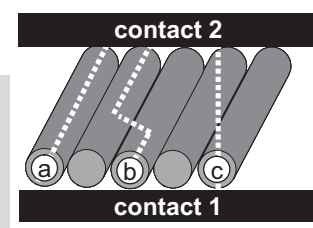


Comparison of Electronic Transport Measurements on Organic Molecules**

By *Adi Salomon, David Cahen,* Stuart Lindsay,* John Tomfohr, Vincent B. Engelkes, and C. Daniel Frisbie**

We compile, compare, and discuss experimental results on low-bias, room-temperature currents through organic molecules obtained in different electrode–molecule–electrode test-beds. Currents are normalized to single-molecule values for comparison and are quoted at 0.2 and 0.5 V junction bias. Emphasis is on currents through saturated alkane chains where many comparable measurements have been reported, but comparison to conjugated molecules is also made. We discuss factors that affect the magnitude of the measured current, such as tunneling attenuation factor, molecular energy gap and conformation, molecule/electrode contacts, and electrode material.



1. Introduction

Over the past few years a sizeable body of experimental charge-transport data has been accumulating in the general area of molecule-based and molecule-controlled electronic device research, often termed “molecular electronics”. In this review we consider these data and ask: Can we compare various measurements of molecular conduction? If so, how well do the data sets agree with each other and, if they do not, can we understand why not? To arrive at answers and to define directions, we review some experimental and theoretical results, which, in our view, reveal important aspects of charge transport through molecules. Factors that influence the current–voltage characteristics of molecules include intrinsic properties such as molecular length, conformation, and highest occupied molecular orbital–lowest unoccupied molecular orbital

(HOMO–LUMO) gap. In addition, the type of molecule–electrode contact and the electrode work function affect measured conductivities.

Figure 1 shows a generic conductor–molecule–conductor junction, which can serve to measure current transport through molecules. There are now a variety of approaches to form molecular junctions,^[1–16] which differ in the types of electrode materials employed, the way in the molecule–electrode contacts are established, and the number of molecules contacted. To make the comparison between the experimental data, as shown in Tables 1,2, we calculate the measured current per molecule.^[17] We do so by taking published currents at a given voltage and dividing them by the estimated number of molecules in the contact area.^[18] This kind of comparison requires that cooperative effects between molecules are, to first approximation, negligible, and that the molecules can be considered to be wired in parallel and conducting current independently. The issue of cooperativity in molecular junctions

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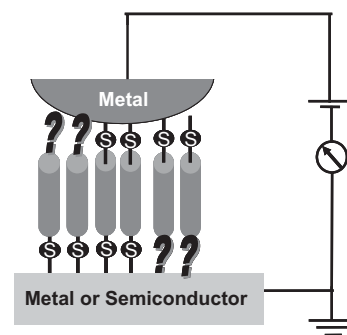


Fig. 1. Schematic cartoon of measurement set-ups and experimental configurations discussed in the text. While only S-mediated bonds to electrodes are shown, this is for illustrative purposes only and other types of bonds (such as the Si–C one, discussed in the text) can exist.

still needs to be addressed experimentally explicitly. However, assuming the molecules are wired independently represents a reasonable starting point for comparison. In some sense, the comparisons we make here can provide a basis for determining whether this assumption is correct. In addition, in the case that the measurement is on an ensemble of molecules, the resulting current per molecule value will be an average that includes contributions from both molecules that are well-coupled to the electrodes and those that are not. These relative contributions may well differ between different contacting methods and measurement approaches. It also means that comparisons with “single molecule” measurements remain incomplete in the absence of clear statistics. With these caveats, the present review is a starting point to use comparisons for insight into current transport via molecules.

2. Theoretical Background

Transport through individual molecules connected between electrodes is expected to be different from bulk transport because of the inherently small size of molecules. A clear indication of this comes from calculations of energy dissipation over a single molecule. A current of 500 fA at 0.5 V (= 0.25 pW/molecule) (cf., entries 13,16 in Table 1), taking $3.5 \times 10^2 \text{ J mol}^{-1} \text{ K}^{-1}$ as the heat capacity of an alkane chain, translates into a temperature increase of $\sim 10^8 \text{ K}$ per molecule. The reason that this calculation does not apply is not just ineffective thermal coupling between molecule and electrode (unlikely to decrease the result by 7 orders of magnitude), but rather that the molecules are much smaller than the mean-free path of electrons in typical metals (a few to tens of nano-



