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Structure and Bonding of Ordered Organic Monolayers of 1,3,5,7-Cyclooctatetraene on the Si(001) Surface: Surface Cycloaddition Chemistry of an Antiaromatic Molecule

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Cycloaddition reactions have been utilized widely in organic chemistry and are now emerging as a method for attachment of organic molecules to silicon(001) surfaces in a controlled way. Scanning tunneling microscopy (STM), Fourier transform infrared spectroscopy (FTIR), and ab initio molecular orbital calculations have been used to investigate the structure and bonding of 1,3,5,7-cyclooctatetraene (COT), an antiaromatic molecule, on the Si(001)- 2×1 surface. STM images show that the COT molecules spontaneously order on Si(001) at room temperature. The individual molecules are separated by 7.7 Å, equal to twice the separation between Si=Si dimers on the underlying reconstructed Si(001)- 2×1 surface. FTIR measurements in conjunction with STM experiments show that the COT molecules bond to Si(001) via the direct interaction of two C=C units with two adjacent Si=Si dimers within a single dimer row. Ab initio molecular orbital calculations show that the lowest-energy geometry bonding of two C=C groups with two Si=Si dimers is a di- σ configuration via a double [2 + 2] cycloaddition reaction. The result of this bonding is a monolayer organic film that terminates in an ordered array of alkene groups exposed to the vacuum.

I. Introduction

Organic films have been utilized in a great number of technological applications because of the ability to control chemical and physical properties of the films by modifying the structure of the organic molecules comprising the film. Yet, a fundamental understanding of the bonding of most organic molecules to silicon surfaces is lacking. Recent experimental^{1–6} and theoretical investigations⁷ have shown that some analogies can be drawn between the reactivity of the Si=Si dimers of the reconstructed Si(001) surface and the reactivity of alkenes. In particular, it is possible for unsaturated organics to undergo an addition reaction in which the π bond of the alkene and the weak π bond of a Si=Si dimer are each broken, forming two new Si–C σ bonds.^{8–16} Recent work on conjugated alkenes further suggests that a surface analogue of the Diels–Alder reaction is possible.^{4,6,7} Because this bonding involves primarily the π orbitals of the C=C groups, it is expected that the reactivity and structure might be sensitive to the electronic structure of the π electron system as well as the physical structure of the molecule.

In a previous investigation, we showed that the molecule 1,5-cyclooctadiene (COD) bonds to Si(001) through only one of the C=C groups, leaving the second exposed at the vacuum. We additionally hypothesized that bonding through only one of the C=C groups occurred because the two C=C groups in this molecule are not coplanar and because the π systems of both C=C units cannot simultaneously achieve good π overlap with two adjacent Si=Si dimers.³ Here, we present an investigation of the structure and bonding of 1,3,5,7-cyclooctatetraene (COT), a conjugated, antiaromatic molecule, with the Si(001) surface. In contrast to COD,¹⁷ the COT molecule is highly symmetric with two sets of coplanar C=C groups.¹⁸ Understanding the bonding of such highly unsaturated molecules

to Si(001) is important because highly unsaturated organic films might be expected to have unusual electronic and optical properties, as well as acting as good sites for attaching other molecules to the surface in a controlled manner.

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 of -2.0 to -2.2 V, utilizing tunneling currents of 150–200 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 BaF₂ windows with a cooled InSb detector. The vacuum chambers are equipped with quadrupole mass spectrometers both for doing residual gas analysis and for checking the purity of the organic molecules introduced into the chamber. For each type of experiment samples were prepared and characterized completely in situ.

The 1,3,5,7-cyclooctatetraene was purchased from Aldrich with guaranteed purity $>98\%$. It was introduced into the chamber through a variable leak valve. For both 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 much higher than the chamber background pressure. Since these are 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 pressure in the chamber. When kept at room temperature for extended periods of time 1,3,5,7-cyclooctatetraene (a yellow liquid) inevitably contains dimeric and polymeric material. Thus, before the STM and FTIR experiments

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were attempted, COT was analyzed in situ with a mass spectrometer. Mass analysis consistently showed COT (104 amu) and its decomposition fragments¹⁹ but nothing at higher masses; this suggests that any dimers or higher polymers either are formed in insignificant amounts or else have vapor pressures that are significantly lower than that of COT, thereby presenting no significant contamination.

