The ability to control the conductance of single molecules will have a major impact in nanoscale electronics. Azobenzene, a molecule that changes conformation as a result of a trans/cis transition when exposed to radiation, could form the basis of a light-driven molecular switch. It is therefore crucial to clarify the electrical transport characteristics of this molecule. Here, we investigate theoretically charge transport in a system in which a single azobenzene molecule is attached to two carbon nanotubes. In clear contrast to gold electrodes, the nanotubes can act as true nanoscale electrodes and we show that the low-energy conduction properties of the junction may be dramatically modified by changing the topology of the contacts between the nanotubes and the molecules, and/or the chirality of the nanotubes (that is, zigzag or armchair). We propose experiments to demonstrate controlled electrical switching with nanotube electrodes.

Recent theoretical studies have explored the use of azobenzene as an electronic switch when contacted by Au electrodes. Promising results were obtained, as a significant change in conductance was seen between the two conformations. Although a mechanism was proposed that allowed for a certain movement of the Au-leads, azobenzene and similar molecules undergoing isomerization transitions require more versatile nanocontacts that adjust appropriately to the change of length in going from one isomeric state to the other. Moreover, the coupling to Au electrodes only leads to a broadening of the molecular orbitals, without essentially perturbing the intrinsic molecular electronic structure. Although this may be a positive feature in some situations, more exciting is the possibility of having nanoscale electrodes with electronic properties that may lead, in contrast to Au electrodes, to a strong modification of the low-energy molecular electronic structure and hence to dramatic changes in conductance. The most attractive candidates are carbon nanotubes (CNTs), which are essentially one-dimensional systems whose conduction character (metallic or semiconducting) can be easily tuned by changing their chirality.

We focus in this paper on the transport characteristics of single trans and cis azobenzene contacted by metallic CNTs with two typical chiralities: armchair and zigzag. In order to improve the molecule-electrode coupling, the hydrogen atoms at the para-positions on the molecules are substituted by NHCO-groups, which have been used as linkers to CNT electrodes in recent transport experiments (A. Holleitner, private communication). Our main aims are to highlight the dependence of charge transport on the electronic structure of the nanotube electrodes, as well as the influence of the linker groups, which are known to play an important role. It turns out that the oxygen atom plays a critical role in determining the conductance near the Fermi level. Finally, the sensitivity in the electrical response of the isomers may be exploited to identify them using electrical transport measurements as well as to realize a molecular switch.

The trans isomer is characterized by a planar structure, but in the cis isomer the benzene aromatic rings are tilted with respect to each other, as seen in Fig. 1. Total energy calculations yield an energy difference between the isomers of ~0.2 eV, the trans state having the lowest energy and smallest highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) gap of ~1.98 eV. On addition of the linkers, the gap slightly increases to 2.03 eV. Conversely, the gap for the cis isomer decreases from 2.55 eV to 2.34 eV. However, the isomer geometries, when the linkers are added, are not appreciably modified after relaxation. In Fig. 1, we show the energetic position of the isomers’ frontier orbitals as well as the optimized geometries.

Let us consider the CNT-azobenzene-CNT molecular junction. The complexity of the system leads to a very structured potential-energy hypersurface with many metastable states; for the sake of simplicity we only consider coaxial arrangements of the left and right CNTs. Different junction geometries varying in the way the molecule is attached to the CNT surfaces were then optimized using conjugated-gradient techniques, and the lowest-energy configurations were used for the transport calculations. We note at this point that the energy differences between the investigated metastable states are roughly of the order of a few meV per atom, so that our transport calculations can be considered as providing expected trends. Other configurations close in energy may lead to slightly different quantitative results. However, the basic conclusions of this paper should not be affected.

Concerning the CNT-molecule contact, two direct covalent bonds are formed between the azobenzene complex and the CNT leads: a C\textsubscript{CNT}-C\textsubscript{1} bond and a C\textsubscript{CNT}-O bond. C\textsubscript{1} denotes the carbon atom belonging to the linker. The bond topology is, however, different.

