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Adsorption of Benzene-1,4-dithiol on the Au(111) Surface and Its Possible Role in Molecular Conductance

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It is a consensus in the field of molecular electronics[1−4] that the transport of charge across a single molecule depends sensitively on the properties of the contact region. In particular, it depends on the details of the interaction between the molecule and the metallic leads, such as the anchoring groups[5,6] and the molecular orientation.[7−12] To advance the design of complex molecular devices, it is crucial to have a detailed understanding of these many aspects that influence the electron transport. To this end, simple systems are fundamental, and a particular example that has been used as a paradigm of the class of conjugated aryl molecules is the benzene-1,4-dithiol (BDT).[13]

In a pioneering work,[14] a self-assembled monolayer (SAM) of BDT was formed at the two ends of a gold mechanically controllable break junction (MCB), with the conductance of a (supposedly) single BDT contacting the two leads measured as a function of voltage. The measured conductance was approximately 2 orders of magnitude smaller than the calculated values[8,10] that followed this experiment. More recent measurements,[13] using a different technique to create the break junction, obtained results closer to the theoretical predictions, albeit still smaller by a factor of ∼10 when compared to recent theoretical values.[12] It has been argued by many authors that the differences between the theoretical and the experimental numbers are a result of the sensitivity of the conductance on the contact details, as discussed above. However, it is somewhat frustrating that even for such a small system we still do not have a full understanding of the transport experiments.

Usually the geometries considered in transport calculations assumed that the BDT was connected to the two Au leads via the S atoms, and that the molecule was either perpendicular or close to a perpendicular configuration relative to the Au surfaces. Moreover, the chosen configurations were somewhat arbitrary, and no attempt was usually made to systematically connect them with the energetics of the system. We point out that low energy adsorption configurations, where the BDT molecules have their phenyl rings closer to being parallel to the surface, may be very relevant for transport. Using state of the art density functional theory (DFT) calculations, we investigate the adsorption of BDT on the Au(111) surface. We show that, unless the coverage is sufficiently high, the most stable configuration has the molecules forming an angle of approximately 64° with the surface normal. We therefore argue that, depending on the experimental procedure, this may be the relevant configuration to be used in the transport calculations. In particular, there is a low energy structure with a BDT layer on the surface of both Au leads which gives a conductance closer to experimental values.

All our adsorption and geometry relaxation results are based on ab initio total energy DFT[15,16] calculations,[17−23] whereas for the transport calculations we have used a code that we have written in our group,[24] which is based on the nonequilibrium Green's function−density functional theory (NEGF−DFT) approach[24−26] and the SIESTA code[17] (see Supporting Information for computational details).

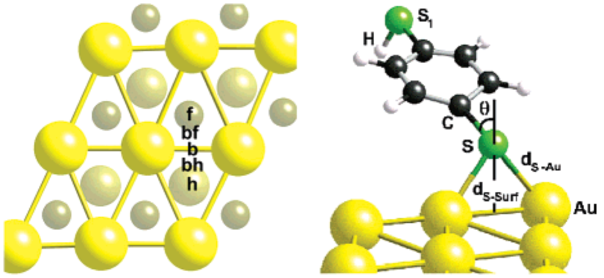

Figure 1. Schematic model (right panel) showing the BDT adsorbed in a Au(111) surface; the labels refer to quantities presented in Table 1. The left panel shows the investigated adsorption sites; the smaller the spheres, the farther from the surface the Au atoms are.

Table 1. Adsorption Energies (in eV) and Geometrical Parameters for the Different Adsorption Configurations Studied. See Figure 1 for the Definition of Symbols and Site Labels (d_{S-Au} is the Smallest S−Au Distance). All Distances are in Å

configuration (label)	E_{ads}	θ (°)	d_{S-Au}	d_{S-Surf}	d_{S-C}	d_{S1-H}
bridge fcc (bf)	1.33	63.9	2.54	2.09	1.81	1.41
bridge hcp (bh)	1.29	64.3	2.55	2.08	1.81	1.41
bent fcc (f)	1.22	42.0	2.56	1.97	1.80	1.38
bent hcp (h)	1.10	38.1	2.57	2.09	1.79	1.38
fcc (f)	1.04	17.3	2.51	1.79	1.79	1.38
hcp (h)	0.98	17.9	2.50	1.84	1.79	1.38

We have investigated a variety of adsorption sites, schematically shown in Figure 1 (see Table 1 for adsorption energies and geometrical parameters; as discussed in the Supporting Information, the precision is ∼0.05 eV).

The configuration with highest adsorption energy (1.33 eV), schematically shown in Figure 2a (top view) and Figure 2b (side view), has the BDT molecules lying almost parallel to the Au surface,[27] with their S atoms at a bridge site, slightly displaced toward the fcc site (site *bf* in Figure 1). Note that the S_1−H bond (see Figure 1) is increased by ≅0.03 Å, indicating that there is an interaction between the H atom and the Au surface, which helps to stabilize this configuration. There is another similar configuration adsorbed at a bridge hcp (site *bh* in Figure 2).

Considering now configurations where the BDT is almost perpendicular to the surface, the most stable structure has an adsorption energy of 1.04 eV and is shown in Figure 2c (top view) and Figure 2c (side view). In this case, the BDT molecules are adsorbed at fcc sites (site *f* in Figure 1), and they are only slightly tilted with respect to the surface normal (see Table 1).

