

## Selective Adsorption of Pyridine at Isolated Reactive Sites on Si(100)

Jill A. Miwa,<sup>‡</sup> Brian J. Eves,<sup>†</sup> Federico Rosei,<sup>‡</sup> and Gregory P. Lopinski<sup>\*,†</sup>

Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, and Institut National de la Recherche Scientifique, Énergie, Matériaux et Télécommunications, Université du Québec, Varennes, Québec, J3X 1S2

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Dative bonding of nitrogen-containing heterocycles offers a strategy for the controlled attachment of aromatic molecules to silicon surfaces. However, while scanning tunneling microscopy shows that pyridine on clean Si(100) initially binds via a dative bonding configuration, slow conversion to a more stable bridging state, destroying the aromaticity, is observed. To restrict adsorption to the dative bonded form, we investigated the interaction of pyridine with isolated reactive sites on partially H-terminated Si(100). While dative bonding on isolated clean dimers is observed, single dangling bonds remain unreacted. This selectivity can be accounted for by the ability of the Si–Si dimers to act as electron acceptors that stabilize the dative bonded species. This observation has important implications for the controlled positioning of single molecules on silicon via dative bonding.

Recent adsorption studies of organic molecules on silicon surfaces have been largely motivated by the prospect of fabricating hybrid organic/silicon molecular devices.<sup>1–4</sup> Aromatic molecules are of particular interest for such applications because of their potential use as molecular wires or switches. Numerous studies have demonstrated that unsaturated molecules react readily with the dangling bonds of clean silicon surfaces via cycloaddition reactions.<sup>1–6</sup> The prototypical aromatic molecule, benzene, exhibits multiple bonding configurations on the Si(100) surface.<sup>7–11</sup> This lack of selectivity is a common feature for molecular adsorption on silicon where multiple bonding configurations with similar binding energies are usually available. In the case of benzene, all three observed configurations destroy the aromaticity of the molecule, an important functionality in the context of nanoelectronics. Controlling the selectivity of adsorption while preserving aromaticity are challenges that need to be addressed to design molecule-based devices with tailored structures and electronic properties.

In addition to these cycloaddition reactions, molecules containing nitrogen have an additional bonding configuration available. The lone pair electrons on the nitrogen can be donated to the silicon, resulting in stable chemisorbed species as demonstrated for several saturated amines on Si(100) and Si(111) and termed “dative bonding”.<sup>12–14</sup> For aromatic heterocycles such as pyridine (C<sub>5</sub>H<sub>5</sub>N), this bonding strategy is potentially attractive as it preserves the aromaticity of the molecule. However, based on the observations for benzene, competitive adsorption between the dative and cycloaddition pathways is expected. Previous experimental and theoretical studies for pyridine on Si(100) have indicated that this is indeed the case.<sup>15–17</sup>

In this letter we report results of scanning tunneling microscopy (STM) investigations of the interaction of pyridine with

clean Si(100) and isolated reactive sites (i.e., single dangling bonds and clean dimers) on H-terminated Si(100). On clean Si(100), while a great majority (over 80%) of molecules are found to initially adopt the dative bonded geometry, gradual conversion to a nonaromatic bridge species is observed at room temperature. To restrict adsorption to the aromatic, dative bonded form, the interaction of pyridine with isolated reactive sites on a hydrogen terminated Si(100) surface was studied. While dative bonded species were observed to form on isolated clean dimers, surprisingly pyridine did not react with single dangling bonds. This observation illustrates the ability of clean dimers to act as electron acceptor sites that stabilize the dative bonding adduct.

Clean Si(100) surfaces were prepared in ultrahigh vacuum (UHV) by flashing a well-degassed sample (Virginia Semiconductor, n-type, 0.6–1.4 Ω cm) to 1200 °C. Pyridine (Anachemica, ACS grade, >99%) was purified by performing several freeze–pump–thaw cycles. STM images were obtained in constant current mode at room temperature using an Omicron STM1. Tips were electrochemically etched from tungsten wire and subsequently cleaned in situ by electron bombardment and field emission.

