

Deformation of a 3.7-nm long molecular wire at a metallic step edge

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 (Received 22 March 2002; published 15 August 2002)

The adsorption of a new molecule constituted of a 3.7-nm long conjugated board equipped with eight lateral legs was studied with scanning tunneling microscopy on the Cu(100) and nanostructured Cu(111) surfaces. The conformation of the adsorbed molecules was extracted by comparing experimental images with calculated ones. In particular, we demonstrate that not only are the legs free to rotate, but also that the central board is distorted at double steps. The van der Waals interaction of the conjugated board with the metallic surface is shown to be responsible for the deformation of the molecules.

DOI: 10.1103/PhysRevB.66.075410

PACS number(s): 68.43.-h

I. INTRODUCTION

Long and conducting molecular wires are expected to be at the basis of the challenging research of monomolecular electronics with the full electronic circuit integrated in a very single molecule.^{1,2} To measure the conductance of an individual organic molecular wire, and to have access to the tunnel transport characteristics along it, the molecule must be adsorbed in a coplanar configuration between two metal electrodes belonging to the external measurement circuit as shown in Fig. 1(a). Due to the progresses in the fabrication of planar and coplanar metal-insulating-metal nanojunctions,^{3,4} the conductance of molecular nanomaterials such as carbon nanotubes⁵⁻⁷ and of small molecules^{8,9} has been measured at ambient conditions. In most of these experiments, the electronic interactions of the molecule extremities with the electrodes are not well defined. In addition, the atomic organization of the electrodes tips—which may also be polluted by unknown contamination—as well as the conformation of the molecular wire in the junction are undetermined.¹⁰ This precludes the control of the measurement conditions and complicates the optimization procedure of the internal chemical structure of the molecular wire for a better conductance.¹¹

Vacuum offers the ideal conditions for this type of experiment thanks to the possibility of mastering the cleanness and the geometry of the contacts between the electrodes and the molecular wire, which allows the molecular configuration shown in Fig. 1(a) to be realized. Nevertheless, experiments in vacuum are still rare because of the difficulties encountered in the fabrication of ultraclean nanometallic wires^{12,13} and in the fabrication of nanojunctions in this environment. In a pseudoplanar geometry [see Fig. 1(b)], the only measurement of the conductance of a molecular wire attained in vacuum was accomplished by Langlais *et al.*¹⁴ on the first member, the *S*-Lander molecule, of the family of Lander molecules. *I-V* characteristics were recorded electrically coupling one extremity of the molecular wire part at to a double Cu(100) step edge and by using the tip of an ultrahigh vacuum (UHV) scanning tunneling microscope (STM) as the second electrode.

The Lander family consists of molecules with a central polyaromatic board, the conducting molecular wire because

of the delocalized π orbitals of the benzene rings. At both extremities, the wire is terminated by fluoranthene groups assuring a more efficient contact point. On the contrary, the 3,5-di-*tert*-butylphenyl substituents act as insulating legs, keeping the board away from the metal surface below.¹⁵ The conformation of two members of the family, the *S*-Lander¹⁶ and *L*-Lander¹⁷ molecules were studied in detail using UHV-STM images to obtain the geometry of the legs when adsorbed on a metal surface. As observed in previous works on porphyrin molecules equipped with the same type of legs,^{18,19} it was pointed out that each σ bond attaching a leg to the board is distorted due to the electronic interactions between the π molecular orbitals of the wire board and the metallic surface. Consequently, the designed distance between the board and the metal surface was experimentally found to be reduced from the expected 0.67 to 0.38 nm. This distance reduction precludes a good electronic contact between the board of the Lander and a metal step edge. Heating up the surface again while the Landers had already been sublimated,¹⁴ may be the way to find some Landers docked in a good conformation to a step edge for intramolecular transport studies. But many of the Landers may have been destroyed at this stage, thus hindering any systematic measurements.

