

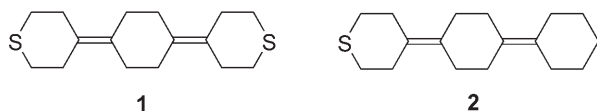
DOI: 10.1002/anie.200503591

Charge Transport in Three-Terminal Molecular Junctions Incorporating Sulfur-End-Functionalized Tercyclohexylidene Spacers**

Yann-Vaï Kervennic, Jos M. Thijssen, Daniel Vanmaekelbergh, Reza Dabirian, Leonardus W. Jenneskens, Cornelis A. van Walree,* and Herre S. J. van der Zant*

Molecular electronics using single molecules as active components is a promising technological concept of fast-growing interest.^[1–3] Two-^[4–8] and three-terminal^[9–14] systems have been studied, often employing π -conjugated compounds with thiol end groups. Experimental results at low temperatures indicate that the three-terminal devices studied so far operate in the weak coupling regime in which the discrete molecular energy-level structure remains essentially intact.

Herein we present charge-transport phenomena in three-terminal molecular junctions based on bis(sulfur-end-functionalized) tercyclohexylidene **1**. Compound **1** and the



monosulfur reference compound **2** are oligo(cyclohexylidenes), which consist of cyclohexane-type rings interconnected by double bonds.^[15] Their σ - π - σ orbital topology allows transannular electronic interactions and mediates charge transport through the partly saturated hydrocarbon framework, as demonstrated by the occurrence of long-range photoinduced charge separation.^[16–18] Photoelectron spec-

troscopy and NBO studies show that there is a strong electronic coupling between the electron lone pairs of the sulfur atoms in bis(sulfur-end-capped) oligo(cyclohexylidenes) owing to σ - π - σ through-bond interactions.^[19] In common with other sulfides, the sulfur atoms can bind to gold substrates by physisorption,^[20,21] thus enabling the formation of self-assembled monolayers.^[22]

The three-terminal devices used consist of gold leads and an oxidized aluminum film that serves as a gate. They were constructed with a technique published elsewhere (see also the Supporting Information).^[23] In short, nanogaps in a 15-nm-thick gold wire were created by using a combination of e-beam lithography and electrochemical etching. This approach allows the creation of gaps with subnanometer precision by monitoring the gap conductance in situ during etching.^[23] For the tercyclohexylidenes (length 1.2 nm), the gap distance was between 1.2 and 1.5 nm. After creation of the gap and drying, the samples were dipped in solutions of **1** and **2** in ethanol (1.0 mM) and dried. Compounds **1** and **2** were available from previous studies.^[19] In all cases (nine junctions) and for both molecules a dramatic decrease in resistance (from > 1 G Ω to the M Ω range) was observed. Ten other junctions were dipped in pure ethanol and did not exhibit an increase in conductance which shows that the decrease in resistance is due to the presence of the tercyclohexylidenes. The zero-bias room-temperature resistance varied from junction to junction (Figures 1 and 3; see also the Supporting Information). These

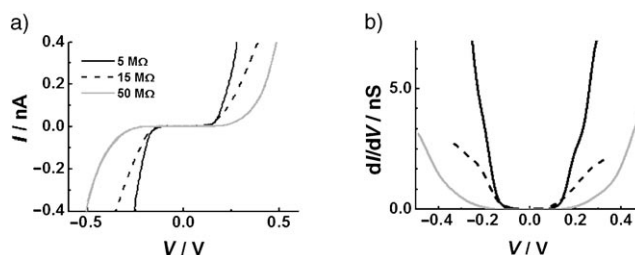


Figure 1. a) Current–voltage characteristics (trace and retrace) of three different molecular junctions based on **1** measured at 7–10 K. b) Corresponding numerically obtained differential conductance (trace only) in the same pattern. Zero-bias room-temperature resistances are indicated in the legend of a).

differences may reflect differences in bonding strength or in molecule-lead geometries, that is, in the exact physisorption of the molecule to the leads.^[24] Another factor may be the number of molecules between the gold leads. We cannot be sure that it concerns only a single molecule, but several reasons suggest that, at most, only a few molecules are involved (see Supporting Information).

