

## Electric Field-Induced Isomerization of Azobenzene by STM

Micol Alemani,<sup>†</sup> Maike V. Peters,<sup>‡</sup> Stefan Hecht,<sup>\*,‡</sup> Karl-Heinz Rieder,<sup>†</sup> Francesca Moresco,<sup>†</sup> and Leonhard Grill<sup>\*,†</sup>

*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany, and Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany*

Received July 28, 2006; E-mail: leonhard.grill@physik.fu-berlin.de; hecht@mpi-muelheim.mpg.de

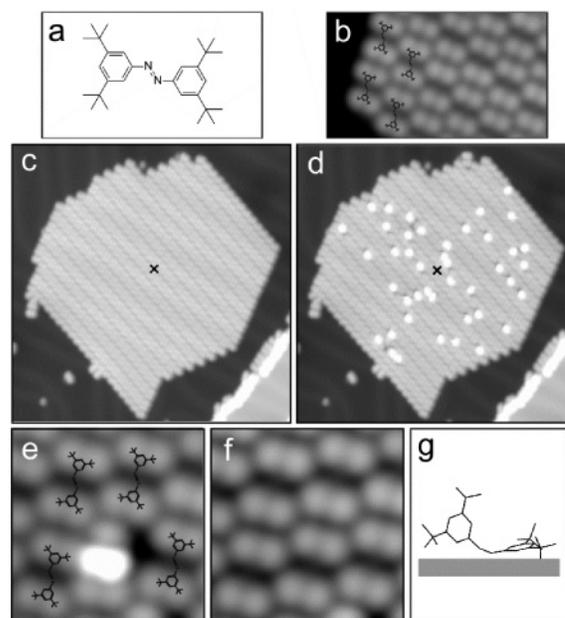
Understanding and controlling conformational changes of molecules adsorbed on solid substrate surfaces is currently one of the most actively pursued goals related to fundamental electronic device miniaturization.<sup>1</sup> Molecular devices can exhibit new operating mechanisms with technological advantages. In particular, the realization of a molecular device operable without electric current is of interest. In the search for molecules suitable for molecular electronics, present research interest is focusing on molecular switches.<sup>2,3</sup> Azobenzene represents a very interesting example of such a molecular switch, and its operating mechanism is based on the *trans*–*cis* isomerization of a double bond.<sup>4</sup> In the electronic ground state, azobenzene adopts two configurations: a nearly planar *trans* and a nonplanar, three-dimensional *cis* form. The reversible switching of azobenzene is well studied in solution and in the gas phase, where the ground state barrier for isomerization is typically overcome by photoexcitation.<sup>4,5</sup> Adsorption and lateral manipulation of azobenzene have been investigated by STM.<sup>6</sup> Moreover, very recent experiments have provided evidence that the isomerization of azobenzene<sup>7</sup> and of the azobenzene derivative Disperse Orange 3<sup>8</sup> can be induced by resonant or inelastic tunneling of electrons.

In this communication, we show for the first time that the reversible isomerization of specifically designed azobenzene molecules can be induced on Au(111) by the *electric field* in the STM junction, without tunneling of electrons.

We chose to investigate 3,3',5,5'-tetra-*tert*-butylazobenzene (TBA), an azobenzene molecule carrying four lateral *tert*-butyl groups (Figure 1a). This substitution pattern increases the separation between surface and the azobenzene  $\pi$ -system, leading to increased surface mobility and potentially lower electronic coupling. It does not significantly alter the electronics of the azobenzene chromophore and does not impart steric hindrance upon the isomerization process, and its set of four symmetrically placed labels facilitates conformational analysis. TBA was synthesized by oxidative dimerization of 3,5-di-*tert*-butylaniline and exhibits the photochemical and thermal isomerization behavior typical for azobenzene derivatives in solution.<sup>9</sup>

The experiments were performed in ultrahigh vacuum at a temperature of 5 K using a home-built STM.<sup>9</sup> Upon adsorption onto a clean Au(111) surface at room temperature, the molecules are mobile and form ordered islands consisting of parallel rows (Figure 1b, c). Each molecule appears as four lobes with a rhombic shape and an apparent height of  $2.7 \pm 0.1$  Å. From the dimensions of the molecule in the gas phase, we infer that the lobes correspond to the *tert*-butyl groups while the central azobenzene part is not visible. All observed molecules were found in the same planar configuration that we assign to the thermodynamically favored *trans*-isomer (Figure 1a).

