The Structure of [4-(Phenylazo)phenoxy]hexane-1-thiol Self-Assembled Monolayers on Au(111)

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The structure of [4-(phenylazo)phenoxy]hexane-1-thiol (AzoC₆) self-assembled monolayers (SAMs) on Au(111) has been investigated with scanning tunneling microscopy (STM) and Fourier transform infrared-reflection absorption spectroscopy (FTIR-RAS). The FTIR-RAS results yield a tilt angle of the molecules close to 0° , which significantly differs from the 30° tilt angle of linear *n*-alkanethiols. In STM images two types of domains are observed that have equal unit cell dimensions and two molecules per unit cell but show different tunneling contrasts, which is attributed to a different arrangement of the molecules within the unit cell. The relationship of the molecular lattice to the substrate lattice is found to be commensurate.

I. Introduction

Self-assembled monolayers on solid surfaces have been investigated to a large extent during the past decade. A thorough overview concerning SAMs is given by Schreiber.¹ SAMs are potentially interesting for industrial applications such as corrosion inhibition, gas sensors, bio-templates, etc.

The by far best analyzed systems are linear *n*-alkanethiols on Au(111).² Since the main driving mechanism for the ordering within the thiol monolayer is the strong interaction between the thiol headgroup and the gold substrates, the idea to attach a functional group to the tail of the alkyl chain in order to achieve ordered arrays of these functional units has been developed. Photochromic thiol molecules could, for example, be useful in the fields of photopatterning or data storage.

The structure of SAMs of various azobenzene-functionalized thiols on Au(111) has been investigated previously by means of real space analysis³⁻⁸ (STM or atomic force microscopy [AFM]) and X-ray diffraction.^{4,8} One important result of these investigations is that the azobenzene moieties form an incommensurate surface mesh. This is in contrast to the typical situation for SAMs of linear *n*-alkanethiols with a commensurate $(\sqrt{3} \times \sqrt{3})R30^\circ$ cell caused by the covalent bond between the sulfur atoms of the thiol groups and the gold atoms of the substrate surface. Apart from this commensurate lattice, there exists a $c(4 \times 2)$ superlattice in most alkanthiol SAMs on Au(111) that was shown to be mainly caused by sulfur \leftrightarrow sulfur interactions resulting in nonequivalent binding sites on the Au(111) surface lattice.⁹ Nonequivalent binding sites are also quoted to explain the incommensurate unit cell in SAMs of $AzoC_6$ on Au(111).³

More often it is assumed that the strong interaction between the azobenzene moieties causes the formation of an incommensurate lattice of the molecular end groups (azobenzene), with the sulfur atoms of the headgroup still occupying equivalent gold lattice sites, i.e., distances between the headgroups on the substrate are still related to the 5.0 Å distances within the Au(111) plane while the spacings between the azobenzene moieties are not. The discrepancy between the latter assumption and the incompatible lattice constants as observed in STM/AFM investigations^{4,7,8,10} has been tried to overcome with the help of the so-called *bundle model*. In this model the alkyl chains of the molecules in a domain have different tilt angles and are leaning inward toward the domain center. Therefore, the domain size is assumed to be limited by the amount of tilting the alkyl chains can undergo.⁴

Different lattice constants were reported for azobenzeneterminated alkanethiol SAMs. For $AzoC_{10}^7$ and $AzoC_{11}^4$ rectangular lattices with two molecules in the unit cell were reported. In both cases a herringbone arrangement of the molecules was suggested for sterical reasons (area per molecule significantly below 20 Å²) and the bundle model was used to explain the SAM structure. On the contrary, Wolf et al.^{3,6} obtained an almost rectangular lattice of $AzoC_6$ with two molecules per unit cell but an area per molecule of about 24.1 Å². The significant difference in lattice constants was attributed to experimental conditions¹⁰ (Wolf et al. investigated their SAMs in ethanol), or the credibility of their results was even called into question.⁸

The main goal of this work is to revisit $AzoC_6$ (Figure 1) SAMs on Au(111) in the light of the results mentioned above. We will attempt to demonstrate that we neither have to assume an incommensurate structure nor do we need the bundle model to explain the observed SAM structure of $AzoC_6$.

