

## Asymmetric Induction at a Silicon Surface

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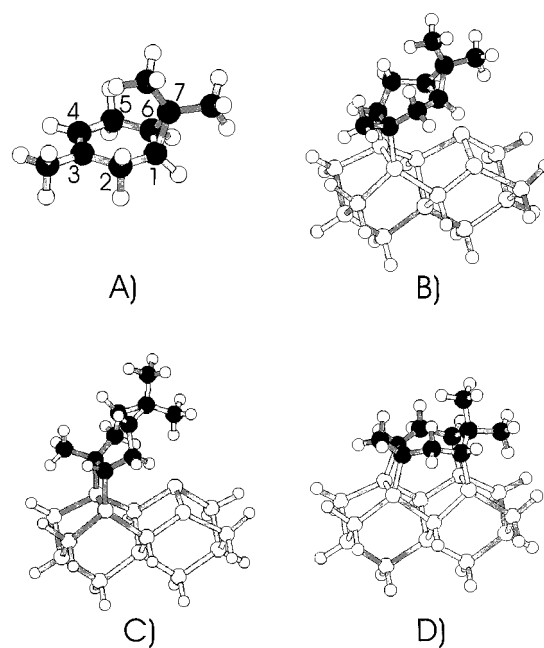
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Received January 11, 1999

Recently, several groups have reported the modification of silicon surfaces via covalent attachment of organic molecules.<sup>1–9</sup> These functionalized surfaces, produced by adsorption in ultrahigh vacuum or various wet chemical methods, have the potential to greatly expand the capabilities of silicon-based microelectronic devices. For example, organically modified surfaces may enable the development of sensors capable of complex molecular recognition tasks such as the ability to discriminate between different enantiomers of the same compound. Progress in this area will require the design of enantiospecific reactions with the silicon surface. In this report we provide the first example of such a reaction. We use scanning tunneling microscopy (STM) to demonstrate that the adsorption of 1*S*(+)-3-carene on the Si(100) surface is enantiospecific, resulting in the formation of a chiral surface.

Previous studies have shown that STM is uniquely capable of directly determining the absolute chirality of individual adsorbed molecules.<sup>10,11</sup> *trans*-2-Butene was observed to undergo a [2+2] cycloaddition to the Si(100) surface leading to the formation of (*R,R*) and (*S,S*) enantiomers that are clearly distinguished.<sup>10</sup> However, in that case, reaction at both the *Re* and *Si* faces of the molecule was equally likely so that equal numbers of the two possible enantiomers were formed, resulting in a macroscopically achiral surface. One approach to achieving enantioselectivity in these reactions is to introduce steric hindrance at one of the faces. To test this hypothesis we studied the reaction of 1*S*(+)-3-carene (3,7,7-trimethylbicyclo[4.1.0]hept-3-ene), a naturally occurring bicyclic alkene belonging to the terpene family, with the clean Si(100) surface. In this molecule a *gem*-dimethyl group significantly restricts access to one face of the double bond (Figure 1A).

The Si(100) surface consists of rows of Si dimers, with two dangling bonds per dimer. Simple alkenes have been shown to react readily with the dimers of this surface in a formal [2+2] cycloaddition, forming two Si–C bonds.<sup>12–16</sup> Carene is expected



**Figure 1.** Optimized structures obtained using the B3P86 density functional and the 6-31G\* basis set. The isolated 1*S*(+)-3-carene molecule (A) is shown along with three possible bonding geometries on the 15 Si atom cluster model of the Si(100) surface: (B) unbridged, (C) reverse unbridged, and (D) bridged.

to react with the surface in a similar manner, its double bond reacting with a single Si dimer as in Figure 1B. Adsorption introduces two additional chiral centers at positions C3 and C4. Addition at the face of the molecule that is partially blocked by the *gem*-dimethyl group results in the formation of a different adsorbed enantiomer (Figure 1C). For the single dimer configuration shown in Figure 1B, it is possible for the molecule to undergo further reaction, opening the cyclopropyl ring on the molecule and forming two additional bonds to the silicon surface (Figure 1D).

Optimized structures and adsorption energies for the configurations of Figure 1 were obtained using gradient corrected density functional methods (B3P86 with the 6-31G\* basis set),<sup>17</sup> employing a 15 Si atom cluster to model the Si(100) surface. Aside from the two dimers, all other edge Si atoms were terminated with hydrogen atoms, whose positions were fixed along bulk Si bond directions in order to prevent excessive relaxation of the cluster. Similar approaches have been used previously to successfully treat adsorption on Si(100) surfaces.<sup>18–21</sup> Adsorption energies are extracted from the total energy of the molecule/cluster system by subtracting the energy of the separated molecule and cluster. The two unbridged structures (bound to a single dimer) have similar adsorption energies, 2.25 (**1B**) and 2.07 eV (**1C**), while the bridged configuration is predicted to be substantially more stable with a calculated adsorption energy of 3.96 eV.

