Liquid Crystals

Publication details, including instructions for authors and subscription information:
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To cite this Article McMaster, T. J. , Carr, H. , Miles, M. J. , Cairns, P. and Morris, V. J.(1991) 'Scanning tunnelling microscopic images of the surface ordering of the liquid crystal 4-n-octyl-4'-cyanobiphenyl', Liquid Crystals, 9: 1, 11 — 18

To link to this Article: DOI: 10.1080/02678299108036759

URL: http://dx.doi.org/10.1080/02678299108036759

LIQUID CRYSTALS, 1991, VOL. 9, NO. 1, 11–18

Scanning tunnelling microscopic images of the surface ordering of the liquid crystal 4-*n*-octyl-4′-cyanobiphenyl

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(*Received 29 March 1990; accepted 6 August 1990*)

Images of the surface ordering of 4-*n*-octyl-4′-cyanobiphenyl, a room temperature smectic liquid crystal deposited upon graphite, have been obtained by scanning tunnelling microscopy. The microscope was operated in air using the constant-current mode. Under certain tunnelling conditions it has been possible to resolve both the aliphatic and aromatic parts of the molecule, and to observe individual benzene rings. Two previously unreported conformations have been observed: an overlapping bilayer structure with spacing 3·7 nm, and a monolayer structure with spacing 2·4 nm. The latter structure may represent the first visual evidence for a surface polar ordered structure.

1. Introduction

A scanning tunnelling microscope (STM) consists essentially of a sharp conducting probe positioned in close proximity to a conducting surface [1]. Figure 1 shows a schematic diagram of a STM. A potential difference is applied between the probe and the surface and, at probe-surface separations of $\lesssim 1$ nm, a tunnelling current flows between the probe and the surface. The tunnelling current decreases exponentially with increases in the distance between the probe and the surface, and thus provides a very sensitive indicator of the probe–surface separation. In the constant-current mode of operation the probe is scanned across the surface and the tunnelling current is maintained at a constant value by controlling the vertical displacement of the probe. Vertical and horizontal displacements of the probe are controlled and monitored by piezo-electric transducers. The vertical displacements of the probe, which arise due to changes in surface conductivity and/or surface roughness, can be amplified and used to display images of the surface or surface adsorbed molecules. STMs are capable of achieving atomic resolution and can be operated in vacuum, gaseous or liquid environments.

Molecular ordering at the surface or interface of a liquid crystal may be markedly different from that within the bulk and the determination of the nature of surface, or interfacial ordering is of both academic and practical importance. STM offers the possibility of imaging the molecular ordering at an interface between the liquid crystal and a conducting surface. Other workers have reported images of liquid crystal molecules adsorbed on graphite [2–7], and on molybdenum disulphide [8]. This paper describes further studies on 4-*n*-octyl-4′-cyanobiphenyl (8CB) which reveal two previously unreported ordered structures.

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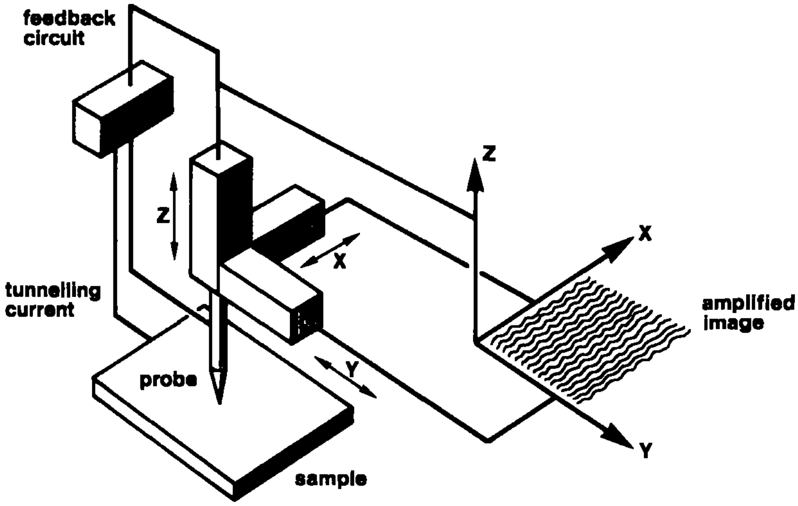


Figure 1. Schematic diagram of a scanning tunnelling microscope. The probe is positioned by three piezo-electric transducers. The movement of the probe is amplified to display the image of the surface of the sample.