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meters at room temperature), so that bulk resistivity is not a valid concept. To a first approximation, the transport is ballistic (coherent) tunneling, although inelastic tunneling can be a significant component of the total current, something that can ultimately lead to dominance of non-tunneling mechanisms (see, for example, discussion in the literature,^[19] and Sec. 3.4). We can describe this tunneling current using the Landauer formula for the linear conductance, G , of the electrode–molecule–electrode junction:^[20]

$$G = \frac{2e^2}{h} T \quad (1)$$

Here T is a function that reflects the efficiency of electron transmission from one contact to the other. This transmission function can be roughly divided into components as follows (see also below):

$$T = T_{lc} \cdot T_{rc} \cdot T_{mol} \quad (2)$$

where T_{lc} and T_{rc} give the efficiency of charge transport across the left and right contacts and T_{mol} reflects the charge transport through the molecule. One can roughly approximate coherent, non-resonant tunneling through molecules as tunneling through a rectangular barrier, in which case

$$T_{mol} = \exp(-\beta l) \quad (3)$$

where l is the width of the barrier, i.e., the length of the molecule, and β is the tunneling decay parameter in units of (length)⁻¹ given by:

$$\beta = 2 \frac{\sqrt{2m^* \cdot \alpha (\phi - (eV/2))}}{\hbar} \quad (4)$$

Here \hbar is the reduced Planck constant, ϕ is the barrier height for tunneling through the LUMO level, $\phi = (E_F - E_{LUMO})$ or through the HOMO level, $\phi = (E_{HOMO} - E_F)$, E_F will be the Fermi level of the electrode (or electrode–molecule composite), m^* is the effective electron mass ($m^* = 0.16 m_0$;^[16,21,22]), V is the bias that is applied across the molecule(s), and α is a parameter used to describe the asymmetry in the potential profile across the electrode–molecule–electrode junction. In the case of symmetric coupling, $\alpha = 1$.^[23,24] Thus, Equation 4 shows that β should slowly decrease (and thus T_{mol} will increase) with voltage and approach zero as $eV \rightarrow 2\phi$. We note that the rectangular barrier picture is a gross approximation to the actual electronic structure of molecular junctions. Considerable theoretical work is underway to calculate accurately tunneling transmission efficiencies based on the symmetry and density of electronic states.^[20,25–27]

The product $T_{contacts}$ represents $T_{lc} \cdot T_{rc}$, the product of transmission coefficients into and out of the molecule at both electrodes (this is, as Eq. 2, a rough approximation). When multiplied by the quantum of conductance, $T_{contacts}$ has the dimensions of conductance and its reciprocal can be viewed as

an effective contact resistance. Weak contacts to the electrodes result in a decrease in $T_{contacts}$ and therefore reduce junction conductance, G . If T_{mol} is sufficiently high, $T_{contacts}$ can dominate the charge transport. This is likely if one or both of the contacts are merely physical (i.e., no chemical bonding). In practice it is very difficult to make perfectly symmetrical contacts unless both contacts are connected via identical chemical bonds to identical electrodes (identical “chemicontacts”). In principle, the nature of the contact can also affect β and not only $T_{contacts}$, because it changes the potential drop over the molecule, and therefore also changes the parameter α .

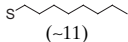
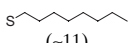
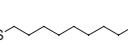
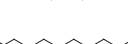
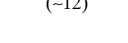
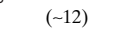
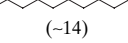
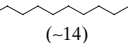
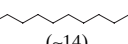
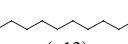

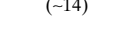
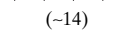
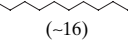
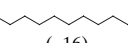
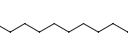
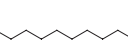
3. Comparison of Currents Through Saturated Alkane Chains (Table 1)

3.1. Dependence of Current on Molecule Length

For various transport measurements through alkane chains, the molecules are chemisorbed on Au or Hg via S atoms. In these studies the current is found to decrease exponentially with increasing molecule chain length, following Equation 3.^[1,4,13,16,28,29] The exponential dependence is observed whether the molecules have one- or two-sided chemicontacts. For one-sided chemically bound systems (see Table 1, entries 1,2,6–9,12–16), rather similar currents are found at 0.2 V through alkane chains of a given length, with the notable exception of entries 2,6. This is so, even though these results were obtained both with sub-microscopic contacts using conducting-probe atomic force microscopy (CP-AFM)^[30] and with macroscopic, solvent-free Hg contacts.^[6,12,14,29] It is not obvious a priori that such different systems should give similar currents, as the contact and/or the electrodes are very different. Therefore, these data suggest that for alkane thiol (i.e., alkane monothiol) and alkane dithiol junctions the contact resistances are either very similar or very small, relative to the electrical (insulating) properties of the molecules themselves, i.e., $T_{mol} \ll T_{contacts}$. Current measurements taken via scanning tunneling spectroscopy (STS) are also in surprising agreement with the above CP-AFM and hanging Hg drop experiments despite uncertainty in the nature of the tip–molecule contact (see Table 1, entries 12–16). Bumm et al.^[31] have also published STS data on alkane thiol monolayers at 1.0 V bias. They report current through C_{12} thiol of ~30 pA per molecule (assuming one molecule in a junction).

