

Letter

Structure analysis of thiouracil on Ag(111) and graphite (0001) by x-ray diffraction and scanning tunneling microscopy

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Abstract. The geometric structures of ordered monolayers of large organic molecules (thiouracil) adsorbed to the surface of Ag(111) and graphite (0001) were analyzed using surface x-ray diffraction and scanning tunneling microscopy (STM), respectively. Although the substrates are different, in both cases the molecules are found to be arranged in parallel zig-zag rows. On graphite (0001) the molecules form a unit cell similar to the $(\bar{1}\bar{1}\bar{1})$ plane of the bulk crystal whereas on Ag(111) the detailed x-ray analysis gives evidence that, in contrast to the bulk structure, all but one of the intermolecular hydrogen bonds present in the bulk are broken. The intact pyrimidine rings are tilted by about 30° with respect to the Ag surface in comparison to flat lying molecules on graphite. An elongation of the C=S bond distance by $0.16(7)$ Å and an increase of the intra-pyrimidine-ring distances by about $0.11(10)$ Å relative to the bulk is observed which can be attributed to the covalent interaction of the molecule with the substrate. We conclude that for an inert surface like graphite, where the molecules merely interact by van der Waals forces, the molecules build a unit cell mainly determined by intermolecular hydrogen bridge bonds and therefore almost unchanged with respect to the bulk, whereas even in the case of a weakly interacting surface like Ag(111) the crystal structure can considerably be altered with respect to the bulk.

1. Introduction

The preparation and characterization of highly ordered monolayers and ultra-thin films of large organic molecules on single crystal substrates has become a rapidly growing field in surface science [1, 2]. In general, this is due to fundamental interest in interface phenomena and to the fact that the organic/inorganic interfaces mainly determine the physical properties of the growing films. More-

over, although the bulk structures of many organic structures are known in great detail, little is known about the geometric structures of surface adsorbed molecules which includes both, their mutual arrangement as well as their internal structure. Among the well established methods for surface structure analysis so far only scanning tunneling microscopy (STM) has been applied for unit cell determination with some routine [3–9] and does not rely on long range order, however STM is not sensitive to structural details such as bond lengths and angles. On the other hand, data taken with techniques providing atomic resolution like low energy electron diffraction (LEED) or surface extended x-ray absorption fine structure (SEXAFS) are difficult to analyze in the case of many atoms to be present in the unit cell. Consequently, investigations employing methods to study the structure of surface adsorbed molecules have up to now mainly dealt with small molecules such as ethene (C_2H_4), acetylene (C_2H_2) [10, 11], thiophene [12], and other small molecules [13]. On the other hand surface x-ray diffraction (SXR) is well established method for the study of surface structures [14, 15], however due to considerable experimental difficulties it has been applied only very recently for the analysis of large surface adsorbed organic molecules [16]. SXR experiments performed on ordered large organic structures so far have only dealt with *n*-alkylthiols [17] which, however, are characterized by comparatively small superlattice unit cells (e.g. 4 times the size of the Ag(111) unit cell as compared with 22 in the present case) and do not provide the atomic coordinates of all the atoms composing the molecules.

In a recent study by Azumi et al. it has been shown by STM that on graphite surfaces the molecular organization of oligothiophenes is similar to the bulk structure determined by x-ray crystallography [18] therefore allowing for 3D-structure prediction based on 2D structure determination. However this may only be possible for inert surfaces like graphite, not for more reactive surfaces.

In the present study we compare the molecular organization of 2-thiouracil (2-TU) adsorbed to a chemically inert graphite surface with the weakly reactive Ag surface. 2-TU is a prototype species for a (substituted) pyrimidine

