In the structure the long alkyl chains lie commensurate with the graphite lattice due to the strong interaction of the chains with the substrate. Owing to the steric considerations described above (see figure 2), the cores and short alkyl chains do not lie

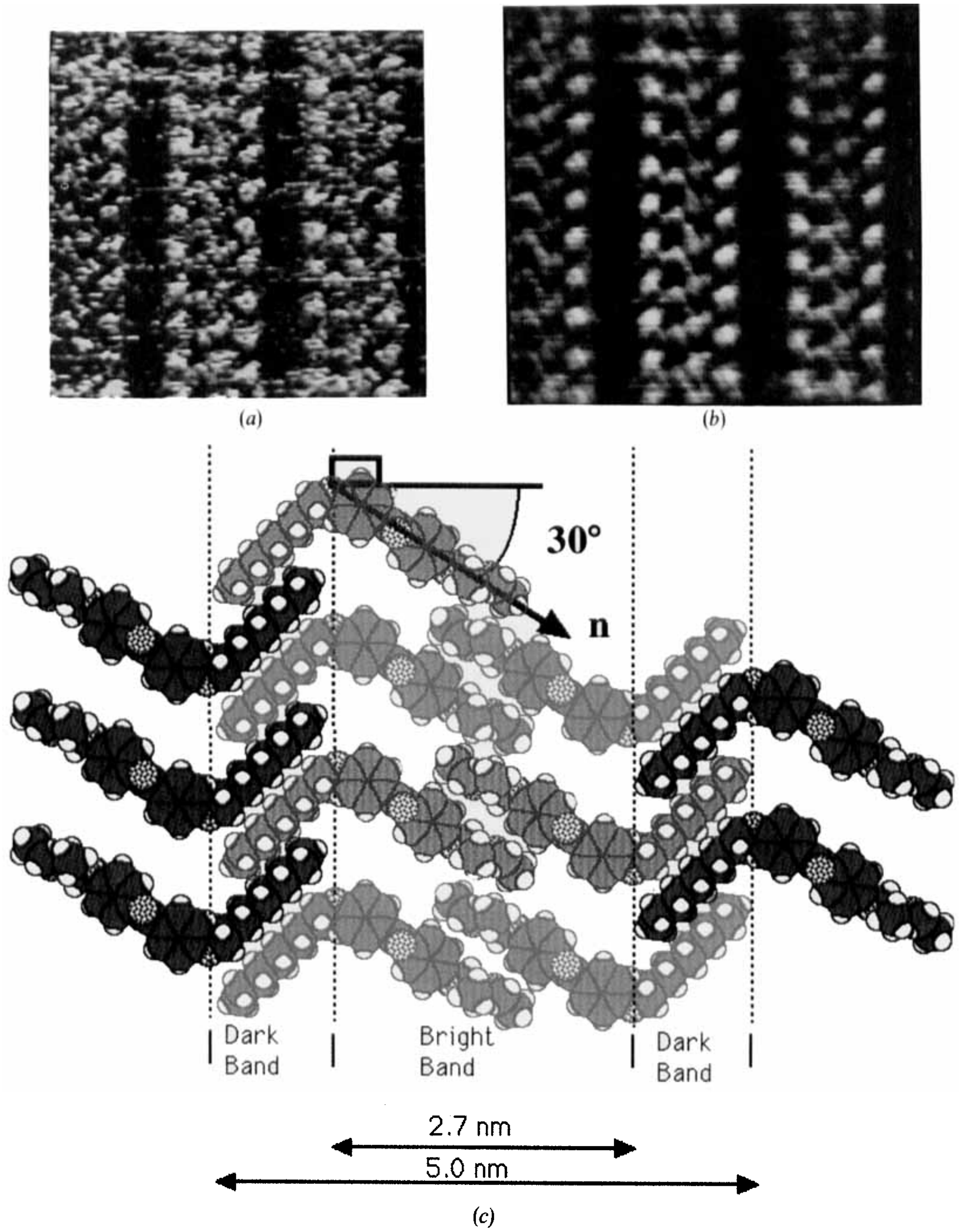

Figure 2. (*a*, *b*) STM image of the ferroelectric liquid crystal W7 on graphite. The figure (*a*) shows the unfiltered image while the filtered image is shown in (*b*). The image was filtered by identifying the strongest peak in the power spectrum and removing all peaks in both the real and imaginary parts with intensities less than 0·01 per cent of the strongest peak. The inverse transform was then calculated. The area of the image is 10·2 nm × 10·2 nm and was collected in the constant current mode with a tip bias of +0·8 V and a tunnelling current of 1 nA. The long alkyl chains appear dark within the image while the aromatic cores appear bright. (*c*) The model shows the packing of W7 molecules on graphite. The line through the core and the chiral chain makes a 30° angle with the layer normal. The model reproduces both the tilt angle and the bilayer width observed in the STM image.