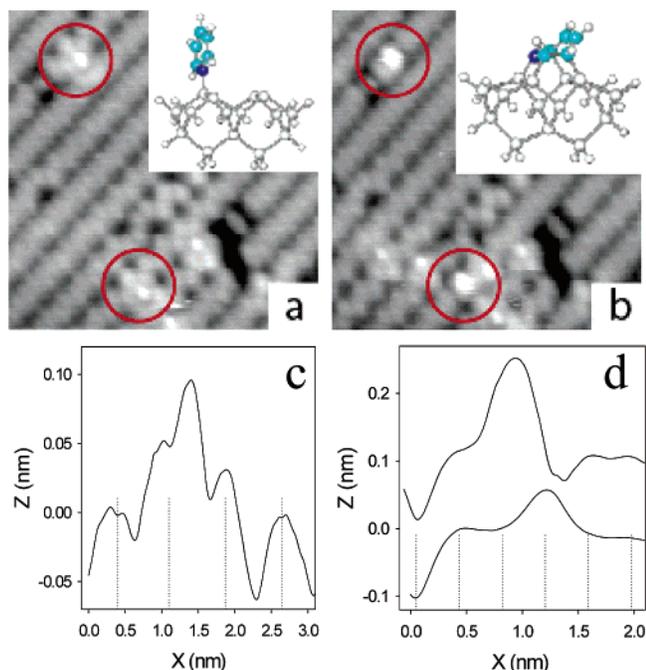
Figure 1 displays two consecutive STM images acquired while exposing the clean Si(100) surface to pyridine. In occupied state images the adsorbed pyridine initially gives rise to paired protrusions on a single dimer as seen in Figure 1a. In this image the two features exhibit an apparent height of ~0.9 and 0.5 Å relative to the surrounding clean dimers, as seen in the representative cross-section (Figure 1c). In addition this asymmetric feature is seen to give rise to a zigzag structure extending for ~2 nm along the dimer row on either side of the adsorbate.

The appearance of the adsorbed pyridine in the STM image is consistent with the dative bonded species shown in the inset of Figure 1a. The paired protrusions in the image can be assigned to the adsorbed pyridine and the remaining dangling

\* Corresponding author. E-mail: Gregory.Lopinski@nrc-cnrc.gc.ca.

† National Research Council of Canada.

‡ Université du Québec.



**Figure 1.** Occupied state STM images ( $7 \times 7$  nm,  $-2$  V,  $40$  pA) during dosing of pyridine on Si(100). In (a) two dative bonded adducts are highlighted and are observed to relax to the “tight bridge” configuration in (b). The insets show model bonding geometries for the dative and tight bridge configurations, respectively. A cross-section (perpendicular to the dimer row) through the highlighted dative bonded pyridine in the top left-hand corner is shown in (c). The dashed lines indicate the center of the dimer rows. Cross-sections (along the dimer row) for the same molecule before (bottom) and after (top) conversion are shown in (d). The deep depression at the left is due to a surface defect and is used to register the two profiles. The dashed lines indicate the position of the dimers along the adjacent row.

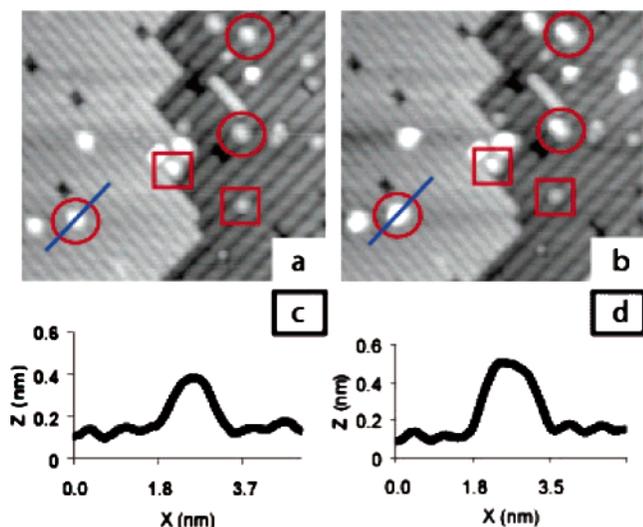
bond of the dimer. At room temperature the dimers of the Si(100) surface exhibit dynamic buckling accompanied by charge transfer from the “down” to the “up” end of the dimer. This charge transfer effect, creating electrophilic and nucleophilic Si atoms on either end of the dimer, strongly influences chemical reactions on this surface.<sup>18</sup> In forming a dative bond, the two lone pair electrons are likely donated to the electrophilic “down” atom of the dimer. To stabilize the dative bonded adduct, the remaining charge on the reacted (“down”) Si atom can be transferred to the unreacted (“up”) atom. Therefore the dangling bond associated with the unreacted atom should be completely filled and should appear somewhat brighter than the surrounding unreacted dimers in occupied state images, as observed. The extended zigzag structures are a result of long-range pinning of the dynamic dimer buckling induced by single dative bonded molecules. This pinning phenomenon is characteristic of the highly asymmetric nature of this bonding configuration. However, in the case of other asymmetric adsorbates, such as propylene, the length scale of pinning is considerably shorter, suggesting that the charge-transfer accompanying dative bonding plays a role in magnifying this pinning effect. Based on the orientation of the adjacent buckled dimers, the larger ( $0.9$  Å) of the two protrusions in Figure 1c can be assigned to the dative bonded molecule while the other feature ( $0.5$  Å) is the completely filled dangling bond.