In this paper, we show that in the Lander series, not only the legs, but also the central molecular wire board is flexible upon adsorbing at a metal step edge. To approach the geometry shown in Fig. 1(b) of an ultraclean and atomically precise planar electronic contact between a molecular wire and a metal electrode, we have fabricated double steps of cobalt on the Cu(111) surface in a controlled way. Upon sublimation, molecular Landers are expected to dock perpendicularly to the islands. For the purpose of this experiment, we have also used a new member of the Lander family, the *D*-Lander molecule¹⁵ whose structure is presented in Fig. 2. In comparison to the *S*-Lander and *L*-Lander molecules, the *D*-Lander molecule is much longer (3.7 nm), thus representing a molecular wire with a realistic length for the integration of some molecular switches along the wire. In order to relate its morphological change upon adsorption to the observations made on the previous members of the family, the *D*-Lander molecule was equipped with eight legs, four of *S*-Lander type and four of *L*-Lander type.

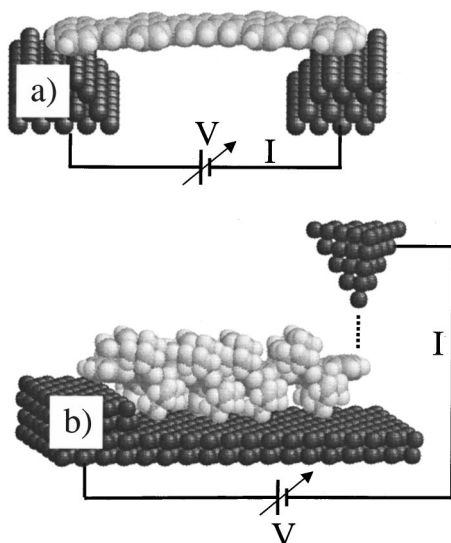


FIG. 1. Two different diagrams for the measurement of the electrical properties of a molecular wire. (a) Ideal case of a molecular wire between two monocrystalline electrodes. (b) The molecular wire is equipped with eight legs (*D*-Lander molecule), the two electrodes are the Cu(100) surface and a STM tip.

II. EXPERIMENTAL

The UHV-STM system used for this study has been already described elsewhere.²⁰ The Cu(100) and Cu(111) surfaces (Surface Preparation Laboratory, Zaandam, NL) were cleaned by the usual cycling procedure of Ar⁺ ion sputtering (600 eV, 3.5 μ A) followed by annealing at 500 °C. Cobalt was evaporated onto the Cu(111) by resistive heating a Co wire (Goodfellow, 0.25-mm thick, purity 99.99+%). Sublimation of the *D*-Lander molecules from a solid powder in a tungsten crucible which was slowly heated was not successful because most of the molecules decomposed during the sublimation procedure. To overcome this problem, another evaporation method was developed. First, the molecules were deposited in the form of a solid powder onto a tungsten wire 0.25-mm thick. Secondly, the filament was positioned in close proximity to the sample whereas the STM tip was kept withdrawn to avoid contamination. Thirdly, a current pulse of ~ 5 A and of a duration of 1 s was applied to the tungsten filament. Thanks to such a procedure, a major fraction of the *D*-Landers molecules were found to adsorb intact on the Cu(100) and Cu(111) surfaces. This method is based on the observation that rapid, high-temperature heating can favor evaporation relative to decomposition.²¹ It can be rationalized by considering that the competitive decomposition and evaporation processes are thermally activated processes with different activation energies. If the activation energy for desorption is higher than the activation energy for decomposition, the production of intact molecules will be favored at high temperatures (assuming that the frequency factor for intact desorption is higher than that for decomposition). Another advantage of this method is the possibility to monitor the deposited amount by STM nearly in real time.

D-Lander molecules are only physisorbed on metal surfaces, therefore, a good control of the interaction of the STM

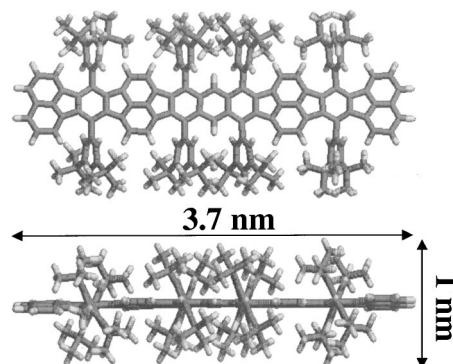


FIG. 2. Top and sideview molecular models of the *D*-Lander molecule after minimization of the energy in vacuum.

tip with the adsorbed molecule is required to avoid the manipulation of the molecule during the imaging stage. Tips were obtained by electrochemical etching of a tungsten wire (0.25 mm),²² heated to eliminate the oxide and sharpened with Ne⁺ autosputtering.^{23,24} Since the conductance of the substrate-*D*-Lander molecule-tip tunnel junction is very low, low tunneling currents below 10 pA and high bias voltages from 2 to 3 V were necessary to keep the tip far away from the surface and avoid such manipulation. Even in these conditions, molecules could be displaced or picked up by the tip apex during a scan. The *D*-Lander molecules and cobalt evaporation and most of the STM experiments were performed at room temperature.

