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# Structure and Bonding of Ordered Organic Monolayers of 1,5-Cyclooctadiene on the Silicon(001) Surface

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The interaction of 1,5-cyclooctadiene with the (001) surface of silicon has been investigated using scanning tunneling microscopy, Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and *ab initio* computational chemistry techniques. Scanning tunneling microscopy images reveal that 1,5-cyclooctadiene molecules adsorb onto well-defined lattice sites and that the molecules are highly ordered both translationally and rotationally. Fourier-transform infrared and X-ray photoelectron spectra show that bonding occurs without dissociation by breaking one  $\pi$  bond of the 1,5-cyclooctadiene molecule and the  $\pi$  bond of one Si=Si dimer of the reconstructed Si(001) surface, forming two new Si–C bonds. Only one of the two unsaturated bonds in each 1,5-cyclooctadiene molecule react, leaving one double bond exposed at the outermost surface. Computational chemistry studies suggest that the surface-bound molecule involves rapid interconversions of several similar low-symmetry conformations.

## I. Introduction

In recent years, there has been a great deal of interest in the growth of organic thin films for a host of technological applications, including lithography, molecular electronics, non-linear optics, and biosensors. Most of these films are disordered due to a lack of control of the interfacial chemistry between the underlying substrate and the organic films. In recent reports,<sup>1,2</sup> we have shown that it is possible to form ordered organic monolayer films on the technologically-important (001) surface of silicon by utilizing the highly specific interaction between the  $\pi$  bond of unsaturated organic species and the  $\pi$  bonds of the Si=Si dimers that comprise the reconstructed Si(001) surface. Cleavage of the  $\pi$  bonds permits formation of two new Si–C  $\sigma$  bonds. Although some details of the bonding and adsorption mechanism are not yet clear,<sup>3–12</sup> scanning tunneling microscopy and infrared spectroscopy studies of cyclopentene on Si(001)<sup>1,2</sup> showed that the resulting films were well-ordered both translationally and rotationally, with the Si=Si dimer bond effectively acting as a template for controlling the locations and rotational orientation of the individual organic molecules. By using 4°-miscut Si(001) wafers it is possible to create films that retain this optical anisotropy on centimeter length scales.

To achieve well-defined growth of multilayer organic films it is necessary to utilize organic species containing more than one reactive functional group. Previous experiments with norbornadiene,<sup>2</sup> which has two unsaturated C=C bonds, found that adsorption occurred without dissociation but that the resulting films were poorly ordered. Here, we show that by using the molecule 1,5-cyclooctadiene (COD) it is possible to form highly ordered organic films in which one reactive group binds to the surface in a selective way, with a second reactive group exposed to the vacuum. The formation of highly ordered organic films from bifunctional organic compounds represents one method for controllably functionalizing the Si(001) surface and is the first step in the growth of ordered multilayer films.

## II. Experimental Section

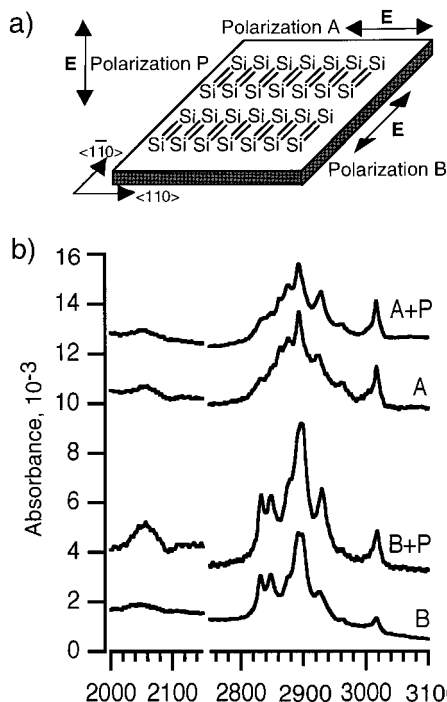
All experiments reported here were performed in ultrahigh vacuum (UHV) systems achieving base pressures of  $<1 \times 10^{-10}$  Torr. The surfaces were characterized by several techniques. Direct observation of adsorbed molecules and molecular layers was achieved using a home-built UHV scanning tunneling microscope (STM). Imaging of the molecules and molecular layers was most effective at sample bias voltages between  $-2.1$  and  $-2.4$  V, utilizing a tunneling current of 200 pA. Fourier-transform infrared (FTIR) absorption spectra were obtained using a multiple internal-reflection geometry and a Mattson RS-1 FTIR spectrometer coupled to a UHV system through BaF<sub>2</sub> windows with a cooled InSb detector. X-ray photoelectron spectroscopy (XPS) experiments were performed using a Physical Electronics system with a monochromatized Al K $\alpha$  source and a multi-channel detector array. For each type of experiment, samples were prepared and characterized completely *in situ*.