Figure 1 also demonstrates that the dative bonded configuration is metastable and can convert to a state with a distinctly different appearance in the STM image. In Figure 1b two dative bonded pyridines highlighted in Figure 1a now exhibit a characteristic two-dimer footprint consisting of a bright feature

centered over one dimer with an adjacent darkened dimer. This type of signature has previously been observed for benzene adsorption on Si(100) where it was attributed to a cyclohexenyl geometry involving bridging between adjacent dimers in a row; referred to as the “tight bridge” structure.<sup>7,8</sup> It is reasonable therefore to interpret this feature as a similar bonding configuration for pyridine, as modeled in the inset of Figure 1b. As seen in the representative cross-section along the dimer row shown in Figure 1d, the darkened dimer (slight depression) appears at the position of the initial dative bonded molecule, while the bright feature is assigned to the remaining double bond on the bridge bonded molecule. By examining the adjacent dimers it is also apparent that the zigzag structure of the dimers adjacent to adsorbed pyridines (seen in Figure 1a) is not observed in Figure 1b. This indicates that conversion to the bridge state lifts the pinning of the dimer buckling, as expected for this more symmetric bonding configuration. We have verified that the observed dative to bridge conversion is not induced by the STM tip. However, tip-induced back conversion to the dative bonded state has been observed, similar to the case of benzene where the STM tip could be used to convert molecules from the “tight bridge” back to the metastable “butterfly” configuration.<sup>7</sup> From the observed rate of dative to bridge conversions the barrier for this process can be estimated to be of the order of  $\sim 0.9$  eV (assuming Arrhenius behavior with a prefactor of  $10^{13}$  s<sup>-1</sup>).

This conversion from dative bonding to a more stable non-aromatic species is consistent with previous observations using other techniques. Tao et al. have used X-ray photoelectron spectroscopy and high resolution electron energy loss spectroscopy (HREELS) to show that at low temperature (100 K) pyridine predominantly adopts a dative bonding geometry, slowly converting to a nonaromatic form as the temperature is increased above 170 K.<sup>15</sup> Theoretical calculations are consistent with these experimental findings, indicating that the dative bonded adduct is energetically less stable than several bridging configurations and that a kinetically viable reaction pathway is available.<sup>15,16</sup> However, Tao et al. have excluded the possibility of bridge bonded pyridines based on their HREELS studies of pyridine-*d*<sub>1</sub>, which indicate that carbon atoms in the 2 and 6 positions do not form Si–C bonds. As a result they attributed the observed nonaromatic bonding configuration to a 1,4 cyclohexadienyl “butterfly” configuration that involves bonding to a single dimer.<sup>15</sup> This type of configuration is clearly inconsistent with the two-dimer footprint observed here. We also note that density functional theory calculations indicate that the “tight bridge” state is more stable than the “butterfly” structure.<sup>15,16</sup> While reconciling these apparently contradictory results requires additional study, we note that the conditions of the two experiments are quite different. The present experiments observe the configurations of isolated pyridine molecules at low coverage, whereas the HREELS results were obtained on surfaces prepared by annealing fully covered surfaces formed at low temperatures. It is possible that at higher coverages intermolecular interactions inhibit formation of the bridging geometry. In contrast to the case of benzene where the butterfly configuration is a metastable state,<sup>7–9</sup> we find no evidence for this type of bonding geometry for pyridine at low coverage. In addition to dative and tight bridge configurations, at somewhat higher coverages a minority (<10%) of adsorbed pyridines are observed to adopt a previously unreported inter-row bonding geometry (not shown), appearing as a bright feature centered between dimers on adjacent rows.