II. Experimental Section

A. Synthesis of [4-(Phenylazo)phenoxy]hexane-1-thiol. 1. Synthesis of 6-Bromohexane-4-azobenzene. 4-(Phenylazo)phenol (1.98 g, 0.01 mol), 1,6-dibromhexane (5.34 mL, 0.035 mol), and potassium carbonate (3 g, 0.02 mol) were dissolved in acetone (30 mL) and were refluxed for 6 h. The orange solution was cooled to room temperature, and 100 mL of water was added. The orange precipitate was filtered off and washed with water and ethanol. The precipitate was then crystallized

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Figure 1. Chemical structure of the [4-(phenylazo)phenoxy]hexane-1-thiol molecule. It is abbreviated as $AzoC_6$ in the text.

from 2-propanol to get 6-bromohexane-4-azobenzene in 80% yield (2.89 g).

¹H NMR (CDCl₃): δ 1.5–1.9 (m, 8H, aliphatic CH₂), 3.43 (t, 2H, J = 6.7 Hz, BrCH₂), 4.06 (t, 2H, J = 6.35 Hz, OCH₂), 7.00 (d, 2H, J = 9.06 Hz, aromatic), 7.42 (t, 1H, J = 7.25 Hz, aromatic), 7.49 (t, 2H, J = 7.6 Hz, aromatic), 7.87 (d, 2H, J = 7.19 Hz, aromatic), 7.91 (d, 2H, J = 9.0 Hz, aromatic).

Anal. Calc for C₁₈H₂₁ON₂Br: C, 59.84; H, 5.86; N, 7.75; Br, 22.11. Found: C, 59.76; H, 6.05; N, 7.81; Br, 22.12.

2. Synthesis of [4-(Phenylazo)phenoxy]hexane-1-isothiouronium Bromide. 6-bromohexane-4-azobenzene (0.86 g, 23.8 mmol) and thiourea (0.23 g, 3 mmol) were dissolved in 30 mL of deoxygenated ethanol. The orange reaction mixture was refluxed for 6 h. After the solution was cooled to room temperature, it was concentrated. The residue was washed with pentane and crystallized from ethanol/pentane to get [4-(phenylazo)phenoxy]hexane-1-isothiouronium bromide in 72% yield (0.75 g).

¹H NMR (DMSO): δ 1.46–1.8 (m, 8H, aliphatic CH₂), 3.15 (t, 2H, J = 7.33 Hz, BrCH₂), 4.09 (t, 2H, J = 6.4 Hz, OCH₂), 7.13 (d, 2H, J = 8.98 Hz, aromatic), 7.52 (t, 1H, J = 7.19 Hz, aromatic), 7.57 (t, 2H, J = 7.36 Hz, aromatic), 7.85 (d, 2H, J = 7.24 Hz, aromatic), 7.9 (d, 2H, J = 8.95 Hz, aromatic), 8.96 (s, 4H, NH₂).

Anal. Calc for $C_{19}H_{25}OSN_4Br$: C, 52.17; H, 5.76; N, 12.81; S, 7.33; Br, 18.26. Found: C, 52.35; H, 5.77; N, 12.29; S, 7.78; Br, 18.1.

3. Synthesis of [4-(Phenylazo)phenoxy]hexane-1-thiol. [4-(Phenylazo)phenoxy]hexane-1-isothiouronium bromide (0.7 g; 1.6 mmol) was dissolved in ethanol (30 mL). An aqueous solution (5 mL) of NaOH (0.06 g) was added. The reaction mixture was refluxed for 3 h and then cooled to room temperature. After neutralization with H_2SO_4 the mixture was concentrated. The residue was dissolved in ether, extracted with water and dried over Na₂SO₄. The ether was evaporated, and the residue was crystallized from ethanol/chloroform to get [4-(phenylazo)phenoxy]hexane-1-thiol in 64% yield (0.34 g).