The 1,5-cyclooctadiene was purchased from Aldrich redistilled and 99+% pure. It was introduced into the chamber through a variable leak valve. Mass spectrometry did not show any significant contaminants. For the FTIR and STM experiments, a directed doser was used to minimize interactions with the chamber walls; as a result, the actual pressure at the sample face is higher than the chamber background pressure. Since these should be proportional to one another, however, chamber pressure was utilized as a measure of overall sample dose. All exposures reported here are nominal exposures based on background pressure in the chamber.

Clean Si(001) samples were prepared by annealing pieces of Si(001) wafers to 1475 K while maintaining the chamber pressure at  $<3 \times 10^{-10}$  Torr. This procedure produces a clean, well-ordered surface exhibiting a  $(2 \times 1)$  reconstruction.<sup>13</sup> Samples having two different levels of doping and two slightly different crystallographic orientations were used. Highly doped ( $<0.15$   $\Omega$ -cm resistivity, Sb- and P-doped) samples were used for STM and XPS experiments, while lightly doped ( $>5$   $\Omega$ -cm resistivity, P-doped) samples were used for infrared spectroscopy experiments to reduce free-carrier adsorption in the bulk. Two slightly different crystallographic orientations of Si(001) were used. On-axis samples were oriented to expose the (001) surface

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**Figure 1.** Infrared absorption of 1,5-cyclooctadiene layer on Si(100) for s- and p-polarized light: (a) definition of polarization directions; (b) absorption spectra obtained with s- and p-polarized light, showing spectral regions corresponding to the Si-H and C-H stretching regions.

with an accuracy  $\pm 0.5^\circ$ . On-axis samples have widely-spaced steps that are a single atom high. Across each single-height step the direction of the Si=Si dimer bond rotates by  $90^\circ$ , producing a surface containing equal amounts of these two different rotational domains of the dimers.<sup>13</sup> We also performed experiments using samples purposely miscut by  $4.0 \pm 0.5^\circ$  toward the  $\langle 110 \rangle$  direction. For such  $4^\circ$ -miscut off-axis ("vicinal") samples, the interactions between adjacent steps are sufficiently strong that pairs of single-height steps collapse to form steps that are two atoms high.<sup>14,15</sup> Because the rotational orientation of the Si=Si dimers is retained across these double-height steps, a precise miscut by  $2\text{--}5^\circ$  toward the  $\langle 110 \rangle$  or  $\langle 1\bar{1}0 \rangle$  directions produces "single-domain" samples having almost entirely one rotational domain of the Si=Si dimers. Thus, it is possible to control the orientation of the Si=Si dimers on the sample by controlling the macroscopic crystallographic orientation of the sample surface.

### III. Results

Infrared absorption spectra reveal a great deal about the interaction of 1,5-cyclooctadiene with Si(001). Using  $4^\circ$ -miscut Si(001) wafers and polarized light, it is possible to probe the absorption along specific crystallographic directions, as depicted in Figure 1a. S-polarized light has its electric field in the surface plane; we refer to orientation "A" as the orientation in which the electric field is perpendicular to the Si=Si dimer bond and orientation "B" as that in which the electric field is parallel to the Si=Si bond axis. P-polarized light has a component of the electric field perpendicular to the surface and another component parallel to the surface. In the geometry utilized here, these two components have nearly the same magnitude. Additionally, the in-plane component of the electric field is nearly identical for s-polarized and p-polarized light.<sup>16</sup>

Figure 1b shows FTIR spectra for s- and p-polarized light for the two different orientations of the Si=Si dimers after exposure to 5 langmuirs ( $3 \times 10^{-8}$  Torr for 166 s) of 1,5-cyclooctadiene at  $50\text{--}100^\circ\text{C}$ . The spectra were measured

