Permethylation Introduces Destructive Quantum Interference in Saturated Silanes

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Supporting Information Placeholder

ABSTRACT: The single-molecule conductance of silanes is suppressed due to destructive quantum interference in conformations with cisoid dihedral angles along the molecular backbone. Yet, despite the structural similarity, σ-interference effects have not been observed in alkanes. Here we report that the methyl substituents used in silanes are a prerequisite for σ-interference in these systems. Through density functional theory calculations, we find that the destructive interference is not evident to the same extent in non-methylated silanes. We find the same is true in alkanes as the transmission is significantly suppressed in permethylated cyclic and bicyclic alkanes. Using scanning tunneling microscope break-junction method we determine the single-molecule conductance of functionalized cyclohexane and bicyclo[2.2.2]octane that are found to be higher than that of equivalent permethylated silanes. Rather than the difference between carbon and silicon atoms in the molecular backbones, our calculations reveal that it is primarily the difference between hydrogen and methyl substituents that result in the different electron transport properties of non-methylated alkanes and permethylated silanes. Chemical substituents play an important role in determining the single-molecule conductance of saturated molecules, and this must be considered when we improve and expand the chemical design of insulating organic molecules.
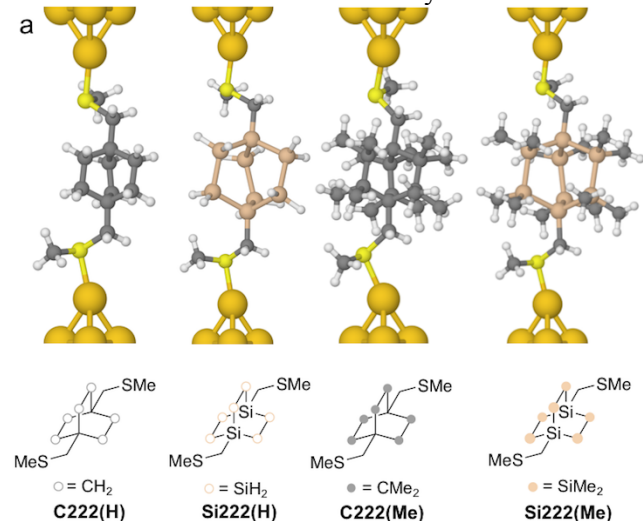
Destructive quantum interference suppresses single-molecule conductance in permethylated silanes when all through-bond paths are constrained and at least one dihedral angle approaches 0°.[1-3] As an extreme case, we recently demonstrated that functionalized permethylated bicyclo[2.2.2]octasilanes are unusually efficient single-molecule insulators.[4-5] Beyond the small dihedral angle, it is not known what is special about the bicyclo[2.2.2]octasilane structure to yield interference effects. Suppression of conductance in alkanes has also been ascribed to gauche conformations.[6-11] Still, previous studies have not found clear signatures of destructive quantum interference in form of a sharp antiresonance feature in the calculated transmission,[10-14] or as negative curvature in the measured differential conductance.[15-17]

Most studies of destructive quantum interference have focused on π-conjugated molecules.[18-21] Linear permethylated silanes have a conjugated σ-orbital system,[22-27] which is reflected in their conductance decay with length and stereoelectronic switching behaviors.[28-30] As alkanes lack electronic conjugation, they are common in chemistry as insulating molecular units,[31] e.g., bicyclo[2.2.2]octane in the Aviram-Ratner molecular rectifier.[32] However, charge transfer and single-molecule conductance studies revealed that cyclohexane and bicyclo[2.2.2]octane are not more insulating than linear alkanes.[33-35]