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 clean well-ordered surface exhibiting a (2×1) reconstruction.²⁰ Highly doped (<0.15 ohm·cm resistivity, Sb-doped) samples were used for STM experiments, while lightly doped (>5 ohm·cm resistivity, P-doped) samples were used for infrared spectroscopy experiments to minimize free-carrier adsorption in the bulk. Experiments were conducted using samples cut precisely along the (001) crystal plane and also on "vicinal" samples purposely miscut off (001) by 4° toward the $\langle 110 \rangle$ direction. For on-axis wafers the surface steps are predominantly one atom high, and the direction of the Si=Si dimer bond rotates by 90° across each step; this leads to a surface containing equal amounts of the two different rotational domains of the dimers, with each domain separated by a single-height step. On the vicinal samples the interactions between adjacent steps are sufficiently strong that almost all steps on the surface are two atoms high.^{21,22} As a result, the rotational orientation of the Si=Si dimers is retained across the step, leading to samples having only one rotational domain of the Si=Si dimers. All STM data shown here were obtained using on-axis samples, and the infrared data were obtained on 4° -miscut samples.

III. Results

Figure 1 shows scanning tunneling microscopy images taken after the Si(001) surface was exposed to saturation coverage, 2 langmuirs (1×10^{-8} Torr for 200 s), of 1,3,5,7-cyclooctatetraene (COT) at room temperature. In Figure 1a a single height step can be seen propagating horizontally through the middle of the image. This image clearly shows that the adsorbed molecules have aligned themselves in rows, and the dimer rows on the upper terrace (Figure 1a, top) and lower terrace (Figure 1a, bottom) are rotated by 90° with respect to one another. Figure 1b shows a higher resolution image of the surface. Here each protrusion is a COT molecule. The (2×1) -reconstructed Si(001) surface consists of rows of Si=Si dimers separated by $a_0 = 3.85$ Å along the row direction and by $2a_0 = 7.7$ Å perpendicular to the rows. In Figure 1b the separation between COT molecules within a dimer row is usually 7.7 Å, equal to $2a_0$; occasionally the molecules are separated by 10.5 Å, equal to $3a_0$. In the perpendicular direction the rows of COT molecules are always separated by $2a_0 = 7.7$ Å, just equal to the spacing between dimer rows. The 7.7 Å spacing along the dimer rows can lead to local regions of (2×2) or $c(4 \times 2)$ order, depending on whether the molecules in adjacent rows are aligned or shifted by $a_0 = 3.85$ Å along the dimer row direction. In the absence of intermolecular forces or molecule-induced strain fields, there is no driving force for preferential formation of (2×2) or $c(4 \times 2)$ ordering.

In Figure 1b each molecule appears to be elongated along the direction of the dimer row, and all molecules appear to be identical. A small number of white protrusions are observed that are attributed to trace contaminants. In addition to this majority species, Figure 1c shows that there is also a small minority of a second type of surface species. In Figure 1c the majority of the features in this image look identical with those

