

Charge-transfer induced isomerization of DCNQI on Cu(100).

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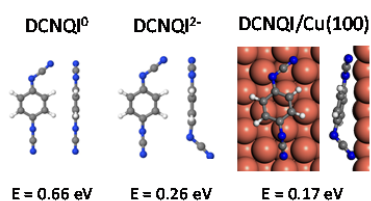
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ABSTRACT. This article reports on the temperature-controlled irreversible transition between the two isomeric forms of the strong electron acceptor DCNQI on the Cu(100) surface. A combination of experiment (time resolved, variable temperature scanning tunneling microscopy, STM) and theory (density function theory, DFT) shows that the isomerization barrier is lower than in gas phase or solution due to the fact that charge transfer from the substrate modifies the bond configuration of the molecule, aromatizing the quinoid ring of DCNQI and enabling a more free rotation of the cyano groups with respect to the molecular axis.

TOC GRAPHICS



KEYWORDS. Isomerization, charge transfer, DCNQI.

TEXT. Molecular isomerization reactions have been proposed as possible switching mechanisms in the field of molecular electronics since, by applying an external stimulus, they can provide a reversible transition between two thermally stable states which differ in some measurable physical property.¹ For the integration in electronic circuits, these molecular switches have to be

deposited on a surface, and although isomerization reactions in solution have been studied for a long time, their study on solid substrates is much more recent.²⁻³ With a few exceptions,⁴⁻⁷ most of these studies have focused on azobenzene derivatives on metal surfaces, where isomerization can be induced by light,⁸⁻⁹ thermal energy,⁹ and the tunneling current¹⁰⁻¹¹ or the electric field¹² from an STM tip. However, it has been shown that different substrates,¹³ different surface orientations,¹³ or even different areas of the same surface¹⁴⁻¹⁵ can suppress the isomerization for the same molecules. In a recent report the surface has been suggested to lower the energy barrier for isomerization, but no specific mechanism could be identified.¹⁶ Steric hindrance, surface defects, charge transfer and/or molecule-substrate electronic states hybridization, which could modify the electronic states of the isomers, and therefore also the potential energy surface, have been suggested as possible mechanisms for modifying the isomerization reaction,^{8, 13, 16} but to our knowledge, no specific mechanism has been demonstrated.

In this work we show through a combined experimental (STM) and theoretical (DFT) study that, contrary to most of the cases reported, molecule-substrate interaction can actually promote isomerization by lowering the energy barrier. In particular, charge transfer from the substrate can change the bond configuration of an adsorbed molecule, decreasing the activation energy and allowing thermal isomerization to take place at lower temperatures than in gas phase or solution.

We have investigated the isomerization reaction of DCNQI (Dicyano-p-quinonediimine, Figure 1) on a Cu(100) surface. DCNQI is an electron acceptor molecule, nearly as strong as 7,7,8,8-tetracyanoquinodimethane (TCNQ),¹⁷⁻¹⁸ and it belongs to a family of molecules which form a large number of charge transfer and coordination compounds exhibiting metallic conductivity.¹⁹ The stereochemistry of DNCQI and its derivatives has been thoroughly investigated.²⁰⁻²¹ For the parent compound, *syn-anti* configurations are interconverted in solution with an activation

energy $E_a \sim 0.5$ eV, although the *anti*-isomer is slightly preferred (80:20), since the dipole moments are reduced in this configuration.²⁰ Theoretical calculations reveal that isomerization takes place via inversion of the cyano group around the imine nitrogen atom, with a gas-phase activation energy of 0.63 eV²¹ (our own calculations give $E_a \sim 0.66$ eV).

