

# *Trans* to *cis* isomerization of an azobenzene derivative on a Cu(100) surface

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**Abstract** This article reports the observation of two stable configurations of an azobenzene derivative on a Cu(100) surface, which resemble the *trans* and the *cis* isomers of the free molecule. Whereas the *trans* form is the only one observed upon adsorption, the *cis* isomer could be produced by manipulation of individual molecules using a low temperature scanning tunneling microscope. Density functional theory substantiates the observation of the two forms and explains that the *cis*-like configuration is the most stable on Cu(100) due to the formation of two chemical bonds between nitrogen and copper atoms. This *cis* isomer shows a less perturbed configuration due to its three-dimensional shape, suggesting that anchoring molecular switches to surfaces through the central azo group is a feasible approach to functionalize metal surfaces with photochromic azobenzene molecules.

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## 1 Introduction

Molecular switches are an attractive endeavor to control the functionality of a molecule (structure, color, conjugation,

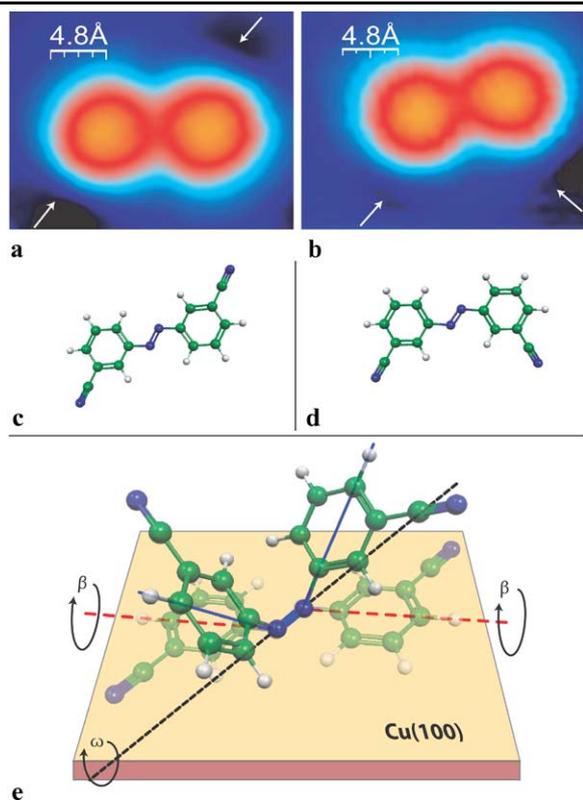
spin and so on) by the use of external stimuli [1]. A molecular switch requires two stable atomic configurations and an accessible conformational/electronic pathway connecting them. Therefore, it represents also an interesting workbench to explore fundamental processes regarding the interaction of light, electrons and external fields with molecular degrees of freedom. The vast majority of studies concentrate on photochromic switches. Among all the processes which can lead to the control of molecular structure with light, *cis*–*trans* photoisomerization is one of the best understood both in solution or in gas phase [1–5]. In particular, azobenzene molecules are one of the simplest examples of *cis*–*trans* photoswitches because they combine a high efficiency with a small structure: two photoactive phenyl rings connected through an azo group. Photoisomerization of azobenzene involves a single excited state, which is populated upon irradiation with ~320 nm and ~420 nm light, allowing effective control of its structure [4, 6–10].

Extensive research efforts have been recently devoted to the functionalization of surfaces with molecular switches, with the goal of building up a new class of materials with controllable properties. From the fundamental point of view, the interest of many studies lies in exploring how the structure and the conformational dynamics of molecular switches, in general, and azobenzene-based compounds, in particular, are modified when adsorbed on metal surfaces [11–16]. Photochromic species have an ubiquitous tendency to mix their aromatic parts with metal states. The bond between metal and molecule introduces an additional degree of complexity in the excited state dynamics. The bonding to a surface distorts the free molecular structure and hinders its conformational motion. Moreover, it allows the rapid quenching of molecular excitations [17]. Hence, the excitation cross section for photochromic molecules on surfaces

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**Fig. 1** (a, b) STM images of the two planar *trans* conformers adsorbed on Cu(100), according to the atomic models (c) and (d), respectively. The locations of the CN end groups are detected as faint depressions (indicated with *arrows*) ((a):  $I_t = 0.26$  nA,  $U_s = -0.72$  V; (b)  $I_t = 0.12$  nA,  $U_s = -0.5$  V). (e) Model of a DMC molecule indicating the intramolecular dihedral angles  $\beta$  and  $\omega$  characterizing the *cis*–*trans* change in configuration for the free molecule. The experimental data was analyzed using WSxM [31]

should be a priori much smaller than in gas phase or solution.

