

Cycloaddition Chemistry on Silicon(001) Surfaces: The Adsorption of Azo-*tert*-butane

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The adsorption of azo-*tert*-butane on the Si(001) surface at 300 K has been investigated using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, scanning tunneling microscopy (STM), and ab initio computational chemistry methods. Although some cleavage of C–H bonds that prevents the formation of a completely ordered layer occurs at room temperature, adsorption onto a 130 K surface occurs molecularly with no bond cleavage. All of the experimental evidence shows that adsorption occurs through the interaction of the N=N azo bond with a single Si=Si dimer bond, in a manner similar to a [2 + 2] cycloaddition reaction. These results show that the use of [2 + 2] cycloaddition reactions to link organic substituents to the Si(001) surface is not limited to alkenes but can be extended to link compounds which have other types of unsaturated bonds to the Si(001) surface.

I. Introduction

The chemistry of silicon surfaces is of fundamental interest for a number of developing technologies.¹ For example, the ability to form an adlayer on a silicon sample that retains its order over the length of the sample would have potential applications in a wide range of areas, such as microelectronics, wavelength-sensitive detection, and biosensing. Of particular interest is the Si(001) surface, which undergoes a reconstruction involving a pairing of surface atoms into dimers.² These dimers are formally held together with a double bond, suggesting some possible concordance between the chemistry of Si(001) and the chemistry of organic alkenes. The interaction of the Si(001) with simple alkenes such as ethylene and acetylene has been studied widely.^{3–12} Recently a great deal of interest has been directed toward the possibility of more complex unsaturated organic molecules interacting with silicon via mechanisms that are analogous to the [2 + 2] and [4 + 2] (Diels–Alder) cycloaddition reactions of organic chemistry.^{13–15} The [2 + 2] reactions have been shown to be facile and to produce monolayer organic films in which the translational and rotational order of the underlying Si=Si dimers is translated into the organic film.^{16–18} By controlling the orientation of the Si=Si dimers, it is possible to create organic films exhibiting anisotropy in their physical properties.^{16–20} Initial results with conjugated dienes show that the Diels–Alder product can be formed^{13–15} although scanning tunneling microscopy data indicate the presence of more than one reaction product.²¹ Recent results for benzene on Si(001) show that not only can it undergo both [2 + 2] and [4 + 2] cycloaddition reactions, but transformations between these products can occur as well.^{22,23}

At the present time, the veracity of analogies drawn between these surface reactions and the vast literature of organic electrocyclic reactions is uncertain. In particular, [2 + 2] cycloaddition reactions of alkenes are usually forbidden by symmetry,²⁴ while the analogous reactions between alkenes and Si(001) are facile. This suggests that the actual mechanism may involve a low-symmetry pathway.¹⁸ In fact, previous work has shown that a range of unsaturated acyclic, cyclic, and hetero-

cyclic molecules can bond to the Si(001) surface through the unsaturated C=C bonds. Thus, while the mechanism is not yet fully understood, the reactivity of alkenes with the Si dimers has been established.

Another class of compounds that may react in a similar fashion with the Si(001) surface consists of the so-called azo compounds, which contain a nitrogen–nitrogen double bond. One previous study of a [2 + 2] cycloaddition reaction of a disilene with an azo compound showed the reaction to be slow thermally but facile photochemically, as expected from symmetry considerations.²⁵ However, azo compounds have been shown to undergo a cycloaddition reaction with alkenes under thermal conditions.²⁶ The above results suggest that the interaction of azo compounds with the Si(001) surface might also be facile. A previous study showed that azomethane adsorbed molecularly on Si(001), but the bonding configuration was not identified.²⁷ If azo compounds also react with the Si(001) dimers via a [2 + 2] cycloaddition, a new class of compounds would be available for the formation of ordered organic layers on Si(001). Herein, we present a detailed investigation of the structure and bonding of azo-*tert*-butane adsorbed on the Si(001) surface, showing that the aforementioned chemistry for bonding of alkenes to Si(001) can indeed be generalized to other unsaturated species: in particular, azo compounds bond to the Si(001) surface molecularly via a di- σ configuration, forming a four-member Si₂N₂ ring at the interface.

II. Experimental Section

The adsorption of azo-*tert*-butane (ATB) on Si(001) at 300 K was investigated using several methods, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared absorption (FTIR), scanning tunneling microscopy (STM), and ab initio calculations. Individually, each of these methods reveals a specific subset of information about the adsorbate–surface system. When taken together, the results from the four techniques provide a comprehensive picture of the adsorption process.

All of the experiments described here were performed in ultrahigh vacuum (UHV) chambers having base pressures of $<1 \times 10^{-10}$ Torr. The Si(001) samples were cut from n-type

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wafers (Wacker Chemitronic), degreased in methanol, and cleaned of residual carbon contamination by exposure to ozone for ~ 10 min. Highly doped crystals (< 0.1 ohm cm, Sb-doped) were used for the XPS and STM experiments, while lightly doped (> 5 ohm cm, B-doped) crystals were used for the IR experiments. Once in a vacuum, the Si samples were degassed at ~ 850 K overnight. The samples were then heated to 1400 K to remove the oxide layer, leaving a clean Si(001) surface. This procedure has been shown to produce the clean, well-ordered (2×1) reconstructed Si(001) surface.²⁸

ATB was obtained at 97% purity (Aldrich). It was further purified by several freeze–pump–thaw cycles. The ATB was introduced into the chamber through a variable leak valve and its purity checked with in situ mass spectrometers in each UHV chamber.

X-ray photoelectron spectroscopy data were obtained using a Physical Electronics system with monochromatized Al $K\alpha$ radiation. Because the X-ray source is monochromatized, this instrument has the capability for very high resolution. To increase surface sensitivity and minimize emission from bulk silicon, the sample was oriented so that the detection angle for the photoelectrons was 65° from the surface normal. The data presented here were obtained using a pass energy of 5.85 eV in the hemispherical analyzer. This setting was found to provide a good compromise between signal intensity and resolution sufficient to distinguish adsorbate atoms in different chemical environments. To distinguish between true chemical shifts and band-bending effects, the Si(2p) peaks were always measured and used as an internal standard. All of the spectra reported here have been adjusted to yield a constant 99.4 eV binding energy for the bulk Si $2p_{3/2}$ line. The same shift (typically < 0.2 eV) was then applied to the binding energies of the C(1s) and N(1s) peaks, ensuring that shifts in the binding energies reported here are solely due to changes in the local chemical environment.