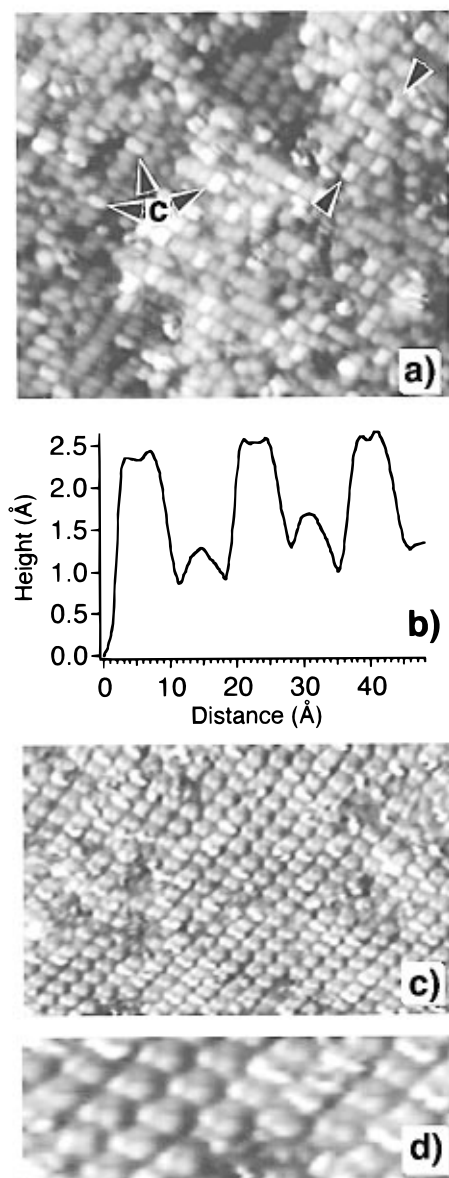
after the sample was cooled to 300 K; similar results were obtained by dosing at room temperature. The spectra are labeled "A", "B", "A + P", and "B + P" to indicate the corresponding directions of the electric field. There are several things to note about these spectra. First, there is little or no absorbance in the Si-H stretching region ( $2000\text{--}2150\text{ cm}^{-1}$ ). Since the Si-H infrared transition dipole is quite strong,<sup>17,18</sup> this demonstrates that there is little or no cleavage of C-H bonds and therefore implies purely molecular adsorption. Secondly, there are strong peaks not only in the C-H region characteristic of alkanes ( $2800\text{--}3000\text{ cm}^{-1}$ ) but also in the region characteristic of alkenes ( $3020\text{--}3080\text{ cm}^{-1}$ ). The observation of alkene stretches suggests that at least some of the molecules have retained this chemical functionality, suggesting that they have bonded to the surface through only one double bond.

A comparison of spectra A and B shows that the frequencies of the individual peaks are almost identical, but with a striking difference in relative intensities. The pronounced difference between orientation A and B indicates that the molecules are strongly aligned along specific crystallographic directions, with this directionality maintained over the entire sample. Finally, we note that the spectra for p-polarized light (A + P and B + P) are almost identical in all respects to those corresponding to purely s-polarized light (A and B) only. This similarity suggests that the infrared transition strength perpendicular to the surface is very small, so that p-polarized spectra are dominated by the parallel component of the electric field vector.

The FTIR results therefore show that (1) the bonding must have occurred though one or both of the C=C bonds in COD, (2) at least some of the time it occurs only though *one* C=C bond, and (3) the alkane C-H bonds are aligned primarily parallel to the surface and have transition dipoles with components in both the  $\langle 110 \rangle$  and  $\langle 1\bar{1}0 \rangle$  directions.

In order to determine the bonding configuration from the FTIR data, it is necessary to know if the majority of the molecules are in a unique bonding configuration. The large anisotropy in the infrared absorbance between the two inequivalent s-polarizations demonstrates that the molecules are aligned rotationally. To determine the bonding geometry and identify the degree of order within the monolayer films, we utilize scanning tunneling microscopy (STM).

