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Isomerization Reactions on Single Adsorbed Molecules

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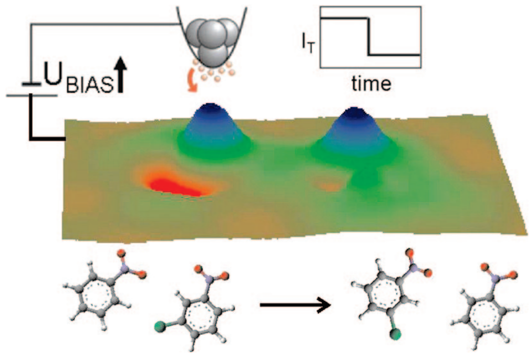

Molecular switches occur throughout nature. In one prominent example, light induces the isomerization of retinal from the compact 11-*cis* form to the elongated *all-trans* form, a conversion that triggers the transformation of light into a neural impulse in the eye.

Applying these natural principles to synthetic systems offers a promising way to construct smaller and faster nanoelectronic devices. In such systems, electronic switches are essential components for storage and logical operations. The development of molecular switches on the single-molecule level would represent a major step toward incorporating molecules as building units into nanoelectronic circuits.

Molecular switches must be both reversible and bistable. To meet these requirements, a molecule must have at least two different thermally stable forms and a way to repeatedly interconvert between those forms based on changes in light, heat, pressure, magnetic or electric fields, pH, mechanical forces, or electric currents. The conversion should be connected to a measurable change in electronic, optical, magnetic, or mechanical properties. Because isomers can differ significantly in physical and chemical properties, isomerization could serve as a molecular switching mechanism.

Integration of molecular switches into larger circuits will probably require arranging them on surfaces, which will require a better understanding of isomerization reactions in these environments. In this Account, we describe our scanning tunneling microscopy studies of the isomerization of individual molecules adsorbed on metal surfaces. Investigating chlorobenzene and azobenzene derivatives on the fcc(111) faces of Ag, Cu, and Au, we explored the influence of substituents and the substrate on the excitation mechanism of the isomerization reaction induced by inelastically tunneling electrons. We achieved an irreversible configurational (*cis*—*trans*) isomerization of individual 4-dimethyl-amino-azobenzene-4-sulfonic acid molecules on Au(111), a reversible configurational (*cis*—*trans*) isomerization of amino-nitro-azobenzene on Au(111), a constitutional (*meta*—*ortho*) isomerization of chloronitrobenzene molecules adsorbed on Cu(111) and Au(111), and a constitutional (*meta*—*para*) isomerization of dichlorobenzene molecules adsorbed on Cu(111) and Ag(111). These studies demonstrate that we can induce a variety of isomerization reactions by electron excitation on a metal surface.

Our model isomerization studies provide a way to manipulate properties of single molecules, changing both their geometric structure and their physicochemical properties. The control of isomerization of single molecules will advance the development of single-molecule electronics and other nanoscale processes.

1. Introduction

In nature, molecular switches are frequent. In many biological systems, specific functions are realized with the aid of photoinduced conformational changes often involving *cis*—*trans* isomerization. One of the most prominent examples is the photoinduced isomerization from a compact 11-*cis*-retinal to an elongated *all-trans*-retinal in the human eye, which eventually leads to vision. Such switches rely on the relative spatial reorientation of molecular groups and are attractive mod-

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els for the development of new technologies. Further progress in molecular electronics requires the understanding and the control of such processes at a single-molecule level.[1−5]

Organic chemistry has demonstrated its potential to synthesize molecular switches.[6] The functional properties of these switching systems were characterized but predominantly in solution or the fluid-crystalline phase.[6] However, integration of molecular switches to larger circuits is hardly imaginable without an arrangement on surfaces. There, it is not immediately obvious whether steric hindrance, bonding to the surface, or alternative de-excitation mechanisms obstruct any switching of molecules in direct contact with surfaces. Thus, it is indispensable to examine molecular switches on surfaces and the influence of the surface on those chemical reactions that are used to establish a switch.

In this Account, we present our investigation of isomerization of individual molecules adsorbed on metal surfaces in a low-temperature scanning tunneling microscope. We recapitulate isomerization of chlorobenzene and azobenzene derivatives on the fcc(111) faces of Ag, Cu, and Au. There are two types of isomers. Both were investigated by us by means of inelastic electron tunneling (IET) manipulation: either there is a rearrangement of the atoms within the same geometrical structure (the constitutional isomer)[7,8] or the molecule changes into another geometrical structure (the stereo isomer).[9−11] The latter might be a conformational or a configurational isomer. The former can be interconverted by rotation around a single bond and the latter cannot. For chlorobenzene and azobenzene derivatives, the effects of different substitutional groups and different substrates are explored.

The possibility to address single adsorbed molecules with scanning tunneling microscopy (STM) and to determine their reaction rate directly in the recorded current was applied before to a variety of elementary chemical reactions involving the modification of extrinsic as well as intrinsic chemical bonds, for example, diffusion[12−16] and bond breaking.[17−20] Unimolecular reactions were still sparse and only qualitative when we started our studies, restricted to a tip-induced molecular deformation,[21] a conformational change due to lateral manipulation,[22] a stochastic change in molecular orientation,[2] and a reversible conformational change of metalloporphyrin molecules.[23]

Meanwhile the configurational change of individual native azobenzene molecules on Au(111) was induced by STM.[24] This isomerization, as well as the one investigated by us, was induced by highly energetic electrons. In contrast, within islands on Au(111), the isomerization of poly(*tert*-butyl-azobenzene) was induced either by an electric field[25] or by light[26] and thermally.[27,28] A conformational change corresponding to a ring rotation was achieved for di-*meta*-cyanoazobenzene on Au(111) via tunneling though the LUMO.[29]

For native and poly(*tert*-butyl-azobenzene), isomerization lifts up one side of the molecule from the surface. In contrast, isomerization of a chlorophyll molecule corresponds to a conformational change in plane[30] comparable to the configurational isomerization of amino-nitro-azobenzene.[9] A different kind of switch with hardly any change in geometry but a measurable change in conductance was realized through the tautomerization reaction of naphthalocyanine molecules adsorbed on thin NaCl layers.[31]

2. Experimental Section

2.1. The Molecules. Figure 1 shows the molecules discussed in this Account. The two azobenzene derivatives (Figure 1a,b) are investigated with respect to their *cis*−*trans* isomerization, where the two phenyls are on the same and opposite sides of the N═N group, respectively. The two chlorobenzene derivatives (Figure 1c,d) exist in the gas phase in three constitutional isomers: *ortho*, *meta*, and *para*. However, we found that isomerization between the two possibilities shown in the Figure 1c,d are largely preferred in particular on Ag(111) and Cu(111).