Recent scanning tunneling microscope (STM) studies have demonstrated that excitations induced by tunneling electrons [12, 13, 16, 18, 19], by photons [15] or by a large electric field at molecules in the tip–surface junction [11, 20, 21] can induce switching between two molecular conformations. So far, the approach followed in most of the works is to preserve the free-molecule properties by working with Au(111), a metal surface well known for its weak interaction to molecular adsorbates, or by decoupling the aromatic moieties with inert bulky groups, like tert-butyl terminations [11, 15, 22–24]. There is a general belief that molecular switches chemisorbed on more reactive metal surfaces will undergo a strong distortion of their electronic and atomic structures and lose all their switching capability.

In this paper we report the irreversible conformational change of a molecular switch on a metal surface, which is mediated by the chemical bond between an azobenzene derivative and a Cu(100) surface. We investigate di-meta-cyano-azobenzene (DMC:  $C_{14}H_8N_4$ , Fig. 1c), consisting

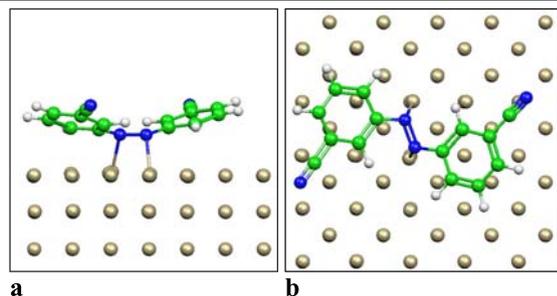
of an azobenzene backbone functionalized with two cyano (CN) groups in meta sites of each aromatic ring [25].<sup>1</sup> Our previous study of DMC on Au(111) revealed that on this surface only the *trans* form is stable, presenting various conformers depending on the relative rotation of their phenyl rings [19]. A *cis*-DMC configuration was not found on Au(111). This was attributed to the large stability of the *trans* isomer, which at the gold surface is further stabilized by the coupling of their  $\pi$ -states with the metal surface. Copper surfaces are more reactive than gold surfaces. However, here we find that a three-dimensional molecular structure closely resembling the gas phase *cis* conformer can be stabilized after manipulation using the tip of a low temperature scanning tunneling microscope. Density functional theory (DFT) simulations confirm that a *cis* configuration turns out to be more stable due to the formation of local bonds between lone-pair electrons of the azo group with copper atoms.

## 2 Adsorption and structure of *trans*-DMC on Cu(100)

Our experiments were carried out in a custom-built low temperature scanning tunneling microscope (STM) under ultra-high-vacuum conditions, at a temperature of 5 K. DMC molecules [25]<sup>1</sup> were deposited using a Knudsen cell at 370 K onto a Cu(100) single crystal at 80 K, previously cleaned using standard sputtering–annealing methods. STM inspection after DMC deposition finds that all molecules appear isolated (Figs. 1a and b). They are imaged as two protrusions (separated by 8.7 Å peak to peak), each one decorated by a faint depression. Tentatively, we may assign this form as similar to the flat *trans*-DMC, and name it so herein, with each protrusion representing the electron-rich phenyl rings, and the depressions accounting for the locations of the CN groups. The latter features allow us to identify two rotamers corresponding to the two CN groups pointing to opposite sites (as in Fig. 1a) or to the same site (as in Fig. 1b), as reported in [19]. Both rotamers are related by a 180° rotation of a phenyl ring around the dihedral angle  $\beta$  (Fig. 1e). Since in gas phase this intramolecular motion is quasi-free and since both rotamers have a very similar stability, we find each rotamer at the surface with the same probability.

The relaxed atomic structure of DMC on Cu(100) has been simulated by means of plane wave density functional theory (DFT) calculations, in the framework of the generalized gradient approximation (GGA) as parameterized by the Perdew–Wang functional [26]. The Cu(100) surface has been modeled with a slab of four copper layers. We have used a  $6 \times 5$  supercell to fit the adsorbed molecule and to

<sup>1</sup>The synthesis of DMC molecules was done by B. Prievisch and K. Rück-Braun, Technische Universität Berlin.