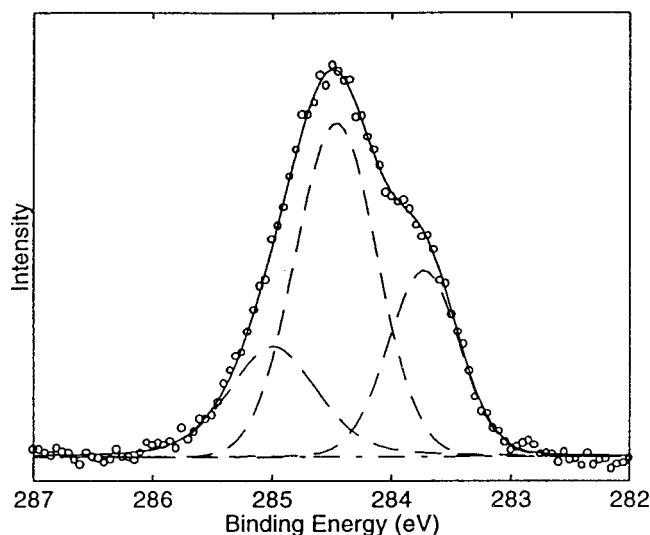
Figure 2a shows an STM image of a Si(001) surface after a nominal exposure to 0.05 langmuir ( $5 \times 10^{-9}$  Torr for 10 s) of 1,5-cyclooctadiene at room temperature. A single-height step propagates through the image from lower left to upper right. Under these imaging conditions, each COD molecule appears as a bright protrusion, labeled c in Figure 2a. Figure 2a shows that all COD molecules appear the same and all are located on top of the dimer rows in what appears to be a unique bonding configuration. Both on the upper terrace (right side of image) and lower terrace (left side of image) the individual molecules appear elongated parallel to the Si=Si dimer bond of the underlying substrate. Each protrusion has a length and width similar to that of one Si=Si dimer. At higher exposures, our experiments show that the adsorption is self-terminating, so that only a single monolayer is formed after a total exposure of approximately 1 langmuir. Figure 2, parts c and d show images obtained after saturation exposure to 3 langmuirs ( $1 \times 10^{-8}$  Torr for 300 s) of COD. These images show that the saturated surface is covered almost entirely by COD molecules aligned into rows. The molecules within a row are separated by  $7.7\text{ \AA}$ , twice the separation between dimers of the underlying substrate. The separation between rows of COD molecules is  $7.7\text{ \AA}$ , identical to the separation between rows of the underlying



**Figure 2.** STM images of Si(001) surface after exposure to 1,5-cyclooctadiene. (a) Image obtained at low coverage showing individual COD molecules and the underlying dimerized Si(001) surface. Image obtained at sample voltage of  $-2.1$  V and current of 200 pA. (b) Height profile along the line indicated in (a). (c) STM image obtained after saturation exposure showing highly-ordered array of COD molecules on Si(001) surface. Image obtained at sample voltage of  $-2.4$  V and current of 200 pA. (d) Magnified view of saturation-coverage surface showing apparent internal structure of molecules on the surface.

Si(001) substrate. The molecules therefore form ordered regions having local  $(2 \times 2)$  and  $c(4 \times 2)$  symmetry.

To identify whether any internal structure of the molecules could be resolved with the STM, we also obtained quantitative height profiles and high-resolution STM images. A height profile (Figure 2b) was measured along the line indicated by arrows in Figure 2a; this profile shows that some internal structure of the COD molecule can be resolved, as each protrusion in Figure 2a can now be resolved into two protrusions separated by roughly  $3 \text{ \AA}$  along the  $\langle 110 \rangle$  direction (parallel to the Si=Si dimer bond of the underlying substrate). The two smaller individual spots arising from each COD molecule can be observed easily in the high-resolution STM image shown in Figure 2d. This internal structure can be observed at lower coverage and under a variety of imaging conditions, indicating that it is a real feature of the molecular electronic structure.