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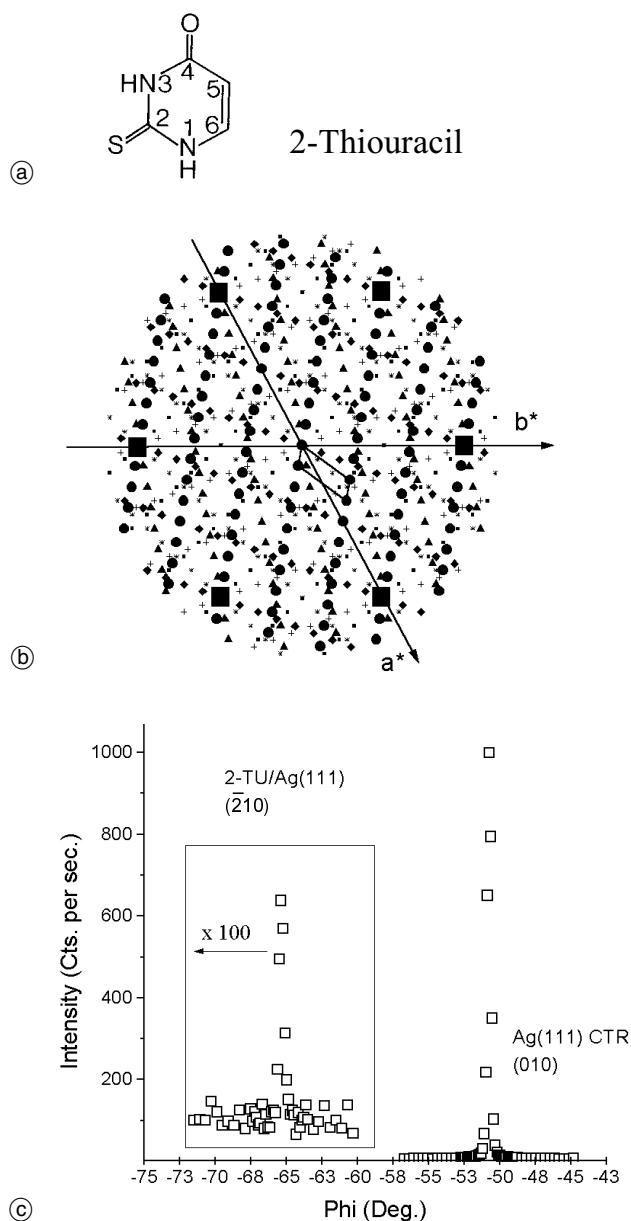


Fig. 1. (a) Structure formula of 2-thiouracil; (b) $(hk0)$ reciprocal lattice plane of the 2-TU/Ag(111)-superstructure. Large solid squares and small symbols represent the first order Ag(111) and superlattice points, respectively. Each class of symbol represents the reciprocal lattice points of one domain. The unit cell of one domain (filled circles) is indicated by the parallelogram; (c) Profiles of the 2-TU $(\bar{2}10)$ -reflection and the Ag (010)-CTR-reflection.

and additionally has been used as a anti-cancer drug in medical applications. The structure formula of the 2-TU molecule is shown in Fig. 1a. 2-TU is derived from the nucleic acid base uracil used in RNA and its bulk structure has been analyzed [19]. The molecular arrangement of 2-TU adsorbed on Ag(111) and graphite (0001) is investigated by SXRD and STM, respectively. Because of differences in the substrate both in surface geometry as well as in interaction strength the arrangements of the molecules are expected to differ considerably. This can be explained by the fact that the 2D molecular crystal lattices are determined by both intermolecular interactions which also govern the 3D lattices (mainly via hydrogen bonds), and by the strength of the lateral variation of the adsor-

bate-substrate interaction. Consequently, for weakly chemisorbed 2-TU on Ag a commensurate superstructure is observed whereas for physisorbed 2-TU (on graphite) an incommensurate structure is formed. Moreover, the SXRD measurements (2-TU/Ag) indicate considerable structural modifications like increased intramolecular and intermolecular bondlengths as compared to the bulk.