2. Experimental

The STM was a commercial instrument supplied by W.A. Technology (Cambridge, U.K.). It was operated in air, in the constant-current mode using tungsten probes. The probes were electrochemically etched in 1 M potassium hydroxide before use. 8CB was chosen because it exhibits a smectic A phase at room temperature. Samples of 8CB were purchased from BDH Ltd. (Advanced Materials Division, Poole, U.K.), and were used as supplied. Specimens for STM imaging were prepared by placing a drop of 8CB on a freshly cleaved surface of highly oriented pyrolytic graphite. The graphite used was a single crystal, type ZYH, obtained from Union Carbide (Geneva, Switzerland). The drop of 8CB was smeared over the graphite surface to a thickness of about 1 mm. The probe was positioned within the liquid crystal and then carefully wound in to tunnelling range. Tunnelling conditions used were typically (0·3–1·0 nA, 0·5–1·0 V), with image acquisition times of 110–160 s for a 256 × 256 pixel raster. The periodic nature of the observed images permitted the use of Fourier transform image processing techniques to remove noise and enhance periodic features.

3. Results and discussion

STM studies of 8CB revealed ordered arrays of molecules extending over large areas of the graphite substrate (see figure 2). Based upon previous STM studies of 8CB [2], and discussions of the mechanisms for producing contrast in STM images of liquid crystals [3, 6], the bright areas of the image shown in figure 2 have been identified as the biphenyl portion of the molecule, and the darker areas in figure 2 have been assigned as regions occupied by the aliphatic alkyl chains. Figure 3 (*a*) shows the Fourier transform of figure 2, and figure 3 (*b*) shows the Fourier filtered image of figure 2. The interlayer spacing was found to be 2·4 nm, which is considerably smaller than the values of 2·9–3·2 nm determined by X-ray diffraction studies for the bulk liquid crystal [9, 10], and also smaller than that of 3·4–3·8 nm reported in previous STM studies [2, 4–6]. In the present studies the periodic spacing of 2·4 nm was observed for tunnelling currents $\geqslant 0{\cdot}5$ nA and bias voltages of 1 V. Figure 4 shows a higher magnification Fourier filtered image of this structure. Under these tunnelling conditions it was possible to image unambiguously the individual benzene rings of the biphenyl group. In addition the octyl chains can also be seen in the darker gaps between the biphenyl regions (see figure 4). The angle of inclination (θ, as defined in figure 5 (*a*)) between the octyl chain and the axis of the biphenyl core was found to be 30°, in good agreement with previous determinations [2, 10, 11]. The images presented in figures 2 and 4 show a degree of structural organization akin to a two dimensional crystalline structure. Thus it is clear that the degree of surface ordering of the molecules is considerably greater than that within the bulk smectic A phase. Figure 4 suggests that both benzene rings are adsorbed flat on the graphite surface, and that neighbouring biphenyl groups sit side-by-side over a period of four molecules. If it is assumed that figure 4 represents the first surface adsorbed monolayer, then there are two possible arrangements of the 8CB molecules (see figures 5 (*b*), (*c*)) which are consistent with the widths of the bright and dark layers, and the identification and relative orientation of the octyl chains and biphenyl groups shown in figure 4. However the structures shown in figures 5 (*b*), (*c*) differ in the orientation of the dipole moment associated with the cyanobiphenyl core. Thus it is possible to construct apolar and polar molecular monolayers which are structurally consistent with figure 4. Two examples of such monolayers are illustrated in figures 5 (*d*), (*e*). Arrows are used to define the dipole moment associated with the 8CB molecule, and the assembly in groups of four molecules is considered to include alternate antiparallel (figure 5 (*d*)) or parallel (figure 5 (*e*)) stacking of the molecular dipoles. The possibility of surface polar ordering in liquid crystals was first discussed by Meyer and Pershan [12], and then later by Parsons [13]. The existence of an adsorbed polar structure, at the interface between 8CB and a glass surface, has been proposed by Guyot-Sionnest *et al.* [11] on the basis of their interpretation of optical second harmonic generation studies. The parallel alignment of dipoles depicted in figure 5 (*e*) would be consistent with both figure 4 and the structure proposed by Guyot-Sionnest *et al.* [11]. In this case the grouping of the 8CB molecules into units of four may signify some underlying registry between the molecular structure of 8CB and the atomic structure of the graphite surface.