The XPS data are fit by a commercial software package (Wavemetrics). The identification of the chemical species that comprise each XPS feature relies on this fitting procedure; therefore, a reliable method of ascertaining the number of individual peaks is necessary. A fit parameter, the so-called reduced chi-square, is used to determine when the fit is a good representation of the data.²⁹ A reduced chi-square of less than or equal to 1.0 indicates that the fit is statistically equivalent to the data. Our fitting procedure iteratively increases the number of individual peaks until the reduced chi-square is less than or equal to 1, thereby achieving good fit quality with the minimum number of statistically justifiable peaks.

Direct imaging of the surface and adsorbed ATB molecules was achieved using a home-built UHV scanning tunneling microscope (STM). All STM images were obtained with a sample bias of -2.6 V and a tunneling current of 2 nA. Fourier transform infrared (FTIR) absorption spectra were collected using multiple internal-reflection geometry. The IR radiation was produced and collected by a Mattson RS-1 FTIR spectrometer, was coupled into the vacuum chamber through a pair of BaF₂ windows, and was detected using an InSb detector. A polarizer was used to define the polarization of the IR light with respect to the surface plane. In all of the studies presented here, p-polarized light was used. Finally, as noted above, lightly doped Si samples were used in the IR experiments in order to reduce free-carrier adsorption in the bulk.

III. Results

A. Structure and Bonding of Chemisorbed ATB on Si(001). Figure 1 shows FTIR spectra obtained by exposing a

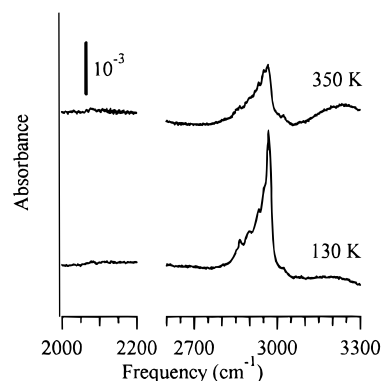


Figure 1. FTIR spectrum of (a) 130 K Si(001) surface exposed to 20 L ATB and (b) the same sample heated to 350 K after adsorption.

Si(001) sample at 130 K to 20 langmuir ($1 \text{ L} \equiv \text{langmuir} \equiv 10^{-6} \text{ Torr sec}$) of ATB. In this spectrum, several features are apparent. First, we note that in the $2800\text{--}3000 \text{ cm}^{-1}$ region, several peaks are observed; this spectral region corresponds to C–H stretching modes of saturated (alkane-like) organic compounds. No other significant intensity is observed in any spectral region between 2000 and 3100 cm^{-1} . In particular, we note the conspicuous absence of any observable intensity in the $2000\text{--}2100 \text{ cm}^{-1}$ region where Si–H molecular vibrations are typically observed. In a previous study with identical samples in this same apparatus, we found that the Si(001)-(2×1)H monohydride surface, which has one H atom per surface Si atom, produced an integrated absorbance of 0.13 cm^{-1} .³⁰ Comparing this value with the integrated absorbance of 0.004 cm^{-1} in the Si–H region in Figure 1 leads us to conclude that the surface hydrogen coverage is less than 3% after saturation with ATB. Thus, we conclude that only a small fraction of the adsorbed ATB cleave a C–H bond during adsorption onto the Si(001) surface at 130 K.

To better investigate the structure and bonding of ATB on Si(001), we utilized other experimental techniques, including XPS. Because we are not able to perform these experiments at 130 K, it was also necessary to characterize the adsorption at 300 K as well as the effect of annealing surfaces initially exposed at 130 K. The upper curve in Figure 1 shows the FTIR spectrum of a sample that was exposed to ATB at 130 K, warmed to 350 K, and then returned to 130 K for the FTIR measurement. (Returning to 130 K is necessary to provide a consistent background signal.) Although the absolute intensity appeared to change slightly (likely due to a thermally induced change in the mechanical alignment of the sample), the FTIR spectra in Figure 1 are almost identical. In particular, the spectra again show no significant intensity in the Si–H stretching region. This indicates that heating the sample from 130 to 350 K does not significantly change the chemical structure of the monolayer film.

In contrast to the above spectra, Figure 2 shows a FTIR spectrum of Si(001) exposed to 20 L of ATB with the sample temperature held at 300 K. In addition to the C–H peaks noted above, two new peaks are observed. One peak is observed at 2086 cm^{-1} , well within the spectral region where Si–H stretches are typically found. A second, very weak, feature is observed at 3082 cm^{-1} , the spectral region in which the C–H stretches of alkenes are typically observed. The presence of a peak at 2086 cm^{-1} indicates that some C–H bond cleavage occurs upon ATB adsorption at 300 K, resulting in surface-bound hydrogen. Because the Si–H infrared transition dipole is much larger than that for C–H, the extent of dissociation cannot be readily quantified from a simple comparison of the intensity of the

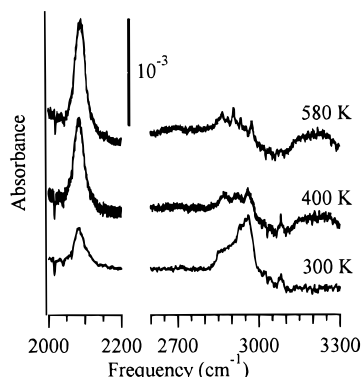


Figure 2. FTIR spectrum of a 300 K Si(001) surface exposed to 20 L ATB and then heated to 400 and 580 K. The lower curve shows the absorbance after 300 K adsorption. The middle and upper curves show the absorbance after heating to 400 and 580 K, respectively.

