

# Chemical control of double barrier tunnelling in $\alpha,\omega$ -dithiaalkane molecular wires†

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Single molecule conductance measurements on 1,4-bis-(6-thiahexyl)-benzene derivatives reveal (i) that benzene rings serve as an effective indentation in the tunnelling barrier, and (ii) that more electron-rich benzene rings give higher conductances, consistent with hole conduction (*i.e.* via the benzene HOMO).

The advent of reliable techniques for measuring the electrical properties of single molecules bridging two metallic contacts has led to an explosion of interest in this field.<sup>1,2</sup> There is still a lack of understanding of basic structure–property relationships in molecular electronics. Attempts to address this are often complicated by the fact that more than one potentially significant parameter (*e.g.* molecular length, conformation, contact geometry, steric and electronic effect of substituents) is varied simultaneously.<sup>3–5</sup> A common approach in molecular electronics has been to search for organic molecular devices capable of basic electrical functions. Molecules designed to act as molecular wires,<sup>6,7</sup> switches<sup>8–10</sup> and diodes<sup>11</sup> have recently been examined theoretically and/or experimentally, and devices have been produced which show rectification and negative differential resistance (NDR) behaviour. This points to the possibility of generating organic devices that mimic inorganic semiconductor junctions, although technological deployment seems some way off.

An architecture that is expected to be important in future generations of devices is the double tunnelling barrier junction.<sup>12</sup> These have been introduced recently into field effect transistors,<sup>13</sup> diodes<sup>14</sup> and bipolar transistors.<sup>15</sup> In these inorganic devices, metalorganic vapour phase epitaxy is used to assemble a ‘well’ or barrier indentation, sandwiched between the two tunnelling barriers.

We recently determined the single molecule conductance of the molecule 6V6 (Fig. 1).<sup>16,17</sup> When contacted to gold electrodes *via* the thiol groups, this can be regarded as the single molecule equivalent of a double tunnelling barrier because the frontier

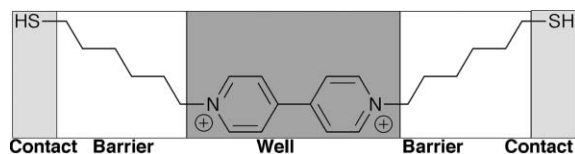


Fig. 1 The molecule 6V6 as a double tunnelling barrier junction.

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orbital energies for the alkyl groups lie far from the gold Fermi energy, while the frontier orbitals for the  $\pi$ -system of the viologen are much closer to the Fermi energy. This is apparent upon comparing the single molecule conductance of 6V6 (0.5 nS)<sup>16,18</sup> with that of dodecane-1,12-dithiol (*i.e.* two back-to-back barriers with no well; 0.028 nS).<sup>19</sup> Even though 6V6 is *longer* than dodecane-1,12-dithiol, it is more conductive due to the influence of the viologen acting as a barrier indentation.

The viologen group in 6V6 is electroactive. When measured under potential control in aqueous electrolyte, the conductance increased approximately six-fold as the potential was swept negative to access the viologen cation radical redox state, giving a value approximately the same as that for a single C<sub>6</sub> alkane barrier (in hexane-1,6-dithiol; 2.5 nS<sup>16,17</sup>), indicating that the viologen radical cation acts as a particularly deep well.

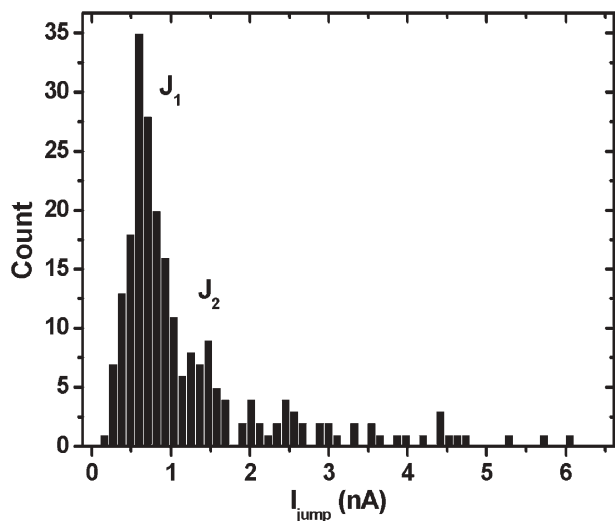
In this paper, we address the following questions. Firstly, do smaller, non-redox-active moieties also act as ‘wells’? Secondly, if so, can they be chemically tuned by altering the electronic structure of the well? Thirdly, is there a relationship between the frontier orbital energies of the well and the conductance of the whole junction? Accordingly, we have made a range of molecules 1–4 in which the contacts and barriers are constant (HS(CH<sub>2</sub>)<sub>6</sub>) and the wells are varied. These are listed in Table 1 together with the HOMO and LUMO energies determined using the SPARTAN04 implementation of DFT (B3LYP/6-31G\*\*).