Table 1 shows up to three orders of magnitude differences in current between CP-AFM data (entries 1 vs. 2 and 5 vs. 6) for alkane thiols. A possible cause for this is the use of a solvent by Cui et al.^[1] to provide a well-controlled environment for the experiments. While indeed this can minimize the tip–SAM (self-assembled monolayer) contact area and eliminate artifacts due to water adsorption on the SAM surface, it is possible that a solvation shell around the tip decreases the electronic coupling of the tip to the SAM, resulting in lower conductances than measured in a dry, gaseous atmosphere.^[4,30]

Table 1. Comparison of currents through saturated, σ -bonded single molecules and monomolecular layers, sandwiched between two electrodes, measured by a variety of different experimental approaches, at two different voltages. Wherever one of the electrodes is a semiconductor the metal electrode is negative versus the semiconductor. Entry "0" refers to calculated tunneling currents (cf. Fig. 2). The last column refers to the literature reference for the currents quoted in the table.

	Junction	Current/molecule [pA] at 0.5 V	Current/molecule [pA] at 0.2 V	HOMO-LUMO gap	Contact area (Number of molecules)	Molecule structure (Estimated length [Å])	Method of measurement (Compressive force in CP-AFM [a])	Reference
0	Au/Vacuum/Au	See Figure 2	See Figure 2	See Figure 2	0.2 nm ²	16	Simmons theory	[32]
1	Au-S-C8/Au [b]	30 [c]	12 [d]	~7 eV [e]	25 nm ² (~100)	 (~11)	CP-AFM (2 nN)	[4]
2	Au-S-C8/Au [b]	0.035 [d]	0.013 [d]	~7 eV [e]	10 nm ² (~40)	 (~11)	CP-AFM (6nN; under solvent)	[33]
3	Au-S-C8-S-Au [g]	1400	310	~7 eV [e]	Single molecule [h]	 (~12)	CP-AFM [f] (6nN; under solvent)	[34]
4	Au-S-C8-S-Au [g]	1300 [c]	520 [d]	~7 eV [e]	25 nm ² (~100)	 (~12)	CP-AFM (2 nN)	[35]
5	Au-S-C8-S-Au [g]	15,000	2,500	~7 eV [e]	Single molecule	 (~12)	Pico-STM	[36]
6	Au-S-C10/Au [b]	0.007 [d]	0.0002 [d]	~7 eV [e]	10 nm ² (~40)	 (~14)	CP-AFM (6nN; under solvent)	[33]
7	Au-S-C10/Au [b]	5.0 [c]	2.0 [d]	~7 eV [e]	25 nm ² (~100)	 (~14)	CP-AFM (2 nN)	[4]
8	Hg-S-C10/p-Si [b]	–	6 [i]	~7 eV [e]	0.002 cm ² (~10 ¹²)	 (~14)	Hanging Hg drop electrode	[12]
9	n-Si-C10/Hg [b]	–	2 [j]	~7 eV [e]	Only current/cm ² reported	 (~13)	Hanging Hg drop electrode	[29]
10	Au-S-C10-S-Au [g]	800	200	~7 eV [e]	Single molecule [h]	 (~14)	CP-AFM [f] (6 nN; under solvent)	[34]
11	Au-S-C10-S-Au [g]	1,200	370	~7 eV [e]	Single molecule	 (~14)	Pico-STM	[36]
12	Au-S-C12/Au [b]	0.2	0.1	7 eV [37]	1600 nm ² (~6400)	 (~16)	Thermally evaporated top contacts (nanopore)	[16]
13	Au-S-C12/Au [b]	0.5 [c]	0.2 [d]	7 eV [37]	25 nm ² (~100)	 (~16)	CP-AFM (2 nN)	[4,38]
14	Hg-S-C12/p-Si [b]	–	0.6 [i]	~7 eV [e]	0.002 cm ² (~10 ¹²)	 (~16)	Hanging Hg drop electrode	[12]
15	n-Si-C12/Hg [b]	–	0.5 [j]	~7 eV [e]	Only current/cm ² reported	 (~15)	Hanging Hg drop electrode	[29]
16	Au-S-C12/(Pt/Ir) [b]	0.55 [k]	–	~7 eV [e]	0.25 nm ² single molecule	 (~16)	STS [l]	[39]
17	Au-S-C12-S-Au [g]	40	10 [d]	7 eV [37]	250 nm ² (~1000) [m]	 (~17)	Crossed wires	[37]

[a] CP-AFM: conducting probe atomic force microscopy. The measured current may increase as function of the tip force. Therefore, we compare between measurements in which the tip force is low. [b] Here C8 or C10 stands for saturated alkane chain (CH₂)_{n-1}CH₃ with $n = 8, 10$. [c] Derived from the low voltage I - V curve data, assuming linear behavior up to this voltage. [d] Divided by the estimated number of molecules in the contact area, using the estimates given in the original papers. [e] The HOMO-LUMO gaps for C12, C10, and C8 will be only slightly different. [f] Au nanoparticles were used as conduit between the Au AFM tip and the dithiol molecule. [g] Here C8, C10, or C12 stand for a saturated alkane chain (CH₂)_n with $n = 8, 10$, or 12. [h] Dithiolate molecules embedded in a monolayer matrix of near identical, monothiol S-(CH₂)_{n-1}CH₃. [i] We have assumed that the coverage is ~20 Å²/molecule. This yields an estimated density of 5×10^{14} molecule cm⁻². The currents are calculated after taking into account the attenuation that results from the Schottky barrier, due to the use of a semiconductor as electrode. This Schottky barrier can be calculated by extrapolating a logarithmic plot of $\ln[J/(1-\exp(-qV/kT))]$ to $V = 0$, which gives ~0.5 eV. Using this barrier we can calculate the reduction in current according to thermionic emission theory. However, since the curves are linear only in the low voltage regime, we cannot extract data at higher voltages. The currents are those obtained at forward bias. [j] As in the preceding footnote, but with a barrier height of 0.6 eV. [k] Current determined by integration of the dI/dV spectra reported in the original paper. [l] Scanning tunneling spectroscopy. [m] By comparison to other charge transport measurements they calculate that the junction contains ~10² molecules. Therefore, we divided the measured current by this value.