¹H NMR (CDCl₃): δ 1.2–1.9 (m, 8H, aliphatic CH₂), 2.55 (q, 2H, J = 7.36 Hz, SCH₂), 4.04 (t, 2H, J = 6.44 Hz, OCH₂), 6.99 (d, 2H, J = 8.97 Hz, aromatic), 7.42 (t, 1H, J = 7.27 Hz, aromatic), 7.48 (t, 2H, J = 7.53 Hz, aromatic), 7.86 (d, 2H, J = 8.45 Hz, aromatic), 7.9 (d, 2H, J = 8.96 Hz, aromatic).

Anal. Calc for C₁₈H₂₂OSN₂: C, 69.64; H, 7.14; N, 9.02; S, 9.05. Found: C, 69.31; H, 7.2; N, 8.94; S, 9.86.

B. Substrate and Monolayer Preparation. At first, mica was freshly cleaved and baked at 750 K for 5 h in a UHV chamber. Subsequently, 50-100 nm gold (Aldrich, 99.5% purity) was deposited onto the mica substrate at a pressure of 10^{-7} mbar. After the deposition, the substrate was annealed at 750 K for another 2 h. This procedure leads to surfaces with atomically flat terraces and grain sizes of typically several hundred nanometers. The samples were taken out of the chamber immediately before immersion and put into a 1 mM solution of AzoC₆ in dichlormethane for about 24 h at room temperature. After removal from the solution, the sample was carefully rinsed with the pure solvent and blown dry with N₂ and investigated with STM. Some samples were additionally annealed at 90 °C for 12 h in order to investigate possible changes in the sample composition following this treatment.

C. FTIR-RAS. Infrared spectroscopy was performed with a Bruker IFS-66 spectrometer equipped with an liquid-N₂ cooled MCT detector and an internal reflection unit Bruker A 518. The optical path was evacuated. An p-polarized beam at an incident angle of 80° to the surface normal was used for the FTIR-RAS measurements. The spectra were taken at a 2 cm⁻¹ resolution, and 1000 interferograms were co-added to yield spectra of high signal-to-noise ratio. The absorbance spectrum is defined as $-\log(R/R_0)$, where R_0 and R are the reflectance of the pure and film-covered gold substrate, respectively. Reference spectra of the bulk compounds dispersed in KBr were obtained in transmission at normal incidence.

D. STM Imaging. All images presented herein were obtained with a Nanoscope III (Digital Instruments) in air at room temperature. The STM tips were cut from a PtIr wire (0.25 mm). To obtain images with molecular resolution of AzoC₆, the tunneling current had to be <5 pA, which in turn implies a rather low scanning frequency <6 Hz. The tunneling voltage applied was in the range of 0.8-1.2 V. Since a low scanning frequency introduces significant distortion into the STM images due to thermal drift of the scanner, special care has been taken to correct the images by recording consecutive STM scans. It can be shown that simple averaging of lattice vectors obtained from two consecutive images, as described in ref 3, does not give correct values unless the amount of drift is very small. However, in that case a drift correction would be obsolete anyway. We use the drift correction procedure described by Staub et al.¹¹ Based on the assumption that the drift vector is constant for two consecutive scans and negligible for a single scan line (which means that the scan lines are always horizontal), this method yields three correction parameters for each of the two images: two scaling factors (horizontal and vertical) and a shear angle.

Other errors such as nonlinear piezo response or nonorthogonality of the scanning axes have been tried to overcome by calibration of the STM for exactly the scanning speed and scanning size used to image $AzoC_6$ samples. This has been achieved by imaging graphite single crystals. Both the correction for drift and the calibration can be written as 2×2 matrices. Before any image analysis, the product of these matrices was applied to STM images using standard image processing software. Because these corrections are based on measurements in distorted images, they implicitly contain experimental errors themselves. Since it would be quite complicated to calculate experimental error bars for measurements in corrected STM images, we assumed the correction methods to be error free and estimated the experimental error bars (2 pixels inaccuracy in the respective FFT images).