In this communication, we explore the cause of the missing destructive σ-interference in alkanes by comparing the electron transport properties of methylthiomethyl-functionalized *trans*-cyclohexane and bicyclo[2.2.2]octane with their corresponding silanes. Shown in Figure 1, we theoretically examine both non-methylated (**H**) and permethylated (**Me**) cyclohexane (*cyclo*-**C6**), cyclohexasilane (*cyclo*-**Si6**), bicyclo[2.2.2]octane (**C222**), and bicyclo[2.2.2]octasilane (**Si222**). Previous theoretical studies

of cyclic and bicyclic carbon and silicon based saturated molecules did not reveal clear trends between the electronic transmission and chemical composition.[5, 36-37] Here, transmission calculations and STM break-junction (STM-BJ) experiments reveal that the lack of obvious interference effects in alkanes is directly correlated with the absence of methyl substituents that are commonly used to chemically stabilize the otherwise reactive silanes.
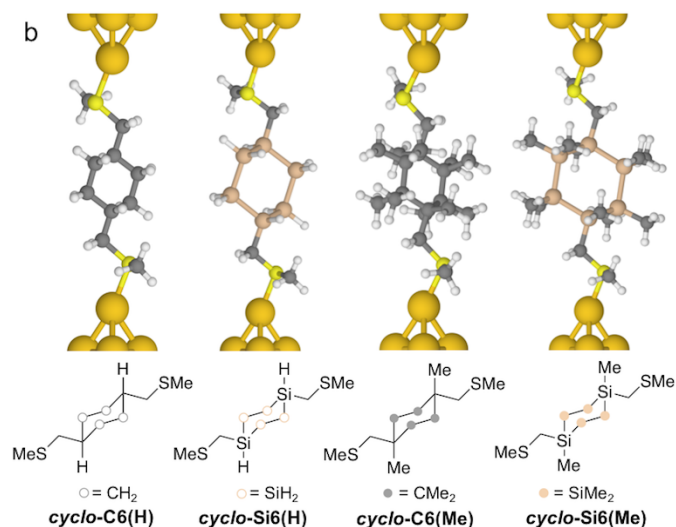

Figure 1. Optimized junction structures of non-methylated and permethylated (a) bicyclo[2.2.2]octane and bicyclo[2.2.2]octasilane and (b) cyclohexane and cyclohexasilane.

To probe the conductance suppression in alkanes and silanes we calculate the Landauer transmission of the eight junctions shown in Figure 1 using density functional theory (DFT). The molecules are optimized to 0.01 eV/Å using the PBE functional and DZP basis set as implemented in the Atomic Simulation Environment and GPAW.[38-40] The molecules are placed between two four-atom Au pyramids on Au(111) surfaces to form single-molecule junctions. Using DZ basis for the Au-atoms, the junctions are relaxed to 0.05 eV/Å with Au-atoms fixed. The transmission is calculated at the same level of theory using the non-equilibrium Green's functions formalism as implemented in Atomistix ToolKit.[41-43] Conformational analysis of all compounds is included in Supporting Information (SI) Part A; briefly, the longest equatorial chair conformations are likely to dominate the transport properties of the *cyclo*-C6 and *cyclo*-Si6 systems, while three similar conformations may all contribute to the transport through **C222** and **Si222** systems.

The four junctions based on the bicyclo[2.2.2]-motif shown in Figure 1a are structurally very similar with bridging (C-C-C-C or Si-Si-Si-Si) dihedral angles in the range of 13°-30° (Table S8). **Si222(Me)** is a clear case of destructive σ-interference, evident from the sharp anti-resonance in its transmission close to the Fermi energy shown in Figure 2a.[3-4] Both non-methylated compounds **C222(H)** and **Si222(H)** have high transmission, i.e., exchanging methyl substituents with hydrogens completely alleviates the destructive quantum interference in **Si222**. The methylated alkane **C222(Me)** does not display a clear antiresonance, but nonetheless its transmission is an order of magnitude lower than that of **C222(H)** around the Fermi energy.
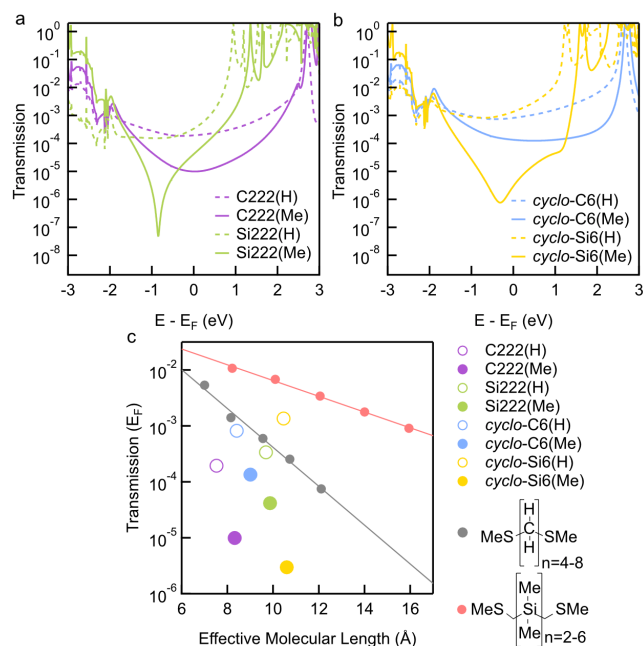
Figure 2. Calculated transmissions of non-methylated and permethylated (a) **C222** and **Si222**, and (b) *cyclo*-**C6** and *cyclo*-**Si6**. (c) Transmission at the Fermi energy plotted against molecular length (sulfur-sulfur distance), with linear alkanes and linear permethylated silanes.