or using Hg drop contacts.^[6,12,14,29] As no such differences are seen with alkane dithiols (entries 3,4), these comparisons emphasize the importance of chemically well defined contacts.

3.2. The Tunneling Decay Parameter, β

By measuring the current as a function of length, the decay factor β for alkane systems generally can be calculated. Often values around 1 \AA^{-1} or somewhat higher are found, reflecting a relatively low tunneling efficiency (β values are also reported as $1/(\text{CH}_2)$ or $1/C$, which translates into numerically slightly lower values per angstrom). There are also a number of reports with lower values from 0.75 down to 0.5 \AA^{-1} .^[4,6,12,14,16,28–30,33,34,40,41] A thorough discussion of the possible causes for this is beyond the scope of this overview. Still, we note that in otherwise identical experiments on junctions with Hg and Si contacts, lower β values ($0.6\text{--}0.7 \text{ \AA}^{-1}$)^[12,28] were found with p-Si than with n-Si ($\sim 1.0 \text{ \AA}^{-1}$).^[42] These different β values probably reflect a difference in electronic structure of the junctions. This can lead to different transport mechanisms, as it is likely that at low bias the p-Si junctions involve HOMO- and the n-Si ones LUMO-assisted transport. This fits theoretical results for intramolecular electron transfer,^[43,44] suggesting lower β for so-called hole, rather than electron tunneling.^[45]

For systems with one chemicontact, β was found to increase with applied bias, in contrast to what is predicted by Equation 4.^[28,33] The increase of β with voltage has been explained in terms of electrostriction^[12] and a concomitant increase in through-space (between chains, in this case) contributions to tunneling, compared to through-bond ones.^[46] Recent results of Wang et al.,^[16] however, show the expected decrease with bias, as do results obtained in CP-AFM with two chemicontacts.^[34] These latter results^[34] can be understood if coulomb blockading caused by the Au particles used as intermediate conduits between the AFM tip and the molecules is taken into account (Lindsay et al., unpublished data). The corrected voltage distribution then results in a β closer to unity. Similar results were obtained recently in experiments where macroscopic leads are used to contact single molecules.^[36]

3.3. Current Transport Mechanisms

Based on the tremendous volume of literature on electron transfer in solvated molecular systems, it is generally assumed that the dominant current transport mechanism in molecular junctions is “through-bond” (TB) tunneling, in which the current follows the bond overlaps along the molecule. However, there will always be a direct component from electrode to electrode, in which the molecule plays the role of a dielectric medium that modifies transport across the gap (“through-space” (TS) tunneling, cf. Fig. 2). The question of which mechanism dominates is more than academic since the rational design of junctions with specific transport behavior

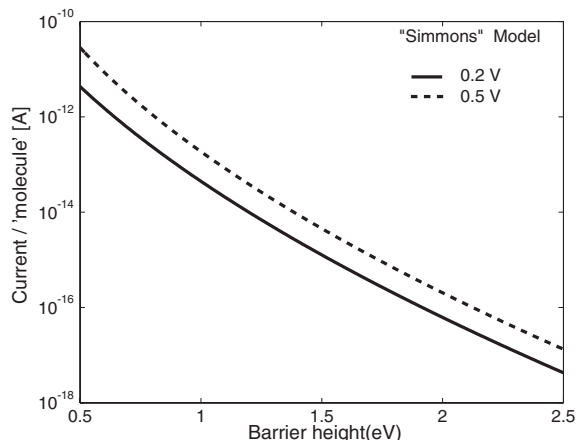


Fig. 2. Tunneling currents densities (current/ 0.2 nm^2 ; 0.2 nm^2 is taken as the footprint of 1 molecule) as a function of the energy barrier height, ϕ_0 , between two conducting media, separated by a 1.6 nm vacuum gap. The currents are calculated according to the simplified, WKB-based model (rectangular barrier) described in the literature [76]. Results are plotted for the two bias voltages used in our comparisons (see Tables 1,2). The formula used is with m the free electron mass, q the electron charge, Planck's constant, and $S = 1.6 \text{ nm}$ (for a C12 alkane, see Table 1).

requires a precise understanding of how the electrons flow. Figure 3 illustrates the difference between TB and TS tunneling for a simple junction composed of tilted alkane chains.

