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Bonding of Nitrogen-Containing Organic Molecules to the Silicon(001) Surface: The Role of Aromaticity[†]

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The adsorption of pyrrole, aniline, 3-pyrroline, and pyrrolidine on the Si(001)–(2 × 1) surface has been studied using Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Both pyrrole and aniline retain their aromatic character after bonding to the surface. Spectroscopic evidence indicates that each of these aromatic molecules can attach to the Si(001) surface via cleavage of one N–H bond, linking the molecule to the surface through a Si–N tether. Isotopic studies of pyrrole show evidence for additional cleavage of C–H bonds. While strong selectivity favoring bonding through the nitrogen atom is observed for the aromatic molecules, the unsaturated molecule 3-pyrroline shows evidence for at least two bonding configurations. XPS and FTIR data show that 3-pyrroline can bond either through the nitrogen atom with cleavage of an N–H bond, or through the C=C bond via the surface equivalent of a [2 + 2] cycloaddition reaction. Pyrrolidine appears to bond only through the nitrogen atom. Potential factors controlling the selectivity in bonding and the role of aromaticity in controlling reaction pathways on silicon surfaces are discussed.

I. Introduction

Recent advances in the field of molecular electronics are fueling an interest in the attachment of a wide variety of organic molecules to surfaces. Previous studies have shown that organic molecules containing one or more unsaturated bonds can link to the Si(001) surface, producing molecular layers with unprecedented chemical and structural homogeneity.^{1–8} Many of these organic–Si(001) reactions are similar to well-known reactions from organic chemistry.^{9,10} The analogy with organic chemistry arises from the fact that the Si(001) surface undergoes a reconstruction involving a pairing of surface atoms, forming surface dimers. These dimers are formally held together with both a strong σ and a weak π bond,^{11–13} making them structurally and electronically similar to the C=C bonds of organic alkenes.

One of the central problems in the field of molecular electronics is the development of well-defined chemical attachment schemes for bonding molecules with delocalized π -electron systems to surfaces without disrupting the π conjugation. Previous studies have showed that unsaturated organic compounds, such as ethylene, cyclopentene, and 1,3-cyclohexadiene, can react with the Si(001) surface via mechanisms that are analogous to the [2 + 2] and [4 + 2] cycloaddition reactions of organic chemistry.^{1,4–8,14–20} More recent studies of simple aromatic molecules such as benzene,^{21–25} toluene,^{24,26} and xylene²⁴ have shown that adsorption is accompanied by a loss of aromaticity. However, some functionalized aromatic molecules such as styrene²⁷ and phenyl isothiocyanate²⁸ interact with Si(001), exhibiting a high degree of selectivity. These substituted aromatic molecules favor bonding through the external substituent group rather than bonding through the aromatic ring. Understanding the factors controlling selectivity

in bonding is important for development of well-defined interfaces between silicon and organic materials for applications such as molecular electronics and chemical/biological sensing.

Molecules containing nitrogen atoms are of particular interest because the lone-pair electrons are good electron donors, giving these compounds particularly useful chemical and electrical properties. Referring to the structures shown in Figure 1, pyrrole (C₄H₄NH, Figure 1a) is an aromatic molecule in which with the nitrogen atom is part of a five-member ring. In this molecule, the two lone-pair electrons of the nitrogen atom and the two C=C bonds form a six-electron conjugated π -electron system. This molecule could be interesting for molecular electronic applications because the polymerized form, polypyrrole, has been shown to be a good organic conductor.^{29–31} The partially unsaturated analogue of pyrrole, 3-pyrroline (C₄H₆NH, Figure 1c), has a single C=C bond that is not conjugated to the N atom. The fully saturated molecule, pyrrolidine (C₄H₈NH, Figure 1d) although structurally similar to pyrrole and 3-pyrroline, is a simple secondary amine. Like pyrrole, aniline (C₆H₅NH₂, Figure 1b) is aromatic, but the NH₂ group is external to the aromatic phenyl ring. Comparison of the bonding of these nitrogen-containing molecules to the Si(001) surface provides an improved understanding of the factors controlling selectivity and electronic properties of the interfaces between extended silicon surfaces and individual molecules.

II. Experimental Section

The experiments described here were performed in several different ultra-high-vacuum (UHV) chambers, each having base pressure of $<1 \times 10^{-10}$ Torr. The Si(001) samples were rinsed in methanol and then cleaned of residual carbon contamination by exposure to ozone for approximately 15 min. The samples were degassed at ~ 850 K overnight in the chamber and then annealed to 1400 K to remove the oxide layer. This procedure produces a clean and well-ordered (2 × 1) reconstructed Si-

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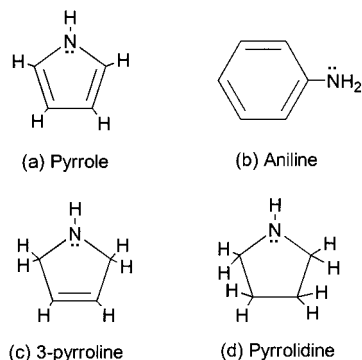


Figure 1. Structures of several N-containing organic compounds. (a) Pyrrole. (b) Aniline. (c) 3-Pyrroline. (d) Pyrrolidine.

(001) surface.¹² Highly doped (0.01–0.02 ohm·cm, Sb-doped) samples were used for the XPS experiments, while lightly doped (15 ohm·cm, B-doped) samples were used in the IR experiments.

Fourier transform infrared (FTIR) absorption spectra were obtained using 8 mm × 20 mm × 0.7 mm pieces cut from a 15 ohm·cm Si(001) wafer polished on the large (001) faces. The 8 mm × 0.7 mm edges were polished for use as a multiple internal reflection prism. Infrared radiation from a Mattson RS-1 FTIR spectrometer was coupled to an ultra-high-vacuum chamber via BaF₂ windows and focused onto the narrow polished edge of the sample; the light exiting from the other end of the sample was collected with an InSb detector cooled to 77 K. Spectra were acquired with 4 cm⁻¹ resolution. The spectra of pyrrole and aniline in the liquid phase were obtained using a Nicolet 740 FTIR spectrometer with a triglycine sulfate (TGS) detector at 1 cm⁻¹ resolution.

X-ray photoelectron spectroscopy (XPS) data were obtained using a Physical Electronics system with monochromatized Al K α radiation (1486.6 eV). To increase surface sensitivity and reduce emission from bulk silicon, the sample was oriented so that the detected photoelectrons were emitted at a takeoff angle of 20° from the surface plane. The Si(2p) peaks were 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 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 and not to changes in band bending. The energy corrections are always <0.2 eV. The integrated intensity of the bulk Si signal was used as an internal standard to ensure that changes in XPS intensities were not from changes in source intensity or sample alignment. XPS spectra were analyzed using standard curve-fitting procedures in which the quality of fit was evaluated through a “goodness-of-fit” parameter, based on a reduced χ^2 .³² In general, a smaller value of “goodness-of-fit” represents a better fit, with values of less than 1 indicating that the fit and the data are indistinguishable within the experimental error.