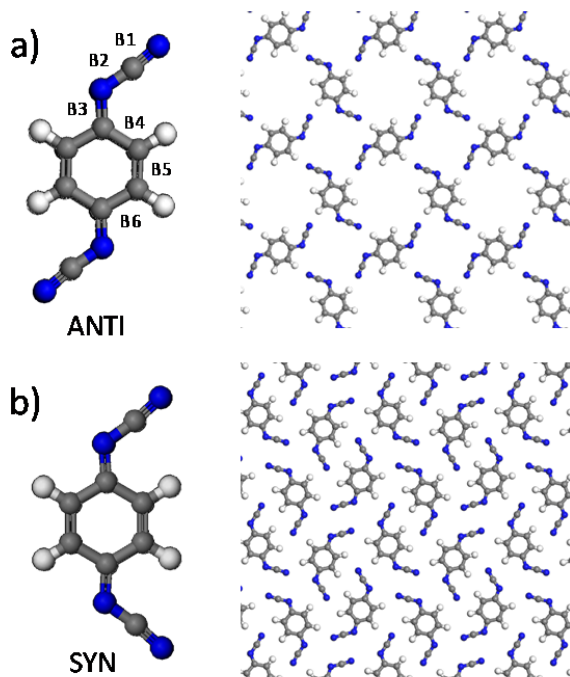


Figure 1. Chemical structure and DFT calculated minimum energy self-assembly of free-standing monolayers of a) *anti* and b) *syn*-DCNQI.

After depositing 0.03 ML of DCNQI on Cu(100) at low temperatures (below 230 K), disordered clusters form on the surface (SI, Figure S1). Increasing the substrate temperature to 235 K leads to the formation of well-ordered 2D islands (Figure 2a). The results of the STM measurements are compatible with a commensurate unit cell that can be described through the epitaxial relationship $\mathbf{b}_I = 3\mathbf{a}_1 + 4\mathbf{a}_2$, and $\mathbf{b}_2 = -4\mathbf{a}_1 + 3\mathbf{a}_2$, where \mathbf{a}_1 and \mathbf{a}_2 are the unit cell vectors of the Cu(100) surface. This type of assembly (denominated LT-phase) is observed in a small

temperature range. Increasing the temperature above ~ 245 K causes the molecules to reorganize into a ~ 1.39 times denser assembly (denominated RT-phase, Figure 2b) with a new unit cell, given by (within the measurement errors) where $\mathbf{b}_1 = 6\mathbf{a}_1$ and $\mathbf{b}_2 = 6\mathbf{a}_2$. Initially both phases coexist on the copper surface (Figure 3a), until the transition from the LT- to the RT-phase is complete (Figure 3d). The RT-phase can also be obtained by depositing directly with the substrate at room temperature. These new RT-phase islands are stable up to at least ~ 440 K.

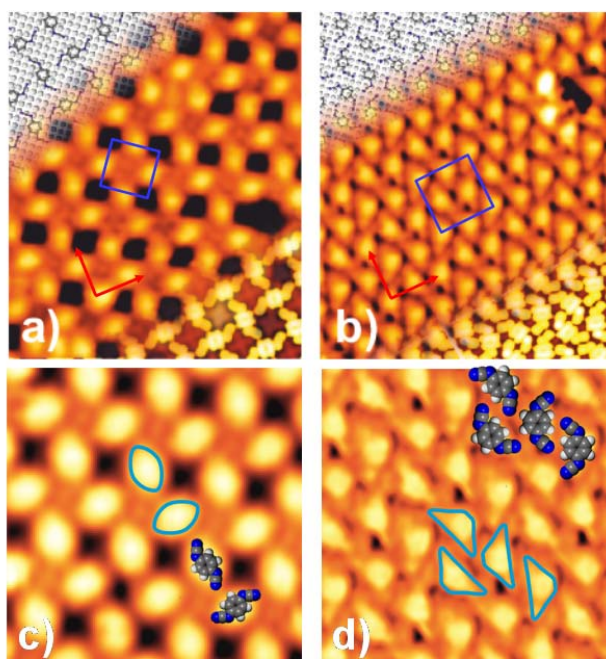


Figure 2. a, b) STM images ($90 \text{ \AA} \times 100 \text{ \AA}$) taken after depositing DCNQI on Cu(100) a) with the substrate at 145 K ($V_b = -1.0 \text{ V}$, $I_t = -0.21 \text{ nA}$; the image was taken at 235 K); b) with the substrate at room temperature ($V_b = -1.24 \text{ V}$, $I_t = -0.48 \text{ nA}$; the image was taken at room temperature). Top left corners show the calculated optimized structures of a monolayer of DCNQI molecules in the (a) *anti* and (b) *syn* configuration on the Cu(100) surface. Bottom right corners show the corresponding simulated STM images. The blue squares indicate the respective unit cells, while the red arrows show the high symmetry directions of the copper surface. c, d)

Higher resolution images showing the difference in the apparent shape of the molecules. The shapes (marked with a light blue line) strongly resemble the c) *anti* isomer for the LT phase; and d) the *syn* isomer for the RT phase (see the SI for details). Some CPK molecular models have also been added for clarity.