The most compelling experiment involving TB versus TS tunneling in molecules is reported by Slowinski et al.^[13,47] They measured current through an alkane thiol SAM on a hanging Hg drop electrode in an electrochemical solution. Current was measured as a function of the monolayer thickness that was varied by two methods: 1) by changing the number of carbons in the alkane chain and thereby its length; 2) expansion of the Hg drop such that the monolayer surface coverage was reduced and the molecules increased their tilt with respect to the surface. In the first scenario, decreasing the monolayer thickness resulted in an exponentially increasing tunneling current with a β value of 0.96 \AA^{-1} . In the second scenario, the increase in current was smaller, with a β value of only 0.12 \AA^{-1} . Thus, for a given chain length, current was not substantially increased by a reduction in film thickness. This result indicates that current predominately follows the σ -bond pathway of the alkane chain, being attenuated primarily by the length of the molecule as the film decreases in thickness and the electrodes are brought closer together. Slowinski et al. postulate a model of electron transport in which the current follows the backbone (TB) of the molecule with a small chain-to-chain and TS contribution, as illustrated in Figure 3.

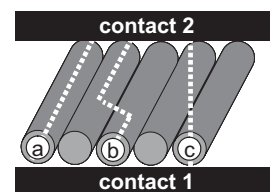


Fig. 3. Schematic illustration of possible mechanisms for (elastic) electronic charge carrier tunneling across molecules (adapted from [13]).

They estimate that the more efficient TB β value is about 0.91 \AA^{-1} , while the less efficient TS value is 1.31 \AA^{-1} .

Qualitative support for TB tunneling comes also from comparing the length dependence of tunneling through monolayers of alkane thiols on Au and Ag substrates. The average tilt angle of these molecules on Ag (12°) is known to be less than the tilt angle on gold (30°). Therefore, a monolayer of a given alkane thiol will be thicker on Ag than on Au. Measured β values are consistent with TB transport as they are the same if calculated in units of inverse angstroms of length and differ if calculated in units of inverse angstroms of monolayer thickness.^[27,35,48] In contrast, Cui et al. can fit the force dependence of their measurements to singly bonded molecules with a simple TS model.^[33] When the molecules are chemically bonded at both ends, the mechanism changes to TB.^[1] These observations might be reconciled with the earlier mentioned ones, if we recall that the currents measured to the singly bonded films are much larger (data taken in ambient) than those measured for singly bonded films under solvent (entries 1 vs. 2, 6 vs. 7 in Table 1). The stronger coupling might change the mechanism from TS to TB. Still, it is clear that more work remains to be done on this important question.^[49]

Another key issue is which orbitals facilitate tunneling, the HOMO or LUMO levels of the molecules in the junction. The ultraviolet photoemission spectroscopy (UPS) data of alkane thiol monolayers on Au that have been reported do not show any evidence for molecular levels within $\sim 5 \text{ eV}$ from the Au Fermi level, suggesting either a low cross-section for the HOMO or a deep-lying HOMO level.^[50,51] It may be possible to decide between these possibilities by probing the LUMO level with complementary inverse photoemission spectroscopy (IPES) and two-photon photoemission (2PPE) data, though we are not aware of any published data.

It is likely that, in addition to these, other types of experiments will be needed to unravel the mechanisms of current transport, even those operative through simple alkane chains. Among these we note temperature-dependent measurements, of which two reports have recently appeared (entry 12 in Table 1,^[16] and work on non-bonded, Langmuir–Blodgett films of eicosanoic acid (C20) between Pt electrodes^[52]). We note that these are often difficult studies and, especially if working with monolayers, one should be aware of this issue,^[53] but a detailed comparison and discussion of temperature-dependent transport is outside the scope of this overview.

3.4. Effect of Molecule–Electrode Chemical Bond

As noted before (cf., e.g., discussions in the literature,^[26,54] and also some more recent references in the paper of Cahen and Hodes^[55]) the way the molecule(s) interact with the electrode materials plays a crucial role in molecule-based electronics. The difference between a system with and without chemicontacts, in terms of current flow through the molecules can be up to three orders of magnitude (for alkane thiol-based

junctions).^[1,28] This was clearly observed by Cui et al., who used a 2-terminal configuration with a conducting AFM tip as one of the electrodes to measure current through a monolayer of octane thiol, chemically bound to only one electrode. They compared the current to that obtained for a single octane dithiol molecule, chemically bound to both electrodes and embedded in a octane thiol layer.^[1] This current is very comparable to that measured by Frisbie,^[35] (see Table 1, entries 3,4) suggesting that the differences between CP-AFM measurements under solution versus those done in ambient (dry gas) conditions are negligible when the contacts are chemicontacts.

Selzer et al. found approximately three orders of magnitude difference in current that passes (at low voltages) between Hg|alkane monolayer|SiO_x–Si junctions with the molecules bound chemically to one electrode (via Hg–S bond) and that without a chemical bond between the molecules and either of the two electrodes.^[12] We note that this huge difference is similar to that obtained with C12 and C18 monolayers (i.e., the absence of the Hg–S bond has the effect of adding (CH₂)₆ at the voltages considered here). This points to the crucial rule that the molecule–electrode contact plays in electronic transport measurements through molecules. These results suggest that the absence of a chemical bond creates an additional barrier.^[56] This leads to a decrease in T_{contacts} and therefore to a reduction in the conductance.

