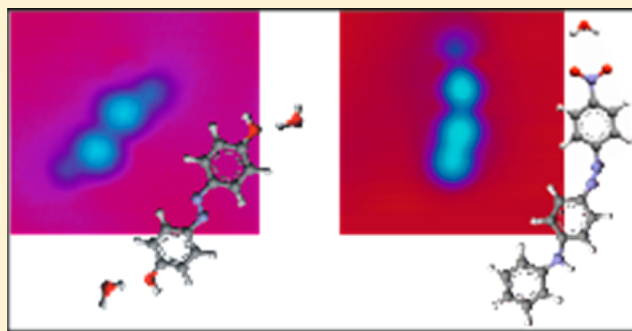


Using the First Steps of Hydration for the Determination of Molecular Conformation of a Single Molecule

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ABSTRACT: Determination of the exact structure of individual molecules is the ultimate goal of high-resolution microscopy. However, the resolution of scanning tunneling microscopy (STM) is intrinsically limited to the extent of molecular orbitals, which frequently do not differ for small changes in the molecular conformation. Here we use the position of water molecules during the first hydration steps of an azobenzene derivative on Au(111) to determine not only the orientation of the end groups with respect to the phenyl rings but also the orientation of the two phenyl rings with respect to the azo group. We investigate the co-adsorption of 4,4'-hydroxy-azobenzene and water molecules on Au(111) by low-temperature STM. The water molecules are attached exclusively to the hydroxyl end groups of the azobenzene derivatives. Predominantly the *trans*-azobenzene molecule with the two hydroxyl groups pointing into opposite directions is adsorbed. As corroborated by the attachment of a single water molecule to 4-anilino-4'-nitro azobenzene on the same inert surface, the method is generally applicable for structure determination of molecules with appropriate end groups. Our study thus gives unprecedented information about the intramolecular orientation based on the first real space observation of the hydration of a functional molecule.



1. INTRODUCTION

Real space information on single molecules provided by scanning probe microscopy gives unprecedented insight into molecular structure, functions, and reactions. The exact structure of a molecule is pivotal for its function and resolving it is consequently the ultimate goal of high-resolution microscopy. For scanning tunneling microscopy (STM), the resolution is intrinsically limited to the extent of molecular orbitals, which frequently do not differ for small changes in the molecular conformation, e.g., a molecular end group rotation. By using short-range chemical forces in tip-modified non-contact atomic force microscopy single bonds within a molecule were visualized¹ giving further fascinating information about the internal structure of molecules² and hydrogen bonding between molecules.³ Though hydrogen bonding might be influenced by both confinement to two dimensions and substrate interaction, this technique provides at the present time the sole possibility to visualize hydrogen bonds in real space and thus unravels fundamental aspects of the molecular interaction on a level that is not accessible otherwise. On the other hand, the water, traditionally considered to be an inert medium, is nowadays increasingly recognized as playing an active role in chemical or biological processes. In future, such processes will be shown as being either solvent-mediated or even solvent-controlled. It is surprising that the question, how the beginning and following water molecules bind to a single functional molecule, has not yet been investigated. Such an investigation is difficult to perform, unless the molecules are immobilized as for instance on a surface.

In this article, we image the first hydration shell of a small dye molecule, 4,4'-hydroxy-azobenzene ($\text{HO}-\text{H}_4\text{C}_6\text{N}=\text{NC}_6\text{H}_4-\text{OH}$) on Au(111). Azobenzene dyes are investigated intensely because of possible functions based on their *cis-trans* isomerization;⁴ Au(111) is one of the least interacting surfaces resulting in a small influence onto the electronic structure of organic molecules. We use the position of water molecules during these first hydration steps around the polar end groups to determine the conformation of the molecule. We confirm the approach at another dye, 4-anilino-4'-nitro azobenzene ($\text{NO}_2-\text{H}_4\text{C}_6\text{N}=\text{NC}_6\text{H}_4-\text{NHC}_6\text{H}_5$), on the same surface. Here, the orientation of the anilino end group with respect to the azobenzene core is reflected in the orientation of water adsorbed at the nitro group.

2. EXPERIMENTAL METHODS

Measurements are performed with a low-temperature STM under ultrahigh vacuum (UHV) conditions. The Au(111) surface is cleaned by repeated cycles of sputtering and annealing. The sputtering gas used is Ne^+ (3×10^{-5} mbar, 1–2 μA , 1.3 keV, 30 min). Annealing is at 900 K for 30 min. 4,4'-hydroxy azobenzene is synthesized according to a published procedure.¹² It is sublimated under reduced pressure at 398 K to reduce the amount of water from the solid to a defined amount. The commercial 4-anilino-4'-nitro azobenzene (from Acros Organics, Disperse Orange 1) has an initial cleanliness of 95%. The solids are filled into a thoroughly outgassed Knudsen cell. Fine tuning of the water content is performed in UHV by annealing the molecules