The junctions of *cyclo*-**C6(H)**, *cyclo*-**Si6(H)**, *cyclo*-**C6(Me)**, and *cyclo*-**Si6(Me)** shown in Figure 1b are all equivalent chair conformers, where the dihedral angles

(C-C-C-C or Si-Si-Si-Si) across the ring are between 47° and 58° (Table S8). The transmissions of these structurally similar junctions are shown in Figure 2b. Similar to **Si222(Me),** the transmission of **Cyclo-Si6(Me)** is suppressed over a broad energy range around the Fermi energy due to an antiresonance. The transmission of these compounds shows the same trend as the bicyclo[2.2.2] systems. The interference effect is completely removed in **cyclo-Si6(H)** and the transmission is similarly high in **cyclo-C6(H)**; the transmission of **cyclo-C6(Me)** is approximately an order of magnitude lower but does not show a clear antiresonance. The transmission of other conformations of the cyclohexyl compounds are discussed in SI part A.

The bond lengths, bond angles, and dihedral angles (see Table S8) of the molecules are only minimally affected by replacing hydrogen with methyl substituents; the electronic transmission, on the other hand, is dramatically affected by this chemical change. Plotting the transmission at the Fermi energy against length in Figure 2c underlines this difference. We systematically predict the permethylated cyclic and bicyclic compounds to have lower conductance than their non-methylated counterparts.

The missing interference in the non-methylated compounds correlates with a change in their molecular orbitals. Shown in Figure S9 and S10, the highest occupied molecular orbital (HOMO) and HOMO–1 interchange when going from permethylated to non-methylated versions of the molecules. It has previously been demonstrated for π-conjugated systems that an interchange in symmetry of two frontier orbitals can induce (or remove) destructive quantum interference.[44-45] The donor character of the methyl substituent perturbs the electronic structure in a way that induces destructive interference. Our results demonstrate that σ-interference is as sensitive to chemical substitution as π-interference,[46-50] and suggest that it may be possible to rationalize the σ-interference effect with molecular orbitals.

In recent work, we found that the primary structural parameter behind the interference in saturated molecules is the constrained cisoid dihedral angles.[1, 3] We reexamine this behavior with transmission calculations for molecules where the backbone dihedral angles are systematically varied. For non-methylated and permethylated linear silanes and alkanes (Figure S6), as well as the four bicyclo[2.2.2] systems (Figure S7), the dihedral angle dependence of the transmission found in previous work[1, 3] remains.

All the permethylated systems considered here exhibit some degree of transmission suppression. As seen in previous work there are clear antiresonances in the permethylated silicon systems;[3] antiresonance-like behavior is also seen in the transmissions of permethylated alkanes at certain dihedral angles (Figure S6 and S7), but it remains unclear if the transmission can be fully switched off near the Fermi energy in a realistic carbon-based molecule by σ-interference. The missing antiresonances are likely to be cases of partial destructive interference. This has been found to happen due to the antiresonance energy being shifted to complex energy values, meaning that the transmission does not go to zero at a real energy.[51-53]