III. RESULTS

A. Adsorption of the *D*-Lander molecules on the Cu(100) surface

Figure 3(a) presents an STM image of adsorbed *D*-Lander molecules at low coverage. Because of their high mobility at room temperature, isolated molecules cannot be imaged on the terraces but only when they are immobilized by defects. In this case, they are trapped at the lower step edge perturbing the diffusion processes of Cu atoms on the steps at room temperature and causing their faceting with an angle of $\pm 15^\circ$ from the $\langle 110 \rangle$ directions. The *D*-Lander molecules are imaged as two rows of four lobes in a nearly rectangular configuration. Each lobe corresponds to the position of one leg of a *D*-Lander molecule. In the inset of Fig. 3(a), the STM image of a *D*-Lander molecule obtained by a more precise scan is presented. In the upper legs row, the third lobe starting from the left is higher than the second one. On the contrary, on the lower row the second is higher than the third causing an alternation of the imaged height of the four central legs [see Fig. 3(b)]. This effect has already been observed for the *S*-Lander molecules,¹⁴ which actually constitute the central part of the *D*-Lander molecules.

No intramolecular contrast can be associated with the central board, as in the case of many molecules of the Lander series.^{13,14,16,17} The central board is maintained by the legs too far away from the surface preventing its molecular orbitals from being electronically coupled with the surface. In Fig. 3, the *D*-Lander molecules are arranged with their axe

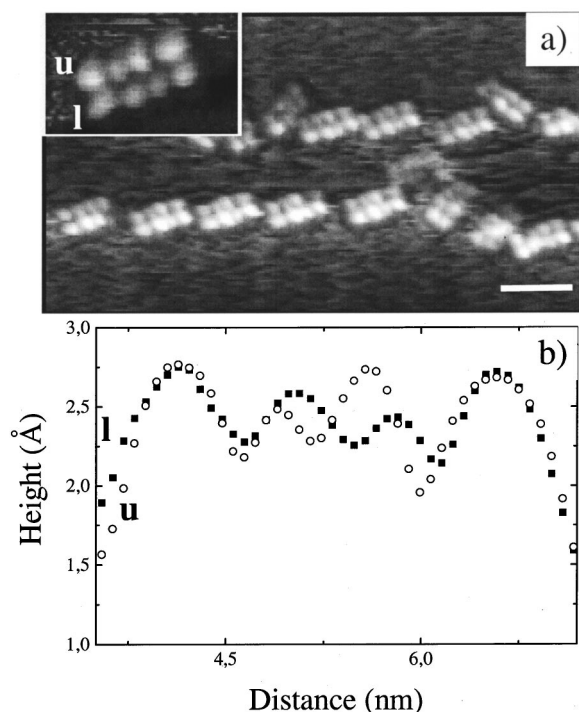


FIG. 3. (a) STM image ($I=10$ pA, $V_{\text{bias}}=2.7$ V) of *D*-Lander molecules adsorbed at Cu(100) steps. The scale bar corresponds to 5 nm. (b) STM profiles of the two legs rows for the *D*-Lander molecule in the inset.

parallel to the step edge. They were also found in other images lying perpendicular to the step edge, although much more seldom.