Figure 2. Infrared spectra of $AzoC_6$: (a) FTIR spectrum of the bulk substance (dispersed in KBr, transmission); (b) FTIR-RAS spectrum of the SAM on Au(111). The curves are shifted and scaled for better comparability. The inset, showing a spectrum of otadecanethiol on Au(111), is provided for comparison. Besides the two CH₂ strechting modes, it exhibits an additional peak caused by the CH₃ tail group of the octadecanethiol molecule.

III. Results and Discussion

A. FTIR-RAS. Figure 2 shows the FTIR spectra of the bulk AzoC₆ (dispersed in KBr, transmission) and that of the corresponding SAM on Au(111)(FTIR-RAS). We find a good agreement in the low-frequency region (1100-1600 cm⁻¹) of the two spectra, which is dominated by modes of the azobenzene group. The high-energy region is mainly governed by the symmetric and antisymmetric stretching modes of the CH₂ group at 2850 and 2920 cm⁻¹, respectively. These modes are the strongest in the spectrum of the bulk sample but are completely absent in the SAM spectrum. The differences between the spectra indicate the alignment of molecules. For FTIR-RAS measurements only the E-field component normal to the substrate contributes to the signal.¹² The transition dipoles of the symmetric and antisymmetric vibrations lie in a plane normal to the long axis of the alkyl chain. Therefore, the absence of these modes can only be explained by assuming the long axis of the alkyl chain to be nearly normal to the surface. However, the relatively short alkyl chain would only yield small stretching mode signals for other tilt angles close to 0° as well. We assume a large error of $\pm 10^{\circ}$ for that reason. A tilt angle close to 0° was also reported for annealed layers of AzoC11 by Caldwell et al.4

The inset in Figure 2 shows a comparable FTIR-RAS spectrum of an octadecanethiol SAM, provided as a kind of reference. This molecule exhibits tilt angles from the surface normal of $\sim 30^{\circ}$ ^{13,14} in SAMs on Au(111). The ν_{as} and ν_s CH₂ stretching modes are clearly visible in the respective spectrum. Although octadecanthiol has an alkyl chain 3 times larger than that of AzoC₆, this gives further confirmation that the tilt angle of AzoC₆ in fact has to be much smaller than 30° .

B. STM Images of $AzoC_6$ Monolayers. Figure 3 shows two typical STM scans of $AzoC_6$ SAMs on Au(111). We find a densely packed monolayer consisting of domains with diameters between 10 and 20 nm separated by so-called "etch pits", which are known from SAMs of simple alkanethiols and are caused by the relaxation of the Au(111) surface reconstruction upon adsorption of the thiol group.¹⁵ Two types of domains featuring a different molecular contrast were observed. Domains of type A (inset in Figure 3a) show a pattern of bright stripes whereas



Figure 3. STM images showing a SAM of $AzoC_6$ on Au(111) ($V_t = 1.2 \text{ V}$, $I_t = 3 \text{ pA}$). Two types of domains are occurring: (a) domain type A with a pattern of bright lines; (b) domain type B with uniform contrast. There is a contrast-enhanced inset in the lower-right part of each image, showing the two different types of contrast. Both domains feature the same nearly rectangular lattice with $a = 6.3 \pm 0.4 \text{ Å}$, $b = 8.2 \pm 0.4 \text{ Å}$, $\gamma = 88 \pm 2^\circ$ (white box in the respective inset).