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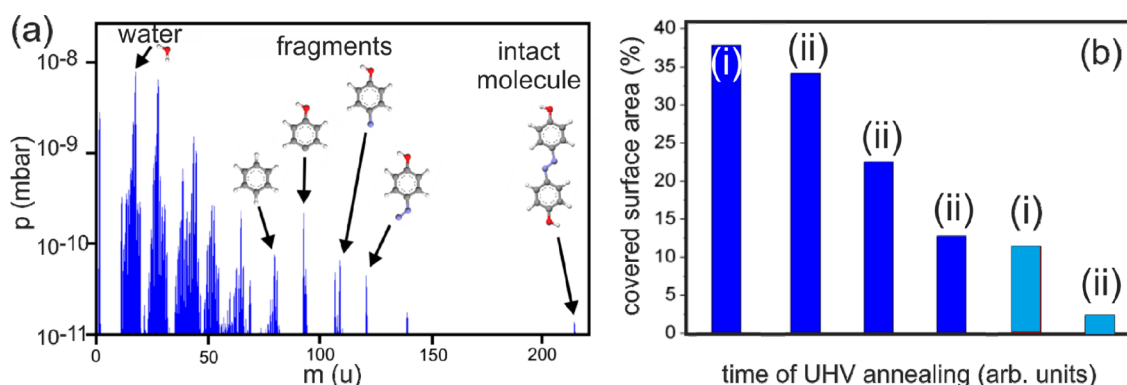


Figure 1. Preparation of molecules: (a) Mass spectrum after 20 h of annealing at 400 K in UHV of 4,4'-hydroxy azobenzene; note that the sensitivity of the spectrometer decreases with increasing mass and that fragments are produced within the spectrometer. (b) Relative area coverage of water as compared to 4,4'-hydroxy azobenzene for different preparations of the molecules, in particular different times of UHV-annealing; different colors indicate different times of ex situ sublimation and different numbers indicate whether UHV-annealing was applied (i) or not (ii).

extensively at around 400 K, while monitoring the evaporated molecules by mass spectrometry (Figure 1a). Via this procedure water:azobenzene surface ratios between 37% and 2% are achieved for 4,4'-hydroxy azobenzene (Figure 1b). For deposition on the surface, the Knudsen cell is heated to 410 and 400 K for the two molecules, respectively. 4,4'-hydroxy azobenzene molecules are deposited with a rate of (7.4 ± 0.5) % ML/min onto the surface at 213 to 233 K. For 4-anilino-4'-nitro azobenzene the Knudsen cell and the surface are held at 400 and 245 K, respectively, and around double the rate is achieved.

After exposure, the sample is transferred to the STM that is operated at a temperature of 5 K. STM images are displayed such that a retraction of the tip from the surface leads to a brighter feature in the STM image. Though only one STM image is shown for each conformation analyzed, the same arrangement is usually found on other parts of the surface as well. Around 500 dihydroxy-azobenzene molecules are imaged with sufficient resolution to make their hydration shell visible. Of these around 50 molecules are analyzed in detail. In particular at high water:azobenzene ratio, some of the dye molecules are covered by water molecules. These structures are not analyzed in the course of this study, but only those for which the dye is clearly identified.

3. THEORETICAL METHODS

For the structural models, the two azobenzene derivatives and water molecules are optimized semiempirically in gas phase using the Parametric Method 3 parametrization of MNDO for the Hamiltonian as implemented in ArgusLab.¹³ The C–N=N–C bond angles of the surface adapted *cis**-isomers are thereby fixed to the values determined experimentally.^{9,14} This approach was used before for 4-amino-4'-nitro-azobenzene and later confirmed by DFT calculations.³ For the anilino-group two different orientations with respect to the azobenzene core are stabilized, both such that the phenyl is in the same plane as the azobenzene core. The orientation of the water with respect to 4,4'-hydroxy-azobenzene is based on the directionality of the hydrogen bonds. From the different possible orientations of the hydrogen atoms not involved in hydrogen bonding, one option is shown, but others are possible. The typical gas phase value of 0.3 nm is used for the O–H...O bond length, in good agreement with the position calculated for one water molecule attached to a 1-hydroxy-4-nitrogen-phenyl. For the water being the hydrogen-bond acceptor and the hydrogen-bond donor the semiempirically calculated O–H...O distance is 274 and 279 pm, respectively, somewhat smaller than the gas phase value. For larger water structures, additional water molecules are positioned into the direction of the additional protrusions with the gas phase O–H...O bond length, and the ice rules are invoked for suggesting a reasonable hydrogen bonding. For 4-anilino-4'-nitro-azobenzene the water position as calculated for nitro-benzene is used giving an O–H...O bond length of ~ 340 pm.