D-Lander molecules could be observed on the terraces only at higher coverages and lower temperature, whereby their hopping rate slows down, as shown in Fig. 4, which was recorded at 150 K by cooling the sample with liquid nitrogen. Even at this temperature, it is generally difficult to detect the Cu(100) surface corrugation between the imaged molecules. The tunneling current is rather noisy in these areas due to molecules diffusing either spontaneously or under the influence of the STM tip. No long-range order was ob-

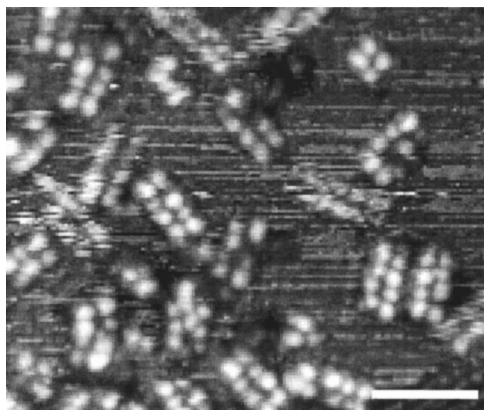


FIG. 4. STM image ($I=10$ pA, $V_{\text{bias}}=3.1$ V) of *D*-Lander molecules adsorbed on a Cu(100) terrace. The image was recorded at 150 K. The scale bar corresponds to 5 nm.

served whatever the deposition or annealing temperature. In Fig. 4, some molecules are imaged with less than eight lobes, probably fragments of the *D*-Lander molecules. As stressed in Sec. II evaporation is in competition with decomposition, hence a few molecules are found dissociated, it is difficult to quantify the yield because some fragments may be very mobile, then the surface should be cooled down to very low temperatures in order to count them.

B. Fabrication of double atomic steps: cobalt islands on Cu(111) surface

As imposed by the design of the *D*-Lander molecules, the electronic interconnection of the extremity of the conjugated board requires a double step edge. But double steps are not thermodynamically stable on many homometallic surfaces such as the Cu(100) surface. After annealing, double steps can only be stabilized by the presence of impurities and are therefore found with a very low density. A method to create double steps on a metal surface consists in gently crashing the STM tip into the surface. As a consequence of the strong local deformation, double steps are indeed generated, but again with too low a density. Following the work of de la Figuera *et al.* on the cobalt deposition onto a Cu(111) surface,^{25,26} we have elaborated a simple method to fabricate double steps in a controlled way. At room temperature and during the initial growth of cobalt layers on Cu(111), cobalt creates triangular islands which are bilayer in structure. Hence, every Co island offers step edges of 3.8 Å corresponding approximately to the required height, where the *D*-Lander molecules may dock and eventually interconnect electronically. After cleaning the Cu(111) surface, a submonolayer of cobalt was evaporated on a Cu(111) surface to form such triangular double step islands. An image of such islands is shown in Fig. 5. The average side length of the island is 5 nm in the middle of the Cu terraces, whereas they form a continuous 1-nm large strip at both sides of the Cu steps. With the objective of interconnecting a single molecule, such formation of islands with a metal different from the one of the substrate is the first step towards a coplanar technology to interconnect single molecules at predetermined, atomically clean, metallic pads, fabricated in UHV on an insulating surface.

C. Adsorption of the *D*-Lander molecules on Co/Cu(111) step edges

An image of a *D*-Lander molecule adsorbed on the Co/Cu(111) surface is presented in Fig. 6. Again recognizable through their eight lobes, *D*-Lander molecules can be found both on top of the Co islands and at the double steps. No molecules were found on the remaining Cu(111) terraces. When adsorbed entirely on a Co island, isolated *D*-Lander molecules are still mobile, but their hopping rate is much lower than on Cu(111) terraces indicating a higher diffusion barrier.

When adsorbed at the Co/Cu(111) double step edge, the isolated *D*-Lander molecules show a multiplicity of configurations. They may lay either parallel or perpendicular to the step edge. If parallel, they are found either at the upper or at