2.2. Experimental Procedure. Scanning tunneling microscopy (STM) measurements were performed with a custom-built low-temperature STM.[32] The ultrahigh vacuum chamber (base pressure below 5×10^{-10} mbar) is equipped with standard facilities for sample preparation and characterization. The single-crystalline surfaces are cleaned by repetitive cycles of Ne^+ sputtering (1.3 kV, 2.2 μA, 45 min) and annealing at 800 K for 10 min followed by 850 K for 2 min for Cu(111) and Ag(111) and at 700 K for 10 min followed by 750 K for 2 min for Au(111).

The fluid molecule *para*-dichlorobenzene is degassed under vacuum conditions by several pump cycles to remove remaining impurities and then deposited by evaporation at room temperature. The other molecules are solid at room temperature. Chloronitrobenzene and *meta*-dichlorobenzene have comparably high vapor pressures at room temperature and are thus leaked into the chamber from a glass crucible after degassing through a different line. The molecules are degassed at 100 °C for *meta*-dichlorobenzene and 110 °C for chloronitrobenzene. The azobenzene derivatives are deposited from a thoroughly outgassed Knudsen cell with a sublimation temperature of 108 °C for 4-dimethyl-amino-azobenzene-4-sulfonic acid and 150 °C for amino-nitro-

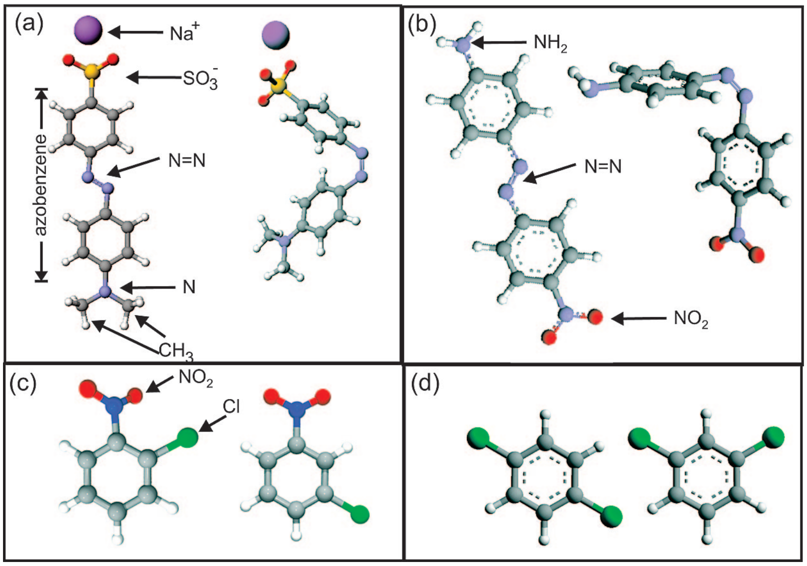

FIGURE 1. Ball-and-stick models of investigated molecules: (a) 4-dimethyl-amino-azobenzene-4-sulfonic acid ($C_2H_6N-C_6H_4N{=}NC_6H_4SO_3^-$ Na^+ in *trans*- and *cis*-configuration; (b) amino-nitro-azobenzene ($NH_2C_6H_4N{=}NC_6H_4NO_2$ in *trans*- and *cis*-configuration; (c) *ortho*- and *meta*-isomers of chloronitrobenzene (Cl-$C_6H_4NO_2$); (d) *para*- and *meta*-isomers of dichlorobenzene (Cl-C_6H_4-Cl).

azobenzene. The molecules are deposited within typically 10−30 s onto the surface held at 17 K except for amino-nitro-azobenzene, which was deposited at 230 K.

Though in a single experiment only one of the isomers is deposited, several isomers and some dissociation products are identified. Thus, the surfaces are catalytically active with respect to isomerization. Except for 4-dimethyl-amino-azobenzene-4-sulfonic acid, the ratio is in favor of the deposited isomer, for example, deposition of *meta*-chloronitrobenzene on Cu(111) gives a ratio of 10:1 for *meta*- to *ortho*-isomer. The *para*-chloronitrobenzene is only very rarely observed on Ag(111) and Cu(111) and *ortho*-dichlorobenzene was never observed on Cu(111) and Ag(111).

After exposure, the sample is transferred into the STM where the measurements are performed at 5 K. To avoid modifying the molecules under imaging conditions unless wanted, we use tunneling parameters on the order of some 10 pA and 100 mV. Voltages are applied to the sample with respect to the tip. The Δh given in the figure captions refers to the apparent height of the highest part of the molecule above the surface plane and is correct by ±5 pm.

The STM images of the azobenzene derivatives are interpreted with the aid of the electrostatic potential mapped (ESP map) onto an iso-electron density as described in detail in ref 33. For the *cis*−*trans* isomerization, the change in shape is thereby the most prominent change in both the ESP map and the STM images. Further details on image identification are given in refs 9−11. We deduce that isomerization has indeed occurred from a clear change in geometry thus derived. The STM images of the benzene derivatives are interpreted based on a Green's function calculation in a tight-binding approach.[34] These reveal that the protrusions found in the STM images correspond to the substitutional groups and their relative position allows identification of the isomers. In the case of chloronitrobenzene, the calculation was confirmed by adsorption experiments of the respective isomers. Further details on image identification are given in refs 7 and 8. Derived ball-and-stick models are displayed in the figures in the same orientation but usually enlarged.