Figure 4. FFT of the type A domain in the upper left part of the STM image shown in Figure 3a. The white lines depict the nearly rectangular unit cell observed in SAMs of $AzoC_6$. The pronounced black line crossing the FFT image is not relevant for our discussion and used to be horizontal in the STM image before the drift correction was applied.

domains of type B (inset Figure 3b) show a more regular tunneling contrast of molecules; i.e., every resolved object appears with the same brightness. The insets were contrast enhanced by application of a correlation averaging procedure.¹⁶

Measurements in the FFT of sections showing type A domains (Figure 4) yield a nearly rectangular lattice with $a = 6.3 \pm 0.4$ Å, $b = 8.2 \pm 0.4$ Å, $\gamma = 88 \pm 2^{\circ}$. The corresponding unit cell area is 52 ± 6 Å². Molecular mechanics calculations in which the van der Waals interactions in an array of rigid



Figure 5. After scanning several times at the same sample location, the stripe pattern of domain A disappears and the regular molecular contrast of domain B establishes. This suggests a tip-induced transition of the azobenzene moiety arrangement from that of domain type A to the one of domain type B.

trans-AzoC₆ molecules (rigid especially means that the alkyl chains could not bend) were optimized resulted in an area per molecule of 21.1 Å² using the force field parameters TRIPOS¹⁷ and 22.2 Å² using the UFF force field.¹⁸ This suggests that there are two molecules in the rectangular unit cell. The primitive and commensurate ($\sqrt{3} \times \sqrt{3}$)R30° cell of alkanethiols (21.6 Å²) is also less than half as large.

Additional confirmation for the assumption of two molecules per unit cell comes from the appearance of the molecules in domain type B. The lattice parameters in this domain are found to be exactly the same as those of domain type A. The only significant difference is that the second molecule in the unit cell appears with the same contrast as the corner molecule. However, in both cases the molecular contrast is not sufficient to allow an exact determination of the mutual arrangement of the two molecules, especially that of the azobenzene moieties, within the unit cell from our STM images. What we can conclude from the different contrast of molecules in the two domain types is that there must be a different arrangement of the molecules within the unit cell. The bright stripes of domain A could be caused by more closely associated azobenzene moieties compared to domain B.

Both calculation methods we performed for an array of $AzoC_6$ molecules as mentioned above resulted in a face-to-face arrangement of the azobenzene moieties, which is in agreement with the arrangement of $AzoC_{10}$ in the crystalline state.⁷ However, calculations performed for a *trans*-azobenzene *crystal* show that there is a herringbone arrangement of the azobenzene moieties.⁴ Also, for several SAMs of azobenzene-functionalized thiols including $AzoC_{10}$, unit cell parameters were found that can only be explained with the herringbone arrangement of the azobenzene moieties within the unit cell.^{4,7,8}

Wolf et al.,³ who not only found similar lattice constants for AzoC₆, but also observed the two domain types A and B, concluded a dimer arrangement of azobenzene moieties for domain type A from the STM image contrast. We sometimes observe tip-induced $A \rightarrow B$ domain transitions. This can be seen in Figure 5. After scanning the same area a couple of times, the characteristic stripes in domain A on the left-hand side have disappeared. We have not observed the opposite change in contrast ($B \rightarrow A$ domain transition) but also have no indication for a single equilibrium phase, as we still find the two phases in annealed samples with more or less unchanged domain diameters. Still, we cannot exclude that the surface is initially, i.e., before the tip-induced changes could occur, completely covered by type A domains.

In the following, we want to address the relationship between the molecular lattice and the substrate lattice. To describe this



Figure 6. Drift-corrected STM image of $AzoC_6$ on Au(111) showing several domains of type A on the same gold terrace (lower half of the image). Two are found to be equivalent by rotational symmetry of the substrate (domains corresponding to the directions S1 and S2), while the domain with its stripes parallel to S3 can only be a mirror domain. Evaluation of the stripe pattern yields the substrate mirror axis m_1 , i.e, the orientation of the molecular layer with respect to the substrate lattice. The gold step parallel to m_1 suggests that the found mirror axis is a $\langle \bar{1}10 \rangle_{Au}$ direction.

relation, we will use the angle $\delta = \angle (a, \langle \bar{1}10 \rangle_{Au})$, where *a* is the short lattice vector of AzoC₆. We find that the angle between the bright stripes of type A domains on the same terrace is often very close to 60°. This fact suggests that these domains are equivalent by rotational symmetry of the substrate, which means that the gold substrate is *at least* determinant for the *azimuthal* orientation of the AzoC₆ lattice. Still, the determination of a substrate lattice azimuth is a difficult task because the SAM completely covers the substrate surface, which prevents the direct observation of the substrate lattice. If AFM is used to image the sample, one can try to increase the cantilever load sufficiently to image the substrate lattice beneath.⁴

