# Stereo-isomerism controls surface reactivity; 1-chloropentanepairs on Si(100)-2×1

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# **Electronic Supplementary Information.**

## 1.0 Experimental

Experiments were carried out at room temperature in ultra high vacuum (base pressure  $5 \times 10^{-9}$  Pa) using an RHK400 Scanning Tunneling Microscope (STM). The STM was operated in the constant–current mode. All measurements were made with a tunneling current of 0.2 nA. STM tips were made by a DC electrochemical etch of 0.25 mm diameter polycrystalline tungsten wire in a 2M NaOH solution under control of a "Schrödinger's Sharpener" (Obligato Objectives, SS03).

Silicon samples (Virginia Semiconductor) were phosphorous doped (n-type, 0.01-0.02  $\Omega$ cm, 250  $\pm$  25  $\mu$ m in thickness). Samples were cleaned in UHV by several cycles of direct current heating to 1240 °C for ~1 min under computer control. The STM images of the surface cleaned in this way showed a (2×1) reconstruction and < 0.2 % of surface defects.

The adsorbate 1-chloropentane (99.9 % pure, from Aldrich) was subjected to repeated freezepump-thaw cycles before being introduced to the UHV chamber through a leak valve for background dosing. Exposures are reported in Langmuir ( $1L = 1 \times 10^{-6}$  Torr s) measured at an uncorrected ion-gauge (Granville Phillips 274) calibrated for N<sub>2</sub>. The corrected doses would be ~ $10 \times$  lower than the stated doses [1].

For studies of electron-induced reaction the STM tip was positioned over a silicon dimer at which the chlorine ends of adjacent chloropentane molecules were physisorbed. The STM feedback loop was switched off and a current of 0.2 nA was maintained at a surface bias of +1.6 V until reaction occurred.

## 1.1 Detailed measurements of the rate of thermal reaction.

For studies of thermal reaction molecules were dosed onto a clean surface maintained at a temperature of 325 K using a bulb heater. Some 113 CP-pairs at the ends of lines (A) and 105 CP-pairs from the middle of lines (S) were observed over a period of 230 minutes using sequential images obtained with non-uniform time intervals. Figure S1 shows a comparison of rates of reaction for A both in isolation, and also at the two ends of a line (close to the buckled dimer, and at the end of a line far from the buckled dimer), a schematic (Fig. S1, right) shows the three positions of A referred to. The measured rates of reaction are identical within experimental uncertainties for A in isolation, and for A within a line close to the end-of-line buckled dimer (the data set shown is different from that given in the main text, and was obtained at 308). Although the rate of reaction *is* distinguishably different for A within a line, far from the buckled dimer, the derived activation energies cannot be distinguished within their uncertainties, and we therefore chose to treat all three species together in our analysis.

The uncertainties in the final derived activation energies for A and S have two components, which are fundamentally different, *relative* and *absolute* uncertainties.

(1) *Relative* uncertainties arise between measurements of  $E_a$  and are due only to uncertainties of the slopes of the straight line fits, which give the first order rate-constants. Conversion of the first order rate constants to activation energies,  $E_a$ , requires that a value of the A-coefficient be assumed. As the reactions studied are for identical molecules on the same surface in slightly different configurations it should be an excellent assumption that the A-factors for the reactions are identical. The relative uncertainties were calculated assuming an A-factor of  $10^{13}$  and arise only from the difference in the measured first order rate constants. The relative uncertainties in the activation energies are of order 3 meV.

(2) *Absolute* uncertainties in the activation energies derive from the uncertainty in the value of the A-factor to be used. A usual approximation for the A-factor and its uncertainty is  $10^{11}$  to  $10^{15}$ , and recent work on halogenated molecules on a silicon surface <sup>2</sup> showed that this is an excellent approximation. Using this range of A-factors gives an absolute uncertainty of  $\pm 0.13$  eV which must be applied to all derived activation energies in the same sense.