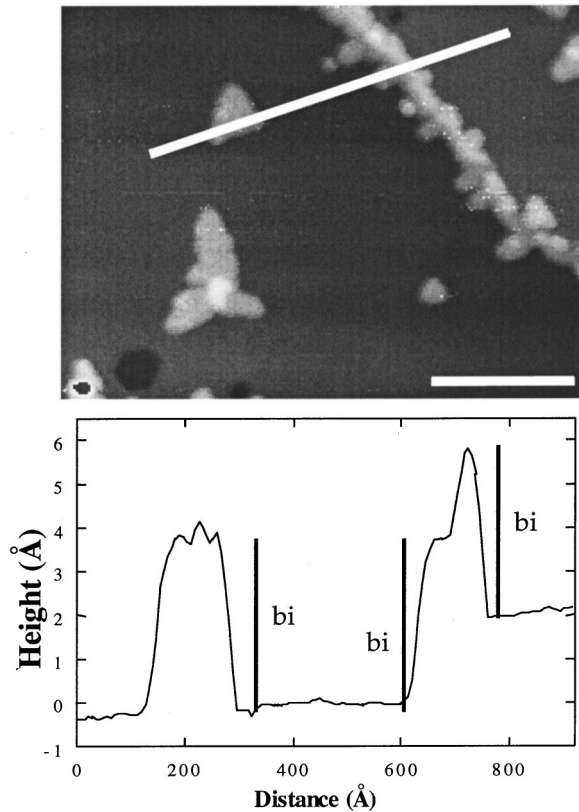


FIG. 5. STM image ($I = 100$ pA, $V_{\text{bias}} = 0.7$ V) of Co islands on a Cu(111) surface. The scale bar corresponds to 10 nm. The profile emphasizes that all the islands are bilayer both on the terraces and at the steps.

the lower side of the step. If perpendicular, they are found in five configurations which are practically equiprobable: all the eight legs at the lower side of the step edge (A), six legs on the Cu terrace (down) and two on the Co one (up) (B), four down and four up (C), two legs down and six up (D), and finally all the eight legs up (E). All these configurations are very stable.

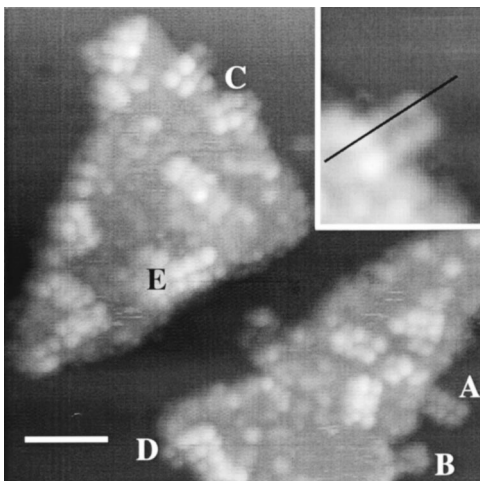


FIG. 6. STM image ($I = 10$ pA, $V_{\text{bias}} = 3.0$ V) of *D*-Lander molecules adsorbed on Co/Cu(111). The scale bar corresponds to 5 nm.

IV. DISCUSSION

In a previous work,¹⁷ we have deduced the conformation of a four leg Lander molecule adsorbed on a Cu(100) surface by comparing the experimental and calculated STM images. Molecular mechanics (based on standard MM2 parameters)²⁷ was used to optimize the geometry of the adsorbed molecules and the electron scattering quantum chemistry (ESQC) technique to calculate the corresponding STM images in the constant-current mode.²⁸ We showed that the four legs are rotated around their σ bond and that this σ bond is also twisted in the frontal plane because of the interaction between the molecular wire board and the metallic surface. We applied the same calculation procedure to obtain the conformation of the *D*-Lander molecules adsorbed on the Cu(100) surface and docked perpendicularly to the Co/Cu(111) step edges.