2. Results and discussion

2.1 Surface x-ray diffraction: 2-TU/Ag(111)

The commensurate superstructure of 2-TU on Ag(111) was prepared in UHV by de-position of the molecules from a Knudsen cell on the substrate surface kept at 340 K in order to obtain a well ordered structure. The relation between the unit cell axes of the superstructure and the substrate is given by the matrix $\begin{pmatrix} 4 & 5 \\ 2 & 3 \end{pmatrix}$, which has already been proposed earlier by LEED [20]. The area of the superstructure unit cell equals to 159 \AA^2 which is 22 times the size of the Ag(111)- (1×1) unit mesh. Integrated x-ray reflection intensities were collected in situ under total reflection conditions of the incident beam by using an 18 kW rotating anode x-ray generator and a sagittally focusing pyrolytic graphite monochromator selecting $\text{CuK}\alpha$ -radiation. From the width of the reflection profiles an average domain size in the order of 500–1000 \AA has been determined. This value is typical for superstructures of the pyrimidine-derivatives investigated so far [20].

Fig. 1b shows a schematic view of the $(hk0)$ -plane of the reciprocal lattice. Large solid squares represent the Ag crystal truncation rods (CTR's) [15], the other symbols correspond to superlattice spots. Each type of symbol represents one of six equivalent domains. The reciprocal unit cell of one domain is represented by the solid parallelogram. A considerably redundant data set consisting of 113 in-plane intensities, $|F_{hk0}|^2$, was measured reducing to a set of 37 independent reflections by symmetry equivalence. In addition the intensities along four superlattice rods (two symmetry independent) were collected up to maximum normal momentum transfer of $q_z = 0.67 \text{ \AA}^{-1}$ (0.75 reciprocal lattice units) yielding a data set consisting of 61 reflections in total. The standard deviations (σ) were estimated from the reproducibility of symmetry equivalent reflections and by the counting statistics. They are in the range of 10–15% for the strong reflections, but are up to 50% for the weakest ones. In this context it must be noted that organic molecules are mainly composed of weakly scattering atoms and exhibit large superstructure unit cells of low symmetry. Consequently, the $|F|$ -values of organic monolayers are extremely small. This is illustrated by Fig. 1c which compares the profile of the $(\bar{2}10)$ 2-TU-reflection with the (010)-CTR reflection of the Ag(111) substrate. The intensity of the latter is equivalent to $1/3$ of a Ag-monolayer [15]. The profile of the superlattice reflection is exaggerated by a factor of 100. The structure analysis was performed by least square refinement using the program SHELX-97 [21]. In order to keep the number of free parameters at a minimum (three rotational and three

translational per molecule) the pyrimidine rings were treated as rigid units, however we allowed for a variation of the overall intra-ring bond distance and for the variation of the bond lengths to the exocyclic ligands O and S. The latter were also fixed to be located within the pyrimidine-ring plane. Temperature factors were kept constant.

The best fit model for the superstructure is shown in Fig. 2a. It is compared with the projection of the bulk structure onto the $(\bar{1}\bar{1}\bar{1})$ plane (Fig. 2b) which is parallel to the molecular stacks. The basic feature of the bulk structure is a chain of molecules linked by hydrogen bonds involving both, $O \cdots H-N$ and $S \cdots H-N$ bonds (as shown by dashed lines). The sequence has a two-molecule periodicity ABAB... . In this way parallel stacks of zig-zag chains are formed. The O-N and S-N distances are 2.83 Å and 3.31 Å, respectively. These values can be considered as typical for hydrogen bonds. The molecules within each chain, (I) and (II), are nearly at the same level, therefore dense lateral packing requires a vertical separation (3.48 Å) of the adjacent chains.

Reduction of the dimensionality induces modifications on the lateral packing. Furthermore, chemical interaction of the S and O atoms with the substrate involves site specific bonding which is related to the commensurability of the structure. As a result of these chemical and steric interactions several modifications relative to the bulk structure are observed in the surface structure: The lateral packing density of the molecules is considerably reduced. Along the molecular chains the $S \cdots H-N$ bonds and one half of the $O \cdots H-N$ bonds are broken. Distances for the S-N and O-N pairs of 4.04(10) and 3.64(10) Å, respectively (see Fig. 2a), are far too large as to be considered as intact