FIG S1. Thermal reaction of an A-pair in various environments. (Left) Rates of thermal reaction obtained by plotting the natural logarithm of survival {N(t)/N} against time [ N is a normalizing constant of magnitude 1, and the same dimensions as N(t) ]. Blue line (triangles): A-pair far from the buckled dimer, B. Pink line (squares): A-pair close to the buckled dimer, B. Brown line (diamonds): A-pair in isolation. The error bars are derived from the standard error ( 1/square root of the count ). (Right) Schematic. The positions of the three types of A-pairs, measured at left, are indicated – the length of the line of CP-pairs was not important in these measurements.

## 1.2 Electron induced reaction thresholds.

Electron-induced reaction thresholds were established for both A and S. For A, electron-induced reactions could be measured for isolated A-pairs and for A-pairs in a line. For electron-induced reaction, isolated S-pairs were observed to convert to A-pairs before reacting, therefore electron induced reactions of S could *only* be studied within a line. For thermal reaction, the case was less clear; thermal switching of isolated S-pairs is always occurring at room temperature, it is therefore not possible to deduce whether direct thermal reactions of S occur (out of a line), or whether (as in the electron-induced case), S converts to A before reaction.

## 1.3 Line profiles of A and S

Line profiles of A and S pairs in a line were measured along the axes shown in Fig. S2. The calculated configurations for A and S have different geometries of the alkyl tails. This difference shows up in the line profiles, where the line profile of S is symmetric about the centre point, while that of A is not.



**Figure S2.** Height profiles of symmetric and asymmetric CP pairs. (a) STM image ( $V_{surf} = -1.5 V$ , 0.2 nA, 75×75 Å<sup>2</sup>) after dosing with 0.3 L chloropentane (1 x 10<sup>-9</sup> torr, 30 s). (b),(c) Height profiles taken along feature 'A' and feature 'S' in a line of three CP pairs are shown in (a). The asymmetric and symmetric shapes are evident in the line profile at its highest point. The *A*-pair is asymmetric about the centre-line shown in (b) as a red dashed line. The *S*-pair is symmetric about the centre-line shown in (c) as a red dashed line. The average height of the feature 'A' and 'S' compared to bare Si are 1.6 Å and 1.3 Å respectively at this imaging bias.

#### 1.4 Switching between A and S

In our room temperature measurements, switching between *A* and *S* was often observed to have occurred between different STM images taken sequentially (therefore on a time-scale of minutes). These switching events were spontaneous and thermally induced, they did *not* take place while the tip was scanning the molecules – processes that occur under the tip are distinguishable because such processes result in an image that shows a "half moon" shape.

An example of switching between S and A is shown in Fig. S3. The principal observable change is not in the configuration of the molecules, but in the brightness and position of the adjacent buckled dimer. As can be seen in the figure, for A, the "up" atom of the adjacent buckled silicon dimer is close to the CP-pair, and very bright. In contrast, for S, the "up" atom of the adjacent buckled silicon dimer is away from the CP-pair, and is not much brighter than the surrounding surface silicon atoms.



**Figure S3. Switching of symmetric and asymmetric CP pairs.** (a, b) Show the same CP-pair imaged at different times at room temperature. The feature is observed to switch reversibly between the asymmetric 'A' (a) and symmetric 'S' (b) configurations shown. The centres of two adjacent silicon-dimer rows are indicated with black dashed tags above and below the images. The position of the adjacent surface buckling (indicated by B in the figure) changes, being closer and brighter to the adsorbed molecules for A than for S. Schematic representations are given for A (c) and S (d). Cl-atoms are shown green, hydrocarbon tails as grey, "up" silicon atoms as open circles, "down" silicon atoms as filled circles and the buckled silicon atom is labeled "B". The centers of the two adjacent silicon-dimer rows are indicated with black dashed tags above and below the schematics

We attribute the lack of switching of *S*-pairs in a line to steric hindrance from the neighboring CP-pair which prevents flipping of the pentane tail of the molecule (this hindrance is absent at the ends of the line,). The long-term stability of the CP-pairs in a line allowed us to study the role of stereoisomerism on reactivity as described below.

