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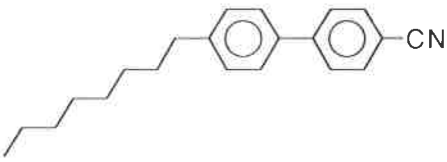
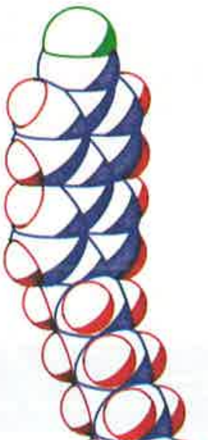
STM Simultaneous Observation of a Liquid Crystal Layer and its Substrate

Organic molecules are mainly electric insulators, so that thick layers are not suitable for STM investigation. In the case of easily crystallizable products, it will be nearly not possible to obtain suitable samples. Very small crystals are large enough to be obstacles for the tip. The substrate material is also very important, it must be flat enough at atomic level, and interacts with adsorbed molecules to immobilize them during the scanning.

Liquid cristals are described to give well organized layers, rather easy to image by STM. This work was done one 8CB **1**, a well known smectic liquid crystal, **2** is the shape of the isolated molecule as calculated by molecular modeling. Images were recorded on a Nanoscope II STM (Digital Instruments, Santa Barbara) (soft version 5.3), in air, under atmospheric pressure and room temperature (20 °C) ; tip was platine-iridium alloy wire (Nanotip, Digital Instruments).



1



2

8CB

The sample was prepared by deposit of a droplet of commercial 8CB (BDH) on a piece of cleaved HOPG (Le Carbone Lorraine). The 8CB was heated at 70 °C (spreading of an isotrope liquid), and a slow cooling (8 to 10 hours) back to room temperature led to a good smectic organisation of 8CB on graphite surface. The observation of that sample by STM gave us images as *figure 1*, which showed a 25 nm × 25 nm area, the alignments seen being identical to that already published. They can be seen on hundreds of nanometers sided areas, these ribbons are made of 8 molecules packs alignments, slided between vicinal packs, as on *figure 2* (5 nm × 5 nm). The hills on *figure 2* are due to the cyanophenyl part of 8CB molecules, aliphatic chains are in the valleys between two alignments of aromatic moieties.

Figure 3 shows a 8 nm × 8 nm area observed with varied tunnelling conditions (tunnel current and bias voltage) at few minutes intervals to avoid a large drif of the observed area ; the differences seen in the contrast of recorded images are very large. For some conditions (ex : buffer 6), only aromatic parts are seen, whereas with wery close tunnel conditions (ex : buffer 5) informations are recorded on all the observed plane, with high density.