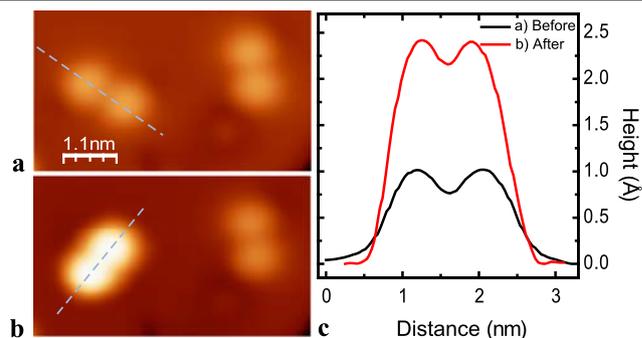


**Fig. 2** Relaxed geometries of *trans*-DMC on Cu(100) obtained by DFT first-principles calculations ((a) side and (b) top views). The surface–adsorbate interaction is dominated by the bonds formed by the N lone-pair electrons with the Cu surface

neglect the spurious interactions with the periodic images. Given the large size of the simulation cell the Brillouin zone has been sampled only with the  $\Gamma$  point. The two bottom layers are kept frozen in their ideal bulk positions, while the top layers and the adsorbate have been relaxed until all the forces on the atoms were lower than  $0.03 \text{ eV/\AA}$ .

According to our calculations, the planar structure of *trans*-DMC is distorted on the Cu(100) surface, as shown in Fig. 2. This distortion can be explained by the balance of the participating interactions. DMC chemisorbs on Cu(100) through the formation of a local bond between the two N atoms at the central backbone and two copper atoms. The N–Cu distance is  $\sim 2 \text{ \AA}$ . Van der Waals forces are not described by the GGA exchange correlation functional. However, the small N–Cu bond length lies already in the repulsive part of the interaction potential between phenyl rings and the copper surface. Hence, both aromatic parts of DMC are pushed upwards, lying at an angle of  $\sim 12^\circ$  from the planar configuration (Fig. 2). The distortion from the planar configuration reduces partially the  $sp^2$  character of the central N=N bridge, thus weakening this bond, on the one hand, and strengthening the bond to the surface, on the other. DFT gives a chemisorption energy of  $0.29 \text{ eV}$ , which probably reflects the balance between energy gained by the formation of local N–Cu bonds and energy employed to bend the molecular structure [27].

The chemisorption of DMC on Cu(100) suggests that conformational changes of the molecule will involve also changes in the Cu–N bond strength and, hence, the whole DMC–metal system has to be analyzed in order to interpret atomic motion. It also poses doubts about the possibility of using molecular excitations (either induced by photons or by electrons) to drive this motion, since the hybridization between N and Cu atoms is probably quenching the excitation very rapidly. To deal with these issues we have carried out further experiments trying to manipulate the shape of a single DMC molecule on the Cu(100) surface.



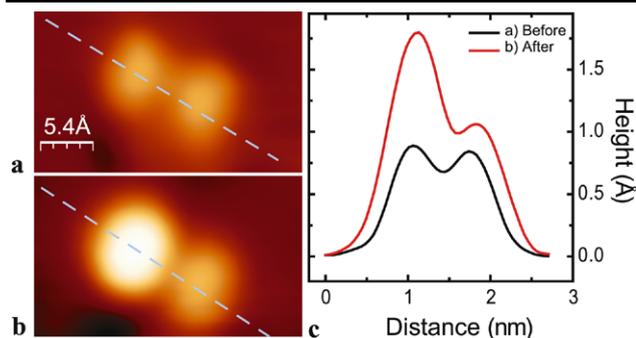
**Fig. 3** STM image of a sample region with two *trans*-DMC molecules (a) before and (b) after positioning the tip on the left-hand molecule and slowly increasing the sample bias in the negative polarity. At about  $U_s = -2 \text{ V}$ , a sudden increase in the tunneling current (not shown) indicates a transformation event ((a)  $I_t = 0.54 \text{ nA}$ ,  $U_s = -0.72 \text{ V}$ ; (b)  $I_t = 0.12 \text{ nA}$ ,  $U_s = -0.5 \text{ V}$ ). (c) Shows the line profiles along the indicated dashed blue lines