# 2.0 Theory

The level of theory used in this work is known to yield accurate adsorption geometries, and energetic (see for example, reference 3), but is also known to be insufficient to recover the phenomena of buckling which is evident in the experimental images. Previous work on pairs of 1-fluoropentane molecules *was* able to recover this surface buckling [4], but to do so required that we reduced the system to a  $1 \times 6$  super-cell and the molecules to fluoro*methane*. For this reduced system we performed DFT simulations at the hybrid level using the HSE03 [5] hybrid functional implemented in VASP [6], including a dopant phosphorus-atom in the super-cell. In this simulation, the image became brighter at the buckled site, B, due to local charging [7]. The high cost of these calculations make them impractical for the simulation of large systems using currently available computers.

### 2.1 Electronic structure calculations

Ab-initio calculations were made using the Vienna Ab-initio Simulation Package (VASP) [8, 9] installed at the SciNet supercomputer [10]. Using VASP 5.2.11, the ground state electronic structure of one or two molecules on Si(100)-2×1 was simulated with ultrasoft pseudopotentials and the PBE parameterization [11] of the exchange-correlation potential, using the semi-empirical DFT-D method of Grimme [12], as implemented in VASP. We simulated a 8×6 supercell for *A* and a 6×6 supercell for *S*. The Si(100) slab contained 8 layers, the bottom layer of which was passivated with hydrogen. The high number of layers was necessary to represent the high elasticity of the silicon lattice. Due to the large number of atoms we limited the simulations of the relaxed geometry to one *k*-point at the center of the surface Brillouin zone. The molecular adsorption sites were determined by placing the bent molecules about 3 Å above the surface plane, with the molecular backbone parallel to the surface. The molecule and four surface layers were then fully relaxed until the forces on individual ions were less than 0.02 eV/Å.

### 2.2 Geometries

Two stable configurations of CP-pairs were found, A and S; their configurations were given in the main Communication; they are shown below in figures S4 and S5. Table ST1 gives the distances between the Cl-atoms of each chloropentane molecule, and the silicon atom beneath.

It is the Cl-atom closest to the surface that reacts in the rate determining step. This is also the Cl-atom that is closest to the buckled dimer. As can be seen, the difference between the distance between the closer Cl-atom and the underlying Si-atom for A and S, differs by less than 0.05 Å.

**Table ST1. Chlorine—Silicon bond lengths for the A-pair and S-pair.** The bond lengths shown were calculated with Grimme's semi-empirical corrections for van der Waals attraction, on the correct surface symmetry for each (see Table ST2 for adsorption energies).

System	Geometry on Si(100)- <i>p</i> (2×2)		Geometry on Si(100)- <i>c</i> (4×2)	
	Si-Cl <sub>far</sub> /Å	Si-Cl <sub>close</sub> / Å	Si-Cl <sub>far</sub> /Å	Si-Cl <sub>close</sub> / Å
A-pair			5.23	2.47
S-pair	4.44	2.44		

#### 2.3 Adsorption energies

Adsorption energies were calculated for both *A* and *S* on both the Si(100) $c(4\times2)$  and Si(100) $p(2\times2)$  surfaces. In the absence of adsorbate the energy of the two surface configurations is known to be almost identical. The molecular physisorption actually occurs at the dynamically flipping surfaces of Si(100)-2×1, and physisorption of a CP-pair results in pinning of some five or six silicon-dimers close to the adsorbates. Local to the *A* adsorbate silicon-dimers are pinned in the  $c(4\times2)$  configuration and local to the *S* adsorbate silicon-dimers are pinned in the  $p(2\times2)$  configuration (as highlighted in Table ST2).

Table ST2. Calculated physisorption energies of the A-pair and S-pair on two symmetries of the Si(100) surface; p(2×2) at left, c(4×2) at right. Calculations of physisorption geometries and energies were made with and without Grimme's semi-empirical corrections for van der Waals attraction. The error of integration is believed to be ~0.01 eV. Bold entries correspond to the best calculation for the correct surface geometry.