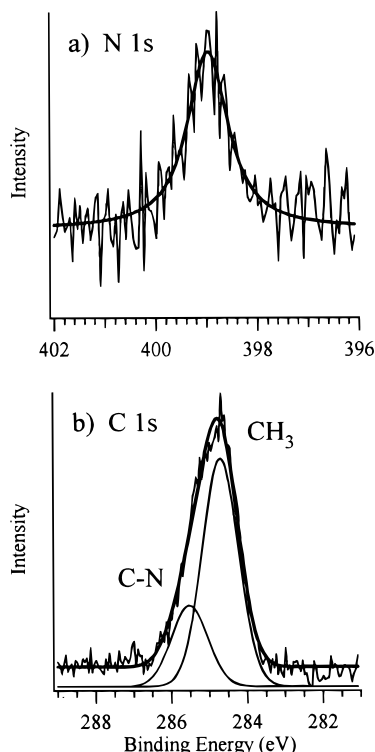


Figure 3. XPS spectrum of a 300 K Si(001) surface exposed to 20 L ATB. Panel (a) shows the N 1s region, and panel (b) shows the C 1s region. The assignment of the individual peaks is discussed in the text.

various features; a more quantitative analysis of the extent of dissociation will be presented below.

To help identify the bonding configuration, XPS spectra were obtained of the C(1s), N(1s), and Si(2p) core levels. Figure 3a shows the N(1s) XPS data for a Si(001) sample at 300 K exposed to 20 L of ATB. The N(1s) region shows only a single peak, with a binding energy of 399.0 eV and a full-width at half-maximum (fwhm) of 0.97 eV, only slightly broader than the resolution of the instrument. Because fitting the data to a Voigt line profile results in a reduced χ^2 of 1.0 (indicating no statistical justification for including more than one peak in the fit) and because the width of this peak is only slightly broader than the instrumental line width, we conclude that although each ATB molecule contains two nitrogen atoms, these N atoms are chemically equivalent after adsorption.

To determine whether the bonding occurs through the N atoms, a comparison of the N(1s) binding energy for this monolayer film with a corresponding measurement for mol-

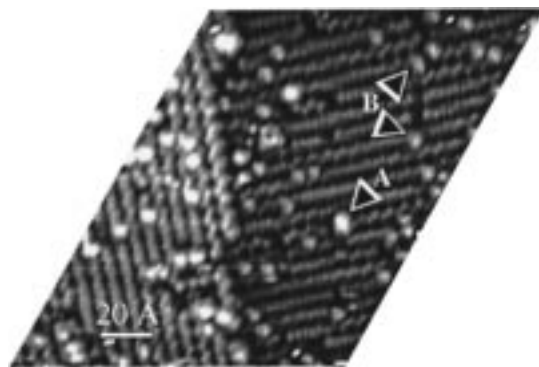


Figure 4. STM image of a 300 K Si(001) surface exposed to 0.1 L ATB. Two distinct features, A and B, are observed.

ecules having an intact azo group is needed. Attempts to condense a thin multilayer film (an ice) of ATB by exposing the sample to 100 L of ATB while cooling the sample failed, presumably due to an inability to cool the sample below ~ 200 K. However, we successfully grew multilayers of another azo compound, azobenzene, on the Si(001) substrate. A thin multilayer film of azobenzene adsorbed on Si(001) showed a single N(1s) peak at 400.8 eV, after correcting to a constant bulk Si 2p_{3/2} binding energy of 99.4 eV. Thus, we find that the N(1s) binding energy of ATB chemisorbed on Si (399.0 eV) is 1.8 eV lower than that for azobenzene ice (400.8 eV). Because the azobenzene ice is known to have an intact N=N bond, this comparison indicates that the N(1s) binding energy is strongly perturbed by chemisorption and suggests that the bonding of ATB on Si(001) likely involves direct Si-N bond formation. As an additional reference point, we measured the XPS spectrum of hydrazine (H₂N-NH₂) adsorbed on Si(001) at 300 K; hydrazine yielded a single N(1s) peak at 398.7 eV, rather close to the value obtained for ATB.

Figure 3b shows the corresponding binding energies of the C(1s) levels for ATB chemisorbed onto Si(001) surface at 300 K. The C(1s) spectrum shows peaks at binding energies of 285.5 and 284.7 eV, with the ratio of peak areas equal to 2.8 ± 0.3 . The stoichiometry of the ATB molecule is such that it has three (primary) methyl carbons for each tertiary carbon. Because the XPS data indicate two types of carbon with a relative abundance of 2.8:1, we conclude that ATB adsorbs on Si(001) at 300 K with little or no cleavage of C-C bonds.

The XPS data are consistent with several possible bonding configurations. One possible adsorption geometry consistent with these data is one in which the N=N bond reacts with a silicon dimer to form a four-member ring, analogous to the manner in which alkenes such as ethylene and cyclopentene bond to the surface. In this configuration, the N=N π bond and the weak Si=Si π bond are broken and two new N-Si σ bonds are formed, while the N-N σ bond and the Si-Si σ remain intact. However, the presence of a single nitrogen peak is also consistent with dissociative adsorption of ATB, in which the N=N bond is cleaved and each N-C(CH₃)₃ fragment bonds directly to a Si atom, forming species such as Si=N-C(CH₃)₃.

Finally, STM images were obtained of Si(001) surfaces exposed to small and large doses of ATB. The lower exposure, 0.1 L, was selected to ensure that the surface was not saturated and to allow for the determination of the position of individual ATB molecules relative to the underlying Si(001) surface. In contrast, the high exposure, 20 L, was sufficient to completely cover the surface, thereby enabling us to ascertain whether ATB will form an ordered layer on the Si(001) surface.

Figure 4 shows a STM image of a 300 K Si(001) surface

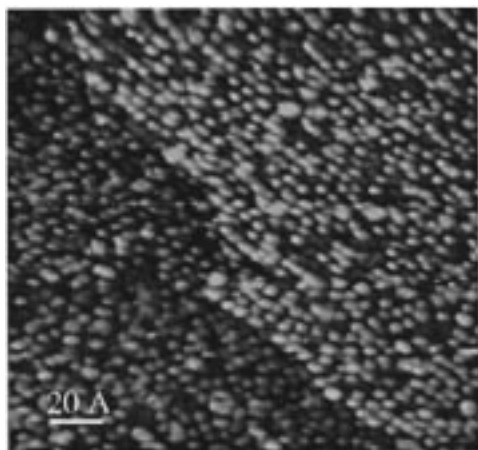


Figure 5. STM image of a room-temperature Si(001) crystal exposed to 20 L ATB.

exposed to 0.1 L of ATB. Rows of dimers are observed on two terraces separated by a single-height step. The dimer rows on these adjacent terraces are perpendicular to one another, as anticipated from the crystallography of the Si(001) surface. Examination of the images reveals two distinct adsorbate features, labeled “A” and “B” in Figure 4. The “A” features appear as high protrusions that are symmetrically located on top of a single Si=Si dimer. In contrast, the features marked “B” are clearly off-center.