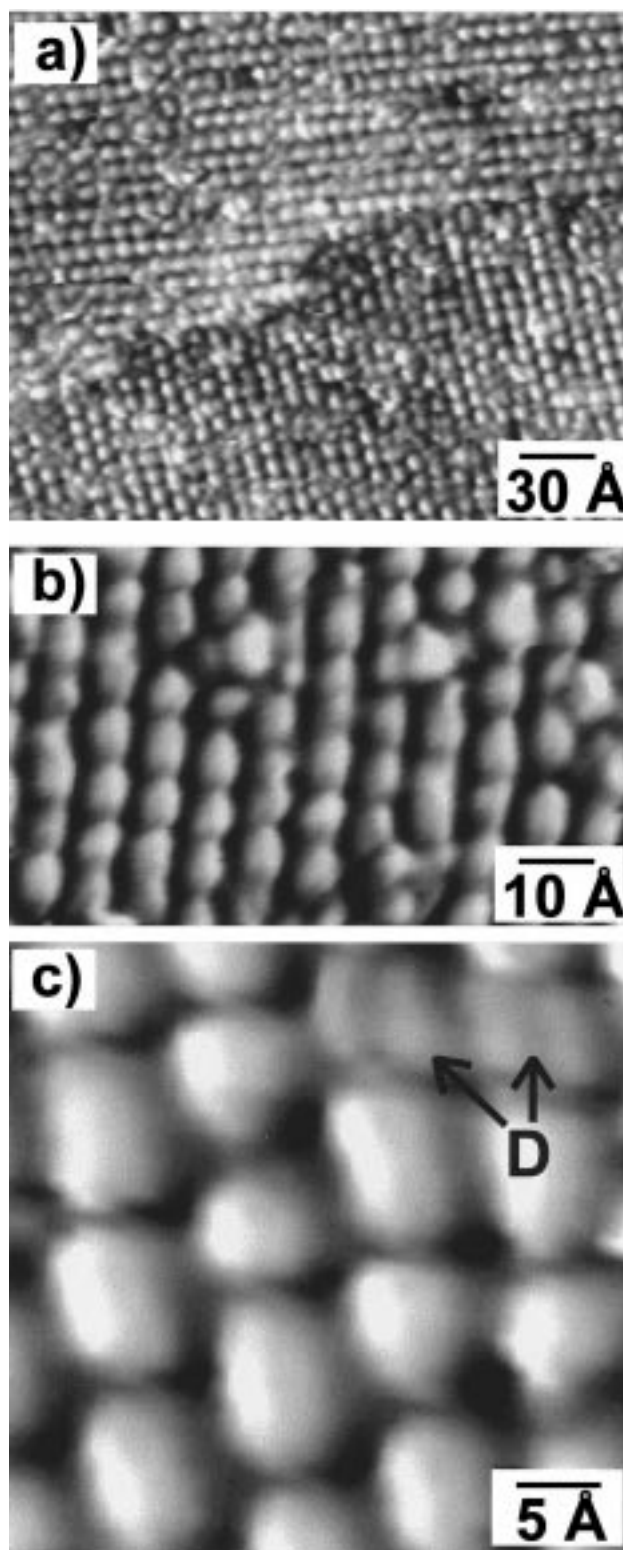


Figure 1. Scanning tunneling microscopy images of the Si(001) surface after saturation exposure to 1,3,5,7-cyclooctatetraene. Images were obtained with a sample bias of -2.2 V and a tunneling current of 150 pA. (a) Large area image with a single height step propagating horizontally through the center of the image. (b) High-resolution image showing the adsorption pattern of the COT molecules. (c) High-resolution image showing the presence of a second minority species ("D") on the surface along with the majority species.

in Figure 1b; however, there are two features in the upper right-hand corner, labeled "D", which appear significantly different. They appear somewhat dimmer in gray scale images and have an apparent internal structure that consists of two adjacent