System	<i>E<sub>ads</sub></i> on Si(100)- <i>c</i> (4×2) / eV		<i>E<sub>ads</sub></i> on Si(100)- <i>p</i> (2×2) / eV	
	with vdW	without vdW	with vdW	without vdW
A-pair	1.20	0.63	1.29	0.55
S-pair	1.19	0.55	1.23	0.42

The calculated adsorption energies were surface dependent in the absence of van der Waals corrections. With van der Waals corrections, the physisorption energies of the *A*-pair and *S*-pair are found to be within 30 meV of one another, in good agreement with experiment.

## 2.4 Energy barriers

Calculation of energy barriers to  $A \leftrightarrow S$  switching were made using the Climbing Image Nudged Elastic Band method [13], and included semi-empirical corrections for dispersion interactions using the method of Grimme [12], as implemented in VASP 5.2.11.

The system to be modeled,  $A \leftrightarrow S$  switching, occurs on a Si(100)-2×1 surface, in which only dimers close to the adsorbate are pinned. All calculations were made with periodic boundary conditions, and therefore required a supercell with a repeating surface symmetry.

Since we cannot simultaneously accommodate the differing surface-symmetries that apply to A and S, we made an estimate of the energy barrier as follows. We first calculated the minimum energy path for  $A \leftrightarrow S$  on a  $p(2 \times 2)$  symmetry surface. The resulting energy barrier was around 0.2 eV. Next, we allowed for the additional energy required by dimer flipping by adding 0.1 eV / Si-dimer [14]. We therefore estimate the total energy barrier for  $A \leftrightarrow S$  (including the flipping of five adjacent Si-dimers) as 0.7 eV. This constitutes a rough upper estimate of the theoretical energy-barrier for  $A \leftrightarrow S$ , including the motion of the substrate, since cooperative effects could lower the total energy-barrier.

## 2.5 Simulation of images

The experimental STM images shown in Figures S4 and S5 were obtained at a surface bias of -1.5 V and with a tunneling current of 0.2 nA. Simulated STM images were generated, using the same -1.5 V surface bias, from the electronic structure of the fully relaxed systems by plotting iso-density contours. The value of the electron density of states was adjusted so that the distance of the contour from the silicon surface dimers was held constant at about 6 Å, which corresponds to the set distance to the surface under the experimental tunneling conditions [15]. Images were simulated using the Tersoff-Hamann approach [16], as implemented in bSkan [17].

Simulated and experimental images are compared below in Figures S4 and S5. The simulated images fail to reproduce the experimental observations because, *inter alia*, the calculations do not recover the "buckled dimer", which is adjacent to the *A* and *S* configurations, and therefore do not recover the brightness in the experimental images which is at one side of the CP-pair (at left, as shown), on a silicon-dimer row adjacent to the adsorbates. In the figures below the positions at which the brightness appears in the STM-images due to the buckled dimer is indicated by a white dot on the lower set of images of each panel. The images were calculated using an  $8 \times 6$  supercell for *A* and a  $6 \times 6$  supercell for *S*. The images have been tiled in the figure. The geometry of the substrates are shown, fading from right to left.



**Figure S4. Simulated and Experimental STM images of an A-pair on Si(100)c(4×2).** Experiment and simulation were obtained using a bias of 1.5  $V_{surf}$ . Top row – Experimental STM image (tiled). Middle row – Simulated STM image (tiled). Bottom row – Simulated STM image (tiled), with the positions of the Buckled dimer indicated by white circles. All images are overlaid onto the surface used for the simulations, the images are faded to the right to show the surface geometry, atoms are shown with van der Waals radii. (Si "up" atoms yellow, Si "down" atoms brown, Cl-atoms green, C-atoms grey, H-atoms white)



**Figure S5. Simulated and Experimental STM images of an S-pair on Si(100)p(2×2).** Top row – Experimental STM image (tiled). Middle row - Simulated STM image (tiled). Bottom row – Simulated STM image (tiled), with position of Buckled dimer indicated by white circle. All images are overlaid onto the surface used for the simulations, faded to the right to show the surface geometry, atoms are shown van der Waals radii. (Si "up" atoms yellow, Si "down" atoms brown, Cl-atoms green, C-atoms grey, H-atoms white)

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