Although submolecular features are hardly resolved due to the strong interaction with the copper surface (see below), a close look at the STM images seems to indicate that the molecular shape is spindle-like in the LT-phase (Figure 2c) with a center of symmetry that is absent in the RT phase, where the molecular shape is more croissant-like (Figure 2d), which suggests that in the LT phase the molecules are in the *anti* configuration, while in the RT-phase they are in the *syn* configuration. This isomer assignment suggested by the STM images is corroborated by the fact that they are the only ones that can explain in a reasonable way both structural arrangements. Figure 1 shows the results of DFT calculations showing the optimized structure of free-standing monolayers composed of *anti*-isomers and *syn*-isomers. The obtained values of the distances, angles and molecular orientations are in good agreement with the experimental results. In the LT-phase each molecule forms four weak hydrogen bonds with the neighboring units, with a binding energy per molecule of 0.43 eV. For the more densely packed RT-phase, the binding energy per molecule is 0.47 eV. We can see (top left corners in Figs. 2a and 2b) that the overall arrangement of the molecular assembly does not change much when the copper substrate is taken into account in the DFT calculations ([see Figure S5](#)), but the difference in binding energy per molecule between the *anti* (0.05 eV) and *syn* configurations (0.14 eV) increases to 0.09 eV when the molecules are adsorbed on the Cu(100) surface. Thus, although the adsorption energy of an isolated molecule is higher in the *anti* configuration (4.33 eV) than in the *syn* configuration (4.21 eV), the layer composed of *syn*-isomers is more stable than the layer of *anti*-isomers.

Figure 3 shows the evolution of a DCNQI layer, deposited at 220 K, when the temperature is increased up to 250 K. At this temperature, the isomerization reaction has already begun, and Figure 3a shows an island composed of *syn* (upper region) and *anti* (lower region) isomers. As time goes by, *anti*-isomers start to detach from the island, decreasing the size of the LT-phase until it completely disappears. On the contrary, the size of the RT-phase has increased slightly. After this sequence, STM images (SI, Figure S6) reveal that now all the island on the surface are in the RT-phase. This shows that the isomerization does not take place while the molecules are forming part of an island, but after detaching from it.

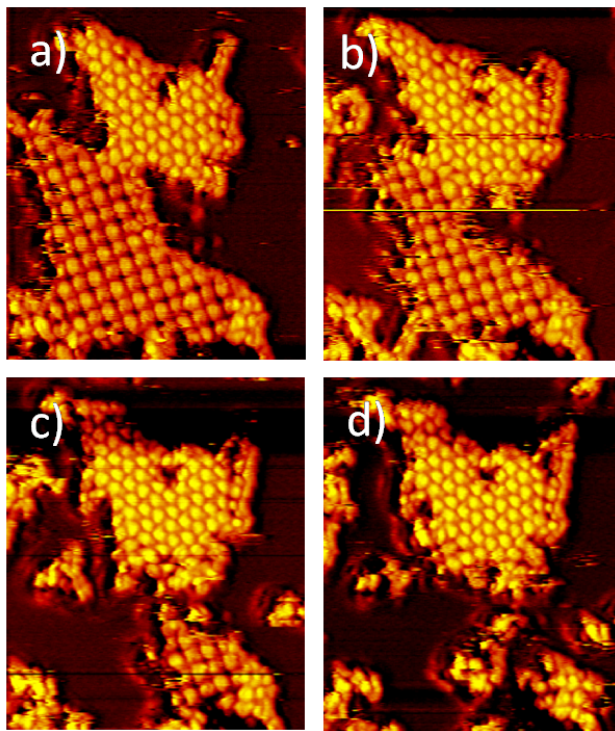


Figure 3. Sequence of STM images (taken every 40 s) of the Cu(100) after depositing 0.2 ML of DCNQI at 220 K. The STM images were taken at ~ 250 K ($200 \text{ \AA} \times 220 \text{ \AA}$; $V_b = -1.7 \text{ V}$, $I_t = -0.23 \text{ nA}$).