The off-center location of the B features indicates that they are associated preferentially with one atom of the Si dimer. Previous studies of hydrogen on Si(001) have found that bonding of a single H atom to a Si=Si dimer yields a “hemihydride” (db-Si-Si-H) moiety with one dangling bond (“db”) per dimer. STM images of the hemihydride moiety show a single bright protrusion (corresponding to the dangling bond) in an off-center position that is very similar to the appearance of the B features in Figure 4,³¹ while infrared spectra show a single vibrational line near 2087 cm^{-1} ,³² close to the 2086 cm^{-1} line observed here for ATB adsorbed on Si(001) at 300 K. The appearance of the A features suggests that they correspond to ATB molecules or molecular fragments. The fact that the molecules appear similar on dimer rows that are running perpendicularly (i.e., on the upper and lower terraces) indicates that the appearance of the molecules in the image is not dominated by the shape of the tip, but is instead a true reflection of the symmetry of the molecules. To assess more quantitatively the surface stoichiometry, the occurrence of A and B features was counted in a large number of images. This process shows that the ratio of B to A features is 3.4 ± 0.7 . If we identify the B features as resulting from individual H atoms and each A feature as resulting from an intact or partially dissociated ATB molecule, then this suggests that, on average, each ATB molecule loses approximately three H atoms when chemisorbed on Si(001) at 300 K.

Figure 5 shows a STM image of a Si(001) surface saturated with ATB (exposure = 20 L). A single-height step runs diagonally through the image from upper left to lower right. Clearly, the ATB molecules adsorb on the dimers since their appearance tracks the dimer rows, rotating by 90° at the step edge. The long-range order is maintained relatively well across the sample. Although some gaps do appear, such defects are most likely due to the dissociation indicated by the FTIR experiment after room-temperature adsorption. Although the ordering observed here is poorer than that observed for organic alkenes interacting with Si(001),^{16,19,20} we believe that the

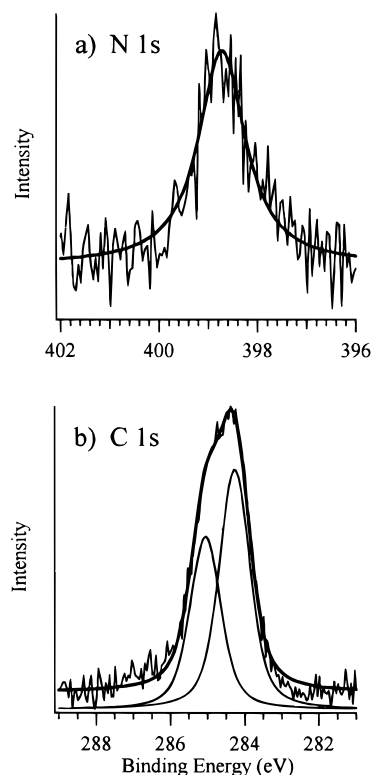


Figure 6. XPS spectrum of a 300 K Si(001) surface exposed to 20 L ATB and then heated to ~580 K. Panel (a) shows the N 1s region, and panel (b) shows the C 1s region.

inability to order is due to the partial dissociation observed at room temperature, which leaves randomly arranged chemisorbed H atoms on the surface. Unfortunately, we were not able to obtain STM images at the low temperature (130 K) where the FTIR data indicate almost no dissociation. Nevertheless, the STM images show that ATB adopts a unique bonding configuration on Si(001) and shows partial ordering. This, in turn, suggests that highly ordered layers might be produced by adsorption of ATB or other azo compounds, particularly if dissociation can be reduced by cooling or by the choice of more stable organic ligands.

B. Stability of ATB Monolayers above 300 Kelvin. To determine the thermal stability of the ATB layer, samples exposed to 20 L of ATB at 300 K were subsequently heated for 2 min to elevated temperatures and then cooled back to 300 K for XPS analysis. Figure 6a shows the N(1s) XPS data for a sample exposed to 20 L ATB and subsequently heated to about 580 K, while Figure 6b shows the equivalent C(1s) data. In Figure 6a, the N(1s) spectrum shows that, upon subsequent heating of the sample, only a single N(1s) peak is observed, but the binding energy has shifted downward from 399.0 to 398.7 eV. The N(1s) peak area remains unchanged by heating. In the C(1s) spectra, Figure 6b shows that, upon heating the sample, the C(1s) binding energies decrease from their 300 K adsorption values of 285.5 and 284.7 eV to lower binding energies of 285.1 and 284.3 eV. Although the overall C(1s) area is unchanged by heating, the ratio of the areas of the two types of C atom peaks decreases from 2.8 to 1.4.

These data indicate that upon heating to 580 K, the ATB molecules dissociate; however, all of the molecular fragments remain on the surface. The decreased C(1s) binding energies suggest the presence of direct C-Si bonds. This finding is in direct contrast to the results of Loh et al.,²⁷ who found that azomethane desorbs molecularly from Si(001) at ~370 K. Our results suggest that the N-N bond or the N-C bond is cleaved,

so that the N species is bound primarily to the less electronegative surface Si atoms.

FTIR absorption data were also acquired for samples heated to 580 K, as shown in Figure 2. As the sample is heated to 400 K, then 580 K, the Si–H stretch grows in intensity, while the intensity of the C–H stretch decreases. As measured by the area under the two peaks, the changes are greatest between 300 and 400 K; essentially no change takes place between 400 and 580 K. The large increase in the Si–H stretch intensity, coupled with the decrease in the C–H stretch intensity, supports our claim that the ATB molecules decompose on the surface as the surface temperature is raised. Because the temperature never rose above the lowest desorption temperature for $\text{H}_2/\text{Si}(001)$, ~ 670 K,³³ we believe that no H leaves the surface in the temperature range investigated here. By comparing the ratios of the areas under the Si–H peaks and under the C–H peaks before and after annealing, we can estimate the “average” number of H atoms that are dissociated from an ATB molecule upon adsorption and after heating. If it is assumed that all of the H atoms that leave an ATB molecule as it is heated to 400 K are retained on the surface to become part of a Si–H moiety, we estimate that the “typical” ATB molecule loses three H atoms upon 300 K adsorption and then loses another five to six H atoms during heating to 400 K. This estimate is in good agreement with the counting statistics from the STM images, which showed two adsorption species with relative populations of 3.4 to 1.