Table 1 Well structures used, and their frontier orbital energies (in eV). R = HS(CH<sub>2</sub>)<sub>6</sub>– in all cases

Molecule	Well structure	HOMO	LUMO
1		–6.25	+0.06
2		–6.62	–0.59
3		–5.23	+0.09
4		–5.97	+0.12

Molecules **1–4** (Table 1) were synthesised (as dithioacetates) and fully characterised by microanalytical and spectroscopic methods.† We then employed the scanning tunnelling microscopy (STM) based  $I(t)$  technique of Haiss<sup>20</sup> to determine the single molecule conductances of **1–4**. A flame-annealed gold-coated glass slide is dipped into a dilute ( $10^{-4}$ – $10^{-5}$  M) solution of the appropriate dithioacetate for one minute to allow the formation of a low coverage monolayer (our recent experience is that it is not necessary to employ  $\text{CH}_3\text{C}(\text{O})\text{Cl}$ –MeOH deprotection<sup>21</sup> prior to monolayer formation). A gold STM tip is then brought to a fixed distance above the gold surface under perfluorodecane, controlled using the set point current. The feedback loop is switched off and the current is monitored as a function of time. As molecules spontaneously form and break bridges between tip and surface, jumps in the tunnelling current are observed (for example, Figure S4 in Supplementary Information) due to conductance through the molecule(s). These jumps are analysed statistically. Fig. 2 shows a typical histogram for such an experiment. For molecules **1–4**, we repeated this experiment at different tip–substrate bias potentials, and the mean single molecule current was then plotted against the bias potential. The slope gives the molecular conductance (Table 2).

The results were checked using a complementary method, the  $I(s)$  technique. Here, the tip is withdrawn while maintaining a constant x–y position, and a current–distance ( $I(s)$  where  $s$  = relative tip–sample distance) curve is collected. We typically observe current–distance behaviour characteristic of the formation of molecular wires (Figure S1, Supplementary Information) with a plateau in the current ( $I(w)$ ) due to conductance through the fully-extended molecule in its lowest-energy conformation. As the tip is withdrawn further, the molecule then detaches at a distance characteristic of its length. Again, the experiment is repeated many times, and the results are analysed statistically as for the  $I(t)$  measurements. The results (Table 2) are valuable in two ways. Firstly, results for the two techniques are in good agreement, giving us added confidence in the  $I(t)$  measurements. Secondly, they provide confirmation that we are dealing with molecular



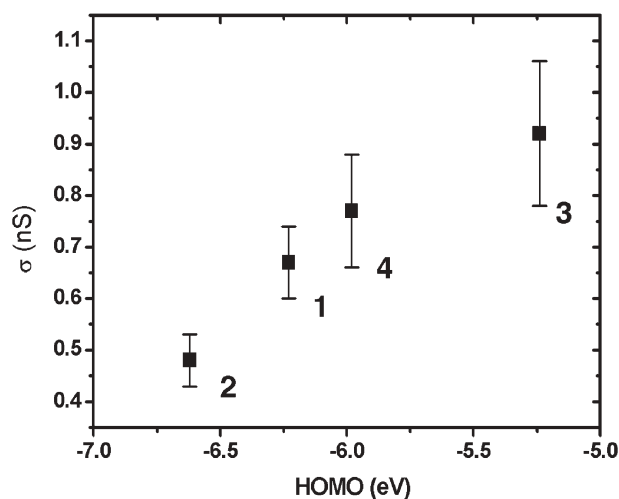
**Fig. 2** Histogram of the current jumps observed in one of the  $I(t)$  measurements on molecule **4**. The tip–substrate potential in this example was +600 mV. The large peak,  $J_1$ , corresponds to jumps involving a single molecule, and the smaller peak  $J_2$  to jumps involving two molecules.

