

## STM Structure Determination of Adenine Bilayers by Moiré Interpretation

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Scanning tunnelling microscopy (STM) has been performed in air at room temperature on bilayers of the nucleic acid base adenine, adsorbed to a graphite surface following evaporation of saturated aqueous solutions. Our results indicate that the upper layer of the bilayer structure shows a structural change compared to the layer adsorbed directly to the graphite. The upper layer has a slightly larger unit cell, and is slightly sheared and rotated with respect to the layer directly adsorbed to the substrate. We can interpret these observations in terms of a model of rows of the adsorbate molecules stabilised by intermolecular hydrogen bonds.

### 1. Introduction

The application of scanning tunnelling microscopy (STM) [1] has proven particularly well suited to study the molecular arrangement of close-packed adsorbate structures physisorbed on the surfaces of inert layered compounds such as graphite. Relevant examples include cyclic aromatic compounds [1], long chain alkane derivatives [2] and cyanobiphenyl liquid crystal derivatives [3, 4]. The physisorption of the purine base adenine (6-aminopurine) onto solid surfaces has first been demonstrated by STM in [5, 6]. In addition to van der Waals interactions, monolayer formation involves specific adsorbate–adsorbate interactions mediated through intermolecular hydrogen bonding.

Here the structure of ordered adenine bilayers has been investigated using a scanning tunnelling microscope. Since the interaction of the first molecular layer with the graphite substrate is different from the layer to layer interaction of the second layer, the epitaxial growth and accordingly the two-dimensional structure of both layers differ significantly. Using a simple model the structure of the two layers visible in the STM images is explained. Additionally the structure of the first layer has been simulated by a molecular mechanics simulation and the stability of the surface has been investigated.

The organisation of the paper is as follows: In Section 2 the experimental set-up is described which was used to obtain the scanning probe microscopic images. Section 3 describes the force field calculations that have been done in order to obtain the energy surface for one adenine molecule in an adenine dimer. Section 4 presents a simple model for the stacking of two adenine layers which explains the observed Moiré pattern resulting in a structure determination of the adlayer.

The mechanisms of physisorption of organic molecules to the solid surface are influenced by both adsorbate–substrate interactions and lateral adsorbate–adsorbate interactions. In most examples, these interactions are predominantly governed by van der Waals forces between the adjacent adsorbate molecules and the surface. The nucleic

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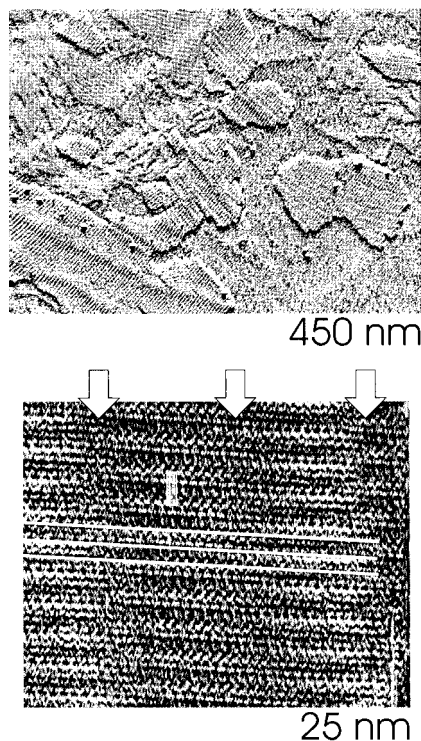


Fig. 1. STM images of an adenine bilayer. Upper panel: Island structures of the adlayer; scan width is 450 nm. Lower panel: Close-up of a bilayer structure showing the typical Moiré pattern. The arrows mark the periodicity of the superstructure, the white lines mark single rows of adenine, and the grey rectangle denotes the unit cell of the 2D crystal; scan width is 25 nm

acid bases and their derivatives are a unique class of organic compounds with biological functions in molecular recognition due to the ability of directed hydrogen bonding. When physisorbed at the solid surface these bonds play a prominent role.