The observations of pyridine adsorption on the clean surface clearly indicate that, as in the case of other organic molecules

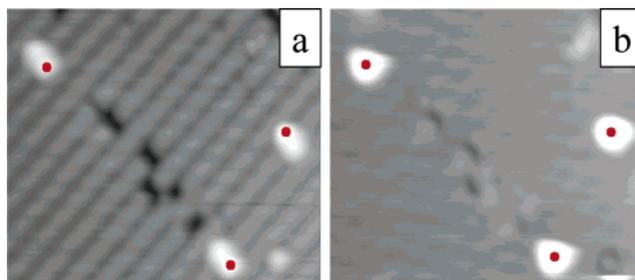


**Figure 2.** (a) STM image ( $17 \times 17$  nm,  $-2.1$  V, 26 pA) of a hydrogen-terminated Si(100) surface with a small number of reactive sites. Examples of clean dimers (circles) and single dangling bonds (squares) are indicated. (b) Shows the same area after dosing the surface with pyridine. The molecules only adsorb to clean dimers and appear as asymmetric protrusions across a single dimer. Cross-sections through the clean dimer before (c) and after (d) the reaction are also shown.

on Si(100), the bonding is not selective with a number (at least three) of coexisting species observed at room temperature. While pyridine is observed to datively bond to Si(100), preserving its aromaticity, slow conversion to a more stable nonaromatic form is observed. To prevent this conversion and preserve aromaticity in the chemisorbed state, the interaction of pyridine with isolated reactive sites on hydrogen-terminated Si(100) was investigated. Hydrogen-passivated silicon has been employed extensively to spatially control the binding of organic molecules on silicon. Incomplete passivation of the surface or controlled removal of individual H-atoms with the STM tip can be used to create a surface with isolated reactive sites. Isolated dangling bonds on H-Si(100) have been used to attach individual molecules,<sup>19–21</sup> or initiate the growth of molecular nanostructures.<sup>22–24</sup>

Figure 2a shows a monohydride-terminated Si(100) surface, created by exposing a clean Si(100) surface to atomic hydrogen at 300 °C.<sup>25</sup> The bright features are isolated reactive sites that can be classified into two categories: (i) features that are symmetric with respect to the dimer row are attributed to clean Si dimers, and (ii) features that are asymmetric are assigned to single dangling bonds. The single dangling bond features are observed to frequently switch from one side of a dimer to the other, consistent with a tip-induced H-atom hopping process previously reported.<sup>26</sup>

Upon dosing with pyridine (Figure 2b), the appearance of the clean dimers is quickly altered, suggesting that a reaction occurred at these sites. In addition to an overall increase in height of these features, a clear asymmetry is seen in both the image and the cross-section (Figure 2d). In contrast, the single dangling bonds remain unchanged, indicating that pyridine did not adsorb at these locations. These single dangling bonds continue to switch from side to side, even after substantial exposure to pyridine, proving that they remain unreacted. (Pyridine bonding to a dangling bond would prevent intradimer H atom hopping.) While only a limited number of reactive sites are shown in Figure 2, an additional number of single dangling bonds were examined for extended exposures, with no evidence of reaction. Since no reaction at single dangling bonds was observed, we can only determine an upper bound on the relative sticking