Pyrrole (C₄H₄NH) was obtained from Fisher Scientific with 99% purity. To help distinguish between the different chemically inequivalent hydrogen atoms on the pyrrole molecule, some experiments were performed using isotopically labeled compounds. Pyrrole-2,3,4,5-*d*₄ (C₄D₄NH) was purchased from CDN Isotopes with 98.6% isotopic purity. Pyrrole-*N-d* (C₄H₄ND) was prepared in our laboratory by hydrogen–deuterium exchange between pyrrole and neutral D₂O, followed by distillation.³³ Analysis via NMR showed that the resulting C₄H₄ND had an isotopic purity of 92%. Aniline (C₆H₆NH₂), 3-pyrroline (C₄H₆NH), and pyrrolidine (C₄H₈NH) were purchased from Aldrich

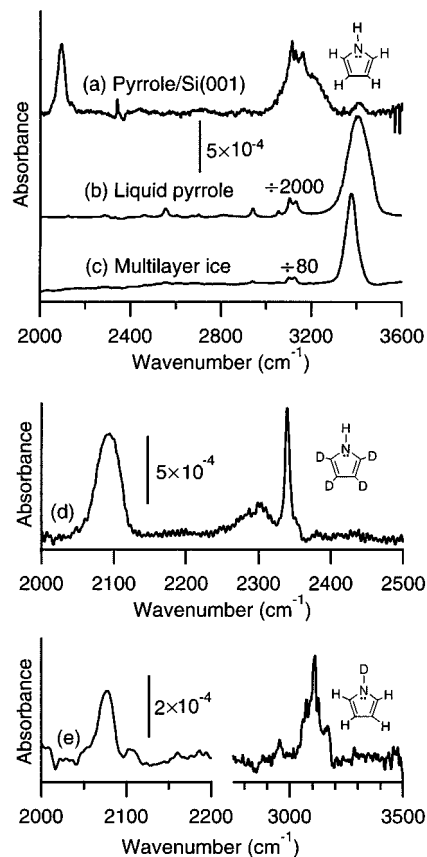


Figure 2. FTIR spectra of pyrrole. (a) Spectrum of a Si(001) surface exposed to 20 L of pyrrole. (b) Spectrum of neat liquid pyrrole. (c) Spectrum of pyrrole ice on a Si(001) surface. (d) Spectrum of a Si(001) surface exposed to 20 L of pyrrole-2,3,4,5-*d*₄ at 300 K. (e) Spectrum of a Si(001) surface exposed to 20 L of pyrrole-*N-d* at 300 K.

with 99% purity. Freeze–pump–thaw cycles were performed to remove all dissolved gases prior to dosing. The purity of each compound was verified in the vacuum chamber using an in situ mass spectrometer. The molecules were introduced to the UHV chamber using a variable leak valve. Chamber pressure was used as an indicator for overall dosage; however the actual exposures at the surface are higher. All exposures are expressed as nominal exposures, in units of langmuirs (1 langmuir ≡ 1 L ≡ 1 × 10⁻⁶ Torr·s).

III. Results

In this study, we investigated several different cyclic molecules, shown in Figure 1. Pyrrole (Figure 1a) and aniline (Figure 1b) are both aromatic molecules. 3-pyrroline (Figure 1c) and pyrrolidine (Figure 1d) are the partially and fully saturated analogues of pyrrole, respectively.

A. Pyrrole. Figure 2a shows an FTIR spectrum of a Si(001) surface exposed to 20 L (1.0 × 10⁻⁷ Torr for 200 s) of pyrrole at 300 K. This spectrum shows a large peak at 2093 cm⁻¹, within the frequency range in which Si–H stretching vibrations are typically observed. No significant absorption is detected in the 2600–3000 cm⁻¹ region, where absorption from alkane-like C–H vibrations are observed. However, strong peaks are observed at 3111 and 3160 cm⁻¹, in the spectral region usually associated with absorption from alkene-like or aromatic C–H vibrations. Finally, a small absorption feature is observed at 3405 cm⁻¹.

To establish whether the surface coverage has reached a saturation limit, spectra were also obtained after exposures of

5 and 100 L. These spectra (not shown) showed that the intensities of all observed vibrational modes increased uniformly up to an exposure of approximately 5 L; higher exposures (up to 100 L) lead to no further change in the spectra. Thus, the spectra obtained after a 20 L exposure are characteristic of the saturated surface.

Figure 2b shows an FTIR spectrum of liquid pyrrole. The spectrum is dominated by a very large peak at 3405 cm^{-1} arising from the N–H stretching vibrations. In the $3000\text{--}3200\text{ cm}^{-1}$ region, several peaks are observed at 3055, 3103, and 3131 cm^{-1} that arise from the alkene-like C–H vibrations. A comparison of the spectra of surface-adsorbed pyrrole (Figure 2a) and liquid pyrrole (Figure 2b) shows that although many of the peak positions, especially in the C–H region, remain unchanged, there are very significant changes in the relative intensities of the absorption. Most notable is the strong attenuation of the absorption due to the N–H stretching vibration for surface-adsorbed pyrrole in comparison with the C–H vibrations. Pure liquid pyrrole has an intense N–H absorption 6 times that of the most intense C–H peak. Upon adsorption this intensity ratio $I_{\text{NH}}/I_{\text{CH}}$ decreases from 6 to only 0.04.

Figure 2c shows a second comparison spectrum, obtained by exposing a cold (116 K) sample to 200 L of pyrrole (2.0×10^{-7} Torr for 1000 s); under these conditions the pyrrole condenses as a multilayer on the surface. The resulting spectrum is very similar to that obtained for pyrrole liquid (Figure 2b), showing an intense N–H vibration and weaker C–H vibrations with an intensity ratio of $I_{\text{NH}}/I_{\text{CH}} \sim 6$.

The presence of the strong Si–H stretching peak at 2093 cm^{-1} in Figure 2a indicates that there is N–H or C–H bond cleavage accompanying pyrrole absorption onto the Si(001) surface at 300 K. To determine the extent of the dissociation and the identity of the bonds broken during absorption, FTIR spectra were obtained of pyrrole-2,3,4,5- d_4 ($\text{C}_4\text{D}_4\text{NH}$) and pyrrole-*N-d* ($\text{C}_4\text{H}_4\text{ND}$) chemisorbed to Si(001). As a point of reference, we determined that the intensity ratio $I_{\text{SiH}}/I_{\text{CH}}$ region for normal pyrrole (Figure 2a) is approximately unity.

Figure 2d shows the spectrum obtained by exposing a Si(001) sample to 20 L (1.0×10^{-7} Torr for 200 s) of ($\text{C}_4\text{D}_4\text{NH}$) at 300 K. Notably, a strong Si–H vibration is again observed at 2093 cm^{-1} . Figure 2d also shows C–D stretching vibrations at 2290 and 2302 cm^{-1} , in the region normally associated with C–D vibrations of unsaturated or aromatic compounds. The sharp peak at 2341 cm^{-1} arises from a small amount of residual CO_2 in the optical path and is also observed in Figure 2a. Because the presence of the CO_2 line makes comparison of integrated peak areas difficult, we instead compare the peak intensities. Comparison of C–H and C–D peak intensities requires correcting for the different transition dipole strengths. The infrared transition dipole for C–D is expected to be approximately half that of C–H.³⁴ The maximum absorbance of the Si–H stretch in Figure 2d is nearly 3 times that of the C–D stretch, while in Figure 2a the Si–H stretch and C–H intensities are nearly identical. Figure 2e shows the spectrum of a Si(001) sample exposed to 20 L (1.0×10^{-7} Torr for 200 s) of pyrrole-*N-d* ($\text{C}_4\text{H}_4\text{ND}$) at 300 K. While both the Si–H and the C–H vibrational modes appear to be less intense (probably due to slight changes in sample alignment), the Si–H line at 2078 cm^{-1} is about 0.6 times the intensity of the C–H stretch at 3110 cm^{-1} . Comparison of these infrared spectra suggests that the Si–H stretching vibrations cannot be attributed solely to cleavage of N–H or C–H bond, but likely arise from a combination of both. However, we note that while the isotopic purity of the liquid pyrrole-*N-d* ($\text{C}_4\text{H}_4\text{ND}$) was determined to