## 2. Experimental

Multilayer structures of the purine base adenine have been prepared on graphite by evaporation of an aqueous solution of adenine on a heated graphite (0001) surface via the sizzling technique [6]. Drops of saturated adenine solution ( $10\ \mu\text{l}$ ) were applied to the surface of

freshly cleaved highly oriented pyrolytic graphite placed on a heat block with a measured surface temperature between 80 and  $110\ ^\circ\text{C}$ . STM measurements were performed with a home built STM using electrochemically (2 mol KOH) etched polycrystalline tungsten tips. The measurements were made at bias voltages around 700 mV and tunnelling currents between 50 and 500 pA. Non-linearities of the piezoelectric scanner were corrected by assuming a perfect threefold symmetry for the atoms of the underlying crystal substrate surface which were imaged by piercing the tip through the adsorbate crystal after reducing the gap resistance.

Figure 1 shows a typical example: an STM image of an island structure of adenine bilayers. The lower panel shows a close-up of a bilayer structure exhibiting a Moiré pattern. The arrows denote a change in the contrast caused by a superstructure in the adenine bilayer.

## 3. Force Field Calculations

A periodic adenine layer adsorbed to a (0001) graphite surface has been simulated using the commercially available computer program Cerius 2 running on a SGI workstation. For the energy minimisation calculations the Dreiding II force field was used, which suitably parameterises organic, biological and main group inorganic molecules and has an explicit hydrogen-bonding term. The potential energy of the adsorbate monolayer system is the sum of the two-, three-, and four-body terms in the energy expression, which is implemented by Cerius 2. Periodic boundary conditions were used

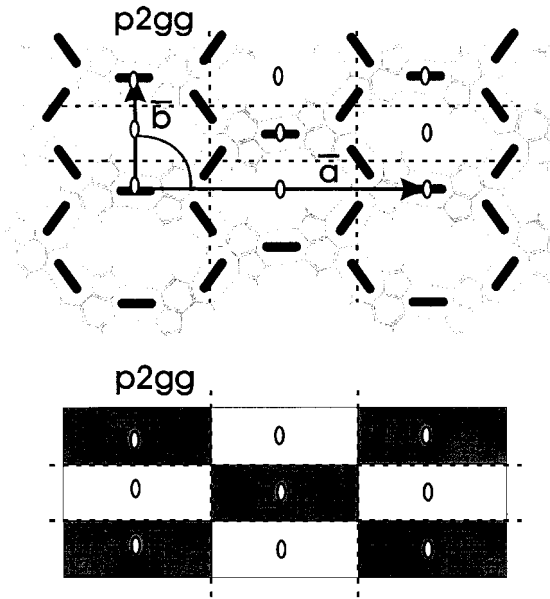


Fig. 2. Upper panel: Molecular mechanics simulation of an adenine monolayer. The  $a$  and  $b$  vectors ( $a = 22 \text{ \AA}$ ,  $b = 8.5 \text{ \AA}$ ) denote the unit cell of the 2D adenine crystal. The symmetry group of the shown structure is  $p2gg$ . The black bars denote hydrogen bonds within the rows, whereas the horizontal dark grey bars denote the hydrogen bonds between rows. The light grey ellipses denote the twofold rotation axes. The dashed lines are glide planes. Lower panel: Simplified model of the unit cell of the 2D adenine crystal. Each grey rectangle represents an adenine dimer bound by hydrogen bonds

in order to obtain a two-dimensional (2D) crystal structure of the adenine layer. Two graphite layers were taken into account in order to represent the half-infinite graphite crystal. The lateral cell dimensions of the model surface were those of the experimentally determined adsorbate cell. Four adenine molecules were put into the model cell. The observed adenine structure has been explained by the molecular simulation (Fig. 2) [7]: The adenine molecules form dimers (light grey bars) and rows (dark bars) bound by hydrogen bonds. The rows are more tightly bound as they contain more hydrogen bonds. As the rows are alternating rotated by  $180^\circ$ , the unit cell belongs to the symmetry group  $p2gg$ . The dashed lines denote glide planes and the light grey ellipses denote