The IET manipulation is initiated by placing the STM tip above a molecule. There the feedback loop is switched off; voltage and current are increased and held at these increased values for typically a few hundred milliseconds to seconds while recording the tunneling current. A sudden change in the $I-t$ characteristics is indicative of a conductance change. This change at the molecule is then verified by imaging. The area below the current curve up to the sharp change is used to determine the reaction yield.

All images shown in this Account are cut outs of larger ones, on which other nonmanipulated molecules are imaged. We use these other molecules to ensure that indeed the molecule under investigation and not the tip changed during manipulation.

3. Results

3.1. Configurational Isomerization of Azobenzene Derivatives. Dye molecules including azobenzene ($C_6H_5N{=}NC_6H_5$) derivatives have a high potential for applications in various optoelectronic devices. These molecules make a

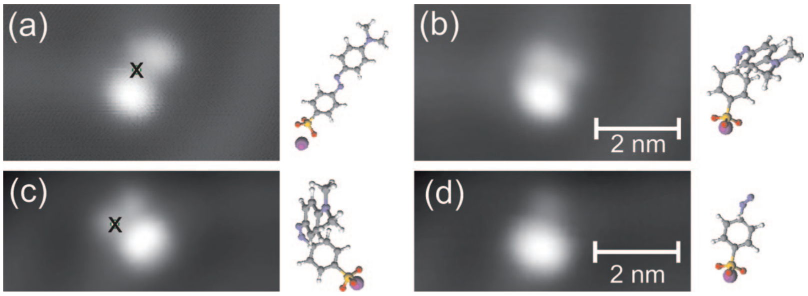

FIGURE 2. IET manipulation of a single 4-dimethyl-amino-azobenzene-4-sulfonic acid molecule ($\Delta h = 150$ pm): (a) molecule in *trans*-configuration before manipulation; the STM tip is positioned above the N═N group of the molecule (position marked by cross), while the manipulation voltage is increased within 1 s from 100 mV to 1 V; (b) after manipulation the molecule is found in *cis*-configuration; $I_{\text{tunnel}} =$ 75 pA; $V_{\text{sample}} =$ 180 mV; (c, d) IET manipulation dissociates the *cis*-molecule at electron energies above 1 V, (c) before manipulation and (d) after manipulation; $I_{\text{tunnel}} =$ 30 pA; $V_{\text{sample}} =$ 180 mV.

reversible light-induced conformational transition of the double N═N bond between an extended (*trans*) and a compact (*cis*) configuration (see Figure 1).

3.1.1. 4-Dimethyl-amino-azobenzene-4-sulfonic Acid. We used IET to change the configuration of a single 4-dimethyl-amino-azobenzene-4-sulfonic acid molecule from *trans* to *cis* (Figure 2). The STM image of this molecule as well as the amino-nitro-azobenzene discussed later, is dominated by the end groups, which appear as protrusions connected by a more shallow protrusion that indicates the N═N group (for details see ref 10). After imaging the *trans*-isomer in Figure 2a, the tip is positioned above the N═N double bond. During the manipulation the voltage is ramped up to 1 V. After the manipulation the molecule is found in the *cis*-configuration (Figure 2b).