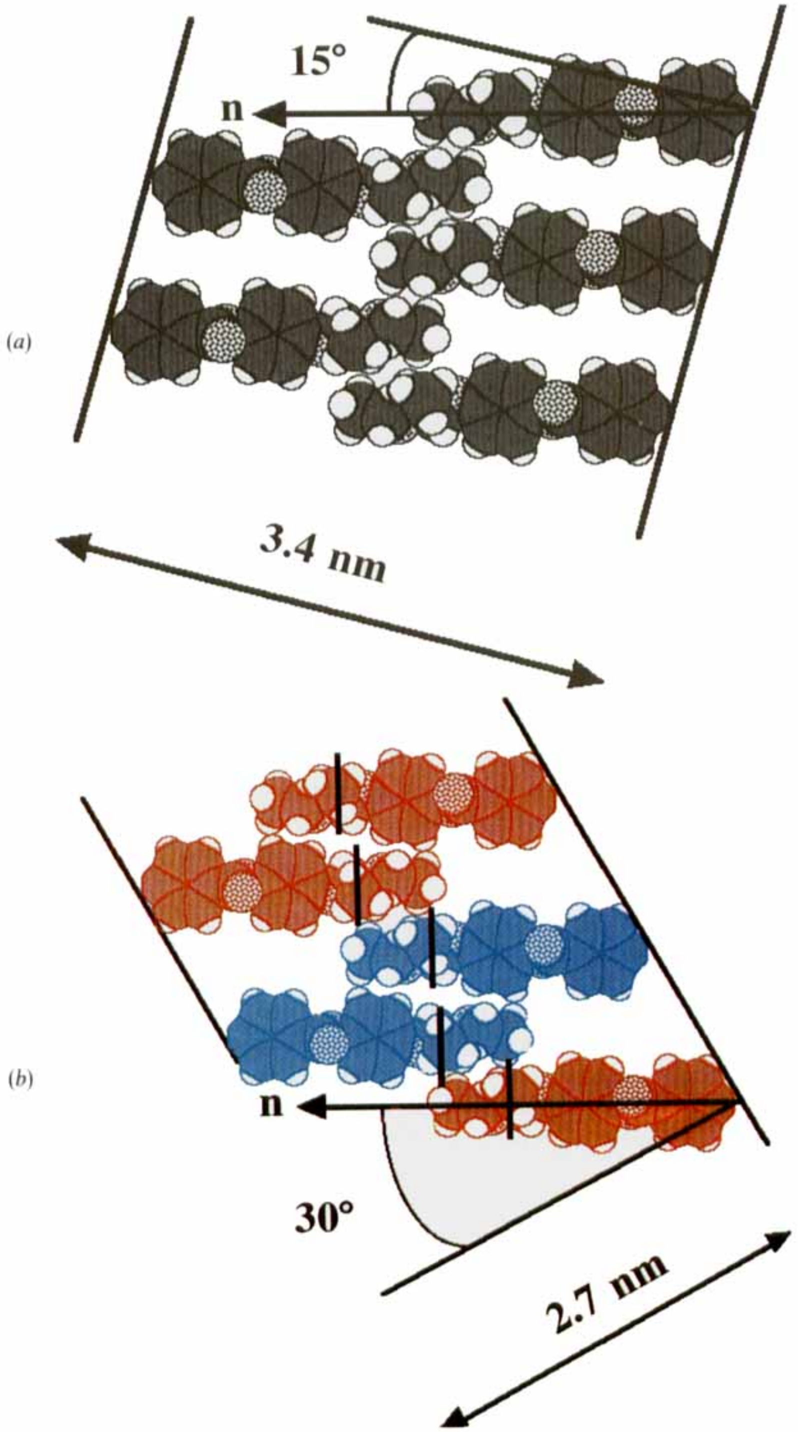

Figure 3. (*a*) A packing structure (long chains omitted) is shown which assumes that van der Waals forces dominate the packing of the short alkyl chains. The resulting tilt angle is 15°. Neither the tilt angle nor the interlayer spacing match the features in the STM image. (*b*) A packing structure (long chains omitted) is shown which assumes that the interaction between the transverse dipoles dominates the packing of the short alkyl chains. To align the transverse dipoles, the molecules form dimers. This arrangement yields a tilt angle of 30°. Both the tilt angle and the interlayer spacing match the features in the STM image.