3.5. Effect of Electrode Material

As theoretically predicted (cf., e.g., work by Datta^[20] or Seminario et al.^[26]), not only the nature of the molecules and the presence/absence of a chemical bond to the electrode but also the nature of the electrode materials can play an important role for current transport. Beebe et al. derived from CP-AFM I – V data the contact resistance for metal tip–molecular monolayer–metal electrode systems where the molecules are singly bound alkane thiols.^[4] They found that this contact resistance decreases with increasing metal work function, for metal–CH₃(CH₂)_nS–metal junctions.^[57] This holds true even when only the metal at the physical contact is changed; another indication that the electrode material is important even if a chemical bond is missing.^[58–60] The work function dependence of the contact resistance provides strong evidence that tunneling in these systems is HOMO-assisted and may be rationalized in terms of a Schottky-like interfacial electronic barrier that results from energy level alignment.^[61] An increase (decrease) in this barrier effectively decreases (increases) T_{contacts} and, thus, the measured conductance.^[62]

As far as the importance of the strength of the bonds is concerned, we note the similarity between the results of Selzer et al.^[12] and those of Liu and Yu,^[29] who studied electrical transport through alkane chain monolayers in Hg–alkane thiol|Si and Si–C–alkane|Hg configuration, respectively. In both systems the molecules are bound only to one electrode, but in one junction the contact is via a S–Hg bond, whereas in

the other it is via the more covalent C–Si one. In one case, the terminal CH₃ group faces a Si–H surface, in the other case, the highly polarizable Hg surface. Still, the observed currents for the two junctions for systems with similar carbon chain lengths are comparable.^[63] While we cannot exclude accidental cancellation of effects, this suggests that within a given bond type bond strength may be of secondary influence only.

4. Comparison of Currents through π -Bonded Molecules (Table 2)

While much work is done with conjugated molecules, fewer systematic data are available on, for example, the length dependence of conduction, than for saturated molecules. This makes comparisons between various studies problematic. Nevertheless, the data collected in Table 2 lead to some interesting observations.

4.1. Efficiency of Charge Transport (Current Magnitude)

As expected from combining a simple Hückel calculation with basic solid-state physics (band) theory, noticeable differences exist between conjugated and saturated molecules in terms of their efficiency for current transport. The lower HOMO–LUMO gap for π -bonded molecules (~ 3 eV), as compared to that of saturated molecules (~ 8 eV), can explain the much higher charge transport efficiency through the former. The tunneling decay parameter β is found experimentally and theoretically to be 0.2–0.6 Å⁻¹ for non-resonant electron tunneling through π -bonded molecules.^[6,68,71] This should be compared to the ~ 0.6 –1 Å⁻¹ mentioned earlier for saturated molecules, indicating that indeed tunneling efficiency is higher for π -bonded systems. The smaller HOMO–LUMO gap for conjugated molecules not only produces a more gentle dependence (β value) in the non-resonant tunneling regime, but, may, ultimately, result in tunneling being replaced by hopping as the dominant charge transport mechanism (see discussion of results of Selzer et al., below).

In terms of absolute current per molecule of given length at a given bias, higher currents were observed experimentally and calculated theoretically for π -bonded molecules than for saturated ones of comparable (and even slightly shorter) lengths (see Table 2, entry g vs. Table 1, entries 7–9; cf. also, for example, the papers by Bumm et al. and Leatherman et al.^[31,75]). Ramachandran et al. compared currents through dithiol phenylene ethylene and carotenoid with alkanes.^[74] The alkanes pass roughly ten times less current than simple estimates based on β ,^[76] the dithiol phenylene ethylene some ten times more, and the dithiol carotenoid over a hundred times more current than expected (see also below).

Kushmerick et al.^[8] measured currents through monolayers of π -bonded molecules and found them to be 1–1.5 orders of magnitude higher than for saturated (σ -bonded) ones of the same length (C₁₂ alkyl dithiol).



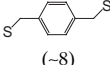
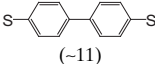
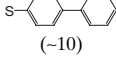
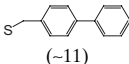
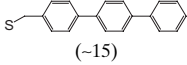
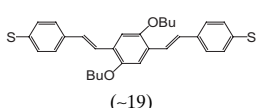
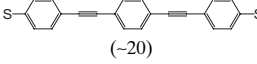
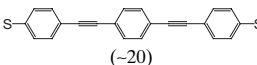
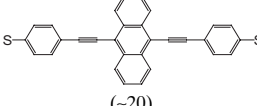
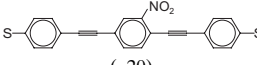
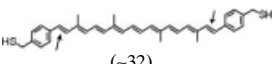
For π -bonded molecules, bound only at one side, (HSCH₂(C₆H₅)₃; ~ 1.5 nm), currents of 130 pA/molecule were measured at 0.2 V by Wold et al.^[68] These numbers can be compared to the 2–6 pA/molecule mentioned above for σ -bonded alkanes (see Table 1, entries 7–9).^[12,29,38] Naturally, such comparisons between different experiments should always be viewed with caution, as the contact resistance for each measurement can be different, due to differences between electrodes and measurement details (cf., Table 1,2). Nevertheless, these comparisons provide clear indications that conjugated molecules indeed pass significantly higher currents than saturated ones.