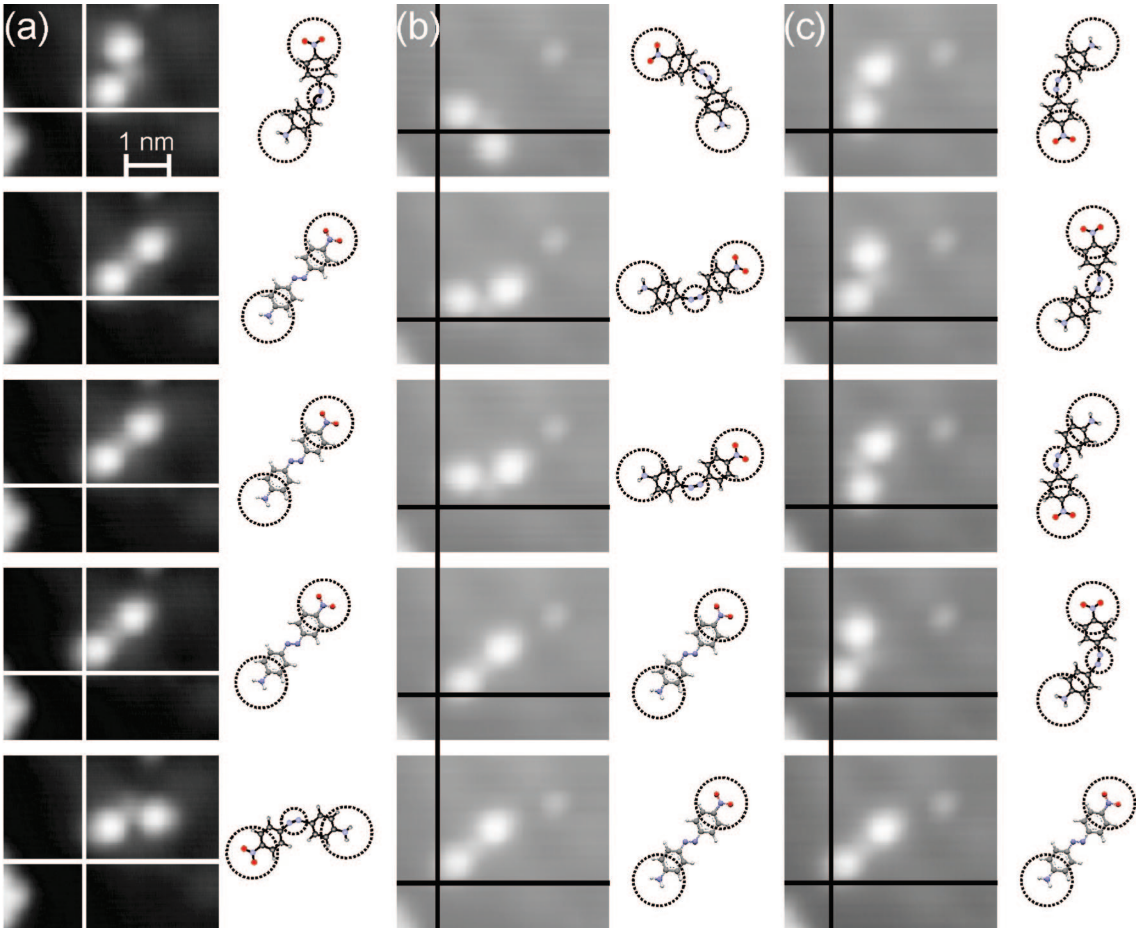

FIGURE 3. Excerpts of an isomerization series of amino-nitro-azobenzene, $I_{\text{tunnel}} =$ 9.4 pA, $V_{\text{sample}} =$ 71 mV, $\Delta h =$ 135 pm: (a) series for manipulation with 650 mV; (b) series for manipulation with 660 mV (c) series for manipulation with 670 mV. Lines are at identical positions within a series and serve to guide the eye for identifying induced diffusion.

Direct comparison of the images before and after the manipulation shows that the NC_2H_6 group (upper protrusion) changes its position, while the Na^+ SO_3^- group (lower protrusion) rests immobile. Methyl groups are known to be not very reactive. As a consequence, they are weakly bound to the surface. Thus, it is plausible that this part of the molecule is moved rather than the more strongly bound Na^+ SO_3^- group.

This example outlines the feasibility of a *trans*−*cis* isomerization on metal surfaces. However, this molecule does not fulfill the requirement of reversibility necessary to employ it as a switch. All attempts have failed to isomerize a 4-dimethylamino-azobenzene-4-sulfonic acid back from its *cis*- to its *trans*-configuration. The IET manipulation either has no effect or dissociates the molecules at manipulation voltages above 1 V (see Figure 2c,d). Even the weakly interacting surface Au(111) would lead to immediate fatigue of the switch.

3.1.2. Amino-nitro-azobenzene. Figure 3a−c depict some examples of a successful series that consists of more than 70 isomerizations of the same amino-nitro-azobenzene molecule by injecting electrons into the N═N double bond. The series starts with a *cis*-configuration (Figure 3a, top image) and within this series at low manipulation voltage, the molecule is reversibly isomerized from *cis* to *trans* and once again back to *cis*. The other two manipulations lead to diffusion of the *trans*-isomer. In the second series at somewhat higher manipulation voltages (Figure 3b), also the *cis*-isomer is excited to diffuse (second manipulation). The first manipulation in this series can be interpreted either as a flip over one of its axes or a double isomerization from *cis* to *trans* to a mirror-symmetric *cis*-configuration. A rotation is unlikely, because the left part of the molecules remains completely unchanged. A similar change, however with a different mirror plane is observed in the first two manipulations of the series shown in Figure 3c, where the flip over process would be over the N═N group. Again, a rotation seems unlikely, because different rotation angles within the series would be expected. The position of the N═N group, which is unchanged in the example shown in panel b but changes in panel c, would be best interpreted as a double isomerization in the former and a flip over process in the latter case. Because the *I*−*t* characteristics are inconclusive (cf. Figure 4c), we are unable to decide this issue.

The high-resolution image of the *cis*-configuration (Figure 4a) shows that the *cis*-configuration is planar on the surface. The increased bond angle (from 111.2° in the gas phase to ∼150° on the surface) allows for the phenyls to lie parallel to the surface. This experimental interpretation has been recently confirmed by DFT calculations,[35] which gives a slightly lower bond angle of 140° (Figure 4b).

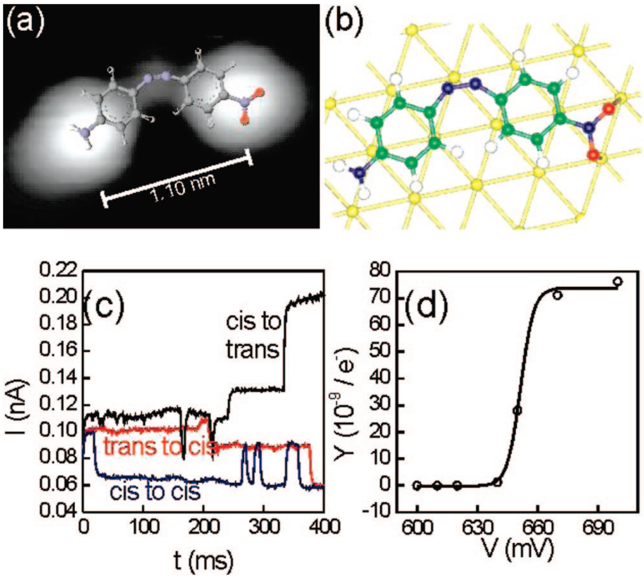

FIGURE 4. Isomerization of amino-nitro-azobenzene (Δh = 135 pm): (a) high-resolution image of *cis*-configuration with I_{tunnel} = 9.4 pA and V_{sample} = 337 mV with superimposed ball-and-stick model as deduced from STM image; (b) DFT calculation of amino-nitro-azobenzene on Au(111);[35] (c) current, *I*, during manipulation; sharp changes are indicative of electron-induced changes to the molecule; (d) isomerization yield, *Y*, vs bias voltage, *V*, for *trans*- to *cis*-isomerization or diffusion.

A steep change in tunneling current (Figure 4c) indicates the success of the manipulation. Often, however, multiple changes are observed, indicating a more complex pathway to the resulting image. If only a single change is observed, the *I*−*t* characteristics allow calculation of the manipulation yield per electron for different electron energies (Figure 4d). The threshold is 650 meV for changes at the *trans*-configuration and 640 meV at the *cis*-configuration. These voltages lie far below the photoisomerization voltages of azobenzene in the gas phase that correspond to ultraviolet (350 nm, that is, 3.55 eV) and blue (440 nm, that is, 2.82 eV) light for isomerization from stable *trans*-configuration and metastable *cis*-configuration, respectively.[36,37] This suggests that the isomerization is not due to excitation into the S_1 state of the molecule as in photoisomerization but is induced in the ground state, where the activation energy in the gas phase is approximately 0.8 eV.