**Table 2** Conductances (standard deviations in parentheses) of **1–4** measured using  $I(t)$  and  $I(s)$  methods, and mean detachment distances (standard deviations in parentheses) measured using  $I(s)$  method

Molecule	$I(t)$ (nS)	$I(s)$ (nS)	$s_{1/2}$ (nm)
<b>1</b>	0.67 (0.07)	0.74 (0.24)	1.83 (0.19)
<b>2</b>	0.48 (0.05)	0.40 (0.09)	2.35 (0.28)
<b>3</b>	0.92 (0.14)	0.90 (0.19)	1.33 (0.14)
<b>4</b>	0.77 (0.11)	0.69 (0.27)	1.38 (0.15)

events, because the mean break-off distances are reasonably consistent with the lengths of the molecules (2 nm S–S distances for the fully-extended, transoid conformers of **1–4** as determined by molecular mechanics). The degree of uncertainty in the detachment distance measurement (see the histogram in Figure S2) is larger than in the determination of conductance because of the range of contact geometries, and the difficulty of maintaining a constant starting-point in the measurements.

The results in Table 2 are interesting in several respects. Firstly, it is clear that the conductances are considerably greater than would be expected for an alkanedithiol of the same length as **1–4**. This indicates that the aromatic units do indeed act as a “well” in the tunnelling barrier for **1–4**. Secondly, it is clear that the conductance varies with substituent; electron-donating groups lead to higher conductances. In Fig. 3, we plot the conductances against the HOMO energy for the aromatic unit, obtained from the Spartan04 implementation of DFT (B3LYP, 6-31G\*\*); equilibrium geometry calculated for the transoid, extended form of **1–4** minimised using molecular mechanics).



**Fig. 3** Plot of conductances determined by  $I(t)$  method (with standard deviations) against HOMO energy for molecules **1–4**.

For molecules such as alkanedithiols in which superexchange is the conductance mechanism, conductance  $G$  decreases exponentially with the length of the molecule ( $G = A\exp(-\beta_N N)$ , equation 1) where  $A$  is characteristic of the metal–molecule coupling and is therefore contact-dependent,  $\beta_N$  is a decay constant characteristic of the repeat unit ( $-\text{CH}_2-$ ), and  $N$  is the number of repeat units. Superexchange is also expected to be the operable mechanism for molecules **1–4**, especially given that the central chemical group (the

“well”) is off-resonance.<sup>18</sup> However, simple barrier tunnelling (equation 1, where the decay constant  $\beta$  or  $\kappa$  is proportional to the square root of barrier height) cannot adequately describe tunnelling across **1–4** since the “well” leads to a double tunnelling barrier with the barrier height only reduced at the well rather than across the entire molecule. Fig. 3 is plotted in linear form since *a priori* the relationship between conductance and the HOMO position is not known and in any case is not likely to follow the simple single barrier tunnelling model implicit in equation 1. The observation that a clearly apparent but rather weak (linear) relationship exists between conductance and HOMO position is noteworthy, and demonstrates that these molecular double tunnelling barriers are not represented adequately by equation 1, for which a reduction in barrier height across the whole molecular wire would lead to a non-linear relationship between conductance and frontier orbital position. Indeed, for a selection of conjugated molecular wires in which a single frontier orbital extends between the two sulfur terminal groups, we observe that  $\ln(\text{conductance})$  scales with the square root of the frontier orbital position, consistent with the barrier tunnelling model of equation 1.<sup>22</sup>

A detailed theoretical description of the mechanism of conduction is outside the scope of this paper. A very recent study of the single molecule conductances of a series of very short conjugated molecules (substituted 1,4-diaminobenzenes) using an STM-based break junction technique found that electron donating substituents resulted in higher molecular conductances, and there was a (very approximate) correlation between the conductance and the Hammett  $\sigma_p$  parameter, consistent with hole transport (*i.e.* one could regard the molecule as being in a ‘positive transition state’ as it conducts).<sup>5</sup> Also, recent thermoelectric effect measurements on conjugated dithiols trapped between gold electrodes in the presence of a temperature gradient gave positive values for the junction Seebeck coefficients, indicating hole conduction.<sup>23</sup> In our molecules, the presence of the alkyl tunnelling barriers means that the aryl substituents are far removed from the gold contacts during measurement, so that possible complications from steric effects, and consequent differences in contact geometry, are much less likely. It is interesting that although the conduction mechanism may well be different for short, conjugated molecules, the effect of substitution is the same.

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## Notes and references

‡ Sonogashira cross-coupling of the appropriate 1,4-dibromo-arene with 6-chloro-hex-1-yne,  $\text{H}_2/\text{Pd}$  reduction of the resulting di-alkyne, and subsequent KSAc-NaI(cat.)-acetone treatment of the 1,4-bis(6-chlorohexyl)arene afforded the corresponding thioacetic acid *S*-{6-[4-(6-acetylsulfanyl-hexyl)-aryl]-hexyl} esters, **1–4**; full details are in the Supplementary Information.

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