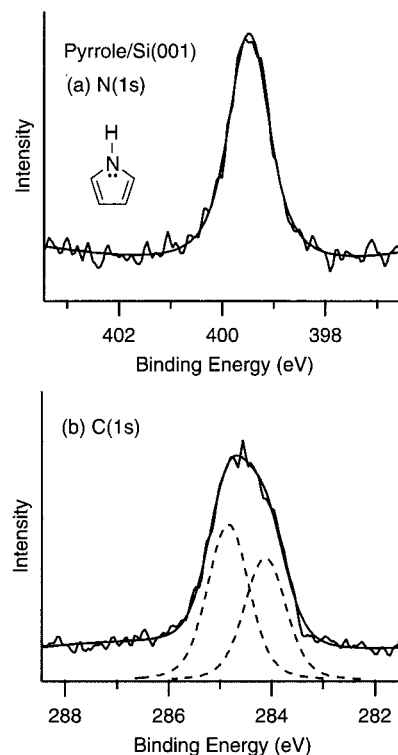


Figure 3. XPS spectra of a 300 K Si(001) sample exposed to 20 L of pyrrole. (a) N(1s). (b) C(1s).

be 92% by NMR, the possibility of some isotopic exchange during dosing cannot be ruled out.

XPS spectra were taken for Si(2p), C(1s), and N(1s) core levels. Figure 3a shows the N(1s) spectrum for a Si(001) sample exposed to 20 L (1.0×10^{-7} Torr for 200 s) of pyrrole at 300 K. Figure 3b shows the corresponding C(1s) XPS spectrum. The N(1s) spectrum (Figure 3a) shows a single peak, with a binding energy of 399.4 eV and a full width at half-maximum (fwhm) of 0.99 eV. Fitting to a single curve yields a reduced χ^2 of 0.79. The narrow width and low χ^2 suggest that there is only one chemically distinguishable form of nitrogen on the surface. Fitting the C(1s) spectrum yields two peaks at binding energies of 284.8 and 284.1 eV with an intensity ratio of 1.2 and a reduced χ^2 of 0.97. The resulting fwhm of 0.96 eV is slightly broader than the effective resolution of the instrument. Alternatively, the C(1s) data can be fit to a single peak at 284.4 eV with a fwhm of 1.76 eV, in agreement with another recent study of this system.³⁵ Since the 1.76 eV line width is significantly broader than the instrumental line width, the C(1s) data shown is better described by the two-peak fit, indicating that there is more than one form of carbon on the surface. Nevertheless, the data can be described either as two discrete forms of carbon with binding energies of 284.8 and 284.1 eV or as a multitude of forms with inhomogeneous broadening leading to an average binding energy of 284.4 eV.

To determine the thermal stability of the pyrrole layer on the Si(001) surface above room temperature, samples exposed to 20 L of pyrrole at 300 K were subsequently heated for 10 min to elevated temperatures and then cooled to 300 K for XPS analysis. Figure 4 shows the resulting N(1s) and C(1s) XPS spectra. At temperatures through 450 K, no changes are observed in the shape or intensities of the N(1s) or C(1s) spectra, as seen in Figure 4b,f. Annealing to 650 K leads to no significant change in the primary N(1s) and C(1s) peaks, but does produce new peaks at 397.7 eV for N(1s) (Figure 4c) and 283.3 eV for C(1s) (Figure 4g). These energies are identical with those previously

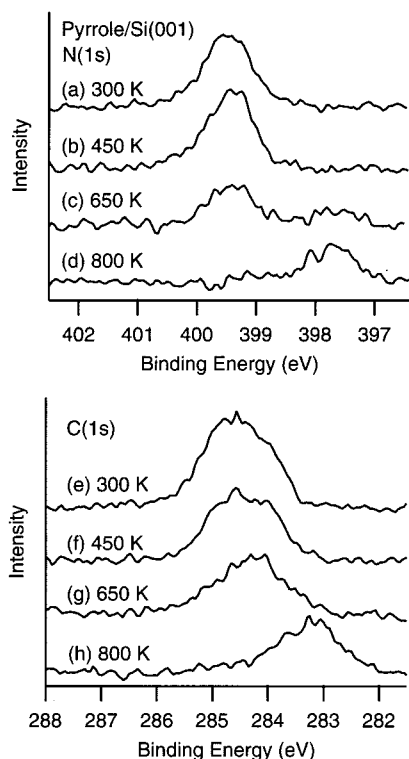


Figure 4. XPS spectra of a Si(001) sample exposed to 20 L of pyrrole at 300 K and subsequently annealed to higher temperatures. (a) N(1s), 300 K. (b) N(1s), 450 K. (c) N(1s), 650 K. (d) N(1s), 800 K. (e) C(1s), 300 K. (f) C(1s), 450 K. (g) C(1s), 650 K. (h) C(1s), 800 K.

observed for silicon nitride^{36–38} and silicon carbide,^{36,37} respectively. Annealing to higher temperature (800 K) leads to almost complete formation of silicon nitride and silicon carbide (Figure 4d,h).

B. Aniline. Figure 5 shows the N(1s) and C(1s) XPS spectra of a Si(001) surface exposed to 5 L (5.0×10^{-8} Torr for 100 s) of aniline at 300 K. The N(1s) spectrum (Figure 5a) shows a single fitted peak, with a binding energy of 398.9 eV, a fwhm of 0.78 eV, and a reduced χ^2 of 0.97. The narrow width and low χ^2 suggest that there is only one chemically distinguishable form of N on the surface. Curve fitting for the C(1s) spectrum (Figure 5b) using one to three peaks yielded reduced χ^2 values of 1.87, 1.30, and 0.97, respectively. These values suggest that fitting to three peaks is justified statistically. The resulting fit yields a major peak at 284.4 eV (71% in total area, 0.71 eV fwhm) and two others, 284.9 eV (24% in total area, 0.71 eV fwhm) and 286.0 eV (4% in total area, 0.71 eV fwhm), respectively.

Figure 6a shows an FTIR spectrum of a Si(001) surface exposed to 10 L (5.0×10^{-8} Torr for 200 s) of aniline at 300 K. This spectrum shows a large absorption feature at 2072 cm^{-1} associated with a Si–H stretch. No significant absorption is detected in the 2600–3000 cm^{-1} region, where alkane-like C–H vibrations are typically observed. However, strong peaks are observed at 3008, 3043, and 3077 cm^{-1} , in the spectral region usually associated with C–H vibrations of aromatic systems. A large peak is observed at 3356 cm^{-1} where the N–H stretching vibrations are typically observed. Finally, a small peak is observed at 3217 cm^{-1} . For comparison, Figure 6b shows an FTIR spectrum of liquid aniline. The spectrum shows high-frequency C–H stretching peaks at 3011, 3039, and 3073 cm^{-1} , nearly identical with those observed in Figure 6a. Two large peaks are observed at 3356 and 3431 cm^{-1} , which are associated with the symmetric and asymmetric N–H vibrations.³⁹ A

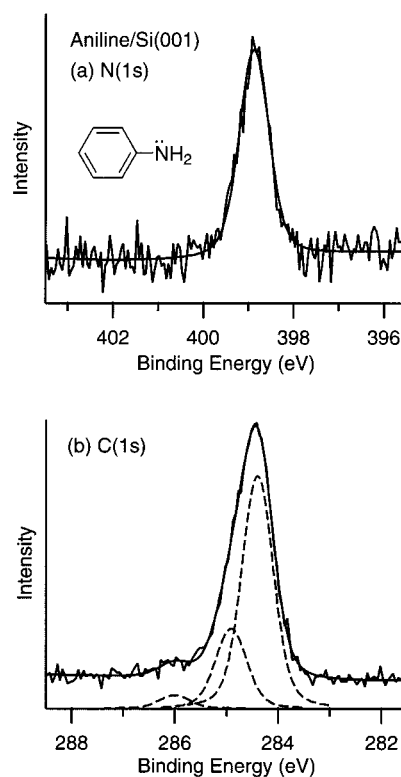


Figure 5. XPS spectra of a Si(001) sample exposed to 5 L of aniline at 300 K. (a) N(1s). (b) C(1s).