IV. Discussion

A. Identification of Bonding Configuration. Previous investigations of ethylene and acetylene show that these molecules can adsorb on Si(001) by breaking the weak π bond of the Si=Si dimers and the π bond of the alkene, forming two new strong Si–C bonds at the interface.^{3,4,6,18,34} This process is formally equivalent to the $[2 + 2]$ cycloaddition reaction of organic chemistry. While the concerted reaction of two alkenes via a $[2 + 2]$ process is forbidden by symmetry considerations,²⁴ experimental results for a wide variety of unsaturated organic compounds have shown that the analogous reactions of alkenes with the Si=Si bonds of the Si(001) surface are facile and can produce well-ordered organic monolayers.^{16,17,19–21} The reaction between alkenes and the Si=Si dimers is likely facilitated by two factors, a transition through a low-symmetry intermediate state and the nonplanarity of the Si=Si dimers.^{30,34}

The goal of the present study is to determine whether a corresponding facile reaction takes place between the N=N bonds of azo compounds and the Si=Si dimers of the Si(001) surface via a $[2 + 2]$ cycloaddition reaction. The resulting geometry, shown in Figure 7a, would involve formation of a four-member Si_2N_2 ring at the interface but would not involve any cleavage of C–H bonds or C–N bonds and might also be used in making well-defined monolayer structures via the interfacial formation of Si–N bonds.

We believe that our experimental results provide particularly strong evidence that the di- σ configuration does in fact represent the correct bonding model for ATB on Si(001). First, we note that any alternative bonding model retaining normal coordination numbers for C and N would either involve cleavage of C–H bonds, C–C bonds, or C–N bonds. Because desorption of molecular fragments into the gas phase is strongly inhibited at low temperature on thermodynamic grounds, we restrict our discussion to alternative bonding configurations for which all species remain bound to the surface. The FTIR results in Figure 1 clearly demonstrate that ATB is able to adsorb on Si(001)

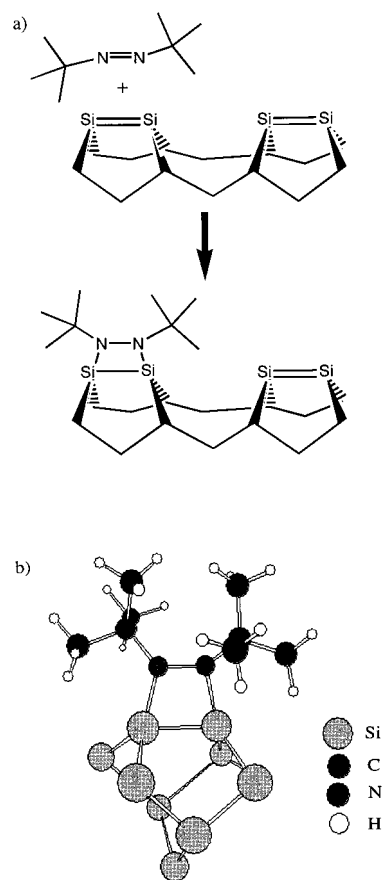


Figure 7. The proposed binding configuration of molecular ATB on 130 K Si(001) (a) and the result of a Gaussian 94 energy minimization calculation for this system (b).

with virtually no cleavage of C–H bonds when the sample is cold during the adsorption process. Cleavage of C–H bonds almost invariably leaves H atoms on the surface; because the Si–H infrared transition dipole is very strong, any significant concentration of surface-bound H atoms is readily detectable. Although C–H bond cleavage is observed after 300 K adsorption both by the appearance of Si–H stretches and by the appearance of a weak C=C–H vibration characteristic of an alkene, no sign of any C–H bond cleavage is evident after low-temperature adsorption. On the basis of our noise level and quantitative measurements of Si–H and C–H bond stretch intensities at varying degrees of thermally induced molecular dissociation, we are able to estimate that fewer than 3% of the ATB molecules undergo any C–H bond cleavage during adsorption at 130 K. A detailed analysis of the infrared spectrum has not been performed, but we note that the form, both in frequency and in relative intensity, of the alkane C–H spectral region for both adsorption temperatures is very similar to that of the C–H stretch modes observed for ATB frozen in a 38 K argon matrix.³⁵ In addition, we are able to rule out cleavage of C–C bonds yielding species adsorbed via a C atom by the absence of any significant component in the C(1s) XPS spectra near 284 eV, which we have previously established as the appropriate energy for carbon atoms bonded directly to Si.³⁶ As will be discussed below, more detailed analysis of the XPS spectra also shows that the core level shifts for N and C atoms are in excellent agreement with the di- σ bonding model.

The limited dissociation upon 300 K adsorption and lack of dissociation at 130 K point to intact molecular adsorption. We further note that heating the crystal from 130 to 350 K does not lead to a noticeable change in the FTIR spectrum. This

TABLE 1: XPS N(1s) Binding Energies for the Adsorption of Nitrogen-Containing Molecules on Si(001)^a

molecule	binding Energies, eV
3-pyrroline, N-Si	398.3
hydrazine	398.7
ATB	399.0
3-pyrroline, N-C	399.2
azobenzene ice	400.8

^a ATB, hydrazine, and azobenzene results from this work; 3-pyrroline data from ref 36.

suggests that the binding configuration at 130 K is stable and likely to correspond to a *local* minimum in the adsorption energy. Without dissociation, few adsorption configurations are plausible for this system. Because our experimental data overwhelmingly support the di- σ bonding model, the remainder of the discussion will be focused in the context of this specific adsorption model.

B. Chemical Shifts and Surface Bonding. Our XPS data strongly suggest that the dominant mode of bonding of ATB on Si(001) is through the formation of direct Si-N bonds, leaving a four-member Si₂N₂ ring at the interface. In this configuration, each N atom is bonded to one other N atom, one C atom, and one Si atom. Bonding to the surface thus involves cleavage of the N=N π bond and formation of a N-Si bond. Although no similar species have been measured with XPS previously, we can make some comparisons with known, related compounds, as listed in Table 1.