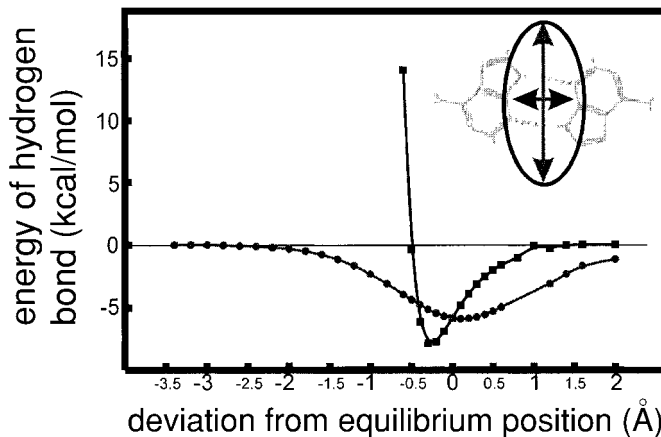


Fig. 3. Graph of the calculated binding energy of an adenine dimer versus amount of translation parallel (squares; dark double-arrow in the inset) and perpendicular (circles; light double-arrow in the inset) to the hydrogen bond direction

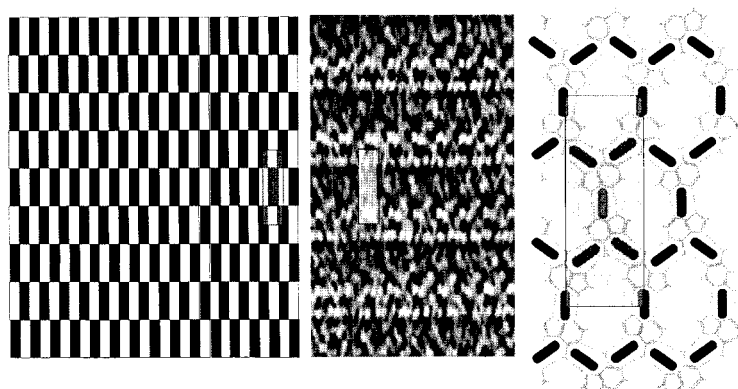
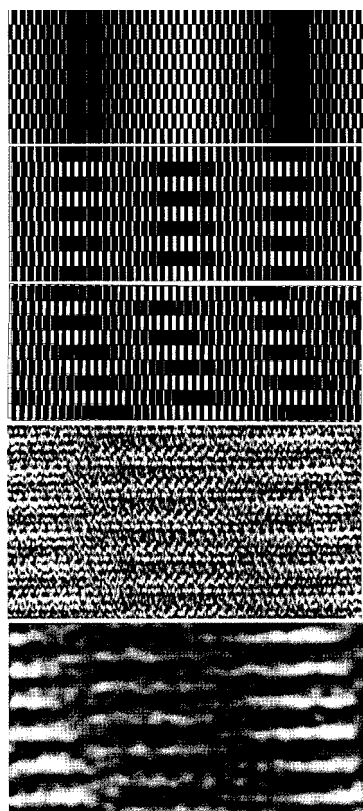


Fig. 4. Abstraction (left panel), STM image (middle panel) and molecular mechanics simulation (right panel). The grey rectangular denotes the unit cell in each respective image

the twofold symmetry axes. The binding energy has been calculated for a single dimer of adenine molecules depending on a translation parallel and perpendicular to the hydrogen bonds. Figure 3 shows a graph of the binding energy. The smooth gradient of the potential perpendicular to the hydrogen bonds shows that it is easy to shift the rows with respect to each other.



#### 4. Moiré Pattern Explanation

- a** The observed super-structure in the STM images can be explained by the following simple model. Figure 4 shows a simplified representation of the adenine layer, the STM image and the molecular model (from left to right). The simplified pattern is composed of black and white areas where every black rectangle represents an adenine dimer. A unit cell is denoted as a grey rectangle.
- b**
- c**

By stacking two adenine layers onto each other and scaling the upper layer by a factor of 1.04 a Moiré pattern emerges as shown in Fig. 5a. It is very important that the second layer is scaled, as a pure shift or rotation

- d**
- e**
- Fig. 5. Moiré for an adenine bilayer: a) Model with adlayer scaled 4% in unit cell vector **b** direction, b) model with adlayer additionally shifted by half a unit cell vector **b** with respect to each other, c) model with adlayer additionally rotated by 0.7°. d) Original STM image of the Moiré pattern of an adenine bilayer, e) low pass filtered STM image resembling closest to model c

would not lead to the observed pattern. In order to be comparable with the observed STM images (Figs. 5d, e), which show a finger-like dark–bright row structure, the upper layer in the Moiré model must additionally be shifted and rotated in the following way: shifting every second row by half a unit cell leads to the pattern of Fig. 5b which resembles the alternating bright–dark finger-like structure of the original STM images. In order to obtain the observed tilt in the Moiré pattern the upper layer must be rotated by  $0.7^\circ$ . Now Fig. 5c closely resembles the experimentally measured STM image.