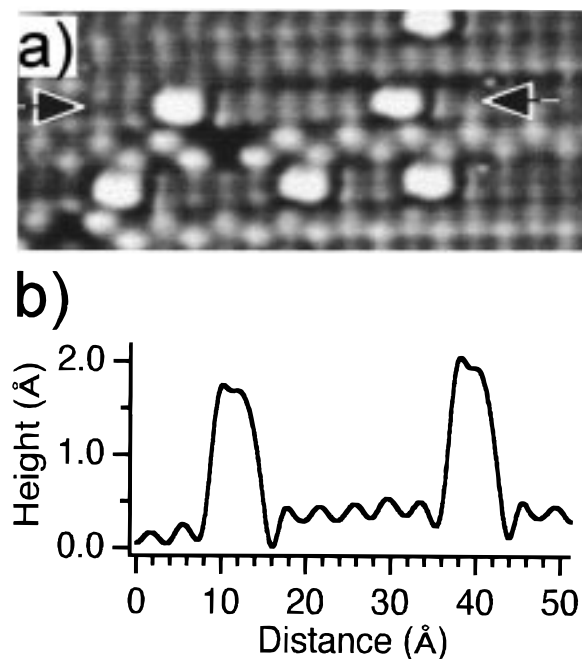


Figure 2. (a) STM image of Si(001) after exposure to 0.1 langmuir (1×10^{-8} Torr for 10 s) of 1,3,5,7-cyclooctatetraene. Image was obtained with a sample bias of -2.0 V and a tunneling current of 200 pA; image size $70 \text{ Å} \times 46 \text{ Å}$. (b) Height profile measured along the line indicated by arrows in (a).

oblong objects oriented parallel both to one another and to the underlying dimer rows. These features are a minority on the surface, and crude counting statistics of several different areas on the surface indicate that they comprise $<5\%$ of the features on the surface. The apparent elongation of the majority species along the dimer row direction and the more complex internal structure of the minority species are observed reproducibly; furthermore, these structures are observed on terraces separated by monatomic steps, confirming that they are real and are not a result of an asymmetric STM tip or other artifact.

The local bonding symmetry of the COT molecules with respect to the Si(001) surface is augmented by images obtained at low coverage. Figure 2 shows a scanning tunneling microscopy image with an accompanying height profile taken after the Si(001) surface was exposed to 0.1 langmuir (1×10^{-8} Torr for 10 s) of 1,3,5,7-cyclooctatetraene at room temperature. The bright protrusions on the surface are the adsorbed COT molecules with only features of the majority type appearing in this image. From this image one can see that the molecules have adsorbed within the dimer rows. It can also be seen again that the molecules appear elongated in the direction of the dimer row and that they encompass the area of two adjacent dimers, with the center of the molecule corresponding to a point midway between two adjacent dimers within a dimer row. Figure 2b shows a height profile measured between the two arrows shown in Figure 2a. This height profile shows that each COT molecule has an apparent height of approximately 1.7 Å above the surrounding dimerized Si(001) surface. The height profile also shows a small dip in the center of each adsorbed molecule; this dip has been seen intermittently in our images, but we cannot confirm that it is real. For features of the majority type the most crucial observations are that (1) the molecules consistently appear elongated in the direction of the underlying dimer rows, (2) that the center of each molecule coincides with the center of a dimer row, midway between two dimers of the underlying Si(001) surface, and (3) that the molecules appear to have two planes of mirror symmetry.

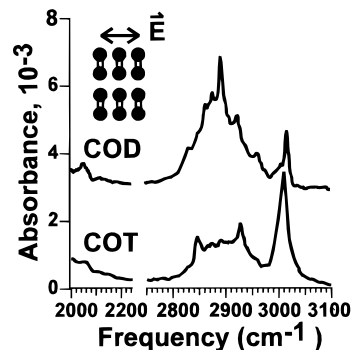


Figure 3. Infrared absorption spectra of Si(001) exposed to COT and to COD. Schematic depiction of incident electric field vector with respect to the Si(001) surface. Absorption spectra of Si(001) surface exposed to saturation coverage (3×10^{-8} Torr, 100 s) of 1,3,5,7-cyclooctatetraene (COT) and Si(001) surface exposed to saturation coverage (3×10^{-8} Torr, 166 s) of 1,5-cyclooctadiene (COD). The figure shows the C–H stretching region ($2800\text{--}3100 \text{ cm}^{-1}$) and the Si–H stretching region ($2000\text{--}2200 \text{ cm}^{-1}$).