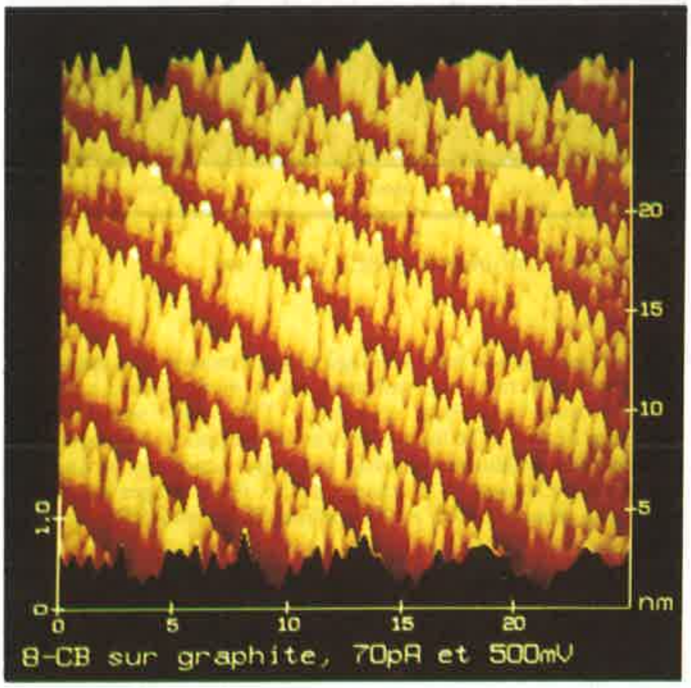


FIGURE 1. - *STM image of 8CB, 25 × 25 nm², 500 mV and 70 pA.*

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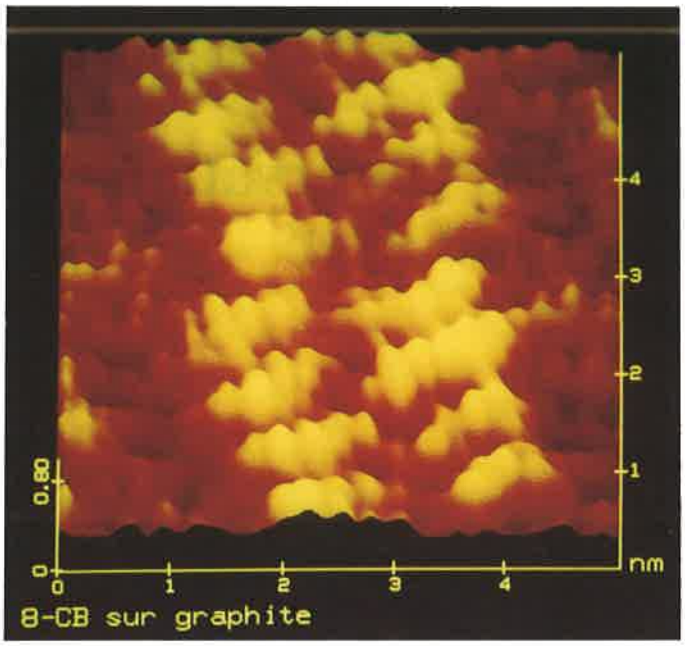

FIGURE 2. - *STM image of 8CB, 5 × 5 nm², − 250 mV and 200 pA.*

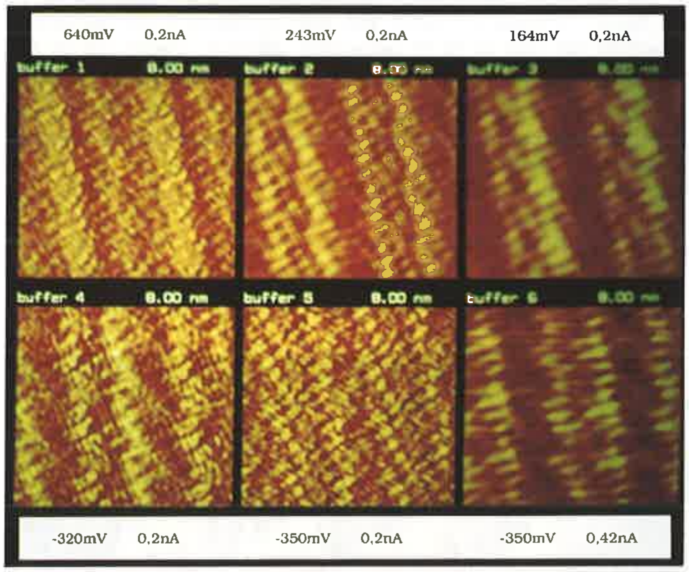

FIGURE 3. - *STM images of 8CB, 8 × 8 nm².*

In the running mode named imaging spectroscopy, the apparatus shifts between two bias voltages for a given tunnel current, between even and odd scannings. This gives simultaneous recording of two STM images for the biasses used. Moreover the tip is height modulated during the same scanning, giving the spectroscopy images (STS images di/ds). Four images are simultaneously recorded 200 × 200 points (STM and STS for each bias).

To test the efficiency of that working mode on our sample *(figure 4)*, tunnel current used was 200 pA, bias switched between − 350 mV and 350 mV and a modulation of 54 pm was used to produce STS images, on a 8 × 8 nm² scale. As in *figure 3*, the image contrast is larger with a negative bias for STM images ; for the STS images, contrast is reversed with the negative bias, and contains informatons on "black" areas of the STM image.