In summary the Moiré analysis leads to the following structure for the adenine bilayer: with respect to the first layer, directly heteropitaxially physisorbed to the graphite substrate, the second layer is stretched in the direction of the unit-cell vector  $\mathbf{b}$  by

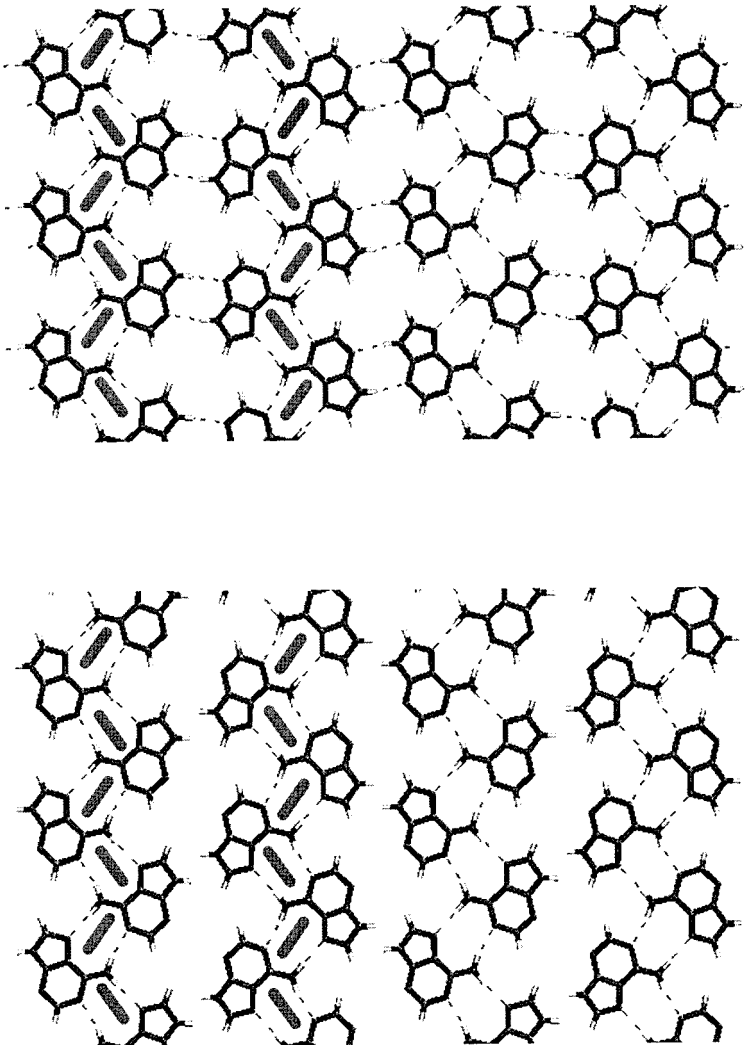


Fig. 6. Structure model of first (above) in comparison with second (below) layer of the growing adenine crystal

a factor of 1.04, the rows are shifted by half a unit-cell vector  $\mathbf{b}$  and the layer is rotated with respect to the lower layer by an angle of  $0.7^\circ$ . This operation changes the unit cell of the second layer from opposite zig-zag to parallel zig-zag as shown in Fig. 6. The binding energy diagram of Fig. 3 shows a broad and smooth minimum, thus making this operation possible and supporting the model.

## 5. Conclusion

In the structure of bilayers of adenine the upper layer deviates significantly from the lower mono-layer structure. This was determined by constructing a simple model for the observed Moiré effect in STM images. The second layer has a slightly larger unit cell vector  $\mathbf{b}$  (approx. 4%) and the rows of the adenine layer are shifted and slightly rotated with respect to each other. The results of the calculated stability of the 2D crystal suggest that the adenine layer consists of molecular rows where the individual molecules are bound tighter to the molecules of the same row than to the molecules of the neighbouring rows. Thus the rows can easily be shifted with respect to each other, resulting in a change in the fundamental symmetry of every other layer suggesting this as an important growth mechanism for a 3D crystal out of the seed of a 2D crystalline layer.

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