Azobenzene carries two lone-pair orbitals at the nitrogen atoms of the N═N double bond. Therefore, isomerization might be due to rotation around the N═N double bond or due to an inversion of one of the N−C bonds with the lone-pair orbital of the nitrogen. Though the rotation seemed very unlikely on a surface because it requires the phenyls to lift up from the surface by about their radius, recent investigations of thermally induced conformational changes of substituted ben-

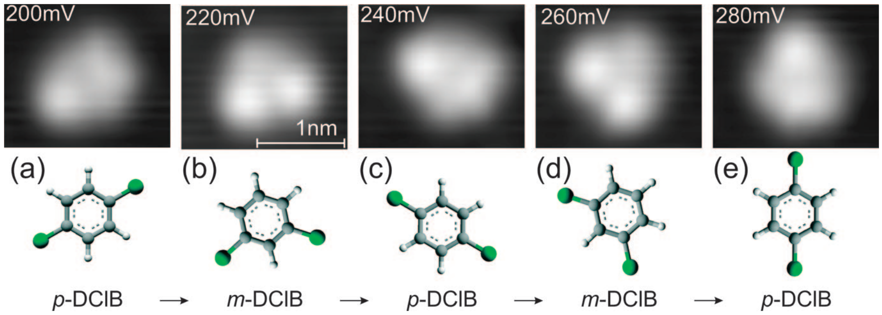

FIGURE 5. Series of isomerizations of dichlorobenzene (DClB) on Cu(111) from scanning at indicated bias and $I_{\text{tunnel}} = 23$ pA; changes to the molecules are not directly observed and are thus probably due to indirect manipulation;[16] this means that they occurred while scanning close to the molecule ($\Delta h = 120$ pm).

zene rings around ethynylene spokes[40] indicate that this process also is feasible. However, calculations showed that inversion, where the N−C bond is exchanged with the lone-pair orbital of the nitrogen, is the preferred pathway for the ground-state isomerization in the gas phase.[41] We thus suggest that the observed isomerization is an inversion of one of the N−C bonds with the lone-pair orbital of the nitrogen.

Comparison of the two investigated azobenzene derivatives presented here points out the importance of the substituents for the use of the molecules as a reversible switch on a surface. Only amino-nitro-azobenzene isomerizes in plane, while the unsubstituted azobenzene[24] and the poly(*tert*-butyl-azobenzene)[26] both isomerize out-of-plane. Thus the careful choice of the appropriate substituent will be indispensible for a useful two-dimensional switch.

3.2. Constitutional Isomerization of Substituted Chlorobenzene Molecules. The constitutional isomerization of chlorobenzene derivatives is based on the exchange of a chlorine atom with a hydrogen atom attached to two different carbon atoms of the phenyl ring. For these molecules, we investigated the excitation mechanism of the isomerization[7] and the influence of both the surface and the second substituent on the isomerization.[8]

3.2.1. Dichlorobenzene. IET-induced constitutional isomerization of individual dichlorobenzene molecules was investigated on Cu(111) and Ag(111).[8] Each chlorine atom leads to a protrusion (Figure 5), and their relative position on the white circle (ring) allows identification of the isomers. The molecules isomerize during scanning at rather low voltages. Figure 5 shows a series of images of a dichlorobenzene molecule absorbed on Cu(111), imaged repeatedly. The first image (Figure 5a) shows the *para*-isomer. The upper right chlorine atom changes its position to form a *meta*-isomer (Figure 5b). Then, the lower left chlorine atom changes to form a *para*-isomer (Figure 5c) that is rotated by 60° with respect to the *para*-isomer in Figure 5a. The same sequence is repeated in Figure 5c−e.

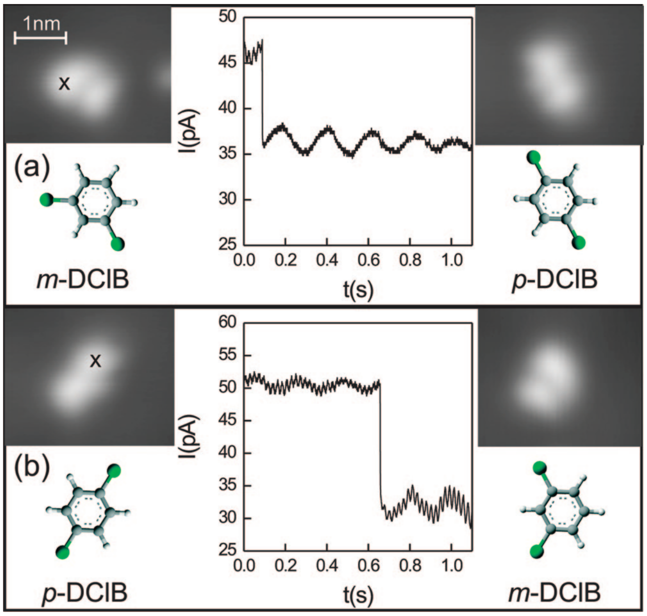

FIGURE 6. Isomerization of dichlorobenzene (DClB) on Ag(111) by IET with $I_{\text{tunnel}} = 23$ pA, $V_{\text{sample}} = 100$ mV, and $\Delta h = 80$ pm: STM images on the left-hand side show the molecule before manipulation; images on the right-hand side show the molecule after manipulation with 200 mV and $I = 50$ pA at positions marked by crosses; the middle panels show current during manipulation; current oscillations in these unfiltered data are a superposition of a building vibration at ~4.9 Hz, and the nitrogen cryostat vibration at 44 Hz (a) from *meta*- into *para*-isomer and (b) from *para*- into *meta*-isomer.

Though sometimes we observe the change during scanning, we have chosen here images where this is not the case. However, when scanning below the isomerization thresholds, we observe no changes. Thus, there is no spontaneous isomerization. This implies that the isomerization is already possible with injection of electrons at some distance from the molecule (cf. ref 43).