The STM studies were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure below  $5 \times 10^{-11}$  Torr. This pressure is sufficiently low to maintain a clean surface for a day or more. A clean Si(100) surface was obtained by flashing a well-

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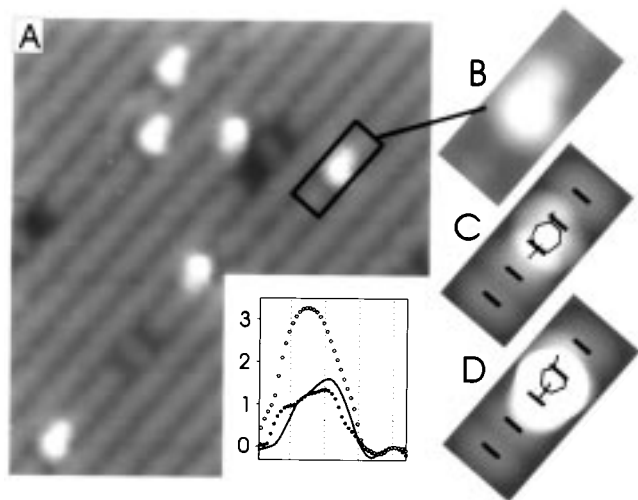
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**Figure 2.** (A) STM image ( $100 \text{ \AA}^2$ ,  $-2 \text{ V}$ ,  $100 \text{ pA}$ ) of  $1S(+)$ -3-carene molecules on Si(100). The inset shows the measured height profile (solid line) through a carene molecule along with calculated profiles for bridged (filled circles) and unbridged (unfilled circles). (B) Enlarged view of a single adsorbed carene molecule. (C) Simulated image for the bridging geometry of Figure 1d. (D) Simulated image for the unbridged geometry of Figure 1b. The gray scale in the two simulated images is the same. The saturation (to white) of the unbridged simulated image reflects the much higher maximum predicted for that structure.

degassed crystal (Virginia Semiconductor, n-type,  $0.005 \text{ } \Omega \text{ cm}$ ) above  $1200 \text{ }^\circ\text{C}$ . Carene (Aldrich, 99%) was degassed by performing several freeze–pump–thaw cycles.

Figure 2A shows an STM image of the Si(100) surface after exposure to a low dose of  $1S(+)$ -3-carene molecules. The bar-like structures running diagonally across the images are the silicon dimer rows. The six bright protrusions are due to adsorbed carene molecules. The protrusions all have a characteristic appearance, consisting of a bright round maximum with a smaller tail asymmetrically positioned off to one side. Four of the molecules are of the same orientation while the other two exhibit the same features but rotated by  $180^\circ$ . The observation of these two different orientations ensures that the tail is not a tip shape artifact. By comparison with the calculated geometries in Figure 1, the larger protrusion can be assigned as primarily due to the *gem*-dimethyl group while the smaller protrusion is due to the C3 methyl. While two orientations of the molecule are observed in the image, these are identical structures related by a rotation and hence with the same chirality. Inspection of several hundred molecules indicates that reaction at one face of the molecule is indeed blocked, confirming that the reaction is enantiospecific. As the observed chirality of the adsorbed molecules is inconsistent with the bonding geometry of Figure 1C we can conclude that this product is not obtained. Recalling that the calculated adsorption energies for the two unbridged structures are nearly equal, it is evident that asymmetric induction has been achieved as a consequence of kinetic rather than thermodynamic factors.

To distinguish between the bridged (Figure 1D) and unbridged (Figure 1B) bonding configurations, the observed molecular features were compared to simulated images for these two geometries. The simulated images are obtained from constant

electron density contours based on the highest occupied molecular orbitals. Within the Tersoff–Hamman approximation,<sup>22</sup> these electron density contours correspond to a constant current STM image. We have previously demonstrated the success of this approach in simulating images of adsorbed benzene on Si(100).<sup>21</sup> While both of the simulated images exhibit the correct chirality, the calculated image for the bridged geometry (Figure 2C) is seen to give better agreement with the observed features. In the simulated image for the unbridged configuration (Figure 2D) the C3 methyl protrusion which gives the image its asymmetric appearance is relatively less distinct with the image being dominated by the protrusion due to the C7 dimethyl group. As seen by the height profiles shown in the inset in Figure 2, the largest distinction between the two simulated images is in the predicted maximum height with respect to a clean dimer— $1.3$  and  $3.3 \text{ \AA}$  for the bridged and unbridged configurations, respectively. The average maximum height of the molecules measured in the STM images varies somewhat with bias voltage,  $1.71 \pm 0.12 \text{ \AA}$  at  $-2 \text{ V}$  and  $1.37 \pm 0.10 \text{ \AA}$  at  $-1.5 \text{ V}$ . The good agreement between the measured and calculated profiles suggests that the molecule adopts the bridging geometry. We note that comparison of infrared spectra in the C–H stretching region with calculations for both geometries did not allow the bonding configuration to be definitively assigned.

If in fact the molecule adopts the bridging configuration, it is likely that the unbridged configuration is a metastable precursor to the more stable geometry. Unlike the case of benzene/Si(100), where a slow conversion from a single dimer to bridging geometry was observed at room temperature,<sup>8,9</sup> no time dependent change in the adsorbate bonding geometry has been observed here. Direct adsorption into the bridge state at room temperature would imply that the barrier for breaking the cyclopropyl ring and forming two additional Si–C bonds is less than  $0.85 \text{ eV}$ . The cyclopropyl ring opening is somewhat surprising as cyclopropane has been reported to not react with the Si(100) surface.<sup>23</sup> Evidently, favorable positioning of the single dimer-bound species together with the opportunity to make repeated attempts at cyclopropyl–dimer reaction leads to ring opening in the case of carene. We speculate that similar ring opening reactions may serve to anchor various other organic molecules on Si(100).

In summary, we have shown that the addition of  $1S(+)$ -3-carene to the Si(100) surface is enantiospecific, resulting in the formation of a chiral surface. This is a significant step toward the design of surfaces capable of chiral recognition. This work also demonstrates that STM is a useful tool for determining the enantioselectivity of a reaction and, together with calculations of the geometric and electronic structure, can be used to extract details of the bonding geometry for a relatively complex molecule. In the present case,  $1S(+)$ -3-carene is most likely adopting a bridging geometry involving an addition reaction of the double bond followed by opening of the cyclopropyl ring, resulting in the creation of four new asymmetric centers with complete enantioselectivity. This bonding configuration is predicted to be highly stable, suggesting that carene-saturated Si(100) surfaces may be stable to air exposure.

JA9900858

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