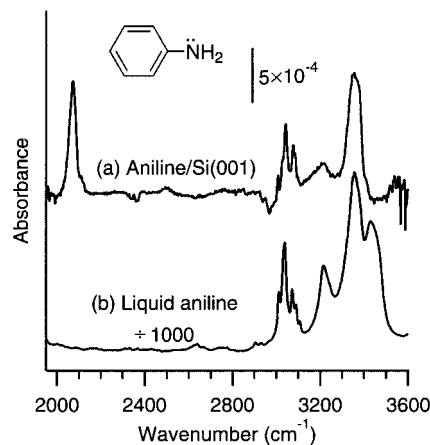


Figure 6. FTIR spectra of aniline. (a) Spectrum of Si(001) surface exposed to 10 L of aniline at 300 K. (b) Spectrum of neat liquid aniline.

moderately strong peak is also observed at 3217 cm^{-1} , which has been previously assigned to a combination band of the ring stretches.³⁹ A comparison of the spectra of surface-adsorbed aniline (Figure 6a) and liquid aniline (Figure 6b) shows that adsorption of aniline onto the Si(001) surface causes the two N–H modes at 3356 and 3431 cm^{-1} (Figure 6b) to collapse to a single mode at 3356 cm^{-1} (Figure 6a) and leads to the appearance of a strong Si–H vibrational feature at 2072 cm^{-1} . However, the C–H spectral region and the ring-stretching combination band at 3217 cm^{-1} remain nearly unperturbed.

C. Nonaromatic Amines. To understand how the electronic structure of the molecule affects its adsorption onto the surface, similar experiments were performed with 3-pyrroline and several saturated amines, including pyrrolidine. Figure 7 shows infrared spectra of Si(001) surfaces exposed to 3-pyrroline. The spectrum in Figure 7a was obtained after a Si(001) surface at 300 K was exposed to 1 L (1.0×10^{-8} Torr for 100 s) of 3-pyrroline.

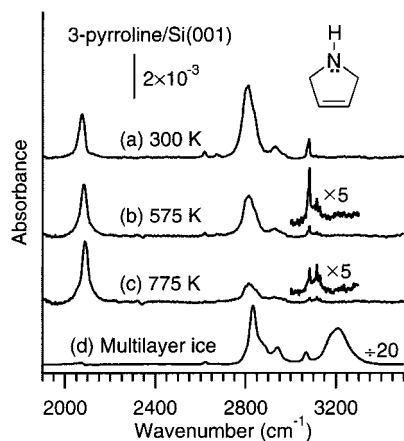


Figure 7. FTIR spectra of a Si(001) sample exposed to 1 L of 3-pyrroline at (a) 300 K and subsequently annealed at elevated temperature: (b) 575 K and (c) 775 K. Spectra are obtained after cooling sample back to 300 K. (d) 3-Pyrroline ice spectrum obtained by exposing the Si(001) sample at 80 K to 1 L of 3-pyrroline.

Significant absorption is observed in the Si–H vibrational region (2086 cm^{-1}), indicating cleavage of either C–H or N–H bonds. The C–H region is dominated by an intense peak at 2810 cm^{-1} and a weaker peak at 2931 cm^{-1} , in the frequency range typically associated with C–H vibrational modes of saturated molecules. In addition, there is a sharp feature at 3080 cm^{-1} , in the region normally attributed to absorption from C–H vibrations of unsaturated or aromatic species. For comparison, Figure 7d shows an FTIR spectrum of a 3-pyrroline “ice”, formed by exposing the Si(001) surface at 80 K to 1 L (1.0×10^{-8} Torr for 100 s) to form a condensed multilayer. Comparison of the monolayer spectrum (Figure 7a) with the multilayer spectrum (Figure 7d) shows that there is a decrease of $\sim 25\text{ cm}^{-1}$ in the position of the most intense C–H peak when the molecule is adsorbed on the surface. However, the peaks at 2931 and 3080 cm^{-1} are nearly identical for the monolayer and multilayer spectra. The most notable difference between these spectra is that the condensed multilayer shows a very strong absorption from an N–H vibrational mode at 3210 cm^{-1} that is almost completely absent for the chemisorbed monolayer.

Figure 7b shows the spectrum obtained when the sample prepared at 300 K (Figure 7a) is subsequently annealed at 575 K for 1 min, while Figure 7c shows a similar spectrum after annealing at 775 K. In both cases the sample was returned to 300 K before acquiring the spectrum. Upon annealing to 575 K, Figure 7b shows that the high-frequency 3080 cm^{-1} peak decreases in intensity. Meanwhile, a new absorption feature becomes visible at 3115 cm^{-1} , in the region normally associated with absorption from C–H vibrations of aromatic rings. The overall increase in the Si–H intensity relative to the C–H intensity suggests that at this temperature cleavage of C–H bonds occurs, resulting in an increase of surface-adsorbed hydrogen atoms. Heating to 775 K (Figure 7c) further increases the intensity of the peak at 3115 cm^{-1} and decreases the absorbance at 3080 cm^{-1} . Although the overall decrease in intensity in Figure 7c may arise from changes in sample alignment due to heating and cooling, such alignment changes should affect the entire spectrum uniformly. Changes in the relative intensity of peaks within a given spectrum (particularly Si–H vs C–H) reflect changes in chemical composition of the sample.

XPS spectra were obtained of Si(001) exposed to 1 L (1.0×10^{-8} Torr for 100 s) of 3-pyrroline. Figure 8 shows the N(1s) spectra for 3-pyrroline adsorbed onto Si(001) at 300 K (Figure

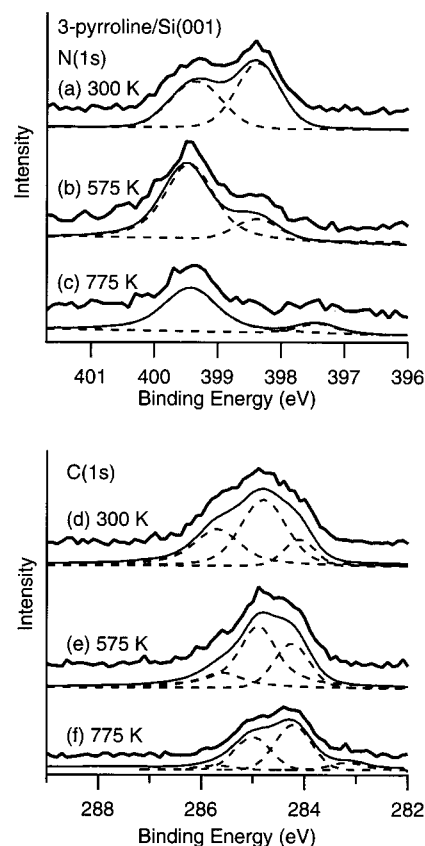


Figure 8. XPS spectra of a Si(001) sample exposed to 1 L of 3-pyrroline at 300 K and subsequently annealed at elevated temperature. All spectra were obtained after cooling the sample back to 300 K. (a) N(1s), 300 K. (b) N(1s), 575 K. (c) N(1s), 775 K. (d) C(1s), 300 K. (e) C(1s), 575 K. (f) C(1s), 775 K.