To further verify these results, we synthesized and characterized the electron transport properties of **C222(H)**, **Si222(Me),** **cyclo-C6(H)**), and **Cyclo-Si6(Me)**. Peralkylated cyclic silanes are traditionally synthesized using the alkali metal-facilitated Wurtz-type coupling reactions.[54] However, this route to cyclosilanes has yields that are extremely low. Potassium *tert*-butoxide was employed to cleave the trimethylsilyl (TMS) group.[55] We convert the TMS substituted cyclohexasilane[56] into **cyclo-Si6(Me)**, a mixture of *cis* and *trans* isomers in a 1:3 ratio. The *trans* isomer was selectively crystallized in diethyl ether at –30 °C (for the crystal structure see SI Fig. **S7**). Synthetic details and NMR characterization of **cyclo-Si6(Me)**, **cyclo-C6(H)**, and **C222(H)** are provided in SI Part C, D. We have previously reported the details for synthesis of **Si222(Me)**.[4] The non-methylated silanes (**Si222(H)** and **cyclo-Si6(H)**) and the permethylated alkanes (**C222(Me)** and **cyclo-C6(Me)**) were not attainable. Synthesis of cyclohydrosilanes is not straightforward and constitutes a substantial challenge for the development of improved synthetic methods.[57]

We apply the STM-BJ technique to measure the conductance of these molecules by repeatedly breaking and forming gold point contacts in the presence of a solution of target molecule in 1,2,4-Trichlorobenzene.[58-59] We collect thousands of conductance-versus-displacement traces and generate 1D and 2D conductance histograms without any data selection. These are shown in Figure 3. We find that all four molecules show well-defined conductance peaks below $1G_0$, and we determine the molecular conductance by fitting a Gaussian function to the peaks in Figure 3a. Moreover, the 2D conductance histograms do not indicate significant conductance switching during the junction elongation. Taken together, this indicates that different transport properties of the four molecules are due to their different structural compositions, rather than conformational fluctuations during the measurement. In agreement with the calculated transmission, we find that **cyclo-C6(H)** and **C222(H)** both have a higher conductance than **cyclo-Si6(Me)** and **Si222(Me).**

Plotting experimental conductance against calculated molecular length in Figure 3b reveals interesting trends. Both **cyclo-C6(H)** and **C222(H)** are shorter than the linear alkane with equivalent number of atoms (n=6, Fig. 2c) and have slightly lower conductance, so evidently there is some degree of conductance-suppression compared to linear alkanes. **Si222(Me)** and **Cyclo-Si6(Me)** are both shorter than the equivalent permethylated linear silane (n=4, Fig. 2c) and, in good agreement with calculations, the conductance is around an order of magnitude lower. All four compounds reported here are effective single-molecule insulators because they are very short molecules with low conductance well below the linear alkane decay

