Selective Functionalization of the Si(100) Surface by a Bifunctional Alkynylamine Molecule: Density Functional Study of the Switching Adsorption Linkage. 2

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The reaction of the bifunctional organic molecule 1-(dimethylamino)-2-propyne (DMAP) on the Si(100) surface has been investigated by density functional calculations employing a two-dimer cluster model. We found that, once in the physisorbed dative bonded well (-20.0 kcal mol^{-1}), DMAP can proceed via a number of pathways, involving the formation of Si−C σ bonds, which lead to thermodynamically more stable configurations. We first considered the cycloaddition of the C≡C triple bond, leading to a Si−C di-σ bonded product (-58.7 kcal mol^{-1}), for which we computed an energy barrier of only 12.5 kcal mol^{-1}, consistently with the observed switching of DMAP adsorption linkage at 300 K. We also explored the dissociative pathway involving the methylene C−H bond cleavage on the dative bonded DMAP, leading to three adsorption products with one (-57.3 kcal mol^{-1}) and three Si−C σ bonds (-58.7 and -60.6 kcal mol^{-1}). The energy barrier for this pathway is computed 24.7 kcal mol^{-1} and may therefore compete at temperature above 300 K with the reaction pathway involving the addition of the alkyne unit.

Introduction

There is currently a great interest in the characterization of organically modified semiconductor surfaces for their potential exploitation in the assembling of microelectronics devices. The Si(100) silicon surface is the semiconductor surface more widely used, and the adsorption of simple organic molecules on this surface can lead to the accomplishment of a new generation of molecular electronic devices.[1−4] Several reactions and techniques for forming bonds between organic molecules and silicon surface are already well established and have been used in the past to modify silicon semiconductor materials.

The Si(100) surface undergoes 2 × 1 reconstruction where two silicon atoms pair together into dimers. The bonding within these dimers has been described in terms of a strong σ bond and a weak π bond and is therefore electronically similar to