For the *D*-Lander molecules on Cu(100), 646 atoms were taken into account to describe the atomic structure of the STM junction, including 278 Cu atoms for the surface and the tip apex, modeled as a pyramidal fcc cluster of five layers and 368 atoms for the molecule. A total of 1180 molecular orbitals were used to describe the electronic properties of the junction, considering all its valence molecular orbitals. The conformation was optimized by making the position of the maxima of the lobes in the longitudinal and lateral directions coincide the same in the experimental and the calculated STM profiles as shown in Figs. 7(a), and 7(c). The agreement in the height of the lobes is not completely satisfying probably because the tip adopted in the calculation has a much sharper shape than the experimental tip. Calculations without relaxation of the distortion of the spacers were not successful. Only by allowing the σ bond to tilt in the frontal and lateral planes, were we able to reproduce the alternation of the lobes in the central part of the image and the experimental distance $l = 0.76 \pm 0.09$ nm between the maxima of the lobes in the lateral direction. The resulting conformation of the molecule with the rotated legs is presented in Figs. 7(b) and 7(d), with the corresponding calculated STM image in Fig. 7(e). The necessity of the relaxation of the legs to match the experimental STM data corroborates our previous results,¹⁷ confirming that even for a long molecule of a Lander series such as the *D*-Lander molecule, the central board remains flat and parallel to the Cu(100) terraces. Its height above the surface amounts to 3.6 Å, a distance at which its electronic coupling with the metallic substrate is very weak (van der Waals interaction). The adsorption energy was calculated with the standard MM2 molecular mechanics routine¹⁷ and amounts to -119 kcal/mol. The deformation energy of the *D*-Lander molecule associated with the rotation and the twist of the legs of the adsorbed molecule was estimated by comparing the energy of this conformation rigidly displaced from the surface with the minimized energy of the free molecule in vacuum. The resulting value is 44 kcal/mol. The energy of the van der Waals interaction of the bare conjugated board without the legs adsorbed on Cu(100) was evaluated to -125 kcal/mol. It follows that the adsorption energy stems from the van der Waals interaction of the polyaromatic board with the copper surface and that the legs

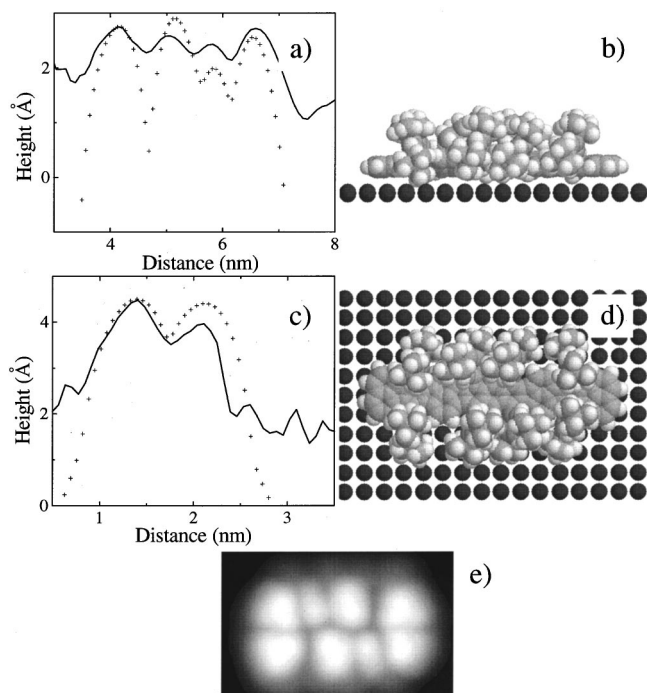


FIG. 7. (a) Comparison between the experimental profile (solid) and the calculated one (crosses) along the longitudinal direction. (b) Sideview of the optimized conformation of the *D*-Lander molecule adsorbed on Cu(100). (c) Comparison between the experimental profile (solid) and the calculated one (crosses) along the lateral direction. (d) Top view of the optimized conformation of the *D*-Lander molecule adsorbed on Cu(100). (e) *Calculated* STM image of the *D*-Lander molecule adsorbed on Cu(100). Note the alternation of the height of the four central legs as in the experimental images.

are too flexible to keep this board away from the surface.

To obtain the conformation of the *D*-Lander molecule on Co/Cu(111) double step edge, 767 atoms were taken into account in the STM junction: 243 Cu atoms for the surface and the tip apex, 156 Co atoms for the bilayer island, and 368 atoms for the molecule. A total of 1301 molecular orbitals were used to describe the electronic properties of the junction, including full valence structure of the molecule with 902 molecular orbitals. In Fig. 8(a) the experimental profile (solid line) along the maxima of the lobes in the longitudinal direction is plotted for the case of a molecule with two legs on the Co island and six on the Cu terrace. To obtain good agreement with the calculated profile (crosses), not only the legs but also the central board were allowed to deform. The polyaromatic wire therefore undergoes a large intramolecular conformation change to adapt itself to the shape of the step edge.