The isomerization experiments were performed by positioning the STM tip at a fixed height above a molecular island with the

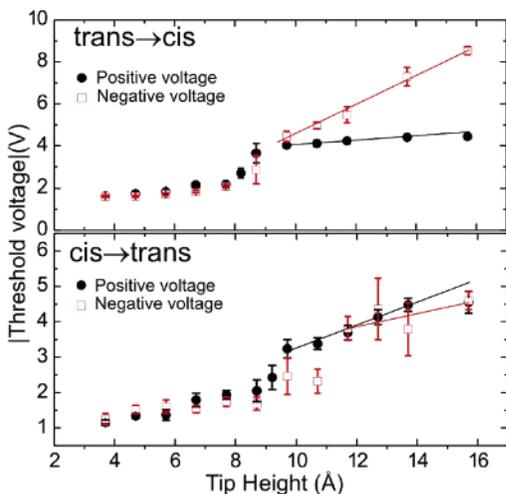


**Figure 1.** (a) *trans*-3,3',5,5'-Tetra-*tert*-butylazobenzene (*trans*-TBA). (b) Corner of a molecular island ( $70 \times 40$  Å<sup>2</sup>). The molecular adsorption geometry is indicated by structural models. (c and d) Switching experiment. (c) Island of *trans*-TBA containing about 400 molecules ( $370 \times 370$  Å<sup>2</sup>). Subsequent voltage pulses (20 s,  $V_m = 2$  V, tip height = 6 Å) are applied at the position indicated by the cross. (d) STM image ( $370 \times 370$  Å<sup>2</sup>) after nine pulses: 43 molecules have been switched to the *cis* form. (e) Zoomed STM image of a molecular island ( $35 \times 35$  Å<sup>2</sup>). One TBA molecule has been switched to the *cis*-configuration (bright lobe), while the other TBA molecules are in the *trans*-configuration. (f) After applying a voltage pulse ( $V_m = 1.5$  V,  $t = 5$  s, tip height = 5 Å), the molecule is switched back to the *trans*-configuration ( $35 \times 35$  Å<sup>2</sup>). (g) Schematic model of an adsorbed *cis*-TBA molecule (side view). In all images, the STM parameters are  $I = 0.1$  nA,  $V = 1$  V,  $T = 5$  K.

feedback loop switched off and applying a voltage  $V_m$  to the sample. After applying subsequent voltage pulses, with the STM tip always at the same position above the island, a collection of STM images was recorded. The images before and after nine equivalent pulses are shown in Figure 1c,d (the complete series of 48 pulses is available as a movie<sup>9</sup>). As one can see, many molecules have changed their appearance, showing a larger apparent height of  $4.1 \pm 0.3$  Å. Typically, the application of a single voltage pulse causes the switching of several molecules in a radius up to 500 Å around the position of the tip. The bright molecules are stable, and their initial appearance can be precisely restored by applying another pulse, as shown in Figure 1e,f. Such switching experiments can be reproduced several hundred times, allowing us to conclude that the observed changes are due to the isomerization of single molecules from the *trans* form to the *cis* form, and back to the *trans* form, as also indicated by the observed shift in the molecular LUMO.<sup>9</sup>

<sup>†</sup> Freie Universität Berlin.

<sup>‡</sup> Max-Planck-Institut für Kohlenforschung.