8a) and after annealing to 575 (Figure 8b) and 775 K (Figure 8c). Figure 8d–f shows the corresponding C(1s) spectra. After adsorption at 300 K, the N(1s) spectrum (Figure 8a) shows two clearly resolvable N peaks at 398.4 and 399.4 eV, with the peak at 398.4 eV comprising 60% of the total area. The room-temperature data show that the molecules are distributed into at least two bonding configurations, as evidenced by the presence of two distinct N(1s) binding energies. The corresponding C(1s) XPS spectrum (Figure 8d) shows three component peaks at 284.1, 284.8, and 285.7 eV, with the center peak (284.8 eV) comprising 55% of the total area.

To identify whether the relative populations of molecules in the two configurations could be altered by heating, spectra were obtained after briefly annealing at 575 and 775 K. Figure 8b,e shows that annealing to 575 K significantly changes the N(1s) and C(1s) spectra. The C(1s) peak at 284.1 eV increases to 1.8 times its original area, while the peak at 285.7 eV decreases to 0.3 times its original area and the 284.8 eV peak decreases slightly. These changes in C(1s) bonding energy are accompanied by changes in N(1s) binding energies. Annealing to 575 K causes the 399.4 eV N(1s) peak to increase to 1.8 times its original value, while the peak at 398.4 eV decreases to only ~ 0.2 of its original area. We note that, while the intensity of individual peaks in both the N(1s) and C(1s) regions change when the sample is annealed, the total areas remain unchanged. The fact that the total area does not change indicates that there is little or no desorption of molecules from the surface, and that the differences in the spectra are due to changes in bonding configuration and/or dissociation.

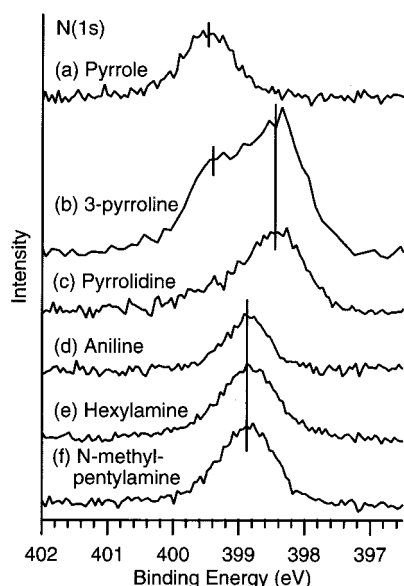


Figure 9. N(1s) XPS spectra for several amines on Si(001) surfaces at 300 K. (a) Pyrrole. (b) 3-Pyrroline. (c) Pyrrolidine. (d) Aniline. (e) Hexylamine. (f) *N*-Methylpentylamine.

After annealing to 775 K, the N(1s) and C(1s) spectra both show substantial changes. Figure 8c shows that after heating to 775 K the N(1s) peak near 399.4 eV has decreased slightly, the peak near 398.4 eV is absent, and a new peak is visible at 397.4 eV, close to the value previously observed for silicon nitride.^{36–38} Similarly, heating the sample results in changes in the C(1s) peaks, as seen in Figure 8f. The C(1s) peaks at 285.7 and 284.8 eV both undergo substantial decreases, while a new peak is observed at 283.2 eV that is attributed to silicon carbide formation.^{36,37} Both the N(1s) and C(1s) spectra show integrated intensities that are significantly smaller than those of the earlier spectra.

We also investigated the adsorption of several other N-containing compounds on the Si(001) surface to help identify specific core-level peaks. Figure 9 summarizes these N(1s) XPS spectra. For reference, Figure 9a,b,d shows spectra of pyrrole, 3-pyrroline, and aniline on Si(001). The XPS spectrum of pyrrolidine (C_4H_8NH) on Si(001) is shown in Figure 9c. Pyrrolidine is a five-member heterocyclic ring with a secondary amino group similar to that of 3-pyrroline. Because it is fully saturated, pyrrolidine is expected to bond to Si(001) through its nitrogen atom, most likely undergoing deprotonation of the nitrogen upon adsorption. The XPS spectrum of this molecule reveals only a single N(1s) peak at a binding energy of 398.4 eV, nearly 1 eV lower in binding energy than we observe for pyrrole, and almost the same as one of the N(1s) peaks observed for 3-pyrroline. Figure 9e,f shows the XPS spectra of the primary amine hexylamine ($C_6H_{13}NH_2$) and the secondary amine *N*-methylpentylamine ($C_5H_{11}-NH-CH_3$). Both these molecules give rise to a single N(1s) peak with a binding energy between 398.8 and 399.0 eV, which we attribute to the formation of a single bond between the nitrogen atom and the silicon surface.

IV. Discussion

Previous studies of simple alkenes and conjugated dienes have shown that bonding to the Si(001) surface occurs primarily through the molecular π systems.^{1,19,20,40,41} While these reactions are somewhat analogous to the [2 + 2] and [4 + 2] “Diels–Alder” reactions of organic chemistry, several studies^{27,42–44} have shown that these reactions likely proceed through a low-

symmetry intermediate and are therefore more like nucleophilic addition reactions between the electron-rich alkene and the Si=Si dimers rather than truly concerted cycloaddition reactions.

Previous studies of benzene,^{21,22,25} toluene,^{24,26} and xylene^{24,26} have shown that purely aromatic systems also will bond to the Si(001) surface, but the behavior is more complex. STM⁴⁵ and FTIR data²⁴ show that benzene can bond into two configurations. One configuration involves a [4 + 2] reaction between benzene and a Si=Si dimer. A second “tight bridge” configuration links one aromatic ring with two adjacent dimers within a single dimer row.^{21–25} While calculations show that the “tight bridge” configuration is more stable thermodynamically because it involves formation of four Si–C bonds, the [4 + 2] configuration appears to be a metastable intermediate.^{23,27} These previous studies establish that bonding of aromatic molecules to the Si(001) surface is thermodynamically downhill (even though it involves loss of aromaticity), and that the high strength of the Si–C bond may lead to nonthermodynamic products.

Previous studies of ammonia (NH_3) have shown that bonding occurs via cleavage of one N–H bond, leaving chemisorbed Si– NH_2 species and adsorbed hydrogen atoms.^{46–48} Although detailed mechanistic studies have not been performed, we believe that in NH_3 and other amines the electron-rich “lone pair” on the nitrogen atom likely interacts at one end of the Si=Si dimer, with subsequent (or concurrent) N–H bond cleavage leading to an N-bonded species. This suggests that the interaction of amino groups and unsaturated C=C bonds with Si=Si dimers may both involve nucleophilic addition processes.