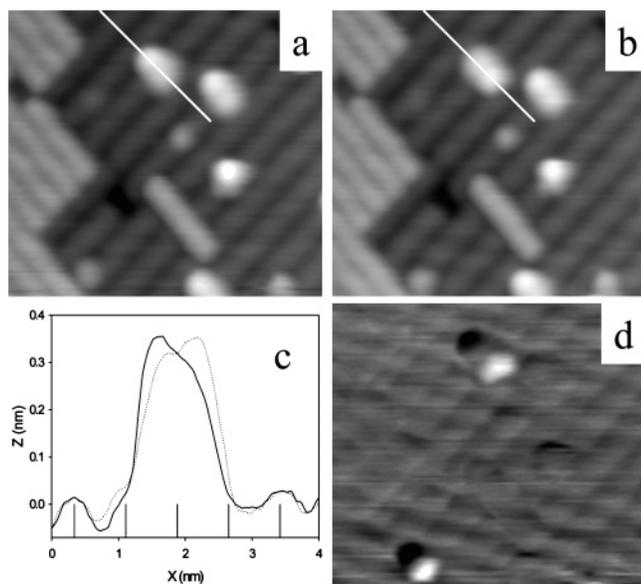


**Figure 3.** (a) Occupied ( $-2.1$  V, 26 pA) and (b) unoccupied ( $+2.1$  V, 26 pA) STM images of a selected area ( $12 \times 10$  nm) showing three isolated dimers with adsorbed pyridine. The dots indicate the same positions on the surface as determined by registering defect sites in the images. The brighter end of the observed asymmetric features in the occupied state image is seen to correspond with the single bright protrusion in the unoccupied state image.

probability at these sites. This analysis indicates that single dangling bonds are at least 600 times less likely to react than clean dimers.

The asymmetric feature observed for pyridine bound to an isolated clean dimer is similar to the paired protrusions observed for datively bonded pyridine on the clean surface. As discussed in the context of adsorption on clean Si(001), both the adsorbed pyridine and the remaining dangling bond on the dimer are expected to appear as bright features in occupied state images (i.e., negative sample bias). However, as discussed above, the remaining dangling bond on a reacted dimer should be fully occupied upon dative bonding. This would imply that this feature should have little unoccupied state character and should appear dark in images taken at positive sample bias. Figure 3 shows occupied and unoccupied state images of a surface region with three reacted clean dimers. Although the unoccupied state image is less resolved, it is clear that the reacted dimers exhibit a single relatively symmetric feature. By registering the two images, it is determined that this unoccupied state feature coincides with the slightly brighter protrusion of the asymmetric pair observed in occupied states. Thus, the appearance of these reacted dimers is consistent with dative bonding to one of the dangling bonds of the dimer. Moreover, the feature that is bright in both polarities can be assigned to the datively bonded pyridine, while the feature that is bright only in occupied state images is the completely filled dangling bond on the unreacted side of the dimer. We note that the adsorbed pyridine is imaged with rather high contrast in the unoccupied state image of Figure 3b, with a measured apparent height of  $\sim 5$  Å relative to the surrounding H-terminated dimers (as compared with  $\sim 3$  Å in occupied states, Figure 3a). This is of the order of the full geometric height of the adsorbed pyridine and considerably “higher” than that of styrene bound to silicon under similar imaging conditions (despite the fact that the styrene is expected to be physically higher). While both these molecules will have similar low-lying electronic states associated with empty  $\pi^*$  orbitals on the phenyl ring, the increased contrast for pyridine suggests that energetically accessible states associated with the vacant lone pair orbitals on the nitrogen atom may play a role in reducing the tunneling barrier in unoccupied states.

These STM observations clearly demonstrate that pyridine selectively adsorbs onto isolated clean dimers via formation of a dative bond. As no bridging configurations are possible without an adjacent clean dimer, these adsorbed molecules remain stabilized in the datively bonded state, preserving the aromaticity of the molecule. It is interesting to note that we do not observe a cyclohexadienyl-like (“butterfly”) bonding configuration on a single dimer, even though such a configuration



**Figure 4.** Sequential STM images ( $-2.1$  V,  $26$  pA) of dimers with adsorbed pyridines are shown in (a) and (b). On the highlighted dimer the brighter side of the protrusion (associated with the pyridine) is seen to switch from the “top” (a) of the dimer row to the “bottom” (b). The contrast on the adjacent dimer remains unchanged. Cross-sections through the indicated adsorbate covered dimer (solid-a, dotted-b) are shown in (c). The image in (d) was obtained by subtracting the images in (a) and (b). Only features that have changed between the two images will exhibit contrast; in this case, the top feature is due to intradimer hopping of pyridine, the bottom feature is due to intradimer H atom hopping.

has been calculated to be thermodynamically stable (with binding energies similar to the dative species).<sup>15,16,27</sup> These DFT calculations agree that a 2,5 butterfly configuration (involving formation of two Si–C bonds) is slightly more stable than the 1,4 species (involving a Si–C and Si–N bond).<sup>15,16</sup> However, the 2,5 species cannot be formed directly from the dative species, suggesting that there is likely a significant kinetic barrier for this type of conversion.