To better understand the bonding to the Si(001) surface, infrared spectra were obtained for Si(001) surfaces exposed at a temperature of $350 \pm 50 \text{ K}$ to 1,3,5,7-cyclooctatetraene (COT) and to 1,5-cyclooctadiene (COD). The spectra shown here were obtained using single-domain (4° -miscut) vicinal Si(001) samples with s-polarized light oriented such that the electric field vector of the light is parallel to the dimer row direction and perpendicular to the Si=Si dimer axis, as indicated in Figure 3. Other polarizations show peaks at the same frequencies, with some changes in intensity. In Figure 3, the spectrum of the COT saturated surface shows several vibrational features in the $2800\text{--}3100 \text{ cm}^{-1}$ region where C–H stretching modes are typically observed, while very little absorbance is observed in the $2000\text{--}2150 \text{ cm}^{-1}$ range where Si–H stretching modes are typically observed. Since the infrared absorption cross section for Si–H stretches is very strong,^{23,24} the absence of any significant absorbance in the $2000\text{--}2150 \text{ cm}^{-1}$ range demonstrates that there is little or no fragmentation of C–H bonds during the adsorption process.

The most prominent peak in the COT spectrum is located at 3009 cm^{-1} . We attribute this peak to the C–H stretch of an alkene group based on two points of comparison. First, the vapor-phase spectrum of COT shows only a single peak in the stretching region at 3011.8 cm^{-1} .²⁵ Additionally, in a previous study of 1,5-cyclooctadiene³ we found that it adsorbed to the surface through only one double bond leaving the second one free; the COD spectrum in Figure 3b shows a peak at 3018 cm^{-1} which we ascribed to a C–H stretch of this remaining alkene group. These data suggest that COT adsorbs molecularly on Si(001) and that a fraction of the double bonds remain intact after adsorption. Although the number of C=C groups remaining cannot be determined from the infrared data alone, we note that the relative intensity of the alkene-like stretching mode is stronger for COT than for COD. Since both molecules have the same packing density on the surface and COD has one alkene group remaining after bonding to the surface, this suggests that COT has at least two alkene groups remaining after chemisorption. The bonding geometries described below all have C–H groups oriented at skewed angles with respect to the $\langle 100 \rangle$ and $\langle 010 \rangle$ crystallographic directions; this reduces the polarization dependence of the spectra and precludes assignment of a bonding geometry based on the FTIR spectra alone.

To identify the geometry of COT on Si(001), we have considered a number of different adsorption geometries. 1,3,5,7-Cyclooctatetraene (COT) is a member of the class of “antiaro-

matic" molecules having $4n$ (where n is an integer) electrons that can interact to form a delocalized π system. In antiaromatic molecules electron delocalization increases the energy of the molecule, so that these molecules typically distort into lower-symmetry geometries that reduce overlap of the atomic π orbitals. A previous study of COT showed it to exist in the gas phase in a nonplane "tub" form D_{2d} symmetry, as shown in Figure 4a.¹⁸ We performed a full ab initio geometry optimization of COT at the 6-31++G** level using the Becke3LYP density functional theory;^{26,27} this computation confirms that the C=C units at opposite ends of the COT molecule are coplanar and are separated by 3.14 Å, slightly shorter than the 3.85 Å separation between adjacent Si=Si dimers.

Figure 4b–e depicts four of the ways in which COT might interact with Si(001). One possibility is for four π electrons of COT to interact with one Si=Si dimer, resulting in a [4 + 2] cycloaddition reaction similar to a Diels–Alder reaction. As shown in Figure 4b, the product of a Diels–Alder reaction would have relatively low symmetry, with one alkene group on one side of a Si–Si dimer and two alkene groups on the other side. Since the highest-occupied molecular orbitals will arise from these alkene groups, filled-state STM images from this geometry would be expected to show only one mirror plane, while the STM images show two planes.