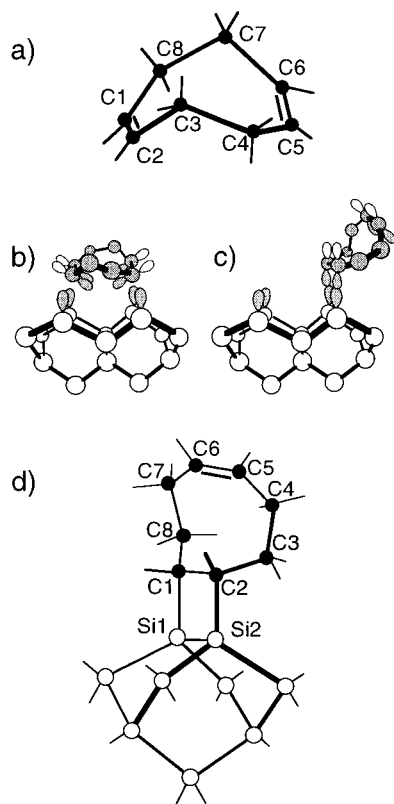
**Figure 3.** XPS spectra of Si(001) after exposure to saturation coverage of 1,5-cyclooctadiene. Large dots denote experimental data, the solid line represents a fit to three Gaussian peaks as described in text, and dashed lines show the individual fit components.

To help identify the local chemical configuration of the carbon atoms, we also used X-ray photoelectron spectroscopy (XPS) to examine the Si(001) surface after saturation exposure to COD. Figure 3 shows a C(1s) XPS spectrum of the Si(001) surface after exposure to 10 langmuirs of 1,5-cyclooctadiene at a sample temperature of  $50\text{--}100^\circ\text{C}$  along with the results of an unrestricted fit of the data to three Gaussian peaks. This fit procedure yielded peaks at binding energies of 283.7, 284.4, and 284.8 eV with integrated intensities of 26.2%, 51.9%, and 21.9%, respectively, or approximately 1:2:1. The XPS data indicates that there are three types of chemically inequivalent carbon atoms. To assign the individual peaks, we note that carbon is more electronegative than silicon; thus, the C atoms bonded directly to the Si surface are expected to be partially negatively charged and to have the smallest core-level binding energies. Previous studies have shown that double-bonded carbon atoms in alkenes have slightly larger binding energies than in alkanes.<sup>19</sup> We therefore assign the peak at 283.7 eV to the two carbon atoms bonded to the silicon surface, the peak at 284.4 eV to the four alkane-like carbons, and the peak at 284.8 eV to the two alkene-like carbon atoms in each surface-bound COD molecule.

#### IV. Discussion

The adsorption of ethylene and other alkenes on Si(001) has been investigated by a number of previous researchers.<sup>1–12</sup> Most of these studies have agreed that bonding occurs by breaking the  $\pi$  bond of the alkene and the  $\pi$  bond of a Si=Si dimer, forming two new Si–C bonds. However, some aspects of this interaction have been controversial. In particular, Weinberg and co-workers have argued that the strain associated with the formation of a four-membered ring at the interface favors cleavage of both the  $\pi$  and  $\sigma$  bonds of the Si=Si dimers.<sup>3,4</sup>

Previous experimental<sup>20,21</sup> and theoretical studies<sup>20,22</sup> have shown that the lowest-energy conformation of COD is a “twisted boat” with  $C_2$  symmetry, as depicted in Figure 4a. We confirmed this at a higher degree of computational accuracy using a fully unconstrained *ab initio* geometry optimization of the cyclooctadiene molecule with the Gaussian 94 program using a large basis set (6-31+G\*\*) and including exchange-correlation interactions through the Becke3LYP density functional.<sup>23,24</sup> Our calculations confirm that the lowest-energy geometry is a



**Figure 4.** Schematic structures for free and surface-bonded 1,5-cyclooctadiene: (a) lowest-energy configuration of COD molecule; (b) endo approach of COD to Si(001) surface; (c) exo approach of COD to Si(001) surface; (d) energy-minimized geometry of 1,5-cyclooctadiene on  $\text{Si}_9$  cluster.

twisted-boat configuration of  $C_2$  symmetry in which the two  $\pi$  bonds are twisted out of a coplanar configuration with a dihedral angle ( $\angle\text{C1C2C5C6}$ ) of  $23^\circ$  and are separated at the midpoint by  $3.20 \text{ \AA}$ , slightly less than the  $3.85 \text{ \AA}$  separation between  $\text{Si}=\text{Si}$  dimers. However, previous studies have shown that at  $300 \text{ K}$  the twist-boat conformer is only  $3 \text{ kcal/mol}$  lower in energy than the chair conformer, and the activation barriers between these and various other conformations are only  $3\text{--}4 \text{ kcal/mol}$ .<sup>21,22</sup> Since at room temperature  $kT$  is  $2.4 \text{ kcal/mol}$ , the geometry of COD at room temperature is best described as a rapidly interconverting mixture of conformations.