### 3 Manipulation of DMC

On Cu(100), DMC monomers remain stable upon STM imaging indicating that the strength of their bond to the surface is larger than observed on Au(111), where diffusion of isolated monomers was easily induced by the tunneling current. On Cu(100) it is possible, however, to induce changes in their structure by increasing the sample bias above a few volts, at either polarity. Figure 3 shows the effect of applying a negative voltage ramp to a single molecule while the STM tip is positioned above the central neck of the DMC molecule. During the ramp, a sudden change in the tunneling current occurs, indicating an irreversible change in the adsorbate. This is confirmed by posterior imaging of the same region. The probed molecule appears much brighter, with a height of  $2.5 \text{ \AA}$ , still showing two protrusions, now separated by  $6.8 \text{ \AA}$ . Neighboring molecules remain unperturbed in the image, with a height of  $1 \text{ \AA}$ , hence excluding any effect due to tip changes.

In some cases, the feature resulting after applying a voltage pulse appears with an asymmetric shape. Figure 4 shows the result of performing a scan on a surface region with a *trans*-DMC molecule using a bias voltage of  $3 \text{ V}$ . After the scan, only one lobe appears higher in the STM image. Such a feature resembles a molecular configuration residing on the pathway between a *cis* and a *trans* state connected by a dihedral angle rotation. In the free-molecule case (and presumably also for physisorbed systems) such an intermediate state is not stable because it breaks the  $sp^2$  conjugation of the di-azo bridge. Here, it reflects the gain in complexity by the formation of chemical bonds with the surface atoms, and poses a warning on the correlation of molecular structures on surfaces with ideal *cis* and *trans* free-molecule configurations.

A possible origin of the manipulated DMC molecules appearing with different shape in the STM images is the

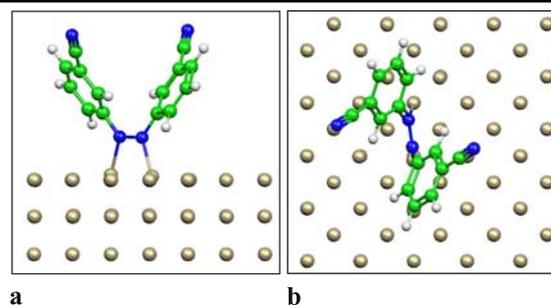


**Fig. 4** STM image of one DMC molecule (**a**) before and (**b**) after scanning using a bias of 3 eV. (**c**) Line profile along the indicated *dashed blue lines*. One of the two lobes of a *trans*-DMC molecule appears with double height. (**a**)  $I_t = 1.7$  nA,  $U_s = 1.3$  V; (**b**)  $I_t = 0.97$  nA,  $U_s = 1.2$  V

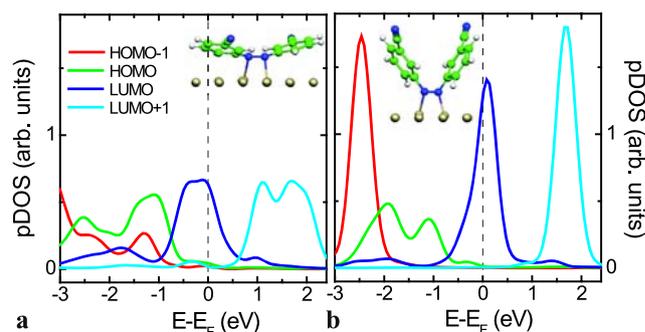
partial fragmentation of the molecular structure. Tunneling electrons may activate the dissociation of an intramolecular bond and, consequently, change its aspect in the STM images [28]. For DMC we would expect to find multiple fragments, most of them with a smaller size than the original molecule. However, we note that the brighter lobes of the modified DMC molecule appear repetitively with double the height of the original *trans*-DMC and a similar separation distance. We suggest that, instead of degradation, the molecular structure has evolved towards a different conformation. A tempting possibility to explore is a three-dimensional configuration resembling the free gas *cis* isomer.

On Au(111) DMC molecules were never found in their *cis* configuration, even after similar attempts of tip-induced manipulation with the STM. The important difference between these two systems is the adsorption state of DMC. On Au(111) a purely physisorbed state is found, where the bonding is dominated by the interaction of the phenyl with substrate states leading to the stabilization of the flat *trans* isomer. In contrast, on Cu(100) the chemical bond between N and Cu atoms (as found for the *trans* isomer, i.e. Fig. 2) may well provide sufficient rigidity to stabilize a three-dimensional configuration of DMC on the metal. In order to find this out, we have relaxed the gas phase atomic structure of the *cis*-DMC isomer on Cu(100) using DFT calculations as described in the previous section. This simulation found a stable three-dimensional form of DMC, which closely resembles the free-molecule *cis* isomer (Fig. 5). This configuration is characterized by the two phenyl rings pointing upwards from the surface by an angle of  $\sim 55^\circ$ . The molecule forms local N–Cu bonds of approximately 2 Å, in a similar fashion to *trans*-DMC (Fig. 2). In fact, the central N=N bridge maintains essentially its orientation with respect to the surface directions.