Figure 1 shows the low-temperature (7–10 K) current–voltage characteristics and differential conductance (dI/dV) traces of molecular junctions based on **1**. Single curves (no averaging) were recorded back (trace) and forth (retrace) with a sweep rate of 10 mV s⁻¹ and proved to be stable for days. Different curves represent devices with different room-temperature resistances, but all are virtually symmetric around $V=0$. In general, currents in the nA range and conductance values in the nS range were obtained. Before

[*] R. Dabirian, Prof. L. W. Jenneskens, Dr. C. A. van Walree
Debye Institute, Organic Chemistry and Catalysis
Utrecht University
Padualaan 8, 3584 CH Utrecht (The Netherlands)
Fax: (+31) 30-253-4533
E-mail: c.a.vanwalree@chem.uu.nl

Dr. Y.-V. Kervennic, Dr. J. M. Thijssen, Dr. H. S. J. van der Zant
Kavli Institute of Nanoscience
Delft University of Technology
PO Box 5046, 2600 GA, Delft (The Netherlands)
Fax: (+31) 15-278-3251
E-mail: herre@qt.tn.tudelft.nl

Prof. D. Vanmaekelbergh
Debye Institute, Condensed Matter and Interfaces
Utrecht University
Princetonplein 1, 3584 CC Utrecht (The Netherlands)

[**] Financial support was obtained from the Dutch Organization for Fundamental Research on Matter (FOM).

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

discussing the data further, it is important to note that in total five junctions based on **1** were characterized which, despite the variation in current magnitude, together evoke a consistent picture.

At low temperatures, a strong influence of the gate voltage on the current is observed for the junctions based on **1** (Figure 2). The gate coupling, that is, the ratio of the gate

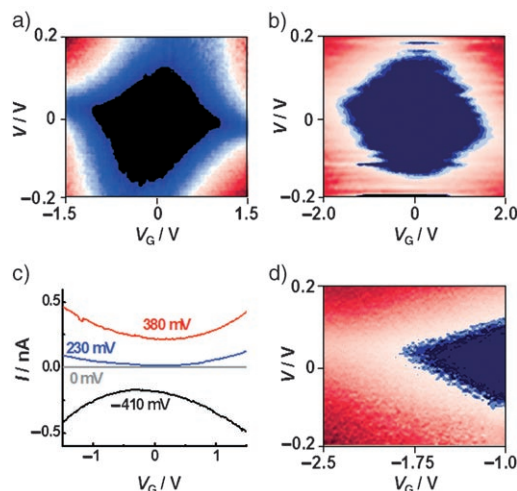


Figure 2. a) Stability diagram at 8 K of the device based on **1** with a room-temperature resistance of 15 MΩ. Plotted is dI/dV as a function of bias and gate voltage. The conductance ranges from 0 (black) to 10 nS (red). b) Stability diagram at 8 K of the sample **1** with a room-temperature resistance of 5 MΩ. The conductance ranges from 0 (blue) to 25 nS (red). c) Current versus gate voltage for the same sample as in a) plotted for four different bias voltages (indicated). d) High-resolution stability diagram of the same sample as in b). The conductance ranges from 0 (blue) to 40 nS (red). The stability diagrams are composed of more than 100 curves.

capacitance to the total capacitance of the molecular island within Coulombic theory,^[25] can be estimated by dividing the diamond height by the width. For both the junctions in Figure 2a,b the gate coupling is about 0.1, implying that a change of 1 V in the gate potential induces a shift of 0.1 eV in the molecular electrostatic energy. Interestingly, the differential conductance plots (Figure 2a,b,d) do not show the sharp features commonly observed in weakly coupled molecular junctions.^[9–13] A related surprising aspect is the absence of well-defined degeneracy points along the gate axis at low bias.^[25] Sharp current peaks are usually observed upon recording the current as a function of gate potential and correspond to the appearance of new charge states when crossing discrete energy levels.^[9,10] In contrast, in the case of **1** the current steadily increases with the gate voltage (Figure 2c) leading to the appearance of a single, broad, diamondlike feature in the dI/dV plots. The absence of sharp Coulombic blockade features makes it very unlikely that gold grains are responsible for the features reported in this study.