In order to confirm the deformation of the central wire, we have also calculated the same STM images and scans without a deformation of this central part. In Fig. 8(b) the *D*-Lander molecule is supposed to be adsorbed only on the Co island, whereas in Fig. 8(c) it rests only on two points of the wire, one on the Cu terrace and the other on the step edge. The corresponding calculated profiles do not fit the experimental data for two reasons: (i) the calculated length

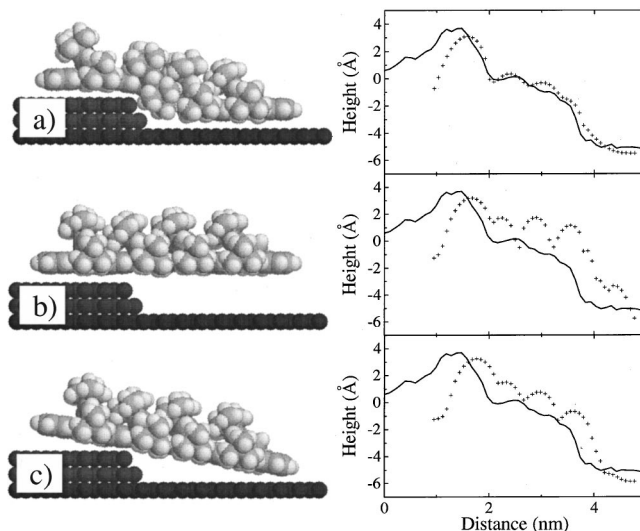


FIG. 8. Sideview of the molecular model of the *D*-Lander molecule adsorbed at a Co/Cu(111) and corresponding comparison between the experimental profile (solid) and the calculated one (crosses) along the longitudinal direction. The experimental profile is extracted from the molecule in the inset of Fig. 7.

of the *D*-Lander molecule is 15% bigger than the experimental one; (ii) the lobes associated with the spacers are much more pronounced and this cannot be rationalized only with the sharpness of the tip.

Here again, the interaction between the central conjugated board and the surface is responsible for the deformation of the central board. The energies of deformation of the *D*-Lander molecule and of the van der Waals interaction between the surface and the *D*-Lander molecule calculated with the MM2 routine are listed in Fig. 9. For the three different

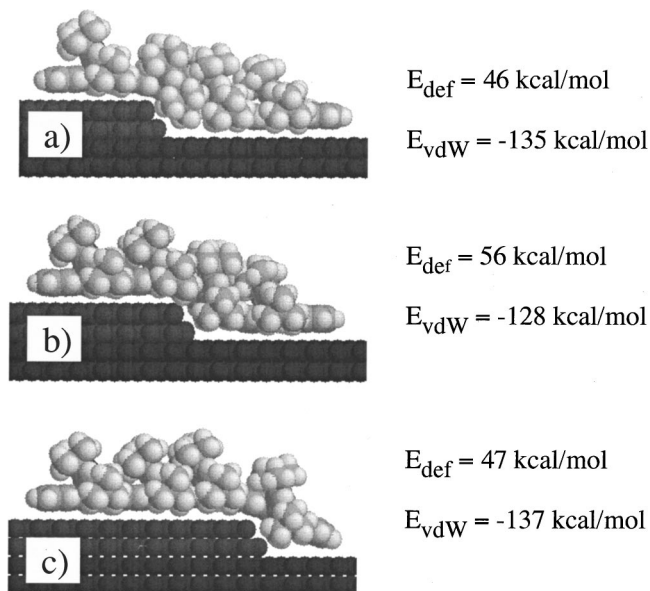


FIG. 9. Sideview of the molecular model of the *D*-Lander molecule adsorbed at a Co/Cu(111) and corresponding calculated energy for the van der Waals interaction (E_{vdW}) and for the deformation (E_{def}).