Under different tunnelling conditions on other 8CB samples prepared in a similar manner a second type of ordered structure (see figure 6) was observed. At high magnification a bright biphenyl image was seen with no resolvable detail. In the darker regions of figure 6, between the bright bands, it was possible to observe isolated bright spots which may correspond to the carbon atoms of the $-CH_2-$ groups within the aliphatic chain. Under these tunnelling conditions an interlayer spacing of 3·7 nm was observed. Once again the degree of molecular order is more consistent with a two dimensional crystal than a liquid-crystalline structure. An interlayer spacing of 3·7 nm can be explained by an interdigitated bilayer structure (see figure 5 (*f*)) showing a smaller degree of overlap than that observed previously [14]. If the cyano group of one molecule overlapped to some extent with the cyano-substituted phenyl ring of its neighbour (see figure 5 (*f*)) then this would explain the 3·7 nm interlayer spacing and the width of the bright region (2·1 nm).

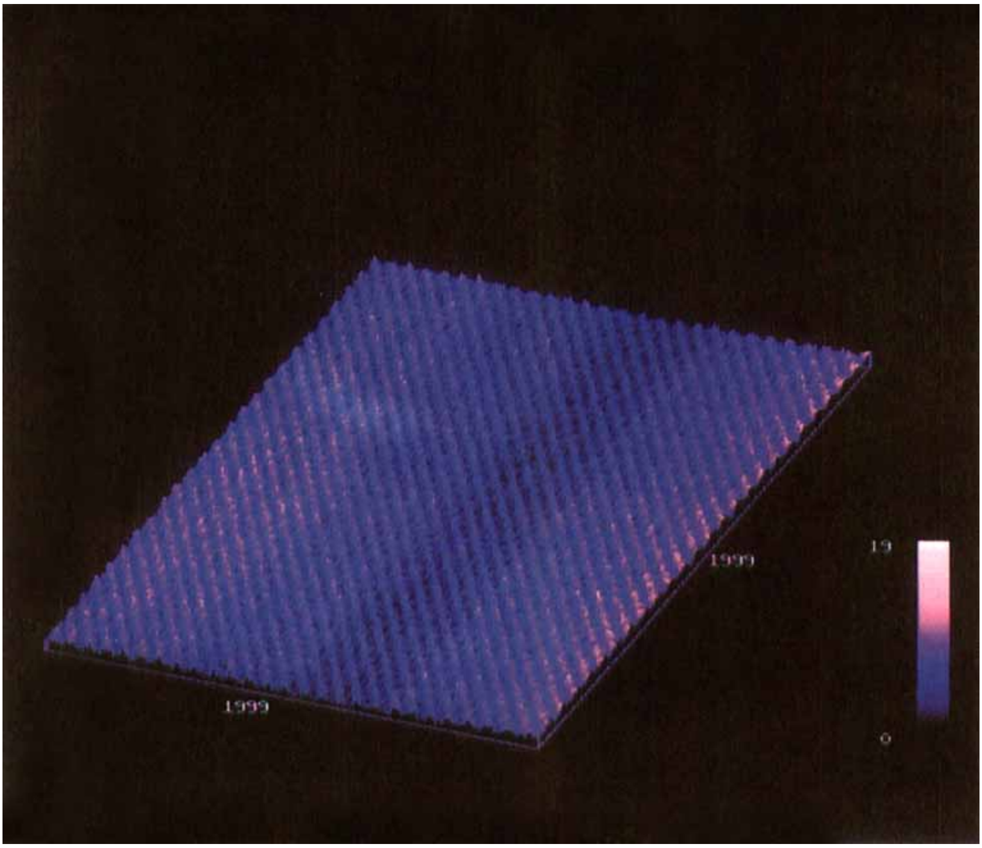
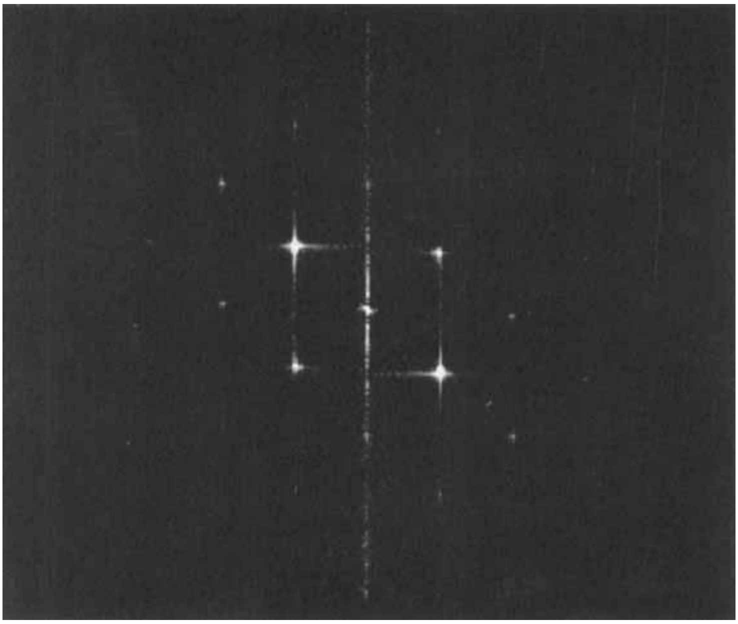