4. RESULTS: HYDROXY AZOBENZENE

Dumbbell shapes with and without additional single protrusions are observed after adsorption of 4,4'-hydroxy azobenzene and water (Figure 2). The circular protrusions are attributed to water monomers due to their apparent similarity to water monomers on a multitude of metal surfaces.⁵ Furthermore, the size of water monomers on Au(111)⁶ is in good agreement to the one of the single protrusions with a FWHM between 0.6 and 0.7 nm observed here. Note that the position of the hydrogen atoms with respect to the tunneling direction influences the apparent height of a water molecule, but the center of the protrusion is (almost exactly) above the oxygen atom for the small tunneling voltages used.⁸ A pure water structure (identified before⁷ on Ag(111) and Cu(111)) is shown in the upper left corner of Figure 2a for direct comparison to the single protrusion in Figure 2b. Indeed, the line scans across this structure and across the water attached to azobenzene show the same shape (Figure 2d, cyan and magenta lines).

The dumbbell shape is attributed to single molecules of 4,4'-hydroxy azobenzene (Figure 2a).⁹ The symmetric dumbbell shape allows us to identify the orientation of the molecular axis (in parallel to the dumbbell) and the position of the azo group (at the neck of the dumbbell). However, fine details about the molecular structure, here the molecular conformation, the low-energetic rotational orientation of the two hydroxyl groups, and the relative orientation of the azo group, cannot be determined from such an image. Note that polar end groups interacting strongly with a metallic surface induce an opening of the C–N=N–C bond angle to allow for a planar form of the *cis*-isomer,¹⁰ named *cis**. Thereby, the distance measured between the two maxima of a double Gaussian fit to the line scans across the maxima is (0.7 ± 0.1) nm for both isomers.⁹ The isomers can thus not be discriminated based on measuring this distance.

Already for the *trans*-isomer, there are six different possibilities of molecular conformation as shown in Figure 3a. These are close to isoenergetic. The hydroxyl groups may point to the same side or to opposite sides of the molecular axis. Two possibilities exist for the hydroxyl groups pointing to the same side. For each of these three arrangements there are two different possibilities for the relative orientation of the azo group. In the following, we differentiate between the prochiral azo group orientations by naming them *re* (right-hand side in Figure 3a) and *si* (left-hand side in Figure 3a).

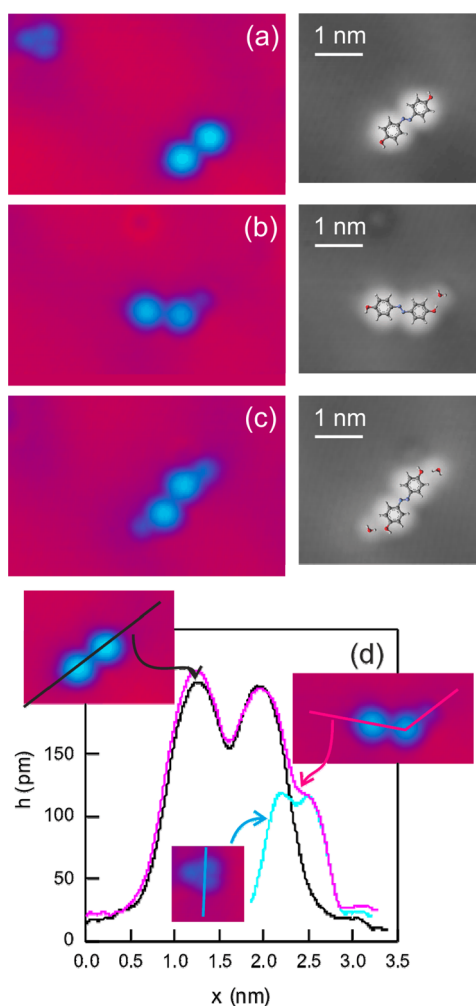


Figure 2. Determination of conformation of 4,4'-hydroxy azobenzene via water attachment. STM images on false color scale; right-hand column shows the same image in gray scale superimposed with a ball-and-stick model derived from Figure 3b, $V_t = 59$ mV, $I_t = 10$ pA: (a) azobenzene molecule without water molecules attached. The ball-and-stick model chosen is not the only one that fits to this symmetric shape, but any other of the conformations shown in Figure 3 fit equally well. (b) Only one water molecule attached to azobenzene molecule. Orientation of hydroxyl group on left-hand side remains undetermined (c) on each side, one water molecule is attached to an azobenzene molecule in majority conformation, in which the hydroxyl groups point to opposite sides of the molecular axis of a *re*-azo group (d) line scans across the structures in panels (a) and (b) as indicated in the insets; across water structure in cyan, across azobenzene molecule without water attached in black, and across azobenzene molecule and attached water molecule in magenta.

The first solvation shell of the molecule is expected to consist of four water molecules as shown in Figure 3. Thereby, each hydroxyl group may hydrogen bond two additional water molecules. Due to the directionality of the hydrogen bond, the position of the water with respect to the molecular axis is characteristic for the molecular conformation, both for the relative orientation of the hydroxyl groups and of the azo group.