We first address the expected N(1s) binding energy. Previous measurements in our laboratory show that the molecule 3-pyrroline,³⁶ which has both an alkene group (C=C) and a secondary amine group, can attach to the Si(001) surface in two ways. One geometry entails binding the C=C group to the surface in a di- σ configuration, leaving a N atom bonded to two C atoms and one H atom exposed to the vacuum and yielding a N(1s) binding energy of 399.2 eV. The other product involves bonding to the surface through the N atom; in this configuration, the N atom is bonded to two C atoms and one Si atom and has a binding energy of 398.3 eV. These measurements show that, for a three-coordinate N atom, substituting Si for H decreases the N(1s) binding energy from 399.2 to 398.3 eV, a decrease of 0.9 eV. Such changes can be explained qualitatively by electronegativity arguments. Using Pauling electronegativities of 3.04 for N, 1.90 for Si, 2.55 for C, and 2.20 for H, one finds that 3-pyrroline bonded to Si through the N atom has an electronegativity sum for attached groups of 7.0 ($\chi = \chi_{\text{Si}} + \chi_{\text{C}} + \chi_{\text{C}} = 1.90 + 2.55 + 2.55$). Similarly, in 3-pyrroline bonded through the C=C group, N has attached atoms with an electronegativity sum of 7.3, whereas in di- σ -bonded ATB, N has attached atoms with an electronegativity sum of 7.49. This simple electronegativity argument suggests that di- σ -bonded 3-pyrroline (399.2 eV experimental) should have a significantly higher binding energy than N-bonded 3-pyrroline (398.3 eV experimental); an extension of this argument suggests that ATB (399.0 eV experimental) should have a N(1s) binding energy very similar to that of di- σ -bonded 3-pyrroline (399.2 eV experimental); the agreement between these values further supports the di- σ -bonding model for ATB adsorption on Si(001).

A previous XPS study by Bu and Lin³⁷ reported that hydrazine (H₂N-NH₂) adsorbs on Si(001) by cleavage of N-H bonds, leaving an adsorbed nitrogen species in which the N-N bond is intact. Experimentally, we performed an XPS study of hydrazine adsorbed on Si(001) at 300 K. We found a single N peak at a binding energy of 398.7 eV. The atoms surrounding the N atom in hydrazine adsorbed on the Si(001) surface have

an electronegativity sum of 7.14, somewhat less than the value of 7.49 for ATB. Our experimental result for the N(1s) binding energy of hydrazine on Si(001), then, bolsters the simple electronegativity arguments that support the di- σ -bonding model for ATB adsorption on Si(001).

Table 2 compares our C(1s) XPS data with similar data for other related molecules on Si(001). All of these systems were investigated in our laboratory and the same fitting and internal standardization procedures were applied to each of them. In Figure 2, the larger peak has a binding energy of 284.7 eV. This value is almost identical to the value of 284.8 ± 0.1 eV found in our previous studies for alkane-like C atoms, and leads us to assign the large 284.7 eV peak to the six carbon atoms in CH₃ groups in each ATB molecule. While the electronegativities of the attached atoms sum to 9.1 for the C atoms in CH₃ groups, this sum is 10.7 for the tertiary C atoms. The greater electronegativity of attached groups is expected to decrease the electron density around the tertiary carbons, leading to a higher binding energy for 1s core electrons. This analysis leads us to assign the peak at 285.5 eV to the two tertiary carbons in the ATB molecule. We also note that, in Figure 3b, no C(1s) intensity near 284.0 eV is observed, which is the energy that we have consistently identified as the binding energy for alkane-like carbon atoms bonded directly to the Si surface.³⁶ The absence of such a peak in the ATB XPS data provides further evidence that no significant formation of Si-C bonds occurs upon ATB adsorption, even for the partially dissociative adsorption at 300 K.

The XPS data, then, indicate that the ATB molecule adsorbs on the Si(001) surface via the N atoms, with both N atoms being equivalent. Furthermore, through comparisons with work on similar systems, our data are also indicative of molecular adsorption that leaves the N-N σ bond intact.

To help propose a binding configuration for ATB on Si(001), we performed ab initio calculations using Gaussian 94³⁸ for an ATB molecule adsorbed onto a nine-atom Si cluster terminated with H atoms at the edges to provide full coordination at the cluster edges. This cluster and its H atom termination are identical to those used in several previous studies.^{13,18,39} The calculation was performed using a hybrid method in which the energy is first calculated at the Hartree-Fock level with the 6-31+G* basis set, and the Becke3LYP density functional⁴⁰ is used to additionally include electron correlation effects.^{13,18} Figure 7b shows the geometry obtained after a multistep geometry optimization. In this optimization, the N=N and Si=Si bonds were initially placed approximately 3 Å apart and approximately parallel to one another; the geometry yielding the minimum total energy was then determined iteratively, with no constraints on the positions or the bond angles. The resulting configuration, shown in Figure 7b, involves a four-member ring between the N atoms of the ATB molecule and a single Si dimer. Additionally, the *tert*-butyl groups of the ATB molecule adopt a trans configuration with respect to the N-N bond, most likely due to steric hindrance. The result of the calculated minimum energy configuration is in agreement with our proposed adsorption geometry based on XPS and STM data. The total binding energy of ATB in this geometry was calculated to be 0.029 hartrees (0.79 eV, 18.2 kcal/mol). We note that the results of our calculations represent a local minimum in the energy but not necessarily an overall global minimum. Yet, in a previous study of the interaction of conjugated dienes with the Si(001) surface, we found the large activation barriers arising from the strongly covalent bonding of related molecules on Si(001) are sufficient to lock in metastable structures.³⁰

TABLE 2: XPS C(1s) Binding Energies for the Adsorption of ATB and Related Molecules on Si(001)^a

carbon species	binding energies, eV			
	ATB	3-pyrroline	cyclopentene	1,5-cyclooctadiene
C, C–Si	not observed	284.1	284.0	283.7
C, alkane C–C	284.7	284.8	284.8	284.4
C, alkene C=C	not observed	285.4	285.4	284.8
C, C–N	285.5	not distinguished		

^a Data for molecules other than ATB are from ref 36.