The presence of two sulfur atoms in **1** is essential for the observed behavior. This is revealed by the strongly different current–voltage characteristics of the asymmetric junctions

based on monosulfide **2**. In **2**, the sulfur-functionalized site is expected to be well coupled to the gold electrode, whereas the other side is—most likely—bound by a weak van der Waals contact. At low temperature, all four devices based on **2** show current–voltage curves with discrete steps. The step size is sample-dependent and varies between 50 and 200 mV; two examples are shown in Figure 3a. The step position changes

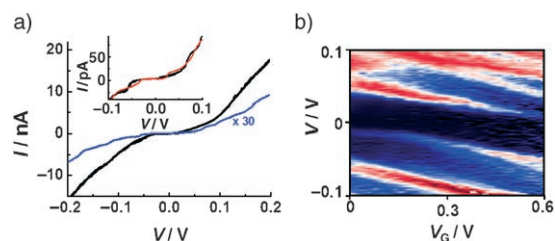


Figure 3. a) Current–voltage characteristics at 5 K of two junctions based on **2** with a room-temperature resistance of 8 MΩ (black) and 500 MΩ (blue). The current level of the blue curve has been multiplied by a factor of 30. Inset: Current–voltage characteristics of the molecular junction with a room-temperature resistance of 500 MΩ for two different gate voltages. b) Stability diagram of the 500-MΩ sample measured at 5 K. The differential conductance ranges from 0 (black) to 3 nS (red).

when applying a voltage to the gate, thus leading to current–voltage characteristics that are generally asymmetric^[26] (Figure 3a (inset), Figure 3b). The steps resemble Coulombic staircases that are regularly observed in asymmetrically coupled quantum dots.^[27] However, it cannot be completely excluded that the steps originate from vibrational modes in the molecules.^[28–30] A remarkable observation that is not yet understood is that at low temperatures junctions based on **1** give larger currents than those based on **2**.

The absence of sharp features and degeneracy points in junctions based on **1** can be rationalized in two ways. First, it suggests the presence of broad transport levels, which must then arise from substantial hybridization between molecule and gold orbitals. A second possibility is that energy levels (which are not necessarily broadened) shift when they align with the chemical potential of one of the leads. Both scenarios rest on a substantial interaction between **1** and the electrodes. In this respect, it is important to realize that the contact between π -conjugated aromatic thiols and gold electrodes leads to decoupling of the sulfur atoms from the aromatic hydrocarbon moiety and the formation of high potential barriers at the molecule–lead interface.^[31,32] The phenomena observed for junctions based on **1** reflect a more-favorable molecule–lead contact. This might be related to a different bonding mode of the sulfur atoms in the alkyl sulfide **1** (compared with the covalent Au–S bond for thiols) and the efficient coupling between the terminal sulfur atoms through the σ – π – σ framework.^[19]

In conclusion, we have shown that electron transport in three-terminal devices prepared by electrochemical etching that contain σ – π – σ conjugated tercyclohexylidene **1** molecular wires is considerably different from that in junctions involving π -conjugated systems. This presumably finds its

origin in a substantial coupling between the molecules and the leads.

Received: October 11, 2005

Revised: February 8, 2006

Published online: March 20, 2006

Keywords: charge transfer · conjugation · molecular electronics · sulfur · through-bond interactions