Figure 1: Low-energy electronic states of azobenzene including the NHCO linkers. The positions of the frontier molecular orbitals of the trans (left) and cis (right) isomers are shown. The HOMO-LUMO gap is slightly smaller in the trans state, which is also the lowest-energy configuration. The presence of the linkers does not appreciably modify the geometric structure of the isomers. Also shown is a density isosurface plot for the HOMO and LUMO orbitals. The trans-HOMO is mainly localized around the N-N dimer with almost no weight on the linker groups. Notice that an extra hydrogen saturates the linker. On attaching the molecules to the CNT electrodes, this H-atom is removed and plays no further role.
ogy, as can be seen from our calculations. The low transmission of states will sensitively depend on the molecule-CNT contact topology, the CNT chirality, thus suggesting that the switching behaviour may proceed through resonant transport. These features arise from the hybridization of surface states with molecular orbitals. The resulting mixed states have a non-negligible overlap with the CNT extended bulk states and thus can contribute to transport. The fact that such states lie within a low-energy window around the Fermi energy (corresponding to a localized state at the zigzag edge) leads, one of the benzene rings slightly rotates out of plane by about 8° so that the relaxed state deviates from the planar geometry found in the isolated molecule. This structural distortion becomes even stronger when attaching the trans molecule to zigzag tubes (14°). On the other hand, for the cis isomer, geometrical modifications on attachment to the leads do not depend so much on the chirality of the CNTs, and consist essentially of a slight reduction of the tilt angle.

Once the geometries were optimized, we first focused on the dependence of the linear conductance on the charge injection energy (Figs. 2 and 3) for armchair and zigzag tubes, as shown in the insets of Figs. 2 and 3. In the former case a hexagon is formed, and in the latter case a pentagon is built. This appears to be a common feature of the bonding topology, as other initial configurations led to similar connectivities upon relaxation. In the trans configuration attached to armchair leads, one of the benzene rings slightly rotates out of plane by about 8° so that the relaxed state deviates from the planar geometry found in the isolated molecule. This structural distortion becomes even stronger when attaching the trans molecule to zigzag tubes (14°). On the other hand, for the cis isomer, geometrical modifications on attachment to the leads do not depend so much on the chirality of the CNTs, and consist essentially of a slight reduction of the tilt angle.

Turning now to the zigzag-azobenzene junctions, the conductance appears to be considerably larger for both isomers than for armchair junctions, as seen in Fig. 3. One should notice at this point that for both chiralities there are essentially two interfering pathways from the CNT to the azobenzene molecule, which merge in the carbon atom belonging to the linker. Our calculations show that the O-C1 pathway completely dominates the charge transport efficiency through the junction, the oxygen atom in the NHCO linker hereby playing a crucial role. Because of its higher electroaffinity, the oxygen tends to deplete the spectral weight on the C1 atom and thus acts as a chemical gate at the atomic scale. This mechanism is very effective for armchair junctions, but fails to have a dominant effect for zigzag junctions. Our density-functional-theory-based calculations as well as a π-orbital model hamiltonian show that, contrary to the armchair system, in zigzag junctions a much larger spectral weight on the C1 atom persists for energies around the Fermi level. The reason for this is that the surface density of states of a zigzag tube has, as is well known, a large spectral weight close to the Fermi energy (corresponding to a localized state at the zigzag edge). Moreover, the strong edge resonance manifests itself in the electrode self-energy, thus leading to a rather complex modification of the lower-lying molecular electronic states which is absent for armchair junctions. Thus, the conductance difference for both junctions is a result of the interplay between local (interface) chemistry and electrode surface electronic structure.

To round off our discussion, we have calculated the current-voltage (I-V) characteristics of the junctions to confirm the possible switching behaviour already suggested by the analysis of the linear conductance. To reveal in a clearer way the effects of chirality on transport, a hybrid armchair-azobenzene-zigzag system was also investigated. The results for the three cases are displayed in Fig. 4.
which showed a similar qualitative behaviour for the two isomers, are always detrimental to junction conductivity. 

Like functions, which would not be directly related to intrinsic electronic structure asymmetries of the molecule as in the paradigmatic case of the Aviram-Ratner molecular rectifiers\textsuperscript{28}. We would further like to mention that our equilibrium treatment of transport is validated by recent non-equilibrium calculations\textsuperscript{27} and transport calculations in the frame of the Landauer approach. The linear conductance $G$ can be obtained from the quantum mechanical transmission probability at zero voltage: $G = G_0 T(E, V = 0)$ (where $G_0 = 2e^2/h$ is the conductance quantum, $e$ is the electron charge and $h$ is the Planck constant). The transmission probability is related to the molecular Green function $g(E)$ and the electrodes’ self-energies $\Sigma_{L/R}(E)$ by $T(E, V) = 4\mbox{Im}[\Sigma_{L}(E)g(E)\Sigma_{R}(E)]$ (ref\textsuperscript{14}). We stress that when calculating the current $I(V)$, the full voltage-dependent $T(E, V)$ is used: $I(V) = (2e/h) \int dE \left[ f_L(E) - f_R(E) \right] T(E, V)$, in the last expression $f_{L/R}(E)$ are Fermi functions of the left and right electrodes. $T(E, V)$ is calculated for the so called extended molecule, which contains the azobenzene molecule, the linkers, and the electrodes’ surface atoms. This allows the molecule-electrode coupling and the molecule electronic structure to be treated on the same footing\textsuperscript{28,29}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Average conductance and current-voltage characteristics of the CNT-azobenzene junctions. Three possible CNT-molecule junctions are shown: zigzag\textsubscript{ZZ}-trans/cis-zigzag, armchair\textsubscript{AC}-trans/cis-zigzag, and armchair\textsubscript{AC}-trans/cis-armchair. A systematic hierarchy can be shown, showing that the trans state is always better conducting than the cis one and that armchair CNTs are always detrimental to junction conductivity.}
\end{figure}