On Ag(111), we use IET for a controlled isomerization of dichlorobenzene (Figure 6). The STM images on the left-hand

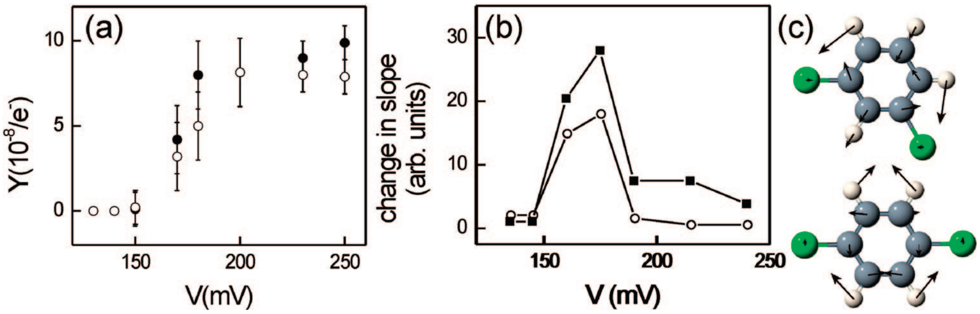

FIGURE 7. IET of dichlorobenzene on Ag(111): (a) dependence of reaction yields, *Y*, on the manipulation voltage, *V*, for the isomerization of the chlorine atom from *meta*- to *para*-isomer (●) and from *para*- to *meta*-isomer (○) at $I = 50$ pA; (b) change in slope of data in panel a for *meta*- to *para*-isomerization (●) and for the opposite reaction (○); (c) schematics of C−C stretch mode at 174 and 172 meV for *meta*- and *para*-dichlorobenzene, respectively.

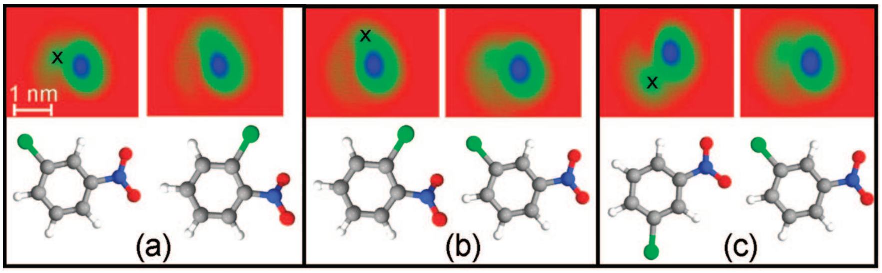

FIGURE 8. Isomerization of chloronitrobenzene on Cu(111) with $I_{\mathrm{tunnel}} = 55$ pA, $V_{\mathrm{sample}} = 100$ mV, and $\Delta h = 80$ pm: In false color STM images, blue ellipses correspond to nitro groups and green circles represent chlorine atoms. The left STM images show molecule before and the right images after IET manipulation indicated by crosses.

side in Figure 6 show the molecule as (a) *meta*- and (b) *para*-isomers, respectively. The molecule is excited by IET with 200 mV and 50 pA. The drops in the recorded current at (a) 0.1 s and (b) 0.7 s correspond to the position changes of the chlorine atom as verified in the STM images at the right-hand side that show the (a) *para*- and (b) *meta*-isomers. The position of the second chlorine atom remains always unaffected by the manipulation, demonstrating a localization of the excitation on the submolecular scale.

We systematically determine the reaction yield through the repetition of the experiment with different manipulation voltages (Figure 7a). The changes in slope (Figure 7b) for the isomerization from *meta*- to *para*-isomer and for the opposite reaction show maxima at (171 ± 7) mV and (169 ± 7) mV, respectively. These threshold energies lie in the energy range typical for vibrational excitations. The excitation mechanism of the isomerization is explained by electron-induced vibrational heating,[38,39] where an inelastically tunneling electron directly transfers energy into a molecular vibration that eventually is transformed into the reaction. Among the vibrations calculated by DFT, there are two modes within the experimentally determined threshold voltage. However, we assign the excitation to the C−C stretch vibration sketched in Figure 7c.[8] This mode has B_{2u} symmetry and leads to an in-plane motion of the hydrogen atoms toward the chlorine atoms, which is certainly favorable for their exchange.

We point out that the scenario in which chlorine and hydrogen atoms are first both detached from the molecule and then reattached in another position on the ring has to be excluded as possible explanation for the isomerization due to energetic reasoning. Instead a collective surface-assisted intramolecular exchange of the atoms is suggested, possibly involving tunneling of the hydrogen atom.

3.2.2. Chloronitrobenzene. Figure 8 shows the feasibility to isomerize a single chloronitrobenzene molecule on Cu(111). Figure 8a (left-hand side) shows *meta*-chloronitrobenzene. The STM image in Figure 8a (right-hand side) after IET corresponds to *ortho*-chloronitrobenzene. It is also possible to manipulate the chlorine atom from different positions back to the *meta*-isomer (Figure 8b,c). The manipulation in Figure 8b shows the reverse isomerization of the *meta* to *ortho* isomerization of Figure 8a, while Figure 8c illustrates the change from *meta*-r to *meta*-l, that is, a change in chirality.

In order to identify the involved vibrations, we investigate the change from *meta* to *ortho* and from *ortho* to *meta* isomers in greater detail by measuring the residence times that the chlorine atom spends in different positions before the isomerizations

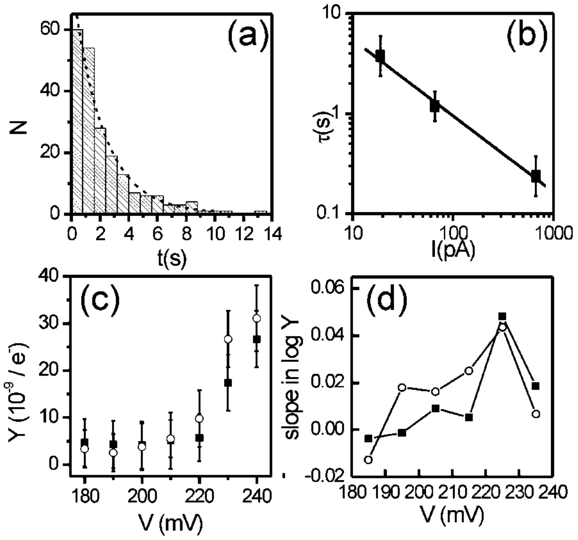

FIGURE 9. (a) Histogram of time, *t*, the chlorine atom spent as the *meta*-isomer before isomerizing to the *ortho*-isomer at 230 mV and 260 pA; dashed line is an exponential fit; (b) time constants, τ, extracted from distributions as shown in panel a for 230 mV as a function of current *I*; solid line is fit to the data ($\tau = I^{-n}$), with $n = 0.9 \pm 0.1$; (c) yields, *Y*, as a function of voltage, *V*, for isomerization from *meta*- to *ortho*-isomer (■) and from *ortho*- to *meta*-isomer (○); (d) changes in slope of log *Y* from panel c; lines serve to guide the eye.