This relaxed structure agrees well with the observed topographical features in the STM data (Fig. 3b). First, the lifted phenyl rings coincide with the higher and closer pro-



**Fig. 5** (**a**) Side and (**b**) top views of the relaxed geometries of *cis*-DMC on Cu(100) obtained by DFT. The surface–adsorbate interaction is dominated by the bonds formed by the N lone-pair electrons with the Cu surface



**Fig. 6** Density of states of (**a**) *trans* and (**b**) *cis* DMC isomers adsorbed on Cu(100) projected on molecular orbitals of the free species. Charge transfer from the surface to the molecule is revealed by the partial occupation of the LUMO-derived resonance. The broadening of the peaks indicates a larger hybridization of the molecular orbitals with the surface states in the case of the *trans* conformer (**a**)

trusions in the modified molecule (Fig. 3). In addition, the top view model in Fig. 5b resolves that, due to the lifted orientation, the phenyl rings appear rotated by  $\sim 45^\circ$  with respect to the relaxed *trans* structure (Fig. 2b). If we take into account that during a transformation event the N=N bond can rotate to an equivalent mirror orientation around the {001} surface directions, we find that rotations of  $\sim 90^\circ$  can also be expected. This agrees well with the situation usually found in our experiment: the orientation of *trans*-DMC on the surface always changes when transformed to the *cis* configuration by an angle typically a multiple of  $45^\circ$  (e.g. Fig. 3).

#### 4 Discussion

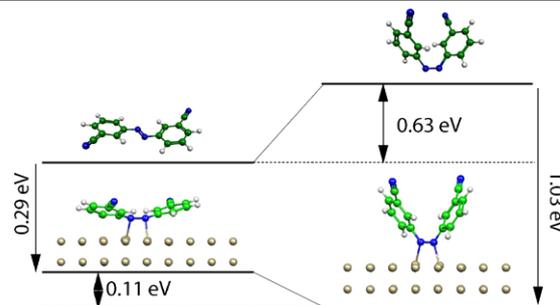
Further insight in the stabilization of a *cis*-like isomer is provided by the projected density of states (pDOS), obtained by projecting the total density of states of the adsorbed system (substrate plus adsorbate) on the molecular orbitals of a free DMC molecule (Fig. 6). The acceptor character of the

molecule is confirmed for both the *trans* and the *cis* configurations, with the lowest unoccupied molecular orbital (LUMO) being partially filled and lying pinned close to the Fermi level. The LUMO is dominated by the  $\pi^*$  orbital, having large weight at the N=N moiety [29]. As this state has antibonding character, the charge transfer is accompanied by a weakening of the central N=N bond (bond length 1.38 vs. 1.26 Å for a free DMC molecule). This may effectively contribute to the distortion of the planar configuration at the surface. However, it cannot explain the larger bending angle of the *cis* isomer, because here the charge transfer is smaller, as we can deduce from the shifted position of the LUMO resonance. In accord with this, the N=N bond length is shorter in the *cis*-DMC isomer (1.32 Å). Hence, the *cis* form is not stabilized by the partial cleavage of the  $sp^2$  N=N bond.

Comparison of the molecular resonances' shape in Fig. 6 provides further evidence that the molecular chemisorption is driven by the non-bonding orbitals, where the N lone-pair electrons reside, instead of by the partial cleavage of the diazo bond. *Trans*-DMC shows a significant distortion and broadening of all molecular states around the Fermi level. However, all these states except the HOMO appear sharp in the *cis* form, indicating that due to the lifted ring geometry the distortion of  $\pi$  and  $\pi^*$  states by the metal surface is reduced. Since the HOMO-derived state corresponds to the non-bonding state [30], its broad shape in both isomers reflects the chemical interaction of lone-pair electrons with copper atoms.