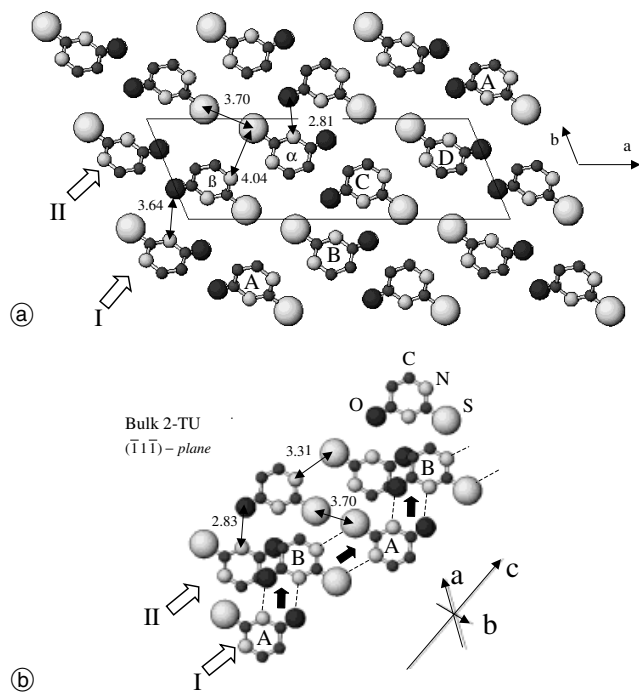


Fig. 2. (a) Structure model for 2-TU/Ag(111). Some interatomic distances are given in Å. Adjacent chains are indicated by the arrows, the sequence of molecules is emphasized by capital letters ABCDA...; (b) Bulk structure projected onto the $(\bar{1}\bar{1}\bar{1})$ plane. The chain periodicity is ABAB... Intermolecular hydrogen bonds are indicated by the dotted lines.

hydrogen bonds. Along the chains there is only one $O \cdots H-N$ distance (2.81 Å) which might be related to an hydrogen bond. As a consequence of the in-equivalent intermolecular distances, the chain periodicity is doubled (ABCDAB...) as compared to the bulk (ABAB...). The reduction of the packing density is somewhat relaxed by the out of plane tilt of the pyrimidine rings which is 31° for ring labeled (α) and 36° for (β). The error bar for the tilt is estimated to lie in the $5-10^\circ$ range. Qualitatively, the tilt of the rings is directly observable by the intensity distribution along the superlattice rods (not shown) which are almost constant with increasing q_z . This is because flat lying molecules would lead to a continuously decreasing intensity with increasing q_z . We may speculate that the tilt might be related to steric requirements necessary to allow the S and O atoms to occupy specific surface sites, but without analysis of CTR data it is not possible to determine the adsorption site of the molecules relative to the surface.

Apart from the modification of the intermolecular arrangement there is also evidence for a modification of the intramolecular structure which can be attributed to the covalent interaction of the molecule with the substrate. In Fig. 3a the bond lengths of the molecule in the bulk structure [19] are indicated by the small bold numbers. Within the pyrimidine ring they vary between 1.338 Å and