In the case of AzoC₆ SAMs we can, however, profit from the stripe pattern of type A domains. Several times we found more than two domains on a single gold terrace. While some domains can be transformed into each other via rotation by 60° or 120°, there are also some that can only be explained by a mirroring operation. This can be seen in Figure 6 for the terrace in the lower half of the image where the axis labeled m_1 has to be a mirror axis of the substrate. However, the hexagonal gold substrate features two nonequivalent mirror axes along the $\langle \bar{1}\bar{1}2 \rangle_{Au}$ and the $\langle \bar{1}10 \rangle_{Au}$ directions, respectively. The fact that m_1 in the present case is parallel to a gold step indicates that it could correspond to a $\langle\bar{1}10\rangle_{Au}$ direction because there is a thermodynamic preference of $\langle \overline{1}10 \rangle_{Au}$ aligned steps over $\langle \overline{1}\overline{1}2 \rangle_{Au}$ aligned steps. This is backed by large scale STM images where series of parallel gold steps were to be seen in relation to the stripe pattern of domain A. If we proceed with that assumption, we find an angle $\delta = 38 \pm 3^{\circ}$ for the rectangular lattice of AzoC₆.

To further investigate the structure, we checked whether the obtained molecular lattice represents an epitaxial structure by using the software EPITAXY,¹⁹ which works with a geometric

 TABLE 1: Experimentally Obtained Lattice Parameters vs

 Those of the Commensurate Model Unit Cell

	a/Å	$b/{ m \AA}$	γ/deg	$\delta/{ m deg}$	\mathbf{C}^{a}
STM	6.3 ± 0.3	8.2 ± 0.3	88 ± 2	38 ± 3	
model	6.3	8.0	87	37	$\begin{pmatrix} -4 & 3 \\ 1 & 1 \end{pmatrix}$

 a The matrix **C** in the last column represents the epitaxial relationship between adsorbate and substrate lattice. The matrix elements are all integers, which indicates a commensurate relationship between the two lattices.



Figure 7. Model for the AzoC₆ SAM on Au(111) lattice structure with a = 6.3 Å, b = 8.0 Å, $\gamma = 87^{\circ}$. The rectangular unit cell (dotted lines) in this model corresponds to the measured unit cell (Figure 3). The equivalent unit cell (solid lines) is commensurate with two molecules per unit cell. A commensurate unit cell fits well with the fact that the self-assembly of thiols is usually established by a chemical bond between sulfur and gold.

lattice match model. This software simply rotates a hypothetical adsorbate lattice with respect to the substrate lattice, varies the adsorbate lattice parameters at each rotation step within predefined intervals, and reports any epitaxial relationship found. In our case the lattice parameters *a*, *b*, and γ were varied within the respective experimental error intervals while the screened range for the angle δ was 0–60°. The calculation yielded exactly one commensurate unit cell (Table 1) within the screened lattice parameter range with an angle $\delta = 37^{\circ}$, which is very close to the experimental value $\delta = 38^{\circ}$.

A model for this commensurate relationship with two molecules per unit cell is given in Figure 7. The rectangular unit cell that corresponds to the unit cell deduced from the STM experiments is drawn with dotted lines, whereas the equivalent commensurate unit cell is drawn with solid lines. From the STM investigations we cannot tell the exact position of the second molecule within the unit cell. If we assume a centered lattice (which is suggested by the appearance of domain type B), the second molecule in the unit cell would have to bend slightly in order to occupy a chemisorption site equivalent to that of the first molecule. A simple trigonometric estimation for this situation results in a tilt angle of about 8° for the alkyl chain of the second molecule, based on the assumption that the first molecule is standing upright. This angle would still be in agreement with the FTIR-RAS results for AzoC₆ SAMs.