Obviously, there is a large difference in angles for the water attached to the *trans*- and the *cis**-isomer with respect to the axis of the dye (Figure 3). An angle close to 0° or larger than 58° corresponds to a *cis**-isomer. All angles between 22° and 44°

belong to *trans*-isomers. After identification of the isomer, the orientation of the hydroxyl groups can be determined. For the *cis**-isomer a symmetric arrangement of the water molecules on both groups is expected, if the angles are symmetric. If not, then the hydroxyl groups point to opposite sides. For the *trans*-isomer, an asymmetry of the angles on the two ends indicates that the hydroxyl groups point to the same side of the molecular axis (lowest row in Figure 3a). If the angles are symmetric and thus the hydroxyl groups point to opposite sides, there is still a unique combination of angles for each possible arrangement as shown in Figure 3a. This difference in angles is large enough to be distinguished using STM, even if the hydrogen bonds deviated slightly from their perfect direction. It is thus possible to determine univocally the orientation of the hydroxyl end groups and the azo group in the center of the molecule.

We use these results to determine the azobenzene's conformation. Figure 2 demonstrates that the attachment of two water molecules is sufficient for such a univocal determination. The single water molecule in Figure 2b is attached at an angle of 45° . The molecule is thus a *trans*-isomer with the following conformation. The hydroxyl group acts as hydrogen-bond donor, and the azo group is oriented *re*. Only the orientation of the second hydroxyl group is undetermined (first or last row of Figure 3a is possible). In the pure water structure, the hydrogen atoms point toward the surface.⁷ A similar height here (cf. Figure 2d) suggests the shown orientation. Attachment of two water molecules reveals the complete structure (Figure 2c). In this case, both angles are 21° corresponding to a point symmetric *re-trans*-isomer with both hydroxyl groups acting as hydrogen-bond acceptor.

Figure 4 demonstrates that from the possible orientations of the hydroxyl groups only the first combination fits to the positions of both water molecules. In this example, the hydroxyl groups point to opposite sides of the molecular axis. In experiment, more than 85% of the molecules exhibit this *trans*-hydroxyl conformation. Thus, most molecules adopt a conformation with the hydroxyl groups in *trans*-conformation with respect to the molecular axis. Furthermore, we do not observe angles indicative for a *cis**-isomer. This is in contrast to the same molecule adsorbed within supramolecular clusters on Ag(111).⁹ From the Knudsen cell, the thermodynamically stable *trans*-isomer is evaporated and thus deposited onto the surface. The surface-adapted *cis**-isomer thus does not form upon adsorption onto Au(111). The *cis**-isomers are either formed upon attachment to the more interacting Ag(111) surface or to other molecules within the supramolecular clusters.

What can we learn about hydration from our study? First, the water is exclusively attached at the hydroxyl groups of the molecules with an O–O bond length of approximately 0.3 nm or slightly larger. This similarity to the assumed gas phase value corroborates that fundamental aspects of hydration might be revealed in a surface study. Second, some co-operative effect must have an influence as we never observed a dye molecule with four water molecules arranged such that each hydroxyl group binds to two water molecules. Instead, attachment of more water molecules leads to the formation of a variety of hydrogen-bonded clusters, some of which are shown in Figure 5. Sometimes, the second water molecule binds to the first water molecule and not to the other hydroxyl group (Figure 5a,b). Starting with the third water molecule, a buckling of the water's apparent height is observed as expected for an ice-like