-
- [1] C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541.
- [2] A. Nitzan, M. A. Ratner, *Science* **2003**, *300*, 1384.
- [3] J. R. Heath, M. A. Ratner, *Phys. Today* **2003**, (May), 43.
- [4] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **1997**, *278*, 252.
- [5] C. Kergueris, J.-P. Bourgoin, S. Palacin, D. Esteve, C. Urbina, M. Magoga, C. Joachim, *Phys. Rev. B* **1999**, *59*, 12505.
- [6] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. v. Löhneysen, *Phys. Rev. Lett.* **2002**, *88*, 176804–1.
- [7] R. H. M. Smit, Y. Noat, C. Untiedt, N. D. Lang, M. C. van Hemert, J. M. van Ruitenbeek, *Nature* **2002**, *419*, 906.
- [8] B. Xu, N. J. Tao, *Science* **2003**, *301*, 1221.
- [9] H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos, P. L. McEuen, *Nature* **2000**, *407*, 57.
- [10] J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruña, P. L. McEuen, D. C. Ralph, *Nature* **2002**, *417*, 722.
- [11] W. Liang, M. P. Shores, M. Bockrath, J. R. Long, H. Park, *Nature* **2002**, *417*, 725.
- [12] N. B. Zhitenev, H. Meng, Z. Bao, *Phys. Rev. Lett.* **2002**, *88*, 226801–1.
- [13] S. Kubatkin, A. Danilov, M. Hjort, J. Cornil, J.-L. Brédas, N. Stuhr-Hansen, P. Hedegård, T. Bjørnholm, *Nature* **2003**, *425*, 698.
- [14] B. Xu, X. Xiao, X. Yang, L. Zang, N. Tao, *J. Am. Chem. Soc.* **2005**, *127*, 2386.
- [15] F. J. Hoogesteger, R. W. A. Havenith, J. W. Zwicker, L. W. Jenneskens, H. Kooijman, N. Veldman, A. L. Spek, *J. Org. Chem.* **1995**, *60*, 4375.
- [16] F. J. Hoogesteger, C. A. van Walree, L. W. Jenneskens, M. R. Roest, J. W. Verhoeven, W. Schuddeboom, J. J. Piet, J. M. Warman, *Chem. Eur. J.* **2000**, *6*, 2948.
- [17] W. D. Oosterbaan, C. Koper, T. W. Braam, F. J. Hoogesteger, J. J. Piet, B. A. J. Jansen, C. A. van Walree, H. J. van Ramesdonk, M. Goes, J. W. Verhoeven, W. Schuddeboom, J. M. Warman, L. W. Jenneskens, *J. Phys. Chem. A* **2003**, *107*, 3612.
- [18] E. P. A. M. Bakkers, A. W. Marsman, L. W. Jenneskens, D. Vanmaekelbergh, *Angew. Chem.* **2000**, *112*, 2385; *Angew. Chem. Int. Ed.* **2000**, *39*, 2297.
- [19] A. W. Marsman, R. W. A. Havenith, S. Bethke, L. W. Jenneskens, R. Gleiter, J. H. van Lenthe, M. Lutz, A. L. Spek, *J. Org. Chem.* **2000**, *65*, 4584.
- [20] D. J. Lavrich, S. M. Wetterer, S. L. Bernasek, G. Scoles, *J. Phys. Chem. B* **1998**, *102*, 3456.
- [21] H. Takiguchi, K. Sato, T. Ishida, K. Abe, K. Yase, K. Tanabe, *Langmuir* **2000**, *16*, 1703.
- [22] R. Dabirian, A. N. Zdravkova, P. Liljeroth, C. A. van Walree, L. W. Jenneskens, *Langmuir* **2005**, *21*, 10497.
- [23] Y. V. Kervennic, D. Vanmaekelbergh, L. P. Kouwenhoven, H. S. J. van der Zant, *Appl. Phys. Lett.* **2003**, *83*, 3782. “Electrochemically fabricated nanometer-sized molecular junctions”: Y. V. Kervennic, PhD Thesis, Delft **2004**, chap. 7. (can be downloaded from <http://med.tn.tudelft.nl/publi/papers.php>).
- [24] X. Xiao, B. Xu, N. J. Tao, *Nano Lett.* **2004**, *4*, 267.
- [25] For an example, see: L. P. Kouwenhoven, D. G. Austing, S. Tarucha, *Rep. Prog. Phys.* **2001**, *64*, 701.
- [26] Asymmetric current–voltage characteristics have also been observed for an asymmetric metal–molecule contact configuration in two-terminal measurements on oligo(phenylene ethynylene) molecules: J. G. Kushmerick, D. B. Holt, J. C. Yang, J. Naciri, M. H. Moore, R. Shashidhar, *Phys. Rev. Lett.* **2002**, *89*, 086802.
- [27] “Single Charge Tunneling”: G.-L. Ingold, Y. V. Nazarov in *NATO ASI Series* (Eds: H. Grabert, M. H. Devoret), Plenum, New York, **1993**, chap. 2.
- [28] W. Wang, T. Lee, I. Kretzschmar, M. A. Reed, *Nano Lett.* **2004**, *4*, 643.
- [29] L. H. Yu, Z. K. Keane, J. W. Cizek, L. Cheng, M. P. Stewart, J. M. Tour, D. Natelson, *Phys. Rev. Lett.* **2004**, *93*, 266802.
- [30] J. G. Kushmerick, J. Lazorcik, C. H. Patterson, R. Shashidhar, D. S. Seferos, C. G. Bazan, *Nano Lett.* **2004**, *4*, 639.
- [31] Y. Xue, M. A. Ratner, *Phys. Rev. B* **2003**, *68*, 115406.
- [32] Y. Xue, M. A. Ratner, *Phys. Rev. B* **2003**, *68*, 115407.