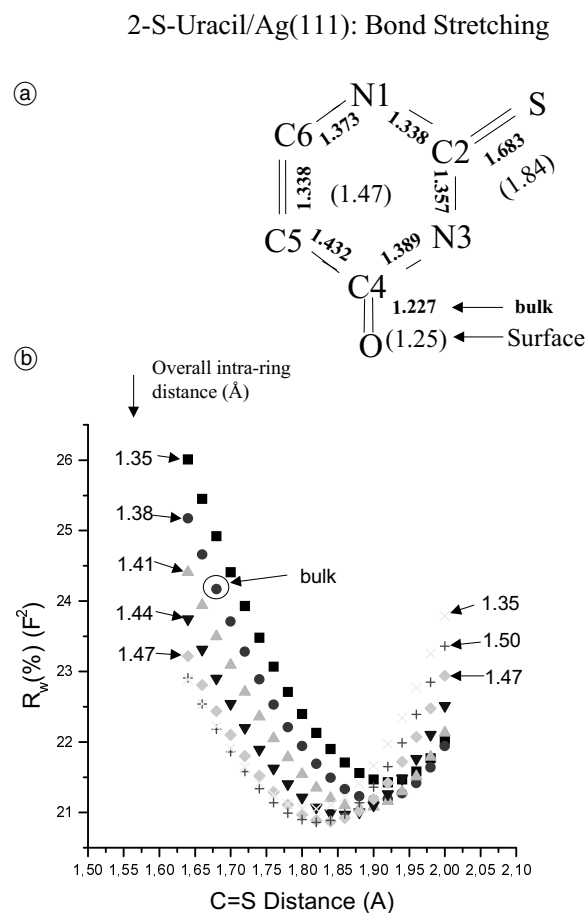


Fig. 3. (a) Internal structure of the 2-TU molecule. Bond lengths are given in Å (bulk: small letters, surface: large numbers in brackets); (b) Weighted residuum $R_w(%)$ as a function of the C=S bond distance. Different curves correspond to different overall bond lengths within the pyrimidine ring as indicated.

1.432 Å, the C=S and C=O double bond length equal to 1.227 Å and 1.683 Å, respectively. The Fig. 3b shows the weighted residuum of the structure factor intensities, $R_w(|F|^2)$ as a function of the C=S bond length. The curves correspond to different bond distances within the ring, where we have assumed one overall value. Allowing for in-equivalent distances within the pyrimidine ring did not improve the fit. There is a significant dependence of the fit quality on both, the C=S and the inner ring distance. The best fit [$R_w = 20.87\%$, Goodness of fit (GOF) = 0.852]¹ is obtained for a C=S distance of 1.84(7) Å and an inner ring distance of 1.47(10) Å. In comparison with the bulk this corresponds to an increase of 0.16 Å for the C=S bond and of 0.11 Å for the inner ring distance. For the latter we reference to the average value of 1.38 Å. The bulk values are indicated by the open circle in Fig. 3b.

We can conclude that the bond length increase of the C=S bond is outside the error bars of the distance determination which is in the range of about 0.05–0.1 Å. However, due to the simplifications necessary to treat the pyrimidine ring adequately the intra-ring distances are less accurate (≈ 0.1 Å), however this still indicates a certain increase of the pyrimidine ring size. Finally, it should be noted that the C=O double bond is not strongly affected, we find a distance of 1.25(5) Å which within the error bar is well comparable with the bulk value 1.227(4) Å. These results suggest, that the adsorbate-substrate interaction can be mostly attributed to the covalent interaction of the S atoms with the substrate leading to a weakening of the S=C bond.

Finally, it should be noted that the high quality of the fit as measured on the basis of $R_w(|F|^2)$, $R_w(|F|)$ and the GOF indicates the high reliability of the structure analysis. Different structure models such as assuming the molecules lying flat on the surface and linked by $O \cdots H-N$ and $S \cdots H-N$ bonds yield agreement factors at least 2–3 as large as those obtained on the basis of the model discussed so far.

2.2 Scanning tunneling microscopy: 2-TU/graphite (0001)

In a second experiment 2-TU molecules were adsorbed on the basal plane of graphite which exhibits similar to the Ag(111) surface a low corrugated hexagonal lattice but with considerably smaller surface energy. The 2-TU films were prepared by the sizzling technique [5], where a μ -liter drop of 2-TU in aqueous solution (0.01 mg/ml) was applied to the surface of highly oriented pyrolytic graphite (HOPG) heated to around 350 K under ambient conditions. This temperature provided enough thermal energy to allow the spreading and diffusion of the molecules and the formation of mono-molecular thin layers besides the evaporation of the water molecules with energies bigger than 10 kcal/mol. The STM measurements were performed at room temperature with a home built instrument using a chemically etched W tip at constant tunneling current (between 100 and 500 pA) with a tip voltage of -1 V. The