The single-molecule data obtained with mechanically controllable break junction contacts (MCB)^[11,19] give currents that are orders of magnitude higher than the per-molecule transport data derived from transport across monolayers (compare Table 2, entry k vs. h–j). Reichert et al. measured ~ 140 nA (at 0.5 V) for a ~ 2 nm long isolated conjugated molecule, bound at both ends,^[70] using a MCB junction.^[11] Their results are in rough agreement with those of Selzer et al. (Table 2, entry l),^[19] who used an electromigrated junction^[73] for isolated molecule measurements on a closely related molecule.^[69,77,78] These high value are remarkable as one could naively expect lower currents in these junctions (vis-à-vis the monolayer junctions) for at least two reasons: 1) the TS tunneling component is expected to be more efficient in a monolayer (through an organic) than through vacuum (the MCB or electromigrated junction cases); 2) intermolecular interaction (in a monolayer) will widen energy levels for charge transport and thereby could increase transmission efficiency. Possibly, for some reason, here resonant tunneling is involved in a much stronger way than in the other measurement approaches. Alternatively, Selzer et al. argue^[19] that, as a result of inelastic scattering and local heating, a more efficient, hopping mechanism starts to dominate the charge transport.

4.2. Conformational Effects

For charge transport through π -bonded molecules, the molecule conformation (which may be reflected in its HOMO–LUMO gap, which is directly related to the extent of bond-alternation) maybe as important as the nature of the electrode–molecule contact.^[8,37,79] Chen and Reed observed a sharp decrease of two orders of magnitude in conductance around 25 K for aromatic-based systems.^[79] At low temperature (~ 10 K) the phenyl rings in these molecules show very little tendency to rotate. Perpendicular phenyl rings are more stable than parallel ones, decreasing the efficiency of charge transport via the molecules. At 30 K, the rings are able to freely rotate with respect to each other, allowing the phenyl rings to assume a planar geometry for part of the time, thus increasing the charge transport efficiency.^[79] Kushmerick et al. observed half an order of magnitude difference in charge transport between OPE and OPV.^[37] These two types of molecules are conjugated and of roughly the same length. How-

Table 2. Comparison of currents through conjugated, π -bonded single molecules and monomolecular layers, sandwiched between two electrodes, measured by a variety of different experimental approaches, at two different voltages. Wherever one of the electrodes is a semiconductor the metal electrode is negative vs. the semiconductor. The last column refers to the literature reference for the currents quoted in the table.

	Junction	Current/molecule [pA] at 0.5 V	Current/molecule [pA] at 0.2 V	HOMO- LUMO gap	Contact area (Number of molecules)	Molecule structure (Estimated length [Å])	Method of measurement (Compressive force in CP-AFM [a])	Reference
a	Au-S-phenyl-S-Au	1300 [b]	300 [b]	~5 eV	Single, isolated molecule	 (~6)	Mechanical break junction	[64]
b	Au-S-phenyl- S/(Pt/Ir)	110 [b]	30 [b]	~5 eV	0.25 nm ² single molecule	 (~6)	STS [c]	[65]
c	Au-S-C-phenyl- C-S/(Pt/Ir)	560 [b]	130 [b]	~5 eV	0.25 nm ² single molecule	 (~8)	STS [c]	[65]
d	Au-S-biphenyl- S-Au	36	4	~5 eV	Single molecule [b]	 (~11)	CP-AFM (~12 nN)	[66]
e	Au-S-biphenyl/Ti	300	7	~5 eV	700 nm ² (~2800)	 (~10)	Thermally evaporated top contacts (nanopore) [e]	[67]
f	Au-S-molecules/ Au [f]	–	500 [g]	~5 eV	25 nm ² (~100)	 (~11)	CP-AFM (2 nN)	[68]
g	Au-S-terphenyl/ Au [f]	–	130 [g]	~5 eV	25 nm ² (~100)	 (~15)	CP-AFM (2 nN)	[68]
h	Au-S-OPV-S-Au [h]	1000 [g]	500 [g]	3.1 eV [37]	250 nm ² (~1000) [i]	 (~19)	Crossed wires	[37]
i	Au-S-OPE-S-Au [j]	500 [g]	200 [g]	3.5 eV [37]	250 nm ² (~1000) [i]	 (~20)	Crossed wires	[37]
j	Au-S-OPE-S-Au [j]	10	4	3.5 eV [37]	Single molecule	 (~20)	CP-AFM (6 nN; under solvent)	[69]
k	Au-S-molecule- S-Au [70]	14 × 10 ⁴	4 × 10 ⁴	3.3 eV [71,72]	Single, isolated molecule	 (~20)	Mechanical break junction	[11] (Fig. 5)
l	Au-S-molecule- S-Au	3 × 10 ⁴	2500	3.3 eV [72]	Single, isolated molecule	 (~20)	Electro-migrated junction [73]	[19]
m	Au-S- caroteno dithiol-S-Au	100	40	2.4 eV [74]	Single molecule [k]	 (~32)	CP-AFM (6 nN; under solvent)	[74]