**Figure 2.** Plot of the threshold voltage as a function of tip height for the *trans*  $\rightarrow$  *cis* isomerization (top) and for the *cis*  $\rightarrow$  *trans* isomerization (bottom) for positive (electric field points toward the STM tip) and negative voltage polarities. The experimental points have been measured by fixing the tip at a specific height (referred to the bare Au(111) surface and calibrated by recording  $I(z)$  curves) and applying a voltage pulse for a fixed time of  $t = 30$  s. Starting from  $V = 0$ , we increased the voltage by increments of 0.1 V until we observed a switching event in a lateral area of  $80 \times 80 \text{ \AA}^2$  from the tip position. Each sequence was repeated 10 times. The linear fit of the data is done for points above 9.5 and 11  $\text{\AA}$  (*cis*  $\rightarrow$  *trans* at negative voltages). The tunneling current is  $7 \pm 1$  nA (*trans*  $\rightarrow$  *cis*) and  $8 \pm 1$  nA (*cis*  $\rightarrow$  *trans*) at a tip height of 3.7  $\text{\AA}$  and  $52 \pm 6$  pA (*trans*  $\rightarrow$  *cis*) and  $67 \pm 6$  pA (*cis*  $\rightarrow$  *trans*) at 6.7  $\text{\AA}$  tip height.

The *cis*-isomer appears with a bright central intensity maximum, while three lateral lobes in triangular shape can be resolved (Figure 1e). From the STM images, we propose a structural model in which one phenyl moiety remains on the surface while the second phenyl ring is pointing upward (Figure 1g). As observed by STM<sup>7</sup> and in agreement with the conformation in the gas phase,<sup>4</sup> the *cis*-isomer is not planar.

We have investigated the dependence of the voltage (necessary for the isomerization) on the tip height for both polarities and isomerization processes (Figure 2). The data show that switching is possible with positive *and* negative voltage polarities, and the threshold voltage is not a constant value, characteristic in the case of electron resonant tunneling,<sup>10</sup> but clearly increases (at large tip heights) when retracting the tip. The isomerization process occurs also at very large tip distances where no tunneling current is flowing (the tunneling current decreases exponentially with the tip–surface distance). Even in the extreme case when the tip is 36  $\text{\AA}$  above the surface, we were able to switch molecules from *trans* to *cis* (after applying a voltage pulse of 6.8 V).<sup>9</sup> Moreover, it is also possible to isomerize molecules when the tip is positioned above the bare surface nearby the island.

All these observations, together with the large lateral extension over which switched molecules are observed, let us conclude that the isomerization of TBA molecules on Au(111) is driven by the electric field in the STM junction, which does not involve tunneling of electrons. This mechanism has not been observed experimentally so far, but was predicted by calculations.<sup>11,12</sup> In the presence of an electric field, the potential energy surface related to the reaction can be deformed, thus leading to an effective lowering of the isomerization barrier. This effect, based on the (de)stabilization of certain molecular configurations, depends on the presence and orientation of an intrinsic dipole moment and also on the polarizability of the molecule.<sup>11</sup>

By performing a linear regression of the data in Figure 2 considering the large tip height regime, we found that for the *trans*

$\rightarrow$  *cis* isomerization the threshold voltage varies with the distance as 0.1 and 0.7 V/ $\text{\AA}$ , while for the *cis*  $\rightarrow$  *trans* it amounts to 0.3 and 0.2 V/ $\text{\AA}$ . Small tip heights are not included because in this region there is a change in slope, probably related to electronic effects that come into play at small tip heights (i.e., large currents). These values are smaller than those calculated for switching TBA molecules by the electric field in the gas phase (about 1–2 V/ $\text{\AA}^{11}$ ), which is likely due to the presence of the surface that enhances the permanent dipole and the polarizability of the molecule. Additionally, the exact variation of these parameters along the reaction path was not included in the model. The different slopes for positive and negative voltages in the case of *trans*  $\rightarrow$  *cis* isomerization as compared to the *cis*  $\rightarrow$  *trans* process (Figure 2) are likely due to the delicate balance between the intrinsic dipole moment of the molecule and its polarizability for the different adsorption geometries and reaction paths.

In conclusion, we have shown that the *trans*–*cis* isomerization of TBA molecules can be reversibly induced on Au(111). The relationship between the applied bias voltage necessary for switching and the tip height shows that the process is caused by the electric field between the STM tip and the sample surface.

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**Supporting Information Available:** Movie of an isomerization sequence and experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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