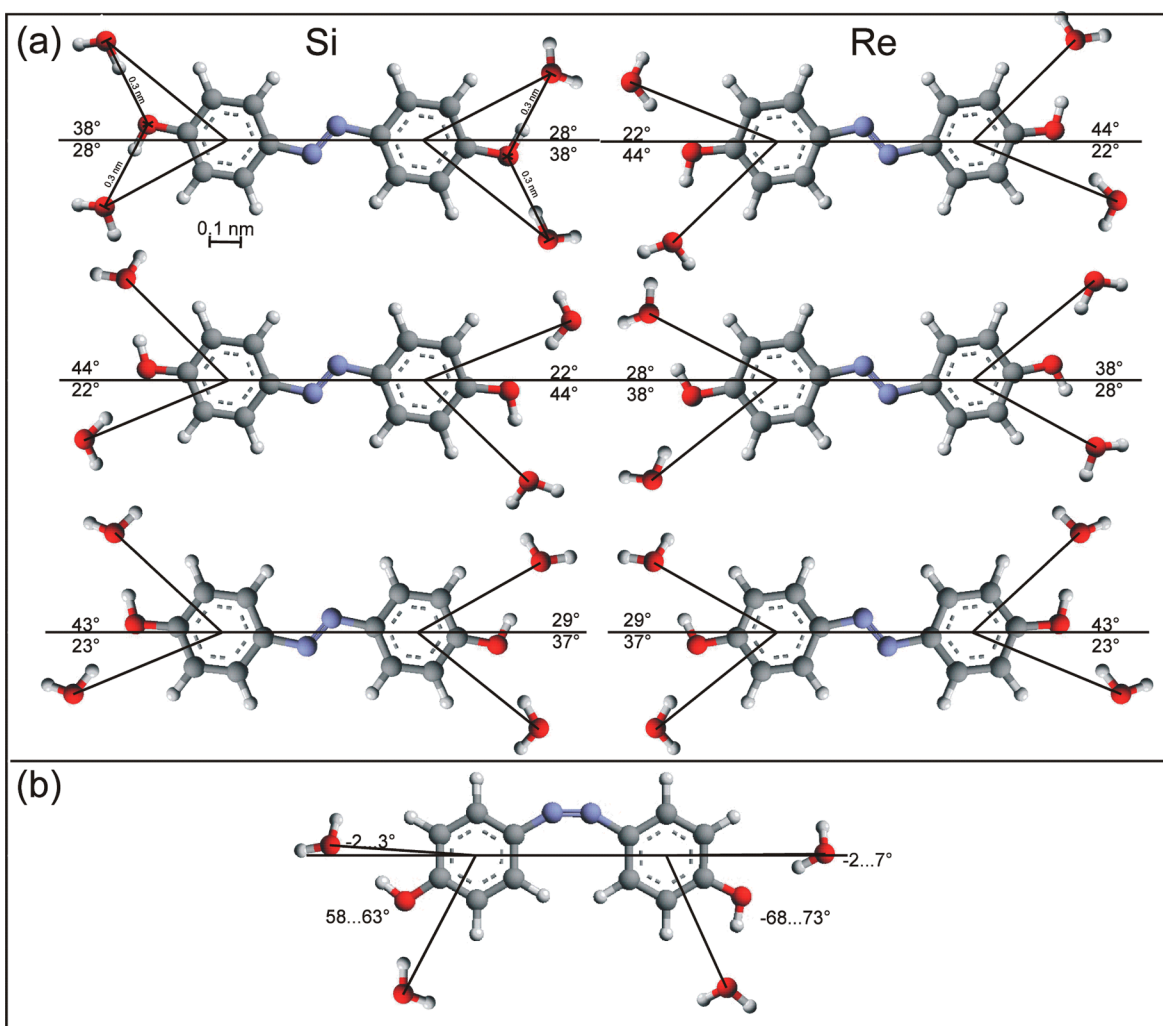


Figure 3. Possible conformations of 4,4'-hydroxy azobenzene on a surface with four water molecules attached each with an O–O bond length of 0.3 nm. Numbers give calculated angles with respect to the molecular axis; the molecular axis is the connection between the centers of the phenyl rings as indicated by the horizontal line: (a) *trans*- and (b) *cis*[±]-isomer.

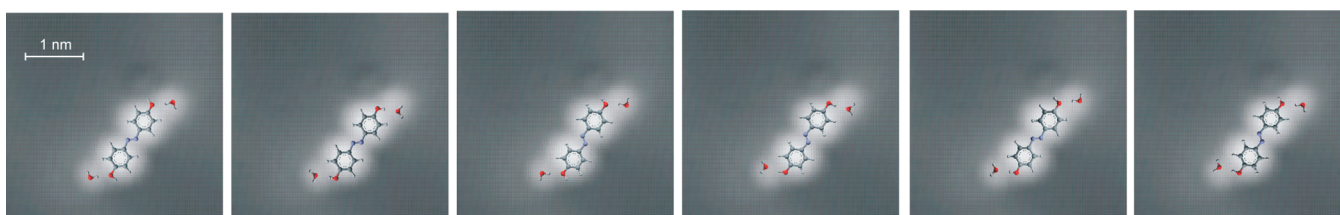


Figure 4. Possible hydroxyl orientations of 4,4'-hydroxy azobenzene superimposed onto STM image of Figure 2c.

network. (Figure 5c). The existence of the molecules of larger apparent height can best be inferred from the false-color images (Figure 5c'). Furthermore, this buckling is observed, if two molecules are attached to the hydroxyl group (Figure 5d–f).⁵ Third, the additional water is able to provide information about the orientation of the first water molecules (Figure 5e,f). The buckling indicates a bilayer-like structure. Finally, further stages of additional water attachment as observed for larger water:azobenzene ratios are shown in Figure 5g–i. Apart from the large diversity of possible networks observed, an important result is that up to two additional molecules are attached in a two-dimensional network (Figure 5g,h). Three-dimensional structures, which cannot be resolved molecularly, are observed only at larger distance from the dye (Figure 5i).