We can use these previous studies to guide selection of the most likely bonding configurations for the molecules studied here. Since interactions of individual C=C groups (such as the nonconjugated alkene group in 3-pyrroline), benzene-like aromatic rings (in pyrrole and aniline), and amino groups (in all three molecules studied here) are all thermodynamically feasible, we expect that multiple reaction products are possible.

A. Bonding Configuration of Pyrrole. The FTIR data for pyrrole on Si(001) shows that the vast majority of the IR intensity remains in the high-frequency regime where alkenes and aromatic C–H vibrations lie. There is little or no absorbance in the 2800–3000 cm^{-1} region normally associated with saturated C–H vibrational modes. The presence of the Si–H stretch indicates that there is significant cleavage of C–H or N–H bonds. The striking decrease in the intensity of the N–H stretching mode upon adsorption on the Si(001) surface (Figure 2a) indicates that the vast majority of the N–H bonds cleave upon adsorption, but leaves open the question of whether C–H bonds also might cleave. The isotopic labeling studies show that significant Si–H stretching vibrations are produced by C_4H_4NH , C_4D_4NH , and C_4H_4ND upon adsorption onto Si(001). A more quantitative comparison of the spectra for C_4H_4NH (Figure 2a) and C_4D_4NH (Figure 2d) shows that the integrated area of the Si–H stretching vibrations are nearly identical, but the ratio of I_{Si-H}/I_{C-D} from C_4D_4NH is nearly 3 times larger than I_{Si-H}/I_{C-H} from C_4H_4NH . The increase in intensity of the Si–H absorption relative to that of the C–D absorption upon deuteration of the ring is attributed primarily to the fact that the intensity of a C–D stretch is expected to be only approximately half that of a comparable C–H stretch.³⁴ Consequently, if all the Si–H vibrations arose from cleavage of N–H bonds and none from C–H bonds, then one would expect I_{Si-H}/I_{C-D} in Figure 2d to be twice the ratio I_{Si-H}/I_{C-H} in Figure 2a. The expected ratio of 2 is less than the experimentally observed ratio of 3, indicating that the number of H atoms that arise from

C—H and from N—H bond cleavage is comparable. This is further supported by noting that the $I_{\text{Si-H}}/I_{\text{C-H}}$ ratio from chemisorbed $\text{C}_4\text{H}_4\text{ND}$ (Figure 2e) is ~ 0.6 times the $I_{\text{Si-H}}/I_{\text{C-H}}$ from $\text{C}_4\text{H}_4\text{NH}$. Overall, the FTIR studies show that the hydrogen on the surface comes from cleavage of N—H and C—H bonds. However, the relative extent of each cannot be quantitatively determined due to possible isotopic exchange during dosing.

Since the frequencies of the C—H stretching vibrations from unsaturated and/or aromatic molecules are typically significantly higher than those from saturated molecules, more detailed analysis of the C—H region can shed light on the fate of the aromatic ring of pyrrole after chemisorption. Most notable is the fact that the FTIR spectrum of adsorbed pyrrole (Figure 2a) shows almost exclusively high-frequency vibrational modes above 3100 cm^{-1} , with little or no evidence for alkane-like vibrations. This, in turn, strongly suggests that the aromaticity of the molecule is retained upon adsorption onto the surface.

Further information about the chemical bonding can be extracted from the XPS data. First, we note that the N(1s) XPS data in Figure 3a shows a single peak at 399.4 eV, with a fwhm close to the resolution of our instrument. The narrow width (0.99 eV fwhm) of this peak and low value (0.79) for the reduced χ^2 suggest that the N atoms are in very similar chemical environments. To correlate the chemical environment with the core level binding energy, however, it is necessary to compare the spectrum of chemisorbed pyrrole with other intact molecules and chemisorbed species of known structure. The N(1s) binding energy of 399.4 eV for pyrrole bonded to Si(001) is nearly 1 eV higher than the binding energy for surface-attached pyrrolidine (its completely saturated analogue) and 0.6 eV higher than the N(1s) binding energy for surface-attached hexylamine and *N*-methylpentylamine. Similarly, studies of ammonia decomposition on Si(001) have reported bonding via N—H bond cleavage to produce Si-NH_x species with N(1s) binding energies of 398.0–398.8 eV.^{38,49} Interestingly, the N(1s) binding energy of chemisorbed pyrrole is significantly higher than that of most compounds that have a nitrogen atom bonded directly to silicon.

We believe that the high binding energy of pyrrole bonded to Si(001) is a direct consequence of the aromaticity of the surface-attached molecule. Aromaticity can have a large impact on XPS binding energies. Particularly notable is the fact that previous measurements of the gas-phase XPS spectra of pyrrolidine reported a binding energy of 404.60 eV, compared with the gas-phase value of 406.18 eV for pyrrole.⁵⁰ This difference of nearly 1.6 eV arises entirely from the fact that the delocalization of electrons that gives aromatic molecules their unusual chemical and physical properties also gives them unusually large core-level binding energies. Applying this same concept to pyrrole, then, leads us to conclude that the large N(1s) binding energy of pyrrole when adsorbed on the Si(001) surface is consistent with the FTIR evidence that the surface-bound pyrrole molecules have retained their aromatic character.

Figure 10 shows several potential configurations corresponding to a [2 + 2] cycloaddition reaction (Figure 10a), a [4 + 2] “Diels–Alder” reaction (Figure 10b), formation of a “tight-bridge” adduct like that found for benzene (Figure 10c),²¹ one configuration formed via N—H bond cleavage (Figure 10d), and one configuration including both N—H and C—H bond cleavage (Figure 10e). Based on the above analysis, the FTIR and XPS data are inconsistent with the configurations shown in Figure 10a–c. The proposed configuration in Figure 10d is consistent with the retention of aromaticity and the absence of detectable N—H stretching vibrations, but does not account for the fact

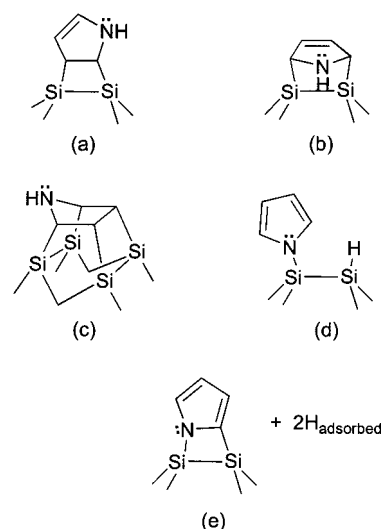


Figure 10. Possible bonding configurations of pyrrole on the Si(001) surface.

that the FTIR data show some C—H bond cleavage. Figure 10e, however, appears to adequately account for all of the experimental data. This configuration would have equal amounts of N—H and C—H bond cleavage, while preserving the aromaticity of the surface-bound molecule. We believe that most molecules bond into the configuration shown in Figure 10d, with some molecules undergoing further C—H bond cleavage to form the adduct shown in Figure 10e.

Another recent study of pyrrole on Si(001) using XPS and high-resolution electron energy loss spectroscopy (HREELS)³⁵ has reported results that are generally consistent with ours. This recent study reported a single sharp N(1s) feature at the same corrected binding energy that we report, and observed modes in HREELS that were interpreted as Si—H stretching vibrations and ring vibrations of an intact pyrrole ring. Since no isotopic labeling or more detailed studies were performed, however, the previous study was not able to distinguish whether any C—H bond cleavage occurred. Our FTIR results clearly show that significant amounts of C—H bond cleavage occur concurrently, so that the single configuration in Figure 10d (also proposed by Qiao et al.) cannot account for all the experimental data. Nevertheless, the previous study and our study both conclude that pyrrole bonds to the surface by cleaving an N—H bond, resulting in a surface-bound complex with a direct N—Si linkage and a structure that preserves the overall aromaticity of the molecule.