1 Joachim, C. & Ratner, M. A. Molecular electronics: Some views on transport junctions and beyond. Proc. Natl. Acad. Sci. USA 102, 8801–8808 (2005).

2 Visoly-Fisher, I. et al. Conductance of a biomolecular wire. Proc. Natl. Acad. Sci. USA 103, 8686–8690 (2006).

3 Champagne, A. R., Pasupathy, A. N. & Ralph, D. C. Mechanically adjustable and electrically gated single-molecule transistors. Nano Lett. 5, 305–308 (2005).

4 Donhauser, Z. J. et al. Conductance switching in single molecules through conformational changes. Science 292, 2303–2307 (2001).

5 Lastapis, M. et al. Picometer-scale electronic control of molecular dynamics inside a single molecule. Science 308, 1000–1003 (2005).

6 Wu, S. W., Nazin, G., Chen, X., Qiu, X. H. & Ho, W. Control of relative tunneling rates in single molecule bipolar electron transport. Phys. Rev. Lett. 93, 236802 (2004).

7 Elbing, M. et al. A single-molecule diode. Proc. Natl. Acad. Sci. USA 102, 8815–8820 (2005).

8 Zhirnov, V. V. & Cavin, R. K. Molecular electronics: Chemistry of molecules or physics of contacts? Nature Mater. 5, 11–12 (2006).

9 Choi B.-Y. et al. Conformational molecular switch of the azobenzene molecule: A scanning tunneling microscopy study. Phys. Rev. Lett. 96, 156106 (2006).

10 Moreasco, F. et al. Conformational changes of single molecules induced by scanning tunneling microscopy manipulation: A route to molecular switching. Phys. Rev. Lett. 86, 672–675 (2001).

11 Dulić, D. et al. One-way optoelectronic switching of photoswitchable molecules on gold. Phys. Rev. Lett. 91, 207402 (2003).
Hugel, T. et al. Single-molecule optomechanical cycle. *Science* **296**, 1103–1106 (2002).

Zhang, C. et al. Coherent electron transport through an azobenzene molecule: A light-driven molecular switch. *Phys. Rev. Lett.* **92**, 158301 (2004).

Zhang, C. et al. Current-voltage characteristics through a single light-sensitive molecule. *Phys. Rev. B* **73**, 125445 (2006).

Guo, X. et al. Covalently bridging gaps in single-walled carbon nanotubes with conducting molecules. *Science* **311**, 356–359 (2006).

Venkataraman L. et al. Single-molecule circuits with well-defined molecular conductance. *Nano Lett.* **6**, 458-462 (2006).

Kobayashi, Y., Fukui, K., Enoki, T., Kusakabe, K. & Kaburagi, Y. Observation of zigzag and armchair edges of graphite using scanning tunneling microscopy and spectroscopy. *Phys. Rev. B* **71**, 193406 (2005).

Aviram, A. & Ratner, M. A. Molecular rectifiers. *Chem. Phys. Lett.* **29**, 277-280 (1974).

Cumings, J. & Zettl, A. Low-friction nanoscale linear bearing realized from multiwall carbon nanotubes. *Science* **289**, 602–604 (2000).

Kwon, Y.-K., Berber, S. & Tomanek, D. Thermal contraction of carbon fullerenes and nanotubes. *Phys. Rev. Lett.* **92**, 015901 (2004).

Frauenheim, T. et al. A self-consistent charge density-functional based tight-binding method for predictive materials simulations in physics, chemistry and biology. *Phys. Stat. Sol. b* **217**, 41–62 (2000).

Pecchia, A. & Carlo, A. D. Atomistic theory of transport in organic and inorganic nanostructures. *Rep. Prog. Phys.* **67**, 1497–1561 (2004).

Fisher, D. S. & Lee, P. A. Relation between conductivity and transmission matrix. *Phys. Rev. B* **23**, 6851–6854 (1981).

Cuniberti, G., Grossmann, F. & Gutierrez, R. The role of contacts in molecular electronics. *Advances in Solid State Physics* **42**, 133–149 (2002).