Our calculation predicts that the Si₂N₂ ring at the interface has a Si–Si dimer bond distance of 2.30 Å, slightly shorter than both the typical Si–Si bond length of 2.37 calculated elsewhere in the cluster and the known value of 2.35 for bulk Si. The N–N distance is predicted to be 1.52 Å; this value is much longer than the 1.24 Å that we calculate for the intact N=N azo bond in free ATB and slightly longer than the 1.48 Å for hydrazine using the same computational method. The calculated Si–N distance of 1.82 Å is slightly longer than the Si–N lengths calculated for H₃Si–NH₂,⁴¹ (SiH₃)₂NH,⁴² and N(Si(CH₃)₃)₃,⁴³ of 1.73, 1.72, and 1.76 Å, respectively. Our calculations also predict that the Si₂N₂ ring at the interface is nearly planar, with a N–Si–Si–N dihedral angle of 2°; the Si–N–N angle and Si–Si–N angles are predicted to be 103° and 78°, respectively, while the C–N–N and C–N–Si angle are both 118°. For comparison, the H–N–N bond angle in hydrazine is predicted to be 104°. Although these bond angles suggest a quite strained ring system, a previous calculation on a Si₂N cluster predicted the cyclic form of that molecule to be only 4.90 kcal/mol higher in energy than the linear form.⁴³ This, in turn, suggests that bond angle distortion in the Si–N system is readily accommodated with comparatively small cost in energy. This conclusion is supported by previous measurements on a related compound containing a four-member ring with alternating N and Si, which showed the Si₂N₂ ring to be planar, with Si–N distances of approximately 1.72 Å.⁴⁴ On the basis of comparisons with these calculations, we believe that the results of our ab initio calculations for ATB present a reasonable adsorption geometry.

C. Molecular Structure and Ordering. As noted above, our scanning tunneling microscopy data show two types of species adsorbed on the surface. We attribute the less common feature that appears as an elongated protrusion centered over a single Si dimer to the ATB molecules adsorbed in the di-σ configuration, and we attribute the more common feature to adsorbed H atoms produced by dissociation of the C–H bonds. As we noted earlier, a statistical analysis of the low-coverage STM images shows that approximately 3.4 H atoms are observed for each ATB molecule, in good agreement with a quantitative analysis of the infrared data that suggests that each ATB molecule loses approximately three H atoms via fragmentation of the *tert*-butyl groups.

In previous studies, we found that a variety of unsaturated hydrocarbons such as 1,5-cyclooctadiene and 1,3,5,7-cyclooctatetraene are able to produce ordered organic monolayers via a similar type of di-σ bonding.^{17,19–21} For ATB, fragmentation of C–H bonds appears to inhibit molecular ordering when the dosing occurs at 300 K. However, the absence of fragmentation at lower temperature suggests that better ordering might take place if the initial adsorption occurs on a precooled surface.

D. Dissociation. Whereas adsorption at low temperature and subsequent annealing upon warming to 350 K leads to little or no dissociation of the ATB molecules, Figure 2 shows that adsorption onto a 300 K sample leads to partial dissociation, as evidenced by the appearance of significant Si–H stretches and

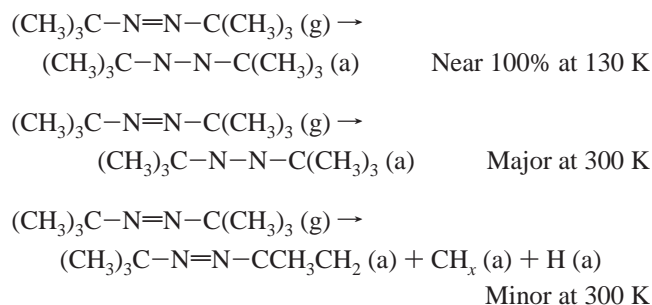
the appearance of an alkene-like stretch at 3082 cm^{−1}. This behavior likely arises from the fact that cleavage of Si–H bonds is a thermally activated process but requires a larger number of available reactive sites compared to purely molecular adsorption. At low temperature, the ATB molecules are able to pack on the surface with a sufficiently high density to prevent dissociation, even when the sample is subsequently warmed to 350 K. In contrast, when dosing occurs onto the 300 K sample, the molecules that first impinge on the surface have sufficient thermal energy to dissociate as well as an ample number of active sites for this to take place in a facile manner. The lack of dissociation at 130 K and the subsequent stability upon warming to 350 K demonstrate that the adsorption configuration is a local minimum in the potential energy well. Once the molecule is adsorbed in the di-σ configuration, it resists dissociation even when heated to slightly above room temperature.

Other compounds containing the *tert*-butyl group have received widespread interest in the microelectronics industry as potential organic precursors in chemical vapor deposition processes; in these studies, dissociation of the *tert*-butyl group plays a critical role in controlling the residual carbon contamination. A previous infrared study of *tert*-butyl phosphine (TBP) and *tert*-butyl chloride (TBC) on Si(001)⁴⁵ found that both of these molecules adsorbed at 300 K with some dissociation, confirmed by the presence of a Si–H stretch peak in IR absorption data. Additionally, the adsorption of TBC on Si(001) also produced an alkene C–H stretch at 3083 cm^{−1} that was attributed to loss of a methyl group and β-hydride elimination in the *tert*-butyl group. The presence of an alkene C–H stretch at 3082 cm^{−1} in our data for ATB adsorption at 300 K suggests a similar process. However, we note that our IR spectrum appears markedly different from that for TBC adsorption on Si(001)⁴⁵ as well as that for the *tert*-butyl radical isolated in an argon matrix.³⁵ These comparisons indicate that N–C bond cleavage does not occur to a significant extent with ATB, since it would be expected to leave a *tert*-butyl group adsorbed to the Si.

The presence of an alkene C–H stretch and its similarity to the results for TBC adsorption on Si(001) indicate that at least part of the observed dissociation of ATB results in the formation of a C=C bond. The spectral location of the alkene stretch is in good agreement with the alkene C–H stretch in isobutene⁴⁶ at 3085 cm^{−1}. A propenyl group could be formed by loss of a H atom and a CH₃ group from the *tert*-butyl group of the ATB molecule. Also, propene could be produced by loss of a H atom and cleavage of the C–N bond. However, the latter process would produce a gas-phase propene molecule, which is expected to desorb; therefore, it could not account for the observed alkene stretch.