line. However, σ-interference in permethylated silanes offers a much more potent suppression of the conductance compared with non-methylated alkanes where the interference effect is missing.
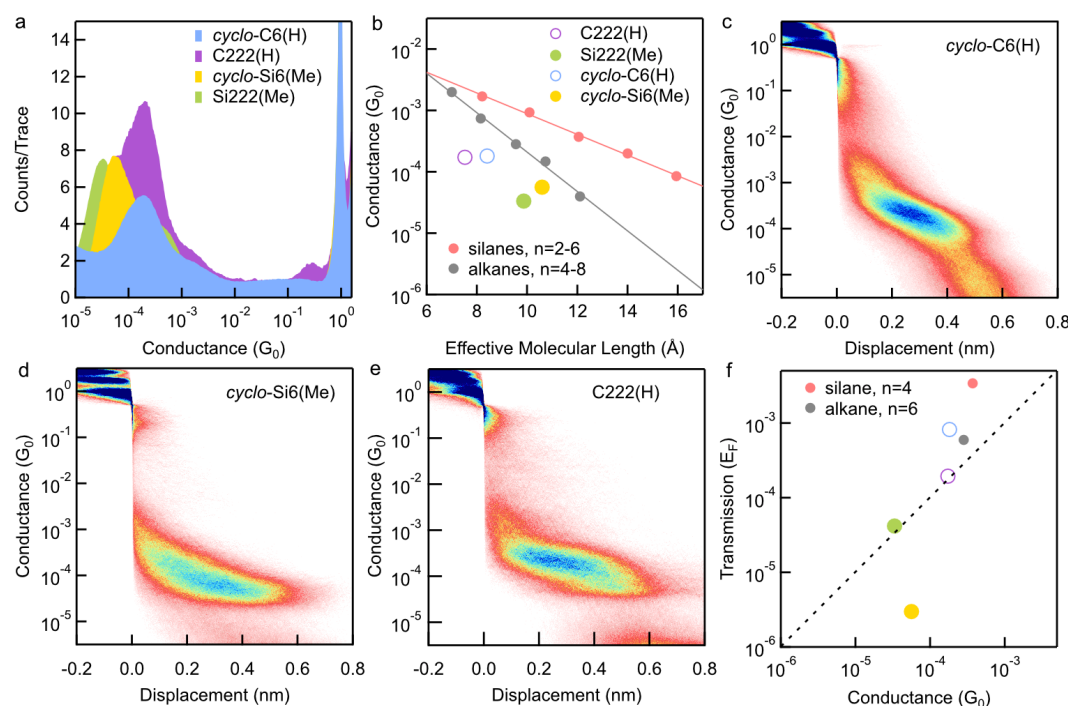
Figure 3. (a) Logarithm-binned 1D conductance histograms of *cyclo*-**C6(H)**, **C222(H)**, *cyclo*-**Si6(Me)**, and **Si222(Me)**, compiled from thousands of measured traces without any data selection. (b) Measured conductance values plotted against the molecular length (sulfur-sulfur distance from DFT-optimized structure) in comparison with linear alkanes and permethylated silanes (structures in Figure 2c). 2D conductance-displacement histograms of (c) *cyclo*-**C6(H)**, (d) **cyclo-Si6(Me)**, and (e) **C222(H)** created by aligning all the measured traces to zero displacement at 0.5 G_0. See Ref. 4 for 2D histogram of **Si222(Me)**. (f) Calculated transmission at the Fermi energy plotted against the experimental conductance.

In Figure 3f, the transmission at the Fermi energy is plotted against the experimental conductance for direct comparison. The good qualitative agreement supports the conclusions based on the calculations that it is the change of substituents that gives the different conductance, less so the difference between carbon and silicon in the molecular backbone. The transmission at the Fermi energy is much lower for ***Cyclo*-Si6(Me)** than for **Si222(Me)**, which is not supported by the experiments. We attribute this difference to the single-molecule conductance being extremely sensitive to the experimental Fermi energy when an antiresonance is present.[3, 60]

A recent study by Gryn'ova and Corminboeuf found that the transmission of carbon-based nanothread oligomers increases when going from secondary to quaternary carbon in the molecular backbone, e.g., from a non-methylated to a permethylated alkane.[61] Here we have demonstrated the opposite trend for short cyclic and bicyclic alkanes and silanes. Upon going from non-methylated to permethylated carbon the transmission of the ***cyclo*-C6** and **C222** systems is reduced significantly due to the induction of destructive quantum interference. In SI part G, we show that for linear alkanes and silanes in transoid conformation, the transmission is also lowest for the permethylated systems. Unlike in more complex carbon

nanothread oligomers,[61] permethylation consistently reduces the conductance in short saturated linear, cyclic, and bicyclic alkanes and silanes.

We have previously studied the current density in linear silanes, and methylation produces no noticeable change in the transport pathway.[14] Yet in the delicate balance that exists when saturated molecules have reduced dihedral angles, this subtle substituent effect makes a huge difference.

Conceptually, it is surprising that a substituent that does not play a role in the transport pathway and is not a strong electron donor/acceptor should influence the conductance to such a large extent. This remarkable susceptibility of the charge transport properties of saturated molecules is unexplored, and may be a viable way of chemically controlling the charge transfer properties of saturated molecular bridges.

To summarize, we have found that methyl substituents are important for introducing destructive quantum interference in the σ-system of methylthiomethyl-functionalized silanes. Consequently, non-methylated alkanes and silanes do not exhibit σ-interference. This work suggests

that organic synthesis could open the door to quantum interference based single-molecule insulators with cyclic and bicyclic alkanes as the molecular backbone.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

Conformational analysis, Transmission of linear and 222 compounds under torsion, synthetic procedures, NMR characterization of compounds, crystal structure of *cyclo*-Si6(Me), molecular orbitals, transmission of linear molecules.

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NOTES

The authors declare no competing financial interest.

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