take place within the molecule as a function of bias voltage (180–290 mV) and manipulation current (26–260 pA). All distributions of residence times within the current and voltage range probed follow a simple exponential law, allowing the determination of the time constants from exponential fits (Figure 9a). According to the vibrational heating model,[38,39] the observed linear dependence of time constants on the tunneling current (Figure 9b) means that the isomerization is induced by a one-electron process. The reaction yields per incident electron as a function of the manipulation voltage exhibits a steep increase (Figure 9c). The threshold voltages are usually determined by displaying the slope between the measurement points versus voltage (Figure 9d). These are not consistent with a single threshold (peak) but a double one with the first maximum at (200 ± 10) mV and the second one around (225 ± 8) mV.

Comparison of the thresholds with DFT calculated vibrational modes[7] shows that the first shallow increase in yield of the molecule can be interpreted as excitation of the C–C stretch mode with 195 meV for the *meta* and 197 meV for the *ortho* isomer. No single vibrational mode of the molecule corresponds to the upper threshold. Thus, we suggest that the isomerization reaction is induced by simultaneous excitation of two vibrational modes by one electron. Simultaneous excitation of the C–C stretch that corresponds to the first threshold and the NO_2 in-plane bend with 21 meV (24 meV) (or possibly an external mode) leads thus to the substantial increase in yield.

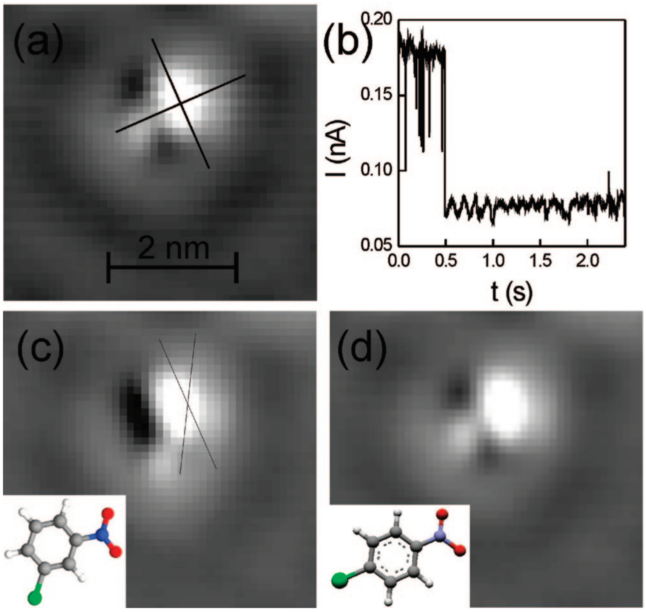

FIGURE 10. Excerpt from a manipulation series of chloronitrobenzene on Cu(111) at 400 mV (Δh = 80 pm): (a) STM image of *para*-isomer; I_{tunnel} = 44 pA, V_{sample} = 100 mV; lines serve to guide the eye for detecting a deviation from a perpendicular geometry; (b) *I*–*t* characteristics during manipulation; (c) STM image after manipulation with I_{tunnel} = 44 pA and V_{sample} = 100 mV; (d) STM image after a second manipulation with 0.4 nA for 2.4 s; I_{tunnel} = 47 pA; V_{sample} = 100 mV.

The threshold energy of approximately 227 mV is significantly higher than the 170 mV for the isomerization of dichlorobenzene on Ag(111) or Cu(111).[8] This clearly shows that the second substituent influences the excitation pathway of the isomerization reaction. Comparison of the rotational adsorption orientation with respect to the atomic surface rows[8] reveals that the nitro group of the chloronitrobenzene, which interacts more strongly with the substrate than the chlorine atom or the phenyl ring, forces the molecule into a different adsorption geometry rotated by ~30° with respect to the orientation of dichlorobenzene. Whether this changes the energetics of the isomerization or the excitability of the vibrations remains to be explored by theory.

The reaction rate of dehydrogenation of substituted thiophenols on Cu(111) at a fixed electron energy depends on the substituents in agreement with a semiempirical model, but the excitation threshold was not presented.[42]

In contrast to our first publication,[7] we are now also able to isomerize the chlorine atom between the *para*- and the *meta*-isomer as shown in Figure 10, though this manipulation required both higher manipulation voltage and higher current than the previously investigated isomerization between the *ortho*- and the

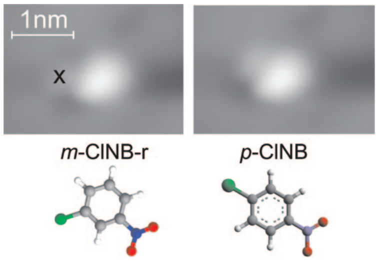

FIGURE 11. Isomerization of *meta*-chloronitrobenzene on Au(111) to *para*-isomer by IET manipulation with 500 mV and 60 pA; I_{tunnel} = 10 pA; V_{sample} = 100 mV; Δh = 125 pm.