The three-dimensionality is most obvious from the line scans in Figure 5j. While the water portion of the structure in Figure 5h is with ~150 pm in the typical range of water bilayer structures, the nonresolvable structure in Figure 5i is around 50 pm higher and thus indicative of a 3D structure.^{15,16} This implies that the molecule seeds the formation of two hydration shells, but its influence on the water structure diminishes at larger distances. For comparison, the hydration layer around a protein shows dynamics distinct from the bulk water up to a distance of 1 nm,¹¹ the same order of magnitude. In contrast to the water molecules that are directly attached to the azobenzene molecule, deviations of the STM image from a model based on gas phase hydrogen-bond distances and angles indicate a

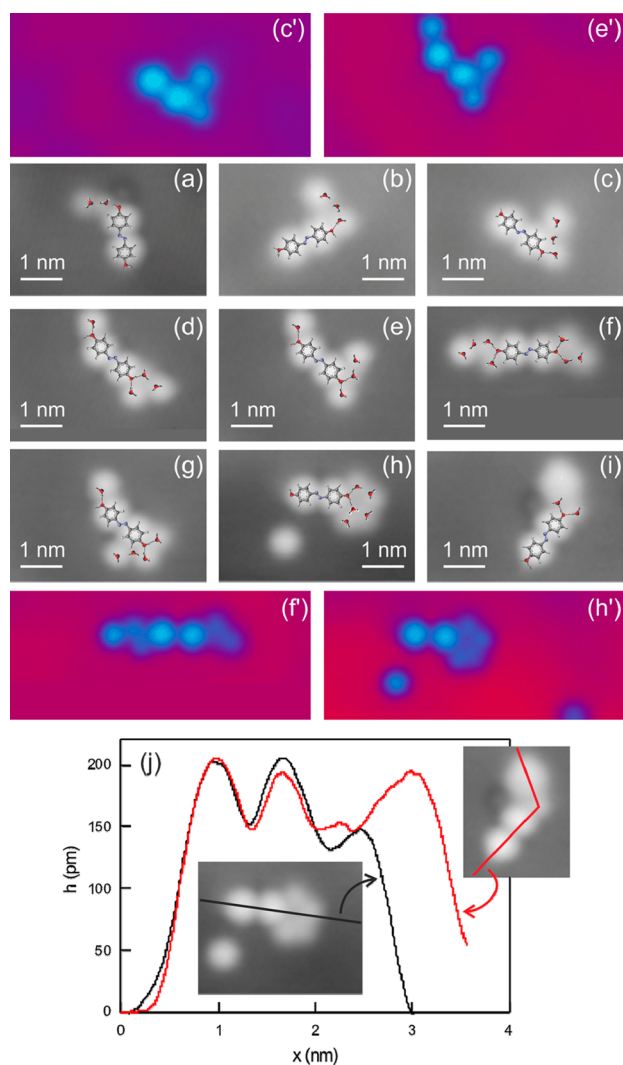


Figure 5. Further hydration of 4,4'-hydroxy-azobenzene on Au(111): (a–c) water molecules hydrogen bond to first hydration layer; (d–f) buckling of water structure; (g,h) larger two-dimensional water clusters; (i) three-dimensional water cluster; (j) line scans across the structures in panels (h) and (i) as indicated in the inset; tunneling parameters: (a,b,e–i) $V_t = 59$ mV, $I_t = 10$ pA (c,d) $V_t = -59$ mV, $I_t = 12$ pA. Note that the positions of the water molecules that are not directly bound to the azobenzene are positioned into the direction of the additional protrusions with the gas phase O–H···O bond length respecting the ice rules. Deviations of the protrusions in the STM images from the water models thus indicated a different bond length or angle.

lengthening of the bonds that are further away from the azobenzene molecule (Figure 5).

5. RESULTS: ANILINO-NITRO AZOBENZENE

To corroborate the approach of structure determination we investigate 4-anilino-4'-nitro azobenzene on Au(111). Previously we showed that 4-anilino-4'-nitro azobenzene molecules form porous clusters consisting of six molecules at 0.1 molecule/nm².¹⁴ Each molecule is imaged as three protrusions. Two of them are exactly above the phenyl rings (Figure 6a). The third one, corresponding to the nitro end of the molecule, is slightly offset from the phenyl ring toward the nitro group reflecting the charge pulling character of this end group. The offset is with (67 ± 7) pm around a fourth of the carbon ring