Using the same working mode with adjusted parameters, we reach the simultaneous observation of the layer of molecules adsorbed on graphite, and the substrate surface with atomic resolution, as seen in *figure 5*. To reach that goal, the tunnel current was 560 pA, a large bias (− 750 mV) yields an image of molecules of the liquid crystal layer (8CB) while a small one (− 60 mV) produces an image of carbon atoms of the graphite support. Scanning frequency was 5 Hz, in height mode (constant tunnel current). The height modulation of 160 pm and sample period of 250 μs were used to give STS images. The scanned area was 10 nm × 10 nm.

From a 5 nm × 5 nm zoomed area of *figure 5*, the graphite surface array was drawn, after, aliphatic chains of 8CB and aromatic parts coinciding with STM image. A further extrapolation and zooming back to all the 10 nm × 10 nm was reached.

The already described model of 8CB surface organization on graphite *(figure 6)* [1] do not fine fit our image. We obtained a

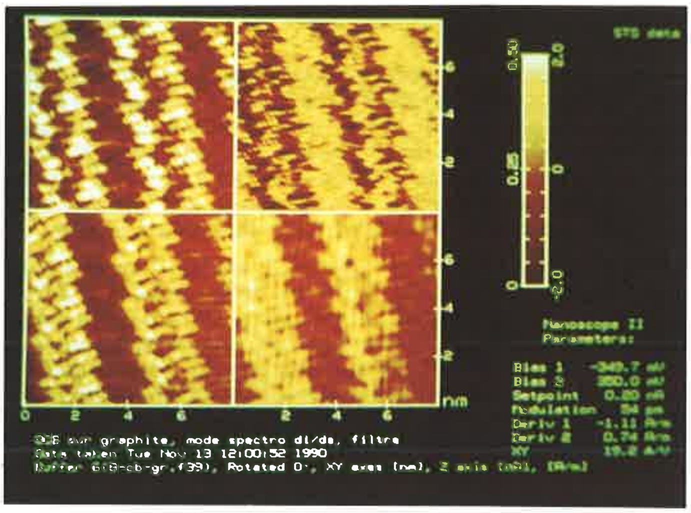

FIGURE 4. - *STM and STS simultaneous images of 8CB, 8 × 8 nm², 200 pA ; a and c : − 350 mV ; b and d : 350 mV.*

a | c
b | d

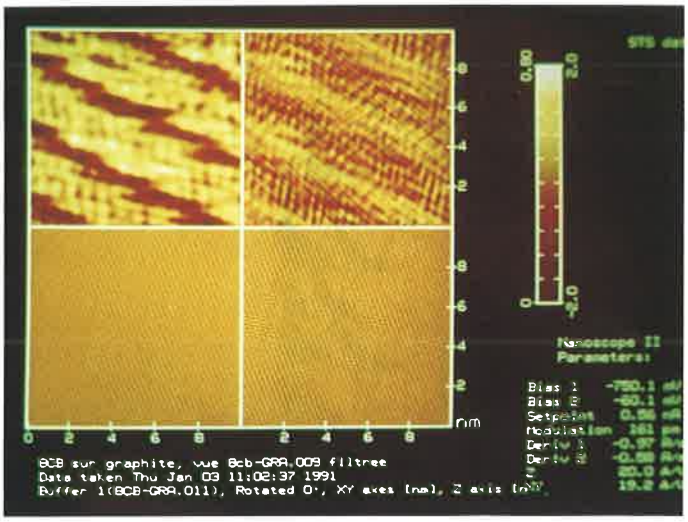

FIGURE 5. - *STM and STS simultaneous images of 8CB and graphite surface, 10 × 10 nm², 560 pA ; a and c : − 750 mV ; b and d : − 60 mV.*