A second method of bonding to the surface is depicted in Figure 4c. Here only one π bond of the COT molecule interacts with a single Si=Si dimer. This mode of bonding is similar to that we identified previously for the 1,5-cyclooctadiene (COD) molecule.³ Although twisting about the unsaturated carbon atoms might permit the molecule to flip between two different conformations, in COT the alkene bonds do not permit this to occur readily because changing from one conformation to the other must proceed through a transition state in which at least one of the alkene π bonds is broken. Since STM images show that the center of each molecule lies midway between two Si=Si dimers, neither of the bonding configurations in Figure 4c nor the average of these two configurations is expected to yield a π electron density with the proper symmetry with respect to the underlying dimers. Irrespective of whether there is rapid interconversion or not, the symmetry of the molecule with respect to the underlying Si=Si dimers appears to be in poor agreement with the STM observations.

Figure 4d,e shows bonding configurations in which two π bonds at opposite ends of the COT molecule interact with two adjacent Si=Si dimers. These configurations both have bonding symmetries in agreement with our STM observations. The bonding geometry shown in Figure 4d involves a C=C unit bonding across two adjacent dimers within a single dimer row, while the configuration in Figure 4e involves bonding of two C=C units to two Si=Si dimers via the di- σ configuration. When compared with the geometry in Figure 4d, the di- σ configuration geometry in Figure 4e involves formation of two four-membered rings, while the cross-dimer geometry in Figure 4e involves a six-membered ring but has a poor match between the 3.84 Å spacing between adjacent Si=Si dimers and the effective length of a C=C bond.

To further understand the adsorption of COT on the Si(001) surface, we performed ab initio molecular orbital calculations of COT adsorbed onto a 15-atom Si cluster simulating two adjacent dimers of the Si(001) surface, as depicted in Figure 4f. The boundaries of the cluster except for the four topmost Si atoms that represent the Si=Si dimers were terminated with H atoms (not shown). Using the 3-21+G* basis set, full geometry optimizations were performed for COT interacting