Thus, the three-dimensional *cis* form is essentially stabilized by the hybridization of the HOMO (mainly located on the N atoms of the azo group) with substrate states. The larger bending angle of the central bridge in the *cis* isomer allows a closer—and thus stronger—interaction of the N lone-pair electrons with the Cu(100) surface,<sup>2</sup> resulting in an overall increase of stability with respect to the *trans* isomer. Flattening the molecule (i.e. *cis* to *trans* isomerization) requires the weakening of this N–Cu bond and the motion of phenyl rings in the repulsive part of the adsorption potential. We cannot exclude that  $\pi$ – $\pi$  attraction between the phenyl rings also contributes to the stabilization of the bent configuration.

Figure 7 shows the direct energy comparison for the two configurations on the Cu(100) substrate. The stronger N–Cu bond for *cis*-DMC results in a larger chemisorption energy of 1.03 vs. 0.29 eV for *trans*-DMC. Hence, a stability reversal occurs: while in the gas phase the *trans* configuration has a lower energy, on a Cu(100) surface the large bending



**Fig. 7** Relative stabilities of the DMC molecule in the gas phase (top) and adsorbed on the Cu(100) surface (bottom). The calculated chemisorption energies for every conformer and their relative energy difference (as free molecule and chemisorbed) are indicated

angle of the *cis* isomer confers a larger stability to the molecule. In agreement with this, we have not succeeded in inducing the reverse isomerization (i.e. *cis* to *trans*) by manipulation with the STM tip. In spite of the stronger chemisorption of *cis*-DMC, all molecules appear as *trans*-DMC after deposition. This is however not surprising. In solid and in gas phases DMC adopts its *trans* form. Furthermore, since chemisorption on Cu(100) requires intramolecular bending, an activation barrier probably exists [27]. Hence, we expect that, upon its arrival onto the Cu(100) surface, DMC first populates a transient and weakly bonded precursor state, in which the *cis* form is not stable.

Both the atomic structure and the pDOS in Fig. 6 indicate that the molecular configurations found on Cu maintain a large degree of the free-molecule character. It is interesting to note that, in spite of the larger chemisorption energy of the *cis*-like conformer, its electronic structure is less perturbed. Both the larger localization of  $\pi$  molecular states into the molecule (deduced from Fig. 6b) and the shorter N=N bond length indicate that this isomer maintains, to a larger extent, the character of the *cis*-DMC molecule, but stabilized at the surface.

Finally, we argue about the possible excitation mechanism inducing the conformational change. Previous works reported that single-molecule *cis*–*trans* isomerization of azobenzene can be induced by inelastic excitation of vibrational states in the ground electronic state [12]. An increase in the electric field at the tip–sample junction can also lead to similar conformational changes [11]. Here, we note that the non-planar structure of the initial *trans*-DMC molecule offers a resulting dipole moment component perpendicular to the surface. This can increase the effect of an electric field on the molecule and activate intramolecular motion. In addition to this, quantum chemistry calculations for a free DMC molecule found that a non-planar geometry is essential to couple DMC anionic states with a three-dimensional conformational change [19]. The low success rate of the isomerization events makes it difficult to provide a certainty on the

<sup>2</sup>The larger bending angle pushes the lone-pair electrons towards the surface, thus strengthening the N–Cu bonds. The N=N axis also rotates slightly. In the *cis*-like configuration this axis becomes more parallel to the direction along two neighboring copper atoms, causing N atoms to approach on-top positions.

leading mechanism. Most probably, it entails a combination of various effects and excitations.

## 5 Summary

In this work we have shown that two stable configurations of a functionalized azobenzene molecule can be found chemisorbed on a Cu(100) surface, which resemble the *trans* and *cis* conformers characteristic of the free molecule. The former bends slightly during the chemisorption process. The latter has a three-dimensional shape and can be induced by applying voltage pulses with the tip of a STM. DFT simulations found that both forms are stabilized through strong local bonds between N lone pair electrons of the central bridge and copper atoms. Interestingly, our results show that at the surface the stability is inverted, i.e. the *cis*-DMC isomer is more stable while, at the same time, its three-dimensional structure keeps its conjugated molecular character less perturbed by the metal surface. An important implication of our results is that, contrary to previous expectations, a chemical bond with the surface (mediated by non-bonding molecular states) is necessary to stabilize a molecular configuration very similar to the photochromic *cis* form. This sets an alternative approach for the effective functionalization of metals with switchable molecular species.

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