STM image of a single domain region of the molecular lattice is shown in Fig. 4a. Bright regions can be interpreted by elevated molecular regions corresponding to suitable tunneling orbitals whereas dark regions correspond to depressions. However, since the tunneling image depends on a superposition between apparent corrugation and electronic structure of the adsorbate system a straight forward interpretation of the image is not possible. Nevertheless, from the periodicity of the features it is possible to derive the molecular lattice and – by applying molecular mechanics minimal energy calculations based on the experimentally determined unit cell parameters [22] – the mutual arrangement of the molecules of the structure. After scan correction and determination of the unit cell and registry of the molecules in the STM images Fig. 4a shows as a result the molecules superimposed over the bright regions in order to emphasize their positions within the lattice periodicity. We suggest that the molecules are lying flat on the graphite surface with unit cell parameter of $a = 10.7 \pm 0.2$ Å, $b = 16.4 \pm 0.2$ Å, $\gamma = 90^\circ$, such forming a coincident mesh with matrix $\begin{pmatrix} 5 & 3 \\ 3/4 & 25/4 \end{pmatrix}$ between molecular superstructure and substrate. The model cell contains four molecules (corresponding to an area of 176 Å²) and the rotation angle with respect to the substrate is 6° . Each molecule is hydrogen-bonded to its neighbors by two double bonds in a zig-zag configuration as shown in the model of Fig. 4b.

The molecular arrangement obtained by STM is remarkably similar to the $(\bar{1}\bar{1}\bar{1})$ plane of the 2-TU bulk structure and differs considerably from the monolayer on

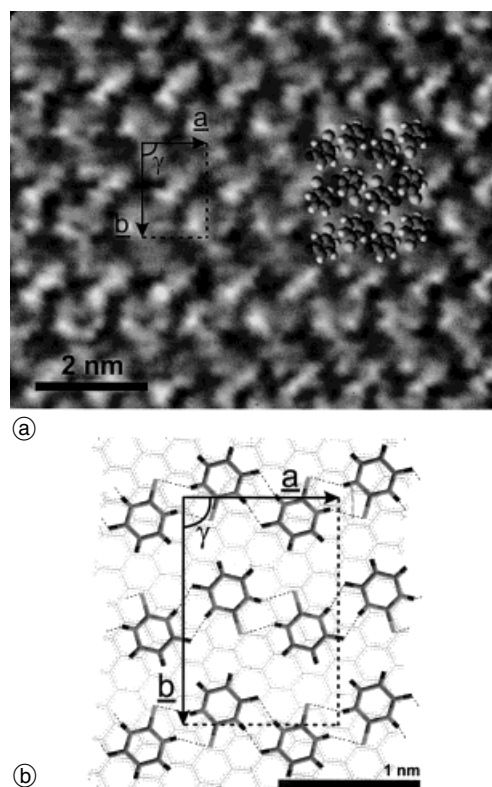


Fig. 4. (a) STM image of a single domain region of 2-TU/graphite (0001); (b) Energy minimized lattice model with tentative hydrogen bonds (dashed lines).

¹ The unweighted residuum, $R_u(|F|)$, is equal to 0.14 for all data and 0.07 for 33 reflections with $|F| > 4$.

Ag(111). This suggests that the molecular arrangement is mainly determined by the intermolecular binding constraints in the case of graphite, whereas on Ag(111) the covalent bond and epitaxial requirements play the essential role for the formation of the 2D adsorbate mesh.

3. Summary

We have investigated the structures of a large organic molecule (2-thiouracil) on flat substrate surfaces using SXRD and STM. Both methods which provide complementary information -SXRD probing the long range average structure whereas STM probes the local structure- are ideally suited for the study of large organic adsorbates, however only very recently SXRD has been applied for this purpose. In both cases [2-TU/Ag(111) and 2-TU/Graphite(0001)] the surface molecular structure is characterized by a zig-zag arrangement of the molecular chains. Although there are fundamental relationships to the bulk molecular arrangement, the SXRD analysis indicates that significant differences exist in detail for both, the inter- and intramolecular structure for the Ag(111) substrate. The reduced dimensionality and chemical interaction with the substrate leads to a modification of the lateral molecular packing. The intermolecular hydrogen bonds characteristic for the bulk structure are broken. In addition we find an elongation of the intra-ring and the C=S bond distances by about 0.11(10) Å and 0.16(7) Å, respectively which can be attributed to the covalent interaction of the molecules with the substrate. In the case of the inert graphite surface STM has shown a very similar structure to the bulk, therefore making 3D-crystal structure prediction based on 2D unit cell determination possible. This may be of great value especially in cases, where bulk crystallization is difficult, however the molecules easily adsorb to a substrate surface.

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