Figure 2. Low magnification unprocessed image of 8CB deposited on graphite obtained in the constant-current mode using a tungsten probe. Tunnel current 0·5 nA, sample bias 1000 mV, area of scan 80 × 80 nm.

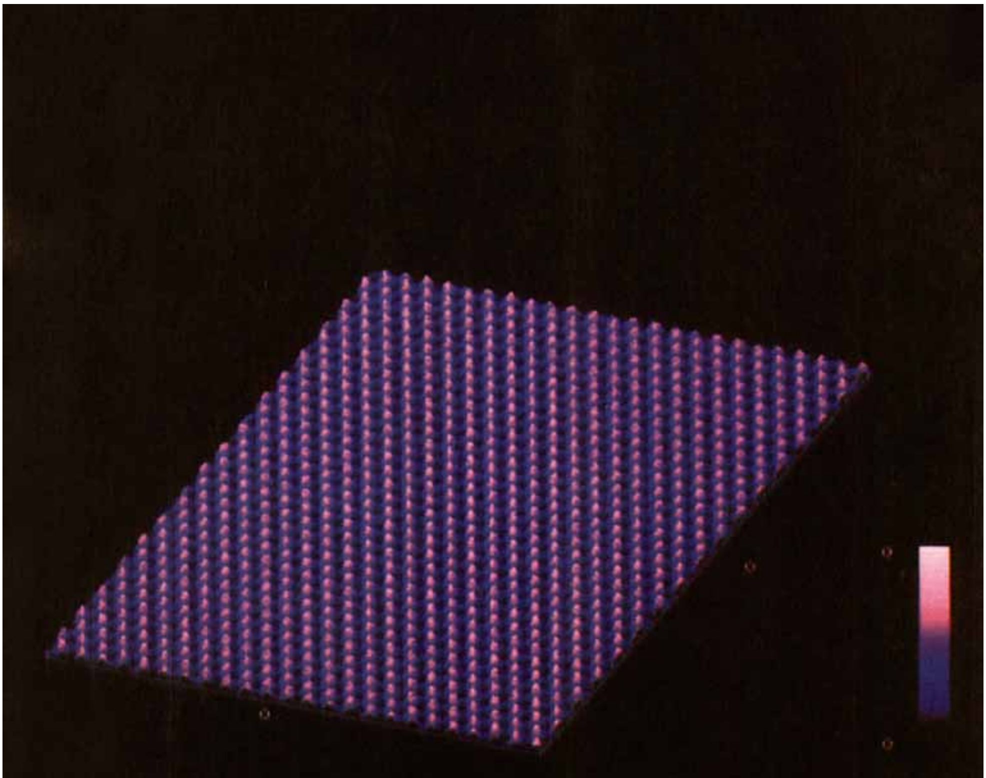
The different structures observed in this study may reflect differences in deposition conditions and the thermal history of the deposition process. The images showing a spacing of 2·4 nm were collected on 8CB samples approximately 12 hours after deposition whereas those showing the spacing of 3·7 nm were measured about 2 hours after deposition. We have previously reported that the different layer spacings were obtained under different tunnelling conditions [7]. Smith *et al.* [6] have noted that for gap resistances below about $5 \times 10^9\,\Omega$, the tip can distort the molecular packing. In our case both spacings were obtained with gap resistances of approximately $2 \times 10^9\,\Omega$, which suggest that the observed differences owe more to sample thermal history than to tip–sample interaction.