a | c
b | d

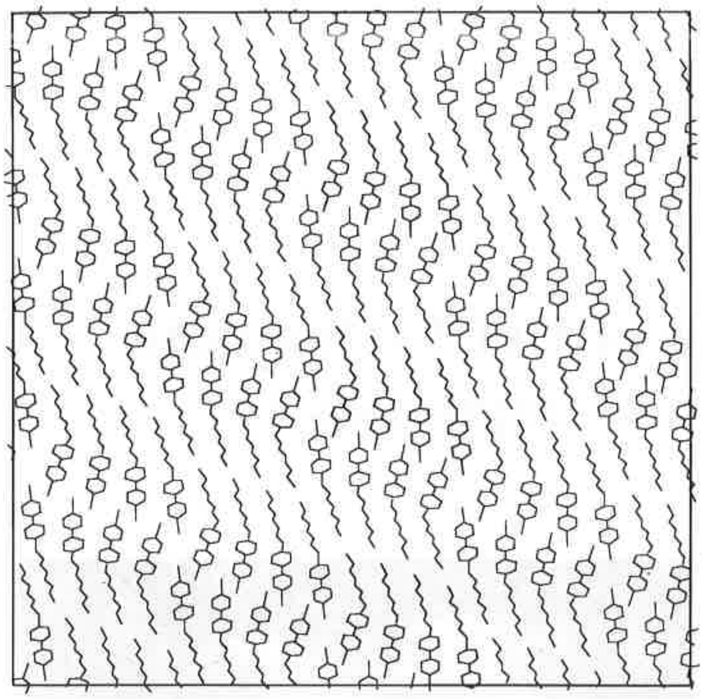

FIGURE 6. - *Bidimensional molecular array of 8CB, as in (6), 10 × 10 nm².*
(D.P.E. Smith, J.K.H. Hörber, G. Binnig and H. Nejoh, Nature, *1990, 344, 641).*

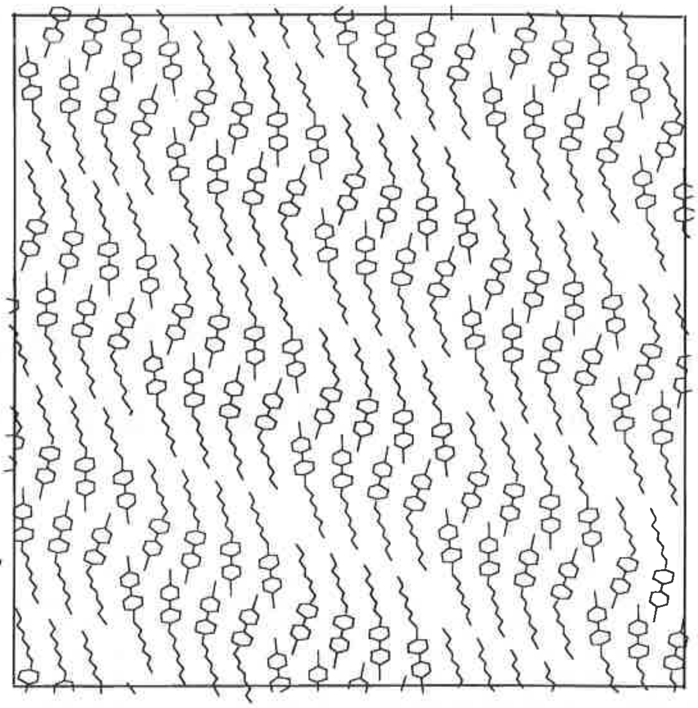

FIGURE 7. - *Bidimensional molecular array of 8CB, deduced from* figure 5 *images, 10 × 10 nm².*
(J.C. Poulin and H.B. Kagan, submitted for publication).

good fitting structure made with alignments of 4 pairs of molecules, translated along an axis linking roughly the 8 cyano groups, as described to give a ribbon. But these ribbons are disposed in an array (*figure 7* [2]) slightly less compact that than described by IBM group [1], we obtained it by a sliding of one 8CB molecule between two ribbons, from the compact array.

If this planar array is superimposed to the STS image of 8CB *(figure 5)* correlations are seen. Fitting of tapes of molecules with STS image was also good, with some contrast in areas corresponding to aliphatic chains.

We are interested in generalizing to the observation of various layers of molecules on different substrates. The STS images obtained simultaneously contain also useful informations. A large number of experiments may be very useful to contribute to a rationalization of different implicated phenomena. This will lead to a better knowledge of the data that STM can deliver in some interesting cases.

References

[1] D.P.E. Smith, J.K.H. Hörber, G. Binnig and H. Nejoh, *Nature*, **1990**, *344*, 641.
[2] J.C. Poulin, H.B. Kagan, (submited for publication).