along graphite lattice vectors. Therefore it appears that packing of the cores and short chains is dominated by the inter-molocular interactions between the liquid crystal molecules. Also, since there is a rather large spacing between the cores of adjacent molecules it seems reasonable that it is the packing of the short alkyl chains attached to the chiral centre which drives the ordering. Since the packing of the short alkyl chains may be dominated either by van der Waals forces or the interaction of the transverse dipoles close to the chiral centre we constructed models for both cases. The packing structures for both the dipole and van der Waals models are presented in figure 3. Either packing structure presented in the models could pack on the graphite lattice. This was determined by overlaying the model structures on to a graphite lattice and fixing the long alkyl chains along graphite lattice vectors. Both models produce structures wherein the aromatic cores are tilted relative to the layer normal. However, the resulting tilt angle is different in each case. The dipole model produces a core tilt angle of 30°, identical to the tilt angle observed in the surface structure, whereas the van der Waals model does not.

If van der Waals forces alone dominate the packing order of the short alkyl chains then a structure with a 15° tilt of the cores is formed. The tilt arises solely from the short chain interaction as segregated polar and non-polar regions are formed. The orientation of the aromatic cores and short alkyl chains in this packing structure is shown in figure 3 (*a*). The long chains are assumed to close pack and are omitted from the figure for clarity. The resulting layer tilt does not agree with the 30° tilt observed in the STM experiment.

The dipole model assumes that the interaction between the transverse dipoles dominates the packing of the short chains. To maximize the interaction between the chiral centres, thereby permitting them to align, the molecules form pairs or dimers which are shown in figure 3 (*b*). (Again the long alkyl chains are omitted from the figure.) The interaction between two dimers is assumed to be governed strictly by van der Waals forces. In figure 3 (*b*), note the inter-dimer versus intra-dimer position of the short alkyl chains with respect to the phenyl rings. The dipole model agrees with both the interlayer spacing and the 30° tilt observed in the STM images.

Current theories for the ordering of bulk smectic C (or S_C^*) liquid crystals often assume the absence of free rotation. In the STM experiment the molecular rotation is frozen in the interfacial structure due to the strong interaction of the alkyl tails with the graphite substrate. This makes it convenient to compare the current theoretical models with the rotationally hindered surface structure observed by STM.

There have been several attempts to explain the origin of the layer tilt in the smectic C phase. McMillan [14] proposed that a molecule exhibiting the smectic C phase must possess central transverse dipoles. As the molecular rotation becomes more hindered with decreasing temperature, the interplay of these dipoles results in the layer tilt. A second theory, proposed by Wulf, considers the zig-zag shape of the molecule [15]. In this model, the layer tilt arises from steric factors as the molecules pack. A recent attempt to explain the origin of the tilt angle and the spontaneous polarization in chiral molecules postulates that the molecules in the ferroelectric phase are ordered with respect to conformational and rotational orientation relative to the tilt plane by a molecular 'binding site' [16]. Such a site should determine the magnitude and sign of polarization depending upon the conformation the molecule adopts in the site.

Experimentally, several molecular features have been found to favour the formation of smectic C phases [17]. For example, the presence of alkyl chains on both ends of the molecule, long alkyl chains, and branching within the chains, all favour the formation of the tilted structure. Although terminal transverse dipoles increase the stability of the smectic C phase they are not prerequisites.

It is interesting to note that the two models in figure 3 yield different tilt angles in the chiral smectic C phase. Steric packing of the cores (van der Waals model) is by itself sufficient to introduce a core tilt of 15°. By introducing the dipole interaction the core tilt is increased to 30°. This value of the tilt is not only in agreement with the tilt of the core observed at the W7–graphite interface structure, but is also similar to the maximum tilt angle of 25° measured for the bulk sample of W7. Therefore, although transverse dipoles are not required for the formation of a tilted structure in the model, the introduction of the dipole interaction significantly enhances the magnitude of the core tilt angle. As the bulk sample is cooled towards the higher ordered smectic phase, this dipolar interaction becomes increasingly important. Also, if the molecular rotation around the aromatic core axis is slowed, the bulk sample may begin to approximate the rotationally frozen surface structure. The interaction of the transverse dipoles would then become increasingly important in the rotationally damped bulk sample.

In summary, our STM studies on a ferroelectric liquid crystal (W7) have revealed many interesting features of the interfacial order existing at the liquid crystal–graphite interface. While some of these features like the crystal-like order and the dimer formation are characteristic of the interfacial order only, the 30° tilt angle of the aromatic cores observed at the interface is similar to the maximum tilt angle in the ferroelectric smectic C phase of bulk W7. Thus STM studies can provide valuable information not only on the interfacial order, but also on some aspects of bulk order.

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