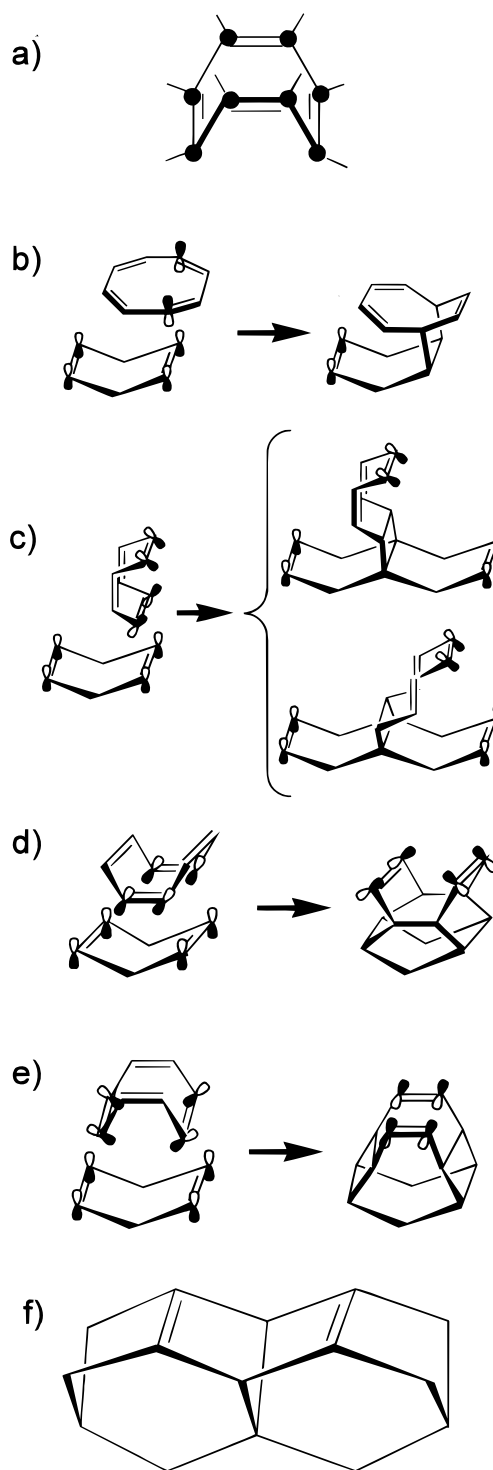


Figure 4. Possible geometries for bonding of COT to Si(001) surface: (a) geometry of free COT molecule; (b) Diels–Alder [4 + 2] addition reaction for planar COT reacting with Si(001); (c) [2 + 2] addition reaction involving only one C=C group in di- σ configuration; (d) [2 + 2] addition reaction involving two C=C groups in cross-dimer configuration; (e) [2 + 2] addition reaction involving two C=C groups in di- σ configuration; (f) 15-atom cluster used for ab initio molecular orbital calculations. Terminating hydrogen atoms at cluster edges are not shown.

with the Si₁₅ cluster in the geometries shown in Figure 4c–e; no counterpoise or other corrections were performed. The “Diels–Alder” geometry shown in Figure 4b was not calculated because the symmetry of this structure is not consistent with our STM images. Bonding via a single alkene group to one

Si=Si dimer, as in Figure 4c, yields a total energy of -4627.530 hartrees; this is 0.09 hartree (2.4 eV, 230 kJ/mol) lower than the sum of COT (-305.837 hartrees) and the Si₁₅ cluster (-4321.603 hartrees). Bonding in the geometry shown in Figure 4d, in which the COT molecule has π -bonded bridges between two adjacent Si=Si dimers, failed to converge to a stable geometry but was significantly higher in energy than both of the other two configurations. Finally, bonding of COT via two alkene groups to two Si=Si dimers in a di- σ configuration, as in Figure 4e, yielded a total energy of -4627.606 hartrees, 0.166 hartree (4.52 eV, 440 kJ/mol) lower than the sum of (COT + Si₁₅) and 2.1 eV (200 kJ/mol) lower in energy than the single-bonded configuration in Figure 4c.

Because the symmetry of this bonding configuration appears to be in good agreement with our STM observations, and because the ab initio calculations show it to be the lowest-energy configuration, we believe that the geometry shown in Figure 4e is the appropriate bonding geometry for COT on Si(001).

IV. Discussion

Previous studies on a variety of linear alkenes,^{5,8,10,15,28-33} cyclic alkenes,¹ nonconjugated dienes (1,5-cyclooctadiene),³ and conjugated dialkenes^{4,6,7} have shown that these molecules chemisorb molecularly to the surface through an interaction between the π system of an unsaturated C=C bond and the π system of a Si=Si dimer. In all cases, the driving force for the reaction is that because the π bond of the Si=Si dimer is very weak, it is energetically favorable to break the π bond of a Si=Si dimer and of an alkene group, to form two new Si-C bonds.

For simple alkenes the adsorption process can be described formally as a $[2 + 2]$ cycloaddition reaction. Reaction leads to the formation of a strained four-membered ring at the Si-C interface, analogous to the reaction of two ethylene molecules to form cyclobutadiene. For conjugated alkenes, however, a second possibility is the $[4 + 2]$ reaction between two C=C groups and a single Si=Si dimer, analogous to the Diels-Alder reaction. Recent theoretical calculations⁷ and experimental observations via infrared spectroscopy⁶ and scanning tunneling microscopy⁴ have shown that conjugated dienes such as 1,3-butadiene^{6,7} and 1,3-cyclohexadiene⁴ can undergo Diels-Alder $[4 + 2]$ reactions with Si(001) via interaction of the four π electrons of the diene with the two π electrons of a Si=Si dimer. Whether the $[2 + 2]$ or $[4 + 2]$ processes dominates is expected to depend strongly on steric constraints. Our STM investigations indicate that for COT the $[4 + 2]$ reaction is very inefficient, and reaction occurs almost entirely by a $[2 + 2]$ process. We attribute this selectivity to the fact that reactions of the $[4 + 2]$ "Diels-Alder" type require the reacting diene to be in a nearly planar configuration to provide simultaneous π overlap with both ends of the Si=Si dimer π orbital. This is readily achieved for molecules such as 1,3-cyclohexadiene; however, even in that case $[2 + 2]$ cycloaddition occurs as a side reaction, leading to the observation of several distinct fragments in scanning tunneling microscopy studies.⁴ For antiaromatic molecules such as COT the planar configuration needed for efficient Diels-Alder reaction is a local energy maximum; consequently, the molecule spends little or no time in the configuration needed for efficient reaction, leading in turn to greater selectivity for the $[2 + 2]$ process. A similar conclusion has been noted in studies of the reactivity of COT with organic alkenes.¹⁸