Acknowledgements We thank A. Holleitner for making us aware of the details of the experiments being performed with azobenzene, and N. Nemec, D. Tomanek, and R. de Vivie-Riedle for discussions and suggestions. This work was partially funded by the Volkswagen Foundation under grant No. I/78 340, by the DFG Priority Program “Quantum Transport at the Molecular Scale” SPP1243, by the MEC under contracts MAT2005-01388, NAN2004-09109-CO4-04, by the CAM under contract No. S-0505/ESP-0200, and by the European Union project “Carbon nanotube devices at the quantum limit” (CARDEQ) under contract No. IST-021285-2. MdV acknowledges the support from the FPI Program of the Comunidad Autónoma de Madrid.

Competing Interests The authors declare that they have no competing financial interests.

Correspondence Correspondence and requests for materials should be addressed to GC (email: G.Cuniberti@physik.uni-R.de).
Supplementary Information

To get further intuition on the enhanced conductivity between the dimer and the chain, we have formulated a minimal single-orbital model (see Fig. S1). The model consists of a semi-infinite armchair (zigzag) CNT, a dimer which mimics the C\(_1\)-O subsystem at the CNT-molecule interface, and a semi-infinite chain connected to the C\(_1\) site, which only fulfills the function of acting as a charge reservoir and will subsequently be treated within the wide-band approximation, i.e. assuming an energy-independent coupling between the dimer and the chain.

With this model, we can qualitatively describe the local chemistry and topology at the CNT-azobenzene interface. Our main goal is to highlight the influence of the charge state at the “oxygen” site—which can be controlled by variations of its onsite energy \(E_{\text{O}}\) as well as the role played by the nanotube surface electronic structure.

We can write an analytical expression for the transmission function in terms of the dimer Green function:

\[
T(E) = 4\Gamma_R \left\{ \Gamma_R^{11} (E) [G_{C_1 C_1}(E)]^2 + |G_{C_1 O}(E)|^2 \right\} + 2\Gamma_R^{12} (E) \text{Re}(G_{C_1 C_1}(E) G_{C_1 O}(E)).
\]

In this equation, \(\Gamma_R^{11}(E)\) and \(\Gamma_R^{12}(E)\) describe the direct and cross coupling of the dimer to the left CNT electrode (the indices 1 and 2 refer to the C\(_1\) and O atoms, respectively), and \(\Gamma_R\) the constant coupling of the C\(_1\) atom to the wide-band lead (WBL) electrode on the right. The dimer Green function can be obtained as solution of a Dyson 2x2 matrix equation \(G^{-1} (E) = E - H_{\text{dimer}} - \Sigma_L (E) - \Sigma_R (E)\).

Three contributions to the transmission function can be clearly distinguished: \(G_{C_1 C_1}\) is related to tunnelling pathways going from the CNT directly through the C\(_1\) atom, \(G_{C_1 O}\) describes pathways passing through the O atom and then through the C\(_1\) atom, and the last term describes interference effects between both pathways. Our calculations show that \(|G_{C_1 O}(E)|^2\) is the dominant contribution to \(T(E)\) for energies around the Fermi level. Additionally this Green function matrix element is the most strongly affected by a shift of the O onsite energies. Thus, we can approximately write: \(T(E \approx E_F) \approx 4\Gamma_R \Gamma_R^{11} |G_{C_1 O}(E)|^2\).

In Fig. S1 we show the influence of a shift in \(E_{\text{O}}\) on the transmission function for both armchair and zigzag junctions (we take the C\(_1\) onsite energy equal to that of the CNT carbon atoms). It turns out that changes in \(E_{\text{O}}\) lead to a dramatic suppression of the transmission for armchair junctions at low energies (left panel of Fig. S1). For the zigzag junction, on the contrary, electronic states lying slightly above the Fermi energy are shifted down (chemical gating) towards the C\(_1\) atom to the right panel of Fig. S1). The value \(E_{\text{O}} = -4\text{eV}\) has been extracted from our DFTB calculation. It is the difference between the 2\(p\) orbital energies of isolated oxygen and carbon atoms. The effect discussed here is nevertheless stable against variations around this value.

Extended calculations, which are not included here, show that this peculiar behavior of the zigzag junction should be attributed to the well-known surface state at the Fermi energy: with zigzag (ZZ) CNT leads the dimer resonances are ultimately shifted (renormalized) by the real part of the surface self-energy, which can, to a good approximation, be written near the \(E_F\) as: \(\text{Re}\Sigma^\text{ZZ} (E) \approx (E - E_F) / (\delta^2 + (E - E_F)^2)\), inducing de facto a pinning of such resonances around the Fermi energy, where the surface state exists with a linewidth \(\delta\). In this way the dimer eigenstates shift into a transport sensitive energy region.