The adsorption energy difference between this configuration and the one shown in Figure 2a is approximately 0.3 eV, with an estimated barrier ≲0.04 eV to go from the perpendicular to the

10.1021/ja0612495 CCC: $33.50 © 2006 American Chemical Society

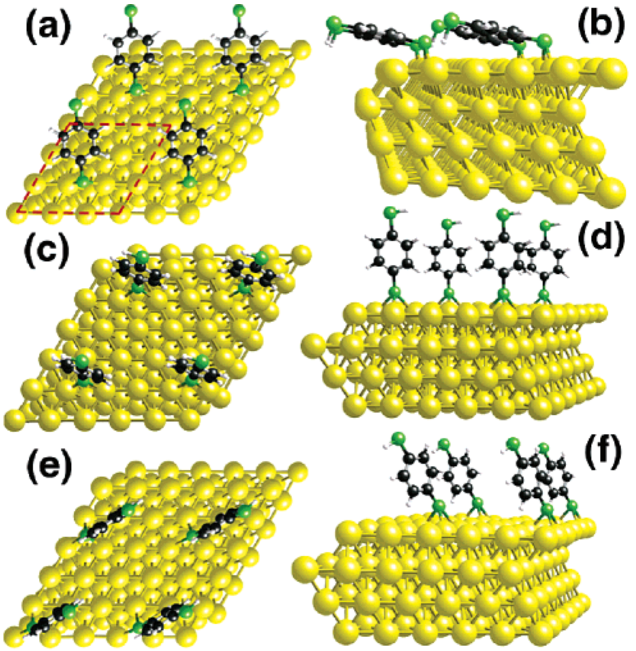

Figure 2. Ball and stick models of the optimized adsorbed configurations for the BDT on a (3 × 3) surface unit cell (marked red in a) of Au(111); (a) and (b) refer to the bridge fcc structure; (c) and (d) to the fcc structure; (e) and (f) to the bent fcc structure (see Table 1).

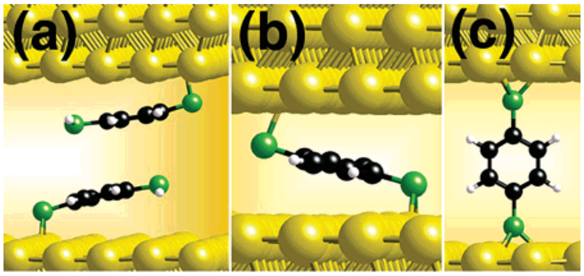

Figure 3. Ball and stick models of the optimized configurations used in the transport calculations (see Supporting Information for details).

parallel BDT configuration. This indicates that the BDT will lie almost flat to the surface where the coverage is not very high.

There is another configuration for the BDT at the fcc site which has higher adsorption energy (1.22 eV), shown in Figure 2e (top view) and Figure 2f (side view). The molecules are also tilted, but the phenyl rings are laterally inclined (see Figure 2f).

Thus, regarding transport experiments, two basic scenarios can be envisioned. In the first one, we imagine that on both Au leads the molecules are lying almost flat to the surfaces (Figure 3a), either because the local coverage is not very high or because of the particular experimental conditions of how the leads were prepared. In this configuration, we expect that the conductance will be smaller than when the BDT makes a direct contact to both Au surfaces. In this latter scenario, there may also be many possible configurations. The molecules may still lie almost flat (Figure 3b) or they can be almost perpendicular to the surface, as in Figure 3c. We have optimized the geometries for the BDT for these three situations, as described in the Supporting Information. Some relevant geometrical parameters are presented in Table 2; *L* is the distance between the two leads; d_{S-Au}, d_{S-Surf}, and θ are defined similarly to Figure 1.

Table 2. Binding Energies (in eV) and Geometrical Parameters for the Different Configurations Used in the Transport Studies (Figure 3). See Text for the Definition of Symbols. All Distances are in Å. The Two Numbers for d_{S-Au} and d_{S-Surf} are for the Two Leads

configuration	E_b^1	E_b^2	L	d_{S-Au}	d_{S-Surf}	θ (°)
3a	1.84	3.67	10.5	2.58/2.62	2.09/2.08	64.2
3b	2.17	2.17	6.9	2.59/2.59	2.08/2.09	57.8
3c	1.77	1.77	10.2	2.60/2.58	1.80/1.80	1.5

We can report the binding energies either per molecule (E_b^1 in Table 2) or per unit cell (E_b^2 in Table 2). This latter one can be thought of as a binding energy per unit area since for the same surface area one can place two monolayers of BDT, one on each surface. The conductances at the Fermi level for the configurations in Figure 3a−c are (see Supporting Information) 0.04 G_0, 0.64 G_0, and 0.51 G_0, respectively. This indicates that the lowest energy configuration for an adsorbed BDT (Figure 2a) can also lead to a low energy configuration, such as that displayed in Figure 3a, which has a conductance in much better agreement with the experimental results than structures, such as those shown in Figure 3b,c. This suggests that further experiments should be performed to investigate these issues.

Acknowledgment. We acknowledge FAPESP, CNPq, and the CENAPAD-SP.

Supporting Information Available: Calculation methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0612495