With this data in mind, the following scenario can be depicted: In agreement with our and other experimental and theoretical results, the *anti*-DCNQI is the more stable isomer²⁰⁻²¹ and DCNQI adsorbs therefore on the copper surface from the gas phase (in the absence of condensation by H-bonding) in the *anti* form. Up to a substrate temperature of 245 K, the thermal energy is not large enough for the molecules to overcome the isomerization barrier between the *anti* and the *syn* form. Therefore, as soon as the molecular mobility is high enough (235 K), metastable LT-phase islands consisting of *anti*-DCNQI start to form. Increasing further the temperature enables the detachment of the *anti*-molecules from the island and their subsequent isomerization ~~while diffusing on the surface~~. The increasing number of *syn*-DCNQI molecules can partially nucleate in the more stable RT-islands, a process that continues until the complete disappearance of the LT-phase. The fact that isomerization takes place only for isolated molecules also explains the observed irreversibility of the isomerization process: once the more stable RT-islands are formed, decreasing the temperature will not dissolve the islands.²²

However, 245 K seems a very low temperature for isomerization to take place if the activation barrier is ~ 0.6 eV. A simple estimation confirms this assumption. Measurements of the island density at a given deposition temperature allow us to estimate the diffusion coefficient and thereby, the average diffusion time t_{dif} . Since isomerization takes place only when the molecules are ~~diffusing on the surface~~ not attached to an island, we can compare the diffusion time $t_{dif} = (4 \pm 3) \times 10^{-2}$ s obtained from the island density at 240 K (see SI for details) with the time t_{iso} needed for an isomerization event to take place at the transition temperature (245 K), which depends on the energy barrier between the two possible states and can be estimated using the transition state theory.²³⁻²⁴ The isomerization rate is $\nu_{iso} = \nu_0 e^{-E_a/k_B T}$. Using the calculated gas-phase activation energy $E_a = 0.66$ eV, and assuming a typical attempt frequency²⁵ of $\nu_0 = 10^{12} \text{ s}^{-1}$ (k_b is the

Boltzmann constant), we obtain $t_{iso} = 1/\nu_{iso} \sim 38$ s, which is three orders of magnitude larger than the diffusion time and renders an *anti* to *syn* transition at 245 K very unlikely, contrary to the experimental results. (See the SI for the details of these calculations.)

To gain insight into this problem, we have performed DFT calculations of the minimum energy conformation of a DCNQI molecule on the Cu(100) surface, both for the *anti* and *syn* isomers. The results (Figure 4) show an isolated DCNQI molecule absorbed with the phenyl ring parallel to the copper surface at a distance of 3.56 Å. The cyano groups, on the other hand, are bent downwards, with the N atoms at a distance of 1.58 Å (the torsion angle is 60.1°). The surface is also distorted, with the Cu atoms close to the N atoms lifted 0.16 Å from the ideal surface termination. Actually, similar molecular and surface distortions have been reported in the case of TCNQ/Cu(100).²⁶ As in that case, there is a considerable amount of charge transfer from the substrate to the molecule, which here amounts to ~ 1.26 e⁻.

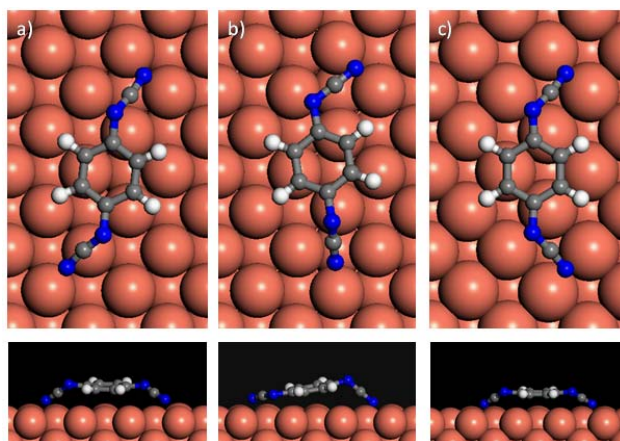


Figure 4. Top and side view of (a) a local minimum structure of the single *anti*-DCNQI molecule, (c) a local minimum structure of *syn*-DCNQI, and (b) the corresponding transition state of the isomerization from (a) to (c).