To determine the bonding configuration of 1,5-cyclooctadiene on the  $\text{Si}(001)$  surface, we start with the fact that the FTIR spectra in Figure 1 show little or no dissociation. This suggests that the basic mechanism of surface bonding in COD is a cycloaddition reaction similar to that proposed previously for ethylene and other unsaturated hydrocarbons.<sup>1,3–7</sup> Although in principle both  $\text{C}=\text{C}$   $\pi$  bonds could react with the  $\text{Si}(001)$  surface, the observation of an alkene stretch in IR and the presence of three chemically inequivalent carbon atoms in XPS suggest that for each molecule only one of its alkene groups reacts with the  $\text{Si}(001)$  surface, with the other extending into the vacuum. We therefore propose that 1,5-cyclooctadiene bonds to the surface using only one of the  $\text{C}=\text{C}$   $\pi$  systems, with the other remaining exposed to the vacuum. This ability to controllably bond one of the two equivalent  $\pi$  systems to the surface is a result of the three-dimensional molecular shape of 1,5-cyclooctadiene.

Although the COD molecule has several different conformations, none of these provide very effective interaction of the  $\pi$  orbitals of both  $\text{C}=\text{C}$  functionalities with the surface. Figure 4b,c schematically depicts the interaction of a COD molecule in the twist-boat conformation with the  $\text{Si}(001)$  surface in two

possible geometries. In order to bond both  $\pi$  systems to the  $\text{Si}(001)$  surface, the molecule must make an “endo” approach as illustrated in Figure 4b. In this case, there is comparatively poor overlap between the  $\text{C}=\text{C}$   $\pi$  system and the  $\text{Si}=\text{Si}$  dimers due both to steric constraints and the fact that the separation between the  $\text{C}=\text{C}$  bonds is small ( $3.20 \text{ \AA}$  for twist boat) compared with  $3.84 \text{ \AA}$  between  $\text{Si}=\text{Si}$  dimers. In the exo-configuration, as illustrated in Figure 4c, there is much better overlap between the  $\pi$  systems and no steric difficulties. We believe that the absence of steric factors would make an exo approach as in Figure 4c more facile.

To explore the likely geometry for bonded on the  $\text{Si}(001)$  surface, we performed Gaussian 94 calculations using a 9-atom Si cluster (one dimer at the surface, four atoms in the second layer, two in the third layer, and one in the fourth) terminated at the edges with hydrogen atoms. The hydrogen atoms were fixed in their equilibrium positions based on earlier calculations on a larger Si cluster, and all nine Si atoms, the eight carbon atoms, and the hydrogens attached to the carbon atoms were allowed to adjust completely freely with no symmetry constraints. Because of the large number of atoms, this calculation was performed at the Hartree–Fock level with the 6-31G basis set. Figure 4d depicts the minimum energy configuration obtained from this calculation. The COD molecule is again found in a low-energy twist-boat configuration. However, breaking the  $\pi$  bond between C1 and C2 permits the molecule to twist more readily; the dihedral angle  $\angle\text{C8C1C2C3}$  goes from  $0.3^\circ$  in pure COD to  $-34^\circ$  for COD on the surface. The remaining double bond retains a locally planar configuration ( $\angle\text{C4C5C6C7} = 0.3^\circ$ ). Although we have not performed calculations on other likely conformers, a simple ball-and-stick model shows that even when C1 and C2 are bonded rigidly to the Si surface twisting motions about C3, C4, C7, and C8 can occur without significant distortions of bond lengths or bond angles, thereby allowing the molecule to readily interconvert among several other conformers.