The selectivity of reaction at clean dimers over single dangling bonds may at first appear surprising since both these types of sites are expected to be rather reactive.<sup>19–24</sup> However, this selectivity can be understood in terms of the ability of a clean single dangling bond to act as an electron acceptor. On moderately doped silicon, the dangling bond will likely be initially occupied by a single electron (i.e., half-filled), so that donation of the two nitrogen lone pair electrons will result in a total of three electrons. As only two electrons are required to form the dative bond, the “extra” electron will have to occupy the antibonding level, destabilizing the resulting bond. In contrast, on a clean dimer, this extra electron can be transferred to the unreacted dangling bond, resulting in a completely filled orbital. This type of electron transfer through the Si–Si dimer bond has been invoked previously to account for the formation of a surface donor–acceptor complex upon coadsorption of trimethylamine and boron trifluoride on Si(100).<sup>28</sup>

Close inspection of sequential images of pyridine datively bonded to an isolated clean dimer indicate that the adsorbed molecule can occasionally move from one side of the dimer to the other, as shown in Figure 4. The probability of this intradimer hopping process was determined to be  $\sim 2\%$  per molecule per image under normal imaging conditions ( $25$  pA,  $-2.1$  V) and appeared to increase significantly at higher tunneling currents. This suggests that this process is mediated by electrons from the STM tip. Normalizing the probability of

a hopping event to the number of electrons passing through the molecule yields an estimate of  $\sim 5 \times 10^{-8}$ /electron, similar to that which has been reported in the case of the tip-induced H-atom switching.<sup>26</sup> We note that intradimer hopping is not observed for pyridine adsorption on the clean surface. This is presumably because of the pinning of the dimer buckling induced by the datively bonded pyridine on the clean Si(100) surface. Pyridine switching sides on the clean surface would require all of the adjacent pinned dimers to flip as well. In the case of the isolated dimer on the H-terminated surface, the datively bonded pyridine cannot gain this extra stabilization.

In this letter we presented STM studies of the chemisorption of pyridine on Si(100) and H–Si(100) surfaces. These molecules react readily with the clean surface, with the majority of molecules initially adopting a dative bonded configuration but slowly relaxing to nonaromatic forms. To maintain aromaticity, adsorption was restricted to the dative bonded configuration by using isolated reactive sites on an H-terminated Si(100) surface. Pyridine adsorbs readily to clean dimers but not to single dangling bonds, demonstrating the importance of the local electronic state environment in stabilizing the dative bonded state. The type of selectivity observed here is expected to apply to all molecules that bind to the surface via transfer of their lone pair electrons. This result has important implications for the controlled placement of single molecules on Si(100) via dative interactions. Not only is a clean dimer required for the placement of these molecules but also the remaining dangling bond on this dimer will be occupied with two electrons (i.e., negatively charged). This is likely to modify the electronic properties of the datively bonded molecule, as Piva et al. have recently demonstrated that charged dangling bonds modulate the conductivity through single molecules on silicon.<sup>29</sup> In addition to applications in molecular scale electronics, adsorption onto isolated reactive sites on the H-terminated Si(100) surface has also been used for atomically precise placement of single dopant atoms. STM tip-induced H-atom desorption can be used to template the adsorption of phosphine ( $\text{PH}_3$ ), which is then decomposed upon annealing to incorporate single phosphorus atoms into the surface.<sup>30</sup> Since the initial interaction of phosphine with the surface likely involves formation of a dative bonded species, our results suggest that a single clean Si dimer is the smallest unit required for this process to proceed; it is predicted that phosphine will not react with isolated Si dangling bonds.

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