We believe that a small amount of methyl group loss from the *tert*-butyl group accounts for the observed alkene stretch in the 300 K adsorption. The fate of this methyl group, however, is unclear. Yates et al. have investigated the vibrational spectroscopy of various CH species on Si(001).⁵ Adsorbed CH₃

is found to have a C–H stretch frequency of 2990 cm^{-1} . This feature would be observable in our IR data, yet we do not find a peak at that frequency. Adsorbed CH and CH₂ species were shown to have a C–H stretch frequency of 2970 cm^{-1} . Unfortunately, this area is obscured by the C–H stretch of the *tert*-butyl group. However, our XPS data do not show a peak at a binding energy of 284.0 eV, which we have previously established as the binding energy for C bonded directly to Si.³⁶ The absence of noticeable peaks in the IR and XPS data does not conclusively rule out adsorbed CH_x ($x = 1, 2, 3$) species. However, based on our signal-to-noise ratios, we estimate the CH_x coverage to be less than 0.1 ML. Considering the above discussion, we present a summary of the proposed adsorption processes below:



Finally, we note that in the gas phase, thermolysis of ATB at or above 453 K results in the formation of *tert*-butyl radicals, 2-methylpropane, 2-methylpropene, and 2,2,3,3-tetramethylbutane.^{47,48} As discussed above, we do not see any evidence for hydrocarbons bound directly to the surface upon adsorption at 300 K. However, after the crystal is heated to 580 K, decomposition of the molecule is evident. Figure 6b shows that a significant fraction of the C on the surface has a 1s binding energy of 284.3 eV, which may indicate that some C is directly bound to the Si surface. Furthermore, the IR spectrum (top curve, Figure 2) shows several peaks whose frequencies do not match those for ATB, indicating a large amount of bond breakage in the molecule. Indeed, the locations of these peaks are consistent with previously determined frequencies for adsorbed CH_x ($x = 1, 2, 3$) species.⁵ At this high annealing temperature, the cleavage of C–N and C–C bonds is quite likely. On the basis of the growth of the Si–H IR peak and the fact that the C and N XPS peaks do not change in area upon heating, we believe that during annealing, the ATB dissociates, depositing various fragments on the surface.

E. Mechanism of Adsorption and Dissociation. The mechanism of cycloaddition reactions at a Si(001) surface is not yet fully understood. A direct cycloaddition process of two organic alkenes has long been known to be symmetry-forbidden under thermal conditions although a facile reaction can be achieved through photochemical excitation to an excited electronic state.²⁴ Although not as well studied, a previous investigation of the [2 + 2] cycloaddition of an azobenzene compound with a disilene was similarly shown to be thermally unreactive but photochemically very facile.²⁵ The apparent barriers to thermal reaction notwithstanding, previous studies of the adsorption of unsaturated alkenes with the Si=Si dimers of the Si(001) surface have shown these reactions to be quite facile.^{3,4,6,18,34} Despite the fact that the Si=Si dimers on Si(001) are formally held together with a double bond (and indeed, the electronic surface states are widely described as π bonding and π^* antibonding levels),^{2,49} some clear differences between Si=Si dimers, disilenes, and organic alkenes exist. One of the most significant differences stems from the fact that, although

disilenes and alkenes adopt a true sp^2 hybridization and a planar configuration about the unsaturated group, such hybridization is not possible for the Si=Si dimers. This causes the gap between the π bonding and π^* antibonding levels on Si(001) to be significantly smaller than the corresponding gaps of disilenes and alkenes (1.0 eV, 2.0–3.0 eV, and ~6.0 eV, respectively).⁵⁰ Perhaps more importantly, the distortion from a planar configuration leads to highly localized regions of increased electron density between the Si atoms, and decreased electron density at the location of the π^* antibonding orbital at the edges of the dimers.

Previous investigations of ethylene¹⁸ and acetylene³⁴ adsorption on Si(001) have suggested that adsorption is facile because the electron-rich region of these alkenes can interact electrostatically with the electron-poor region at the edges of the Si=Si dimers. Such interaction in turn permits facile reaction via a “side-on” approach in which the reaction proceeds through the formation of a three-member ring involving one Si atom and the two C atoms of the alkene. We believe that a similar mechanism is likely to be operative for the adsorption of ATB. In this case, such a mechanism might lead to a three-member ring composed of one Si atom of the dimer and two N atoms. The N atoms are expected to be particularly electron-rich due to their high electronegativity. As a result, the approach of the electron-rich N atoms to the electron-deficient region at the side of a dimer would be rather favorable. The ATB molecule could then shift toward the other Si atom of the dimer to make the four-member ring. To allow the N atoms access to the Si atom, this type of mechanism would require the *tert*-butyl groups to be in a near-cis configuration initially. However, the size of the *t*-butyl groups likely prevents this arrangement to a large degree. Consequently, during the side-on approach, the C and H atoms will be close enough to the other Si atom (or perhaps to another dimer) to react with it. This process would result in the loss of H atoms from the ATB molecule as well as an occasional loss of a methyl group, accounting for the observed Si–H stretch and alkene C–H stretch, respectively. If the steric hindrance of the *tert*-butyl groups does indeed prevent the molecule from approaching the surface in a cis configuration, the calculated minimum energy conformation of a trans geometry does not require a cis to trans conversion from the transition state. Such a conversion, involving movement of bulky *tert*-butyl groups about a ring system, is expected to be unfavorable. We therefore believe that the adsorption of ATB on Si(001) may proceed through a side-on approach intermediate, in which a three-member ring is temporarily formed. The steric bulkiness of the *tert*-butyl groups leads to some C–H dissociation at 300 K, but the N–N bond is not cleaved. The dissociation is clearly thermally activated, as it is not observed at 130 K. A four-member ring with the *tert*-butyl groups in a trans configuration is ultimately the most stable adsorption geometry.

V. Summary

We have shown, then, that ATB is able to bond to the Si(001) surface through an interaction of the π bond of the azo group with the π bonds of the Si=Si dimers, leading to the formation of two new Si–N σ bonds. Although some fragmentation is observed when this reaction occurs at 300 K, our studies at low temperature indicate that the fragmentation is thermally activated and can be avoided by performing the adsorption step using precooled surfaces. Steric interactions then stabilize this configuration to temperatures well above room temperature. The azo compounds, therefore, represent an additional class of

molecules that may be utilized to form ordered organic layers on a Si(001) surface.

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