[a] CP-AFM: conducting probe atomic force microscopy. The measured current may increase as function of the tip force. Therefore, we compare between measurements in which the tip force is low. [b] Current determined by integration of the dI/dV spectra reported in the original paper. [c] Scanning tunneling spectroscopy. [d] A small number of these molecules was inserted into a self-assembled monolayer of alkanethiols on Au. [e] As the currents are very asymmetric, the value reported here is for that obtained when the Au-S contact is biased positive. [f] Oligophenylene derivatives. [g] Divided by the estimated number of molecules in the contact area, using the estimates given in the original papers. [h] OPV: oligophenylene vinylene; here 2, 5-di(phenylethynyl-4'-thio)benzene. [i] By comparison to other charge transport measurements they calculate that the junction contains $\sim 10^3$ molecules. Therefore, we divided the measured current by this value. [j] OPE: oligophenylene ethylene. [k] The dithiolate molecules were embedded in a docosanethiol (C₂₂H₄₅SH) monolayer.

ever, in OPE the phenylene rings rotate freely at room temperature, whereas the two butyl groups prevent this perpendicular configuration in OPV. The conductance is reduced when the rings are perpendicular to each other, as in the former, while the molecule coplanarity enhances charge transport, as in the latter.

We note the earlier mentioned higher currents through carotenoids than through phenylene ethylene, both with chemicontacts on the two ends. The difference may be due to the role that facile rotations about σ -bonds play in the case of OPE.^[74,80]

4.3. Contact Effects with π -Bonded Molecules

For π -bonded molecules the presence of a chemicontact to the electrode appears to be much less important than for saturated ones. Kushmerick et al. find only one order of magnitude difference in current^[81] for conduction via conjugated molecules (OPE) in junctions where either only one end of the molecule or both sides were bound to the electrodes (via Au-S bonds).^[37] It is possible that the π -orbitals of the molecule overlap with the metal spill-over electron density, resulting in a relatively high T_{contacts} value, even without a chemicontact.

All these experiments^[8,37,79] suggest that electrode-molecule contact, the rotational configuration, and HOMO-LUMO gap of aromatic-based molecules all are important for charge transport. We should, though, keep in mind that these are probably not independent variables.

5. Conclusions and Outlook

Comparison of data in Table 1 on saturated alkane thiol molecular junctions shows that many of the published data on these systems agree rather well with each other. This is true for a variety of different approaches to junction formation and methods of measurement. Notable disagreement exists among the alkane thiols, between entries 2 (C8) and 6 (C10) and the other entries, the former currents being ~ 3 –4 orders of magnitude less than the latter ones. This is likely due to contact effects of taking these measurements under solvent. Further experimentation is needed to determine what causes this additional barrier to transport, whether it is due to a solvent shell around the AFM probe, a reduction in contact area, or a combination of both. When the physical contact is replaced by a chemical one, as in the case of alkane dithiol junctions, the disagreement between measurements made in solvent and in ambient vanishes (see Table 1, entries 3–4). Overall, the consistency among most of the entries for saturated alkane chains in Table 1 suggests that in the case of molecular junctions, composed with such molecules, it is probably a good assumption that the molecules conduct in parallel, independently and primarily TB.

Conjugated molecules are shown to be more conductive than saturated molecules of the same length. All in all, though, there is a wider spread of results than for the saturated alkyl chains. In part this is probably due to the fact that only rarely molecules that are identical (and not just of comparable length) have been measured by different methods/groups. The most striking difference is between the single molecule MCB junction currents observed by Selzer et al.^[19] and Reichert et al.^[11] and any of the other values. While possible reasons for this were given above, confirming one or more of these will require additional, carefully designed experiments.

In general, conjugated molecular systems offer more efficient length-dependent tunneling than saturated ones, as observed both in the magnitude of the currents and in smaller β values. Fewer studies exist, however, and there is a lack of experimental evidence for the voltage dependence of β and the effect that contact type (chemical versus physical) and electrode material have on conductance and β . It will be interesting to compare how conjugated junctions behave in these regards with respect to their saturated counterparts. It may be anticipated also that intermolecular coupling may be enhanced in the case of conjugated monolayers such that a significant amount of cooperative tunneling may exist.

Finally, one should try to use contacts that are chemically as well-defined as possible. Clearly, if at all possible what we have called here chemicontacts, made by actual (mostly covalent) chemical bond formation, is to be preferred. However, this can cause synthetic problems, especially if one is interested in asymmetric contacts, as few suitable molecules with different binding groups on two ends of the molecule are available and their preparation will often be far from trivial. In any case, also if it is not possible to have chemicontacts to all electrodes, it behooves to heed a “know thy contacts” credo.

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