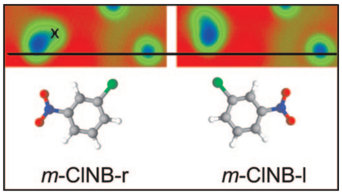

FIGURE 12. Isomerization of chloronitrobenzene on Au(111) by IET where indicated by cross with simultaneous diffusion at 300 mV; line serves to guide the eye to detect the diffusion; I_{tunnel} = 10 pA; V_{sample} = 100 mV; Δh = 125 pm.

meta-isomer. Note that the chlorine is not exactly perpendicular to the long axis of the nitro group ellipsoid. In a separate experiment, where *para*-chloronitrobenzene was deposited on Cu(111), we found that it dissociated upon adsorption. Thus, we conclude that the artificially created *para*-isomer has a different bonding angle to the ring than the gas-phase isomer, which is not stable on Cu(111).

We have also induced isomerization of chloronitrobenzene on Au(111). Here, isomerization into the *para*-isomer is also possible as demonstrated in Figure 11. Again, the chlorine position is not exactly at the normal direction to the nitro group ellipsoid.

In contrast to isomerization on Cu(111), diffusion is sometimes induced simultaneously with the isomerization as shown in Figure 12. This difference is easily understood in view of the smaller interaction and thus lower diffusion barrier of most molecules on Au(111) than on Cu(111).

3.2.3. Manipulation of Substituents between Different Molecules. In Figure 13 we demonstrate that we can move the substituent not only within a molecule but also between molecules. Figure 13a shows a nitrobenzene radical ($NO_2C_6H_4$) from dissociative adsorption of chloronitrobenzene and a *meta*-chloronitrobenzene molecule. IET manipulation with 700 mV detaches the chlorine atom. The subsequent manipulation reattaches the chlorine atom to the other nitrobenzene rest.

The line scans in Figure 13d,e show that the detached chlorine atom is at 60 pm apparent height, considerably higher imaged than if it were attached to the phenyl. This underlines that during the constitutional isomerization of chlorobenzene derivatives, the chlorine is indeed chemically bound to the molecule and not just physi- or chemisorbed.

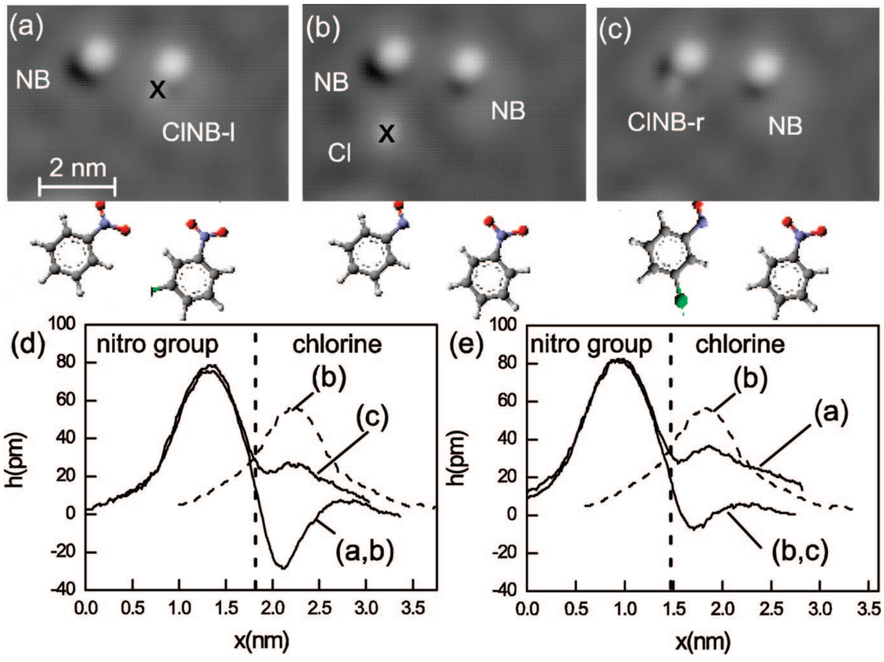

FIGURE 13. Manipulation of substitutional groups between chloronitrobenzene (ClNB) and nitrobenzene (NB) on Cu(111): (a to b) detachment of chlorine atom from molecule; (b to c) attachment of chlorine atom to molecule on left-hand side; (d) line scans of molecules on left-hand side (solid line) and of chlorine atom (dashed line); (e) line scans of molecules on right-hand side (solid line) and of chlorine atom (dashed line); I_{tunnel} = 50 pA; V_{sample} = 100 mV; Δh = 80 pm.

4. Conclusion

In summary, we have demonstrated that controlled constitutional and (geometric) configurational isomerization of several single molecules on Au(111), Ag(111), and Cu(111) is feasible by IET-STM.

We show that on Au(111) *trans*−*cis* isomerization of 4-dimethyl-amino-azobenzene-4-sulfonic acid can be achieved by electron-induced manipulation, while the reverse process is obstructed, because the energy barrier for dissociation is lower than that for isomerization. In contrast, for amino-nitro-azobenzene, the process is reversible. This demonstrates that on surfaces the substitutional groups have a second importance besides the tuning of the isomerization wavelength; they govern the functionality of the azobenzene molecule, that is, the ability to isomerize while in contact with the surface.

For the constitutional isomerization of chlorobenzene derivatives, we showed that the isomerization is induced via inelastic electron tunneling, where the excitation threshold voltages depend on the surface and on the second substituent. Some of the thresholds can only be explained by the simultaneous excitation of two vibrational modes by one electron. For chloronitrobenzene on Cu(111) and Au(111), we find that the weaker interaction of the molecules with Au(111) leads also to an alternative reaction.

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BIOGRAPHICAL INFORMATION

Karina Morgenstern studied Physics and Computer Science at the University of Bonn, Germany, and the University of Tennessee, Knoxville, TN. She received her Ph.D. thesis in Physics in 1996 from the University of Bonn after working at the research center in Jülich, Germany, in the field of surface science. During her Ph.D. studies, she spent six months at the University of Aarhus, Denmark. After a postdoctoral stay at the University of Lausanne, Switzerland, she started a habilitation at the Free University in Berlin on metallic and molecular nanostructures. She finished this habilitation in 2002 and then obtained a Heisenberg fellowship from the German National Science Foundation. Three years later she became full professor of Solid State Physics (W3) at the University of Hannover. Her main research interests are real space investigations of nanoscale physics and chemistry.

FOOTNOTES

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