B. Bonding Configuration of Aniline. The FTIR spectrum of aniline chemisorbed on Si(001) shows that a significant fraction of the absorbance due to N—H stretching vibrations is retained. However, the presence of strong Si—H stretching vibrations shows that adsorption is accompanied by cleavage of either N—H or C—H bonds. Comparison of the spectra of surface-adsorbed aniline (Figure 6a) and liquid aniline (Figure 6b) shows that the C—H spectral region and the combination band of ring stretches at 3217 cm^{-1} are almost identical for both spectra, suggesting that the benzene ring in aniline remains unperturbed. The collapse of the two N—H modes observed for liquid aniline into a single N—H mode observed for the surface-adsorbed aniline is consistent with cleavage of one N—H bond.

Further information about how aniline binds to the surface can be obtained from the XPS data. We note that the N(1s) XPS data shows a single peak at the binding energy of 398.9 eV. This energy is almost identical with the N(1s) binding energies shown in Figure 9e for hexylamine (a primary amine)

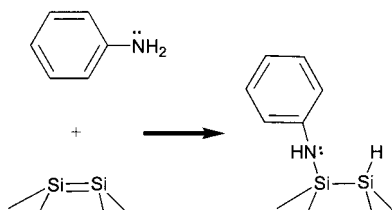


Figure 11. Bonding configuration of aniline on the Si(001) surface.

and Figure 9f for *N*-methylpentylamine (a secondary amine). Infrared data (not shown) for both hexylamine and *N*-methylpentylamine confirms that they bond to Si(001) by cleaving one N–H bond.⁵¹ Consequently, the N(1s) XPS spectra of hexylamine and *N*-methylpentylamine can be used to identify the expected core level shift for a nonaromatic nitrogen atom bonded to a Si(001) surface.

The similarity in N(1s) binding energy between aniline and these compounds suggests that aniline also bonds to the Si(001) surface via cleavage of one N–H bond. The nitrogen atom directly bonds to the silicon surface, as depicted in Figure 11. A previous study of aniline found that bonding aniline to the Si(001) surface lowered the N(1s) binding energy by 1.2 eV compared with a multilayer film.⁵² X-ray photoelectron spectra, combined with ab initio calculations and scanning tunneling microscopy studies, led to the conclusion that bonding occurred via cleavage of one N–H bond, as shown in Figure 11.⁵³ Importantly, this geometry leaves the aromaticity of the aniline molecule intact. Our XPS and FTIR data are consistent with this interpretation.

Detailed interpretation of the C(1s) spectra is difficult. The combined contributions to the signal from possible C–N, C–Si, and aromatic carbons complicates interpretation. The C(1s) XPS data for aniline bonded to Si(001) shows two primary peaks at 284.4 eV (71% in total area) and 284.9 eV (24% in total area). The largest peak (284.4 eV) has a binding energy that is almost the same as the 284.3 eV observed for solid benzene, naphthalene, and tetracene.^{54–56} Furthermore, the amino group could be expected to slightly increase the binding energies of the carbon atoms adjacent to it, perhaps accounting for the peak at 284.9 eV. Although exact assignments cannot be made at this time, we note that the C(1s) data is at least consistent with the proposed structure in Figure 11.

C. Bonding Configuration of 3-Pyrroline. While the N(1s) XPS data for pyrrole shows only a single bonding configuration, the XPS spectrum of 3-pyrroline in Figure 8a clearly shows two types of nitrogen atoms after bonding to the Si(001) surface. Since alkene bonds are known to react with the Si=Si dimers of the Si(001) surface via the equivalent of a [2 + 2] cycloaddition reaction, it is logical to assume that the two most likely bonding configurations would be the N-bonded configuration shown in Figure 12a and the [2 + 2] adduct in Figure 12b.^{1,18}

The FTIR spectrum at 300 K in Figure 7a shows a high frequency absorption feature at 3080 cm⁻¹ associated with an alkene-like C–H stretching mode. The presence of this peak suggests that a significant number of C=C bonds in 3-pyrroline remain intact when the molecule is adsorbed on the Si(001) surface. The absence of any detectable N–H vibration in the 3200–3500 cm⁻¹ region indicates that almost all of the N–H bonds are cleaved. The deprotonation of the nitrogen atom results in surface hydrogen, as evidenced by a strong Si–H absorption. It is not possible from the FTIR data to establish whether a significant amount of C–H bond cleavage also occurs.

Although the presence of more than one bonding configu-

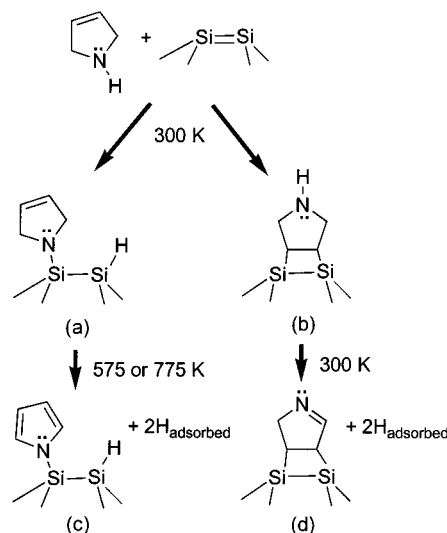


Figure 12. Illustration of different bonding configurations of 3-pyrroline on Si(001) surface.

ration complicates the interpretations, we note that the C(1s) and N(1s) XPS spectra obtained at different temperatures (Figure 8) show that the intensity of the C(1s) peak at 285.7 eV is correlated with the N(1s) peak at 398.4 eV and the C(1s) peak at 284.1 eV is correlated with the N(1s) peak at 399.4 eV. The C(1s) peak at 284.8 eV cannot be correlated with either of the N peaks.

The N(1s) binding energy of 3-pyrroline at 398.4 eV is almost identical with the 398.4 eV value for pyrrolidine (the saturated analogue of 3-pyrroline) chemisorbed on Si(001), suggesting that the peak may arise from N atoms bonded directly to the silicon surface. The temperature-dependent changes in the 398.4 eV peak correlate with those of the C(1s) peak at 285.7 eV. This 285.7 eV energy is significantly higher than the energies observed previously for tetrahedrally coordinated carbon atoms bonded to silicon, but is consistent with C=C species. For example, cyclopentene bonds to Si(001) through the C=C bond. Each surface-bound cyclopentene molecule has two carbon atoms with binding energies of 284.2 eV that are bonded directly to silicon and three alkane-like carbon atoms with a binding energy of 284.9 eV. A small amount of physisorbed cyclopentene also present on the surface gave rise to a C(1s) peak at 285.5 eV, corresponding to an intact C=C species.¹⁸ Based on the above evidence, we attribute the 398.4 eV N(1s) and 285.7 eV C(1s) peaks to molecules bonded to the surface through the N atom accompanied by N–H bond cleavage, as depicted in Figure 12a.

To assign the second bonding configuration, we note that the high binding energy (399.4 eV) of the second N(1s) peak suggests an unsaturated or even an aromatic form of nitrogen. This N(1s) peak correlates with the C(1s) peak at 284.1 eV; the low binding energy of the C(1s) peak is most consistent with alkane-like carbon atoms bonded directly to the Si(001) surface like those present in the geometries in Figure 12b,d. However, the high energy of the N(1s) peak and the absence of any N–H vibration are most consistent with a chemisorbed molecule having a N=C bond like that in Figure 12d.