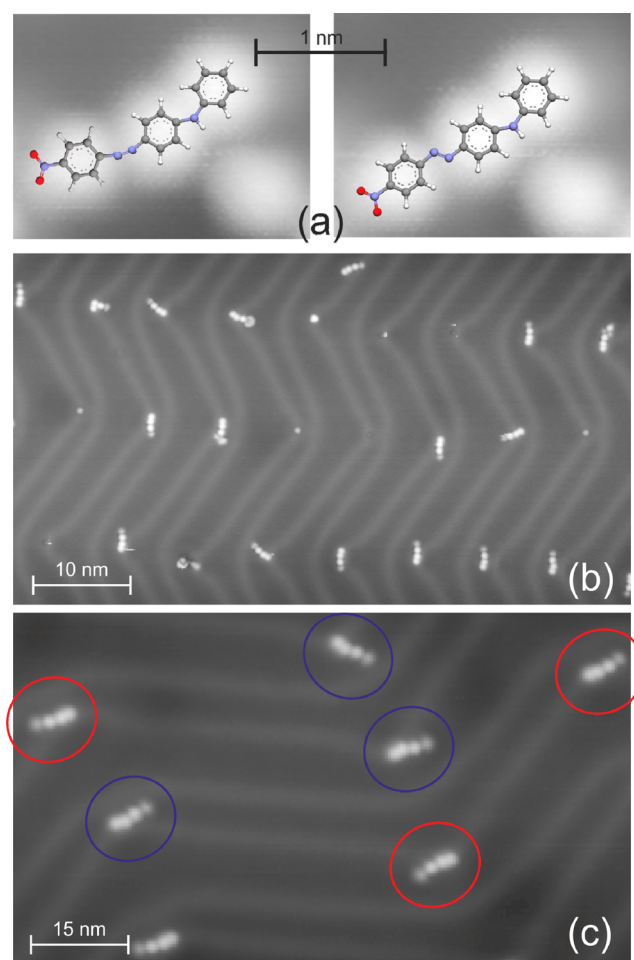


Figure 6. 4-anilino-4'-nitro azobenzene on Au: (a) at 0.1 molecules/nm² with ball-and-stick models from [14] (b,c) at dilute coverage with a azobenzene:water ratio of 1:1; molecules with the water protrusion on the same and opposite side of the azobenzene axis as the anilino protrusion are encircled in red and blue, respectively: (a) 125 mV, 310 pA; (b) 59 mV, 182 pA (c) –100 mV, 0.69 nA.

diameter. Thereby, the nitro group has a slightly larger distance to the middle protrusion than the anilino group.¹⁴ Within the supramolecular clusters, only two conformations exist. The three protrusions feature angles of $\alpha_{\text{mol}} \approx 11^\circ$ and 24° for the *trans*-isomer and for the surface-adapted *cis**-isomer, respectively (Figure 6a).¹⁴ Note that for both adsorbed isomers, also the anilino group seems planar, in contrast to the molecules in gas phase.

In order to hydrate the dye, we prepare a sample with a dye-to-water ratio of approximately 1:1. The molecules tend to attach to the elbow sites of the Au(111) herringbone reconstruction (Figure 6b), which hinders clustering of the molecules at the dilute coverage investigated here. The calculation shows that the first water molecule attaches to the nitro group with the two hydrogen atoms pointing toward the oxygen atoms of the nitro group (c.f. Figure 8a). Indeed, four protrusions are observed in most elbows (Figure 6c). The three protrusions with different distances but equal apparent heights of approximately 150 pm (Figure 7b) correspond to the molecule (cf. Figure 6a). The fourth one has the smaller apparent height of a single water molecule (cf. Figure 2d). A closer look of the orientations present in Figure 6c reveals two types of arrangements marked with two different colors. Either

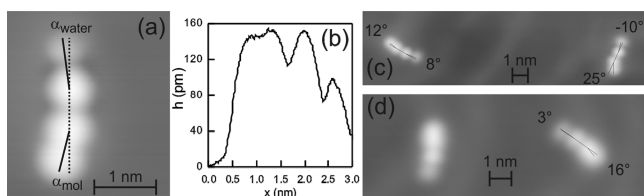


Figure 7. Water attachment to 4-anilino-4'-nitro azobenzene. (a) High-resolution image, marking the angles measured, here $\alpha_{\text{mol}} = 166^\circ$ and $\alpha_{\text{water}} = 172^\circ$ (b,c) several different conformations with α_{mol} and α_{water} , as shown, tunneling parameters: (a) 90 mV, 31 pA; (b) -100 mV, 0.48 nA; (c) 133 mV, 12 pA.

the outer two protrusions are on the same side of the azobenzene core or on opposite sides.

In the following we measure two angles: α_{mol} , the angle within the molecule, and α_{water} , the angle between the azobenzene core of the molecule and the water protrusions (cf. Figure 7a). Thereby, α_{mol} is always positive. A positive/negative α_{water} means that the outer two protrusions are on the same/different sides of the molecular axis. Some of the measured angles are indicated in the high-resolution images in Figure 7c,d. The angles expected to be measured are shown in Figure 8a alongside with the ball-and-stick models. Assuming planar molecules, there are two possibilities for the orientation of the anilino group for both, the *trans*- and the *cis**-isomer. In agreement with the experimental observation, the two protrusions corresponding to the anilino group and to the water molecule are expected on opposite sides of the azobenzene core for two combinations and on the same side for the other two combinations. An angle within the *trans*-isomer of $\alpha_{\text{mol}} = 32^\circ$ and 10° translates into an angle to the water of $\alpha_{\text{water}} = 11^\circ$ and -8° , respectively. An angle within the *cis**-isomer of $\alpha_{\text{mol}} = (22 \pm 2)^\circ$ transforms into an angle to the water of $\alpha_{\text{water}} = -17^\circ$ and 20° . In other words, the angle measured by the position of the water reflects the molecular conformation and should confirm the conformation as deduced from the angle within the molecule. The theoretically determined angle pairs are represented by crosses in the α_{water} vs α_{mol} plot in Figure 8b and compared to measured values. Despite being a minority species, the *re*-molecules

follow the expected trend. One and two molecules adopt the *re-trans* and the *re-cis** conformation, respectively.