As a consequence of the electronic redistribution, the molecular bond lengths also experience significant changes (Table 1): the phenyl ring becomes almost aromatic, and bond B3 increases appreciably its length, acquiring a marked single bond character and facilitating the rotation of the cyano group. As should be expected, all these changes are very similar to what happens to the doubly charged DCNQI molecule in gas phase (Table I). In the case of doubly charged DCNQI in gas phase, the lengthening of bond B3 facilitates the rotation of the cyano group, and the calculated energy barrier for isomerization decreases down to a value of $E_a = 0.26$ eV. (Actually, charge redistribution not only decreases the barrier, but also modifies the isomerization mechanism, which now becomes almost pure rotation around the imine N atom, see SI, Figure S8).

Table 1. Bond lengths (in Å) of the neutral DCNQI molecule (DCNQI^0), in the dianion state (DCNQI^{2-}), and adsorbed on the Cu(100) surface. (See Figure 1 for bonds assignment).

	DCNQI^0	DCNQI^{2-}	$\text{DCNQI}/\text{Cu}(100)$
B1	1.18	1.19	1.20
B2	1.32	1.30	1.29
B3	1.32	1.38	1.40
B4	1.45	1.43	1.42
B5	1.36	1.39	1.41
B6	1.45	1.42	1.42

When the molecule is adsorbed on the surface, the calculation of the energy barrier is much more complicated, because if we assume that isomerization takes place during the molecule diffusion, the exact initial and final states are not exactly known. We have, however, explored different

possibilities, and found that, in every case the energy barrier is much lower than for the neutral isolated molecule, and even lower than for the doubly charged molecule in gas phase. For example, in the case shown in Figure 4, the barrier for going from *anti* (left) to *syn* (right) is only 0.17 eV. If we use this value to calculate the isomerization time, we obtain $t_{iso} \sim 3.1 \times 10^{-9}$ s, which is almost seven orders of magnitude lower than the diffusion time, and consequently explains the possibility of isomerization at 245 K on the Cu(100) surface.

Charge transfer at the organic/metal interface has long been recognized as an important parameter that may modify the energy level alignment and then the charge injection barriers, affecting the functionality of electronic devices. It has also been shown that charge transfer may also have other consequences both on the molecule and/or the metal surface, causing, for example, molecular distortion or substrate mediated self-assembly²⁶⁻²⁸ and allowing chemical reactions not present in solution.²⁹ With the exception of a few cases,³⁰ these effects of charge transfer are usually considered in a disconnected way. Here we have shown that, in some cases, charge transfer can modify the molecular bond configuration, e.g., by facilitating the rotation of specific chemical bonds and decreasing isomerization barriers. This, in turn, can also modify the islands structure on the substrate. In summary, we have demonstrated, for the DCNQI/Cu(100) system, the causal connection among the strong molecule-surface interaction, charge transfer, the isomerization reaction and the surface islands structure, being an example of crucial interface effects in organic device architecture.

EXPERIMENTAL METHODS

The experiments were carried out in an ultra-high vacuum chamber with a base pressure of 10^{-10} mbar. The Cu(100) crystal was previously cleaned by sputter (1 kV Ar⁺ ions for 10 min) and

annealing (800 K for 10 min) cycles. The DCNQI molecules were evaporated from an effusion cell held at ~365 K onto the Cu(100) crystal which, placed onto the STM, could be held at any temperature between 145 and 300 K during deposition.

DFT calculations using the PBE³¹ exchange-correlation functional were performed with the projector augmented wave (PAW) method,³² as implemented in the VASP package.³³ (See the SI for computational details).

ASSOCIATED CONTENT

Computational details of DFT calculations. Additional STM images. Calculation of the average diffusion time. Gas phase calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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