Rapid interconversion between several conformers is supported by the fact that the STM images of COD molecules show what appears to be a mirror plane bisecting the center of the  $\text{Si}=\text{Si}$  dimer bond, while the model depicted in Figure 3d is distinctly asymmetric. Because STM senses the time-averaged position while the various isomers probably interconvert on time scales of microseconds or less, the STM images should be interpreted as reflecting the local electronic structure of the time-averaged position of the adsorbed molecule. It should be noted that due to the  $\text{sp}^3$  hybridization, each COD molecule lies predominantly on one side of the  $\text{Si}=\text{Si}$  dimer. In the STM images this suggests that there are two types of molecules on the surface differing by a  $C_2$  rotation about the center of the  $\text{Si}=\text{Si}$  dimer bond and corresponding to COD molecules bonding to different sides of the  $\text{Si}=\text{Si}$  dimer. These two bonding geometries must be present in equal amounts due to the symmetry of the underlying  $\text{Si}(001)$  surface. In principle, it should be possible to identify these rotational isomers through careful measurements of the location of the protrusions attributed to COD molecules relative to the locations of the surrounding  $\text{Si}=\text{Si}$  dimers in STM images such as Figure 2a. However, our attempts to identify these rotational isomers were thwarted by the relatively large size of the individual COD molecules and the limited accuracy of STM position measurements.

In Figure 4d, the structure of surface-bonded COD involves a four-membered  $\text{Si}_2\text{C}_2$  ring at the interface; this configuration implies that only the  $\pi$  bond of the silicon dimer is broken, with the  $\sigma$  bond intact. This “di- $\sigma$ ” bonding configuration is based on a similar configuration proposed in early studies of

ethylene on Si(001) and leaves all Si and C atoms at the interface with a coordination number of four.<sup>25,26</sup> More recent experimental studies have suggested that both  $\pi$  and  $\sigma$  bonds of the Si=Si dimers are broken during adsorption of ethylene on Si(001), leaving each Si atom with an unterminated dangling bond.<sup>3-7,10,11</sup> Yet, previous *ab initio* calculations<sup>27-30</sup> have found the Si-Si  $\sigma$  bond to be intact, as we have depicted in Figure 4d. Our calculations, at the 6-31G level for COD on Si(001) and also at the Becke3LYP/6-31+G\* level for ethylene on Si<sub>9</sub> clusters like those in Figure 4d, both predict that upon adsorption the Si-Si dimer bond lengthens to 2.42 Å, slightly longer than the 2.35 Å bond length found for unstrained Si-Si bonds by these same calculations but significantly shorter than the 3.84 Å separation that would be predicted if the Si atoms were in their bulk-truncated positions. Calculations for ethylene and for 1,5-cyclooctadiene on a Si<sub>9</sub> cluster yielded almost identical bond lengths, albeit with a twisting of the Si-Si dimer as described above for COD. The nature of the apparent discrepancy between experimental evidence and theoretical calculations for alkenes on Si(001) will be investigated in future studies. At the moment, it remains unclear whether the Si-Si  $\sigma$  bond is intact (leaving a 4-membered ring at the interface) or broken (leaving two 5-membered C<sub>2</sub>Si<sub>5</sub> rings and two "dangling bonds").

A comparison with prior STM studies of unsaturated hydrocarbons on Si(001) provides further insight into the role of steric interactions in controlling adsorption and ordering. In these prior studies, we showed that ordered overlayers of cyclopentene molecules readily formed on Si(001),<sup>1</sup> while norbornadiene (which, like 1,5-cyclooctadiene, contains two unsaturated C=C bonds) produced only disordered surfaces.<sup>2</sup> Several previous studies have shown ordering of ethylene on Si(001). In comparison with norbornadiene, we find that COD produces surfaces that are much better oriented both translationally and rotationally. This is most likely a result of the fact that the exo approach for COD is essentially unhindered while the endo approach is strongly hindered, leading to a strong preference for a unique bonding configuration at the Si-C interface. In contrast, for norbornadiene both the endo and exo approaches encounter steric difficulties; this in turn leads to little preference for a specific bonding configuration for norbornadiene and a poorly-ordered overlayer. Additionally, the smaller separation of 2.37 Å between C=C bonds in norbornadiene<sup>31</sup> produces a much poorer match to the Si(001) dimer spacing.

## V. Summary and Conclusions

We have shown in this paper that it is possible to grow highly ordered organic monolayer films on the Si(001) surface using the bifunctional compound 1,5-cyclooctadiene. Although each cyclooctadiene molecule has two alkene groups, steric interactions and mismatch of the spacing between C=C groups and that of the underlying Si=Si dimers results in reaction at only one end of the molecule, with the remaining alkene group exposed to the vacuum. Our results thus show that it is possible to prepare ordered arrays of chemical functionalities such as

C=C units on the Si(001) surface that might provide a means for further chemical functionalization of the surface in a way that preserves translational and/or rotational order.

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