Note that the *si-trans* conformer dominates in supramolecular structures at larger coverage with $(86 \pm 4)\%$.¹⁴ Surprisingly, most of the single molecules here adopt a conformation, whose molecular angle is in between the values for the *si-trans* and the *si-cis** conformation. This implies that the two distinct angles observed in the supramolecular structures in ref 14 are stabilized by the bonding to neighboring molecules and that the molecule can be deformed at the deposition temperature of 250° .

The unexpected large spread in α_{mol} for the remolecule is reflected in the angle of the water to the molecule, α_{water} . There is a clear correlation between the two angles. The difference between the two angles depends linearly on α_{mol} as shown in Figure 8c. A change in angle could result from other C–N=N–C opening angles than determined for the molecule within supramolecular clusters. However, in this case both angles should either increase or decrease, i.e., $\Delta\alpha \approx 0$. In the gas phase calculations, we find a correlation of the angle between azo and nitro group direction in dependence of the orientation of the anilino phenyl, which follows the opposite trend. For a near to planar geometry of the whole molecule it varies between 172° and 180° . This qualitative agreement suggests that the change in α_{mol} reflects a change in anilino group orientation. The exact change in angles may be reproduced by a sophisticated *ab initio* calculation that includes the substrate.

The distinct angles measured for the water and their clear correspondence to different angles within the molecule prove that our method as proposed based on the measurements of the hydration shell of 4,4'-hydroxy azobenzene is applicable to other systems. In other words, even if we had not known α_{mol} , we could have inferred the angle of the anilino group with the azobenzene core just from α_{water} alone. The method is thus able to determine bond angles within molecules.

6. CONCLUSION

We investigate the co-adsorption of water with two azobenzene derivatives on Au(111) by low-temperature STM. The directed attachment of the water to the polar end groups is used to determine the predominant conformation of the derivatives on the surface. For two identical end groups, at least one water

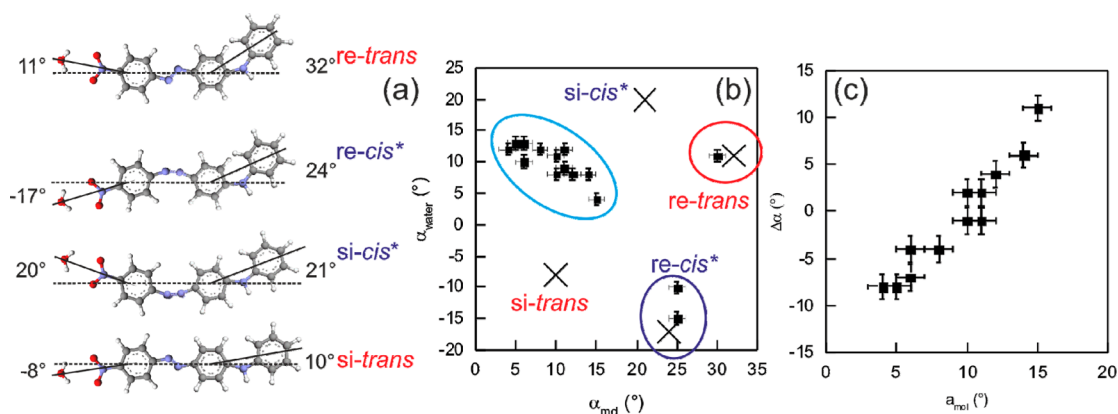


Figure 8. Water attached to 4-anilino-4'-nitro azobenzene. (a) Possible conformations on a surface with one water molecules attached each. Numbers give angles α_{water} on right-hand side and α_{mol} on left-hand side with respect to the molecular axis; the molecular axis is the connection between the phenyl's center of the azobenzene core; the corner on the left-hand side is intentionally placed slightly off-center from the phenyl in accordance with the shift of the protrusion (cf. Figure 6a). (b) Angle to water α_{water} vs angle within molecule α_{mol} ; crosses indicate angle pairs from (a). (c) Difference $\Delta\alpha = \alpha_{\text{mol}} - \alpha_{\text{water}}$ vs α_{mol} ; line is linear fit yielding a slope of 1.56.

molecule adsorbed at each end is sufficient for determination of the conformation of an individual molecule provided the water molecules are well resolved. We propose that the method is generally applicable for structure determination of polar molecules by choosing the proper polar end groups, designing the molecules correspondingly, and adding a sufficient amount of water. Our study thus gives unprecedented information about the intramolecular orientation based on the first real space observation of the hydration of a functional molecule.

Concerning hydration, our results confirm experimentally the well-established picture of hydrogen bonding to polar functional molecules. The developed strategy may be extended to the hydration of the hydrophobic residues by adding further hydration shells to the molecules and thus move toward an understanding of hydration of nonpolar specimen; a topic that is poorly understood at present.

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Notes

The authors declare no competing financial interest.

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