The presence of these unsaturated or possibly aromatic surface-bound species is further evidenced from the annealing data in Figure 7. As the temperature is increased, the increase in relative intensity of the Si–H vibrational modes suggests that additional C–H bond cleavage takes place. The carbon atoms could form new bonds to the surface or could produce

TABLE 1: N(1s) and C(1s) Binding Energies (in eV) of Some N-Containing Organic Molecules on the Si(001) Surface

	element, bond				
	C, C–Si	C, alkane	C, alkene	N, N–Si	N, N=C
pyrrole			284.1	399.4	
			284.8		
3-pyrroline	284.1	284.8	285.7	398.4	399.4
pyrrolidine		285.0		398.4	
aniline			284.4	398.9	
hexylamine		285.5		398.8	
N-methylpentylamine		285.5		398.9	

more highly unsaturated surface products. However, the FTIR spectra in Figure 7 show new peaks at 3115 and 3129 cm^{-1} . The high vibrational frequencies indicate that the adsorbed species form new unsaturated bonds. The vibrational mode at 3115 cm^{-1} is sufficiently high to lead us to conclude that at least some of the surface products may be aromatic in character, and may consist of surface products similar to those produced by adsorption of pyrrole (Figure 12c).

D. Behavior of N-Containing Compounds on Si(001) Surfaces. Table 1 summarizes the XPS results for pyrrole, 3-pyrroline, pyrrolidine, aniline, and several alkylamines. All these molecules appear to bond to Si(001) predominantly through the N atom, with cleavage of an N–H bond and possibly C–H bonds. Previous studies have shown that cleavage of N–H bonds occurs readily when ammonia (NH_3) interacts with Si(001), resulting in surface-adsorbed NH_2 fragments.^{46,47,57}

Perhaps the most notable result of this study is that both pyrrole and aniline appear to retain their aromatic character upon adsorption. We note that previous photoelectron spectroscopy studies of aniline ($\text{C}_6\text{H}_5\text{--NH}_2$)^{52,53,58} and 1,4-phenylenediamine ($\text{H}_2\text{N--C}_6\text{H}_4\text{--NH}_2$)⁵⁹ likewise concluded that bonding occurs via cleavage of one N–H bond while preserving the aromatic nature of the adsorbed molecules. Similarly, a recent XPS study of pyrrole concluded that it likewise bonded by cleaving the N–H bond, leaving the aromatic ring intact.³⁵ Our studies provide new infrared evidence for retention of aromaticity for both pyrrole and aniline upon bonding to the Si(001) surface. More importantly, a more systematic study of aniline, pyrrole, and its saturated analogues helps to establish some general trends for understanding the chemistry of organic amines on the Si(001) surface.

The retention of aromaticity when pyrrole or aniline is bonded to the Si(001) surface is somewhat surprising in light of the fact that benzene,²¹ toluene,^{24,26} and xylene²⁴ all *lose* their aromaticity upon adsorption to Si(001). Infrared spectra of benzene, toluene, and xylene show that upon bonding to Si(001) the high-frequency C–H stretches characteristic of the aromatic rings are replaced by much lower frequency vibrations characteristic of tetrahedrally coordinated carbon atoms, with no evidence for C–H bond cleavage.²⁴ However, molecules consisting of aromatic rings modified with electron-rich substituent groups, such as styrene ($\text{C}_6\text{H}_5\text{--CH=CH}_2$)²⁷ and phenyl isothiocyanate ($\text{C}_6\text{H}_5\text{--N=C=S}$),²⁸ show a strong propensity for bonding through the substituent groups rather than via the ring. Furthermore, *ab initio* calculations for styrene²⁷ and phenyl isothiocyanate²⁸ showed that the preferential bonding through the external groups could not be explained on the basis of simple thermodynamics because the four Si–C bonds formed when these molecules bond to Si(001) through their aromatic ring (giving a surface adduct similar to that of benzene)²³ yielded overall enthalpies of adsorption that were nearly identical with those that would be expected for bonding through the external substituent groups. More detailed calculations for styrene

showed that the preferential bonding via the external vinyl (C=C group) rather than the aromatic ring was dynamic in origin, arising from the fact that the vinyl group could readily interact at the edge of a Si=Si dimer to attach styrene via its vinyl group.²⁷ These prior studies suggest that the electron-donating ability of the substituent group can strongly affect the distribution of surface adducts.

It remains unresolved whether similar kinetic considerations or thermodynamic effects are controlling the product distributions for aniline and pyrrole on Si(001). The selectivity observed for pyrrole and aniline, strongly favoring bonding through the N atom and leaving the aromatic ring unperturbed, could arise from the ability of the “lone-pair” electrons on the nitrogen atom to donate electron density to the Si=Si dimers, making the interaction between the nitrogen atom and the Si=Si dimers a kinetically favored pathway. Alternatively, the energy of the N–H bond of aniline (88 kJ/mol)⁶⁰ may be sufficiently low to make bond cleavage thermodynamically favored over the various cycloaddition products analogous to those observed for benzene, toluene, and xylene.

For the nonaromatic molecule 3-pyrroline, the presence of multiple products and the irreversible changes between these products as a function of temperature clearly point toward kinetic factors as controlling the product distribution. In this molecule, the single alkene group is not conjugated to the nitrogen lone pair, so that the adsorption chemistry of the alkene group and the amino group are expected to be independent of one another. In the case of 3-pyrroline this leads to at least two products, some of which are bonded through the nitrogen atom and some of which are the products of a [2 + 2] cycloaddition reaction. We note that while [2 + 2] cycloaddition reactions are symmetry forbidden in the high-symmetry [$2\pi_s + 2\pi_s$] suprafacial–suprafacial geometry,⁶¹ recent studies have shown that these reactions are facile on the Si(001) surface because they can readily proceed through a low-symmetry pathway that resembles a nucleophilic addition reaction between the electron-rich alkene group and the electron-deficient region at the end of a Si=Si surface dimer.^{42–44} Since the amino group⁵¹ and C=C bond^{5,6,8} are both known to react the Si(001) with high reaction probability, a quantitative understanding of the product distribution for 3-pyrroline on the Si(001) surface will likely require a detailed understanding of the molecular dynamics during the adsorption process.

This study shows that molecules with aromatic rings show a strong preference for retention of the aromaticity, while molecules with similar structure have diverse chemical bonding configurations when they have multiple functional groups. The ability of pyrrole and aniline to retain aromaticity after bonding to the Si(001) surface has a number of important implications for bonding of conjugated π -electron systems to silicon surfaces in a highly controlled way.

V. Conclusions

The above results show that retention of aromaticity is a strong driving force controlling selectivity in bonding of multifunctional molecules to the Si(001) surface. Our results indicate that the lone-pair electrons of nitrogen can act as nucleophiles to form Si–N covalent linkages to the Si(001) surface and that the conjugation of these electrons to other unsaturated bonds can have a significant influence on the resulting surface adducts. The difference in selectivity between pyrrole and its partially saturated derivative 3-pyrroline permits one to distinguish between the structural and electronic factors controlling the adsorption process. Through an increased

understanding of these factors, it may be possible to design and implement improved strategies for tethering complex molecules to surfaces in a highly selective manner.

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