The shape of the COT molecule also influences its reactivity with Si(001) in a second way. In a previous study of 1,5-cyclooctadiene (COD), we found that chemisorption occurred via interaction of only one C=C π bond with the

Si(001) surface, leaving one π bond exposed to the vacuum. In contrast, COT appears to be able to bond via two C=C groups, as depicted in Figure 4e. The ability of COT to bond through two alkene groups, and the inability of COD to do the same, can be attributed primarily to differences in the shapes of these molecules. Since in COT the puckering of the molecule virtually eliminates delocalization of the π electrons, it is likely that bonding of the two alkene groups to the two Si=Si dimers takes place in two sequential steps. In both COD and COT the separation between opposite C=C groups in the free molecules is approximately 3.1 Å, shorter than the 3.84 Å separation between Si=Si dimers. However, in COD the C=C groups are twisted by 23° with respect to one another,^{3,17} while in COT they are parallel to one another.¹⁸ The COD molecule undergoes rapid conformational changes,¹⁷ and the intermediate CH₂ groups between the C=C bonds might produce steric interactions that prevent COD from adopting the configuration necessary for bonding through both C=C groups. In contrast, the puckered shape of the COT molecule keeps the intermediate C-H groups away from the surface; this may minimize undesirable steric interactions and permit COT to adopt the correct orientation for bonding through two C=C group.

Our ab initio calculations suggest that bonding the COT molecule at two locations rather than only one involves only a small cost in energy. Bonding through one π system is predicted to lower the energy by 2.4 eV, while bonding through both π systems lowers the energy by 4.5 eV; this suggests that strain associated with imperfect match of the bond distance and angles contributes only approximately 0.3 eV to the overall energy of the system. Analysis of the energy-minimized structure shows that this is achieved by bringing the COT molecule closer to a planar configuration, with the terminal C-C groups separated by 3.4 Å and the adjacent Si dimers slightly pulled together, separated by 3.73 Å instead of 3.85 Å on the free, reconstructed Si(001) surface.

The net result of COT adsorption on Si(001) is the formation of an ordered organic layer consisting of C=C alkene groups, aligned parallel to the dimer rows (perpendicular to the Si=Si dimer bond) of the underlying surface. Since each COT molecule retains two unsaturated C=C groups on the surface after bonding and occupies the area of two Si=Si dimers, the density of C=C groups on the COT-exposed Si(001) surface is the same as the density of Si=Si dimers, approximately 6.7×10^{14} alkene groups/cm². The high density of alkene groups suggests that it might be possible to induce cross-linking reactions to form organic polymers on the surface. It is likely that the lateral separation of >3 Å between C=C groups is too far to directly cross-link these alkene groups to form a monolayer polymer film. However, it is anticipated that these C=C groups will behave similarly to alkenes in liquid phase and that conventional synthetic organic chemistry techniques can be utilized to convert these alkene groups to other functional groups and/or to polymerize the surface using a suitable copolymer.

V. Conclusions

The interaction of 1,3,5,7-cyclooctatetraene with the Si(001) surface produces an ordered overlayer in which each molecule bonds to the Si(001) surface through two $[2 + 2]$ cycloaddition reactions. Each adsorption event leaves two C=C groups exposed to the vacuum. The net result of this is an ordered array of C=C alkene groups on the Si(001) surface. It is anticipated that the very high density of C=C groups exposed at the surface should be amenable to other types of functionalization and polymerization.

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