On the other hand, the two molecules in the unit cell could in fact occupy nonequivalent adsorption sites. Although it is widely assumed that the sulfur of the thiol group is covalently bound to Au(111) lattice sites of one type (hcp hollow or bridging sites), more recent investigations have shown that this is not the case at least for alkanethiol SAMs on Au(111).^{9,20–23} As the structure of the SAM represents a minimum in the total potential energy of the system, which is the *sum* of all substrate \Leftrightarrow adsorbate interactions and intermolecular interactions, the energetic gain resulting from a specific arrangement of the two $AzoC_6$ molecules in the unit cell could be sufficient to "force" the second molecule into a different position relative to the substrate lattice.

Whatever the actual situation is like, the commensurate unit cell represents the "natural" situation of a SAM on gold and does not stress-limit the domain size of the SAM, as is the case for the *bundle model* proposed for similar azobenzene-functionalized thiols.^{4,7,8}

As already mentioned, Wolf et al.³ declared the structure of $AzoC_6$ SAMs incommensurate, for the following two reasons: (i) they find that domains grow undisturbed over gold steps and (ii) they observe similar lattice constants for $AzoC_6$ SAMs on Au(111) as well as polycrystalline gold films, concluding that there is no influence of the Au lattice. We want to discuss these two arguments in the following.

Sometimes we also find domains of $AzoC_6$ that seem to extend undisturbed over terrace steps, which at first glance seems to question the commensurism of the SAM. Terraces separated by a monoatomic step have their lattices shifted along the $\langle \bar{1}10 \rangle_{Au}$ directions by 1.442 Å. If the same type of domain of a commensurate monolayer grows on both sides of the step, there will be the same shift in the adsorbate lattice. However, this shift would even be smaller than the apparent width of bright stripes in domains of type A. In our opinion it is hardly possible to judge whether there is such a small shift in the respective STM images or not, especially since the area around a gold step is usually not well resolved.

Regarding the second argument, one easy explanation for the similar lattice constants for polycrystalline gold films could be the well-known fact that these films also frequently exhibit (111)-oriented terraces. Still, the order within an AzoC₆ SAM on polycrystalline gold could be mainly governed by interactions of the azobenzene moieties; i.e., the lattice constants would represent an energetic optimum for a 2-dimensional array of molecules without substrate. However, if these lattice constants differ only slightly from those of a commensurate surface mesh on the Au(111) lattice, it is in fact very likely that commensurate growth occurs. The amount of energy necessary to distort the molecular lattice of a SAM on Au(111) from the optimal arrangement would be very small and could therefore easily be made up by the energetic gain from the chemisorption at preferred substrate sites. The agreement between our experimental values and the ones measured by Wolf et al. and their correspondence with the commensurate unit cell (Table 1) fit perfectly into this scenario. Additionally, the existence of substrate influence on the SAM structure is in our case easily proven by the observation of rotational domains.

For the striking agreement between the commensurate model and the experimental values, we strongly suggest that $AzoC_6$ SAMs grow in a commensurate structure on Au(111).

IV. Summary and Conclusion

The structure of AzoC₆ SAMs on Au(111) was investigated using the STM and FTIR-RAS techniques. FTIR-RAS measurements show that the molecules in the SAM stand almost perpendicularly to the substrate surface. STM investigations reveal two types of ordered domains with two different arrangements of two AzoC₆ molecules in a nearly rectangular unit cell. These two arrangements exhibit different tunneling contrast. One of them shows a pattern of bright stripes (type A), while all molecules of the other arrangement appears equally bright (type B). Under the influence of the STM tip during scanning we observe transition from domains of type A to domains of type B. We confirmed the larger lattice constants reported for $AzoC_{6}^{3}$ compared to the lattice constants reported for $AzoC_{10}^{7}$ and $AzoC_{11}^{4}$ We further showed that in contrast to SAMs of other azobenzene-functionalized thiols, the SAMs of $AzoC_{6}$ most likely form a commensurate lattice, which is the usual situation for SAMs on Au(111).

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