cases of a *D*-Lander molecule docked on the Co/Cu(111) step edge, both the van der Waals and the deformation energy are nearly independent on the adsorption geometry. The van der Waals energy is two to three times higher than the deformation energy. In this case, the deformation energy is due not only to the deformation of the spacers but also to the deformation of the wire: hence we tried to separate the two contributions. The deformation energy of the wire was estimated by comparing the energy of a free bare conjugated board with the energy of a board having the curvature of a molecule adsorbed at the double step rigidly removed from the surface. The resulting value is 12 kcal/mol for case (b), whereas it is lower for cases (a) and (c), only about 1 kcal/mol. It is much easier to bend the conjugated board between the first and second pairs of legs (or the third and fourth pair) than in the middle. This large energy difference can be ascribed to the presence of two five member carbon rings introducing a natural curvature on either side on the central part, whereas a flat configuration is favored for the anthracene group in the middle of the *D*-Lander molecule. As with the spacers, the conjugated board is too soft in comparison with its van der Waals interaction with the metallic surface. For the two extreme configurations of Figs. 8(b) and 8(c) involving no deformation of the wire, we obtained the values of 25 and -25 kcal/mol for the adsorption energy. They are much higher than the adsorption energy of the deformed molecule substantiating the statement derived from the comparison of the profiles that they are very unlikely. Structurally distorted molecules have attracted the attention of chemists for many years, and in particular nonplanar sterically overcrowded polycyclic aromatic hydrocarbons.^{29–32} Due to the high energy of these target compounds, their syntheses often require drastic conditions such as prolonged heating in high boiling point solvents or flash vapor pyrolysis, and most frequently proceed in low yields. However, the total energy owing to steric constraints never exceeds a few tenths of kcal per mole compared with the Van der Waals absorption energy of more than one hundred kcal per mole (see above).

Concerning the tunnel transport properties of the adsorbed *D*-Lander molecules, it turns out that this deformation of the central board positively affects its conductance. The I/V curves displayed in Fig. 10 were calculated for the central wire without spacers in the configuration of Fig. 1(a), lying flat (solid) or deformed as in Fig. 9(b) (dotted). The electrodes were modelled with 240 Cu atoms, whereas 534 molecular orbitals were taken into account. The conductance at low voltages is bigger for the deformed central molecular wire than for the rigid one, in agreement with the fact that the HOMO-LUMO gap of the wire decreases by 0.25 eV when the board is deformed. This is a nonstandard way of increasing the conductance of a molecular wire which may be useful for molecular device applications.¹ This deforma-

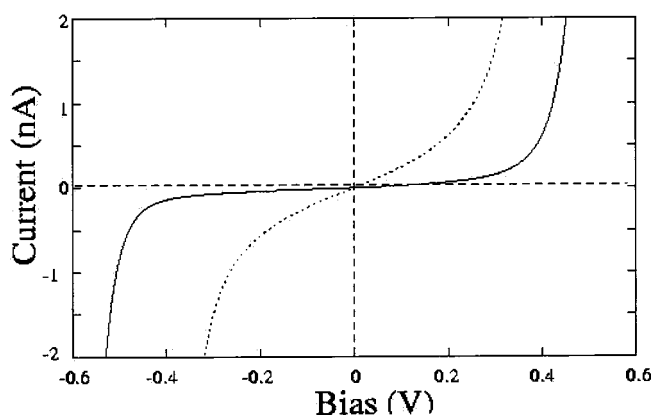


FIG. 10. Calculated $I(V)$ curves for the rigid conjugated board (solid) and for the deformed one (crosses) in the geometry defined in Fig. 1(a).

tion overshadows the study of the tunnel transport properties of this central molecular wire in the designed full planar conformation.

V. CONCLUSIONS

On a surface, a perfect electronic interconnection between a molecular wire and two atomically well defined electrodes requires either two electrodes embedded in an insulating surface or that the molecule carrying the molecular wire adapts itself to the corrugation created by the two interconnecting electrodes. The Co/Cu(111) islands can be considered as an intermediate model between the pure double step edge on a homo-metallic surface¹⁵ and the experiment aimed at where the two pads will be fabricated on an atomically clean surface. A Co island is similar to a metallic nanopad ready on the Cu(111) surface for the interconnection with the molecular wire to occur. The molecular wire board carried by the *D*-Lander molecular can interconnect only by its ends. Unfortunately, this molecule prefers an intermediate adsorption configuration with a few legs up the Co/Cu(111) step edge causing a large deformation of the molecular wire. As a consequence, the conductance of this wire is different from the one of planar configuration. This points out for the future that the delicate chemical structure will need to be optimized in order to successfully maintain such a molecular wire at the edge between the metallic pads and an insulating surface.

ACKNOWLEDGMENTS

This work was supported by the European Community within the context of the “Information Society Technologies” programs NANOMOL IST-1999-12603 and BUN IST-1999-11565.

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