When 8CB is cooled below its crystallization temperature [6], tight binding of the alkyl chains to the graphite substrate is observed. The spacings observed in this work and other studies [2, 4–6] may correspond to a less tightly bound state

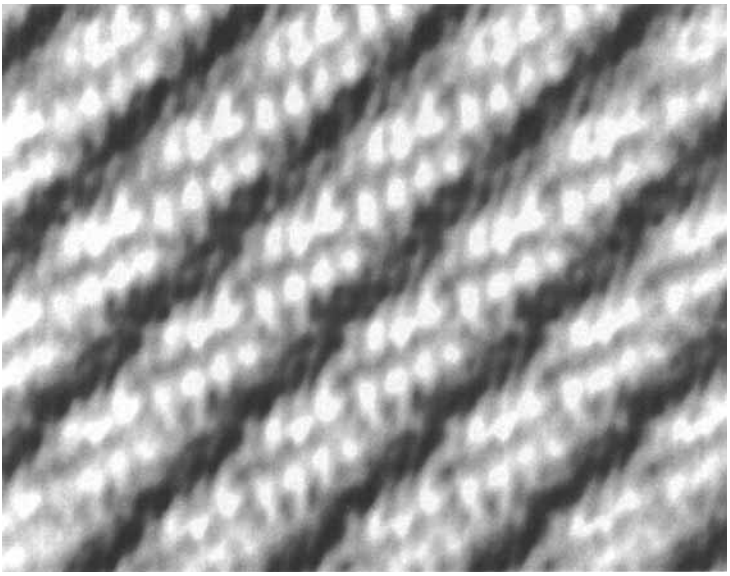
Figure 3. Effects of image processing on figure 2. (*a*) The Fourier transform of figure 2 used to enhance periodic structures, (*b*) Fourier filtered version of figure 2. Area of image 61·5 × 61·5 nm.



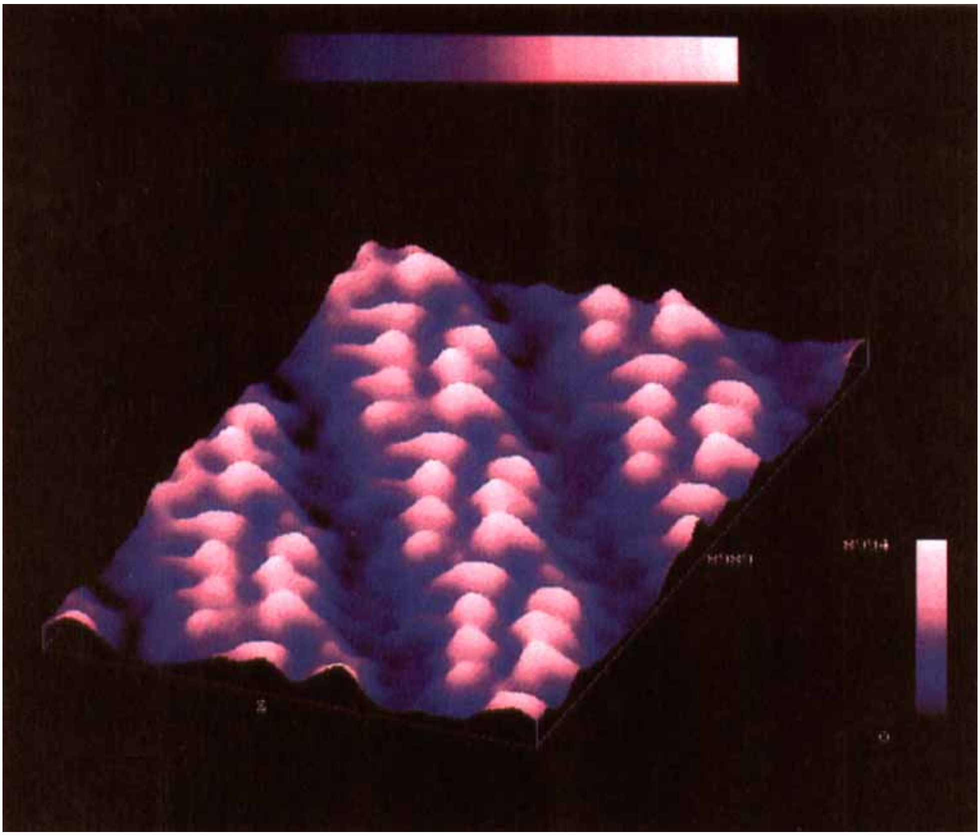
(*a*)



(*b*)



(*a*)



(*b*)

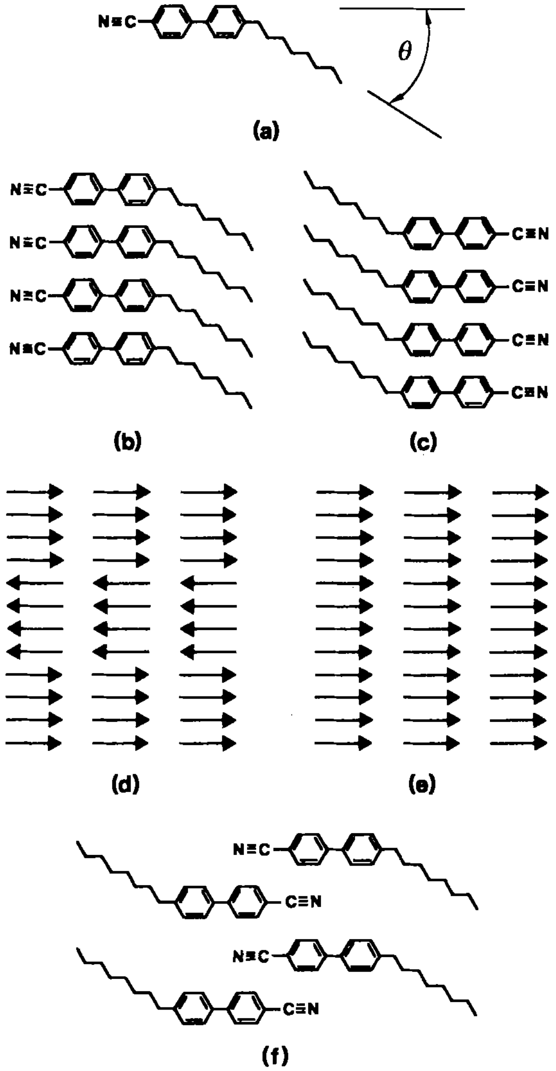


Figure 5. Schematic diagrams indicating structure and orientation of 8CB. (*a*) 8CB molecules showing the angle θ between the biphenyl core and the alkyl chain; (*b*) and (*c*) alternative stacking arrangements of 8CB molecules consistent with the images obtained in figure 4; (*d*) and (*e*) possible stacking arrangements of the 8CB dipole moments consistent with data in figure 4; (*f*) interdigitated bilayer structure consistent with data reported in figure 6. The arrows shown in (*d*) and (*e*) represent the dipole moments associated with the 8CB molecules.

intermediate between the bulk liquid crystal and the bound surface structure. Molecular orbital calculations [6] indicate that the marked difference in height between the phenyl and alkyl portions of 8CB, as observed in figure 4 (*b*), is due to differences in the electronic density of states and is not simply topological in origin.

Figure. 4. (*a*) Fourier filtered image of raw data. Tunnelling current 0·5 nA, sample bias 1000 mV, scan size 11·8 × 9·4 nm. (*b*) Three dimensional representation of part of figure 4 (*a*), area 5·9 × 6·0 nm.

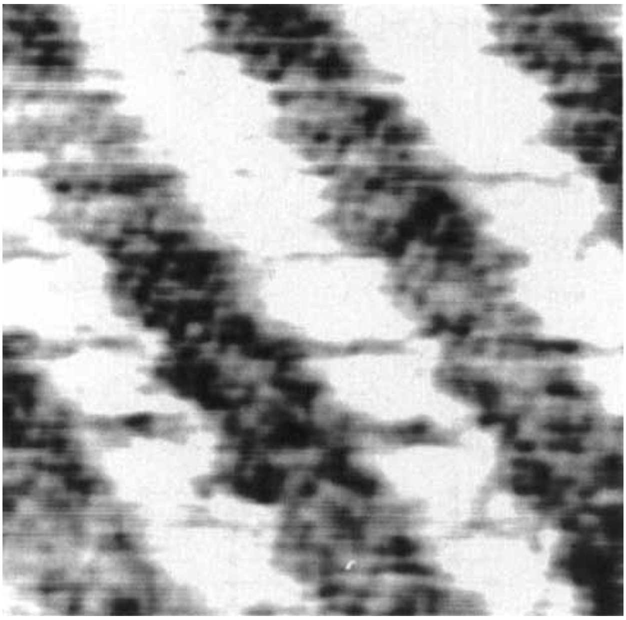


Figure 6. High magnification image of 8CB. Tunnel current 0·3 nA, bias voltage 500 mV, scan area 10 × 10 nm. Post acquisition image processing consisted of low pass filtering, and a five point two dimensional smoothing.

The authors wish to thank the referees for helpful comments and for drawing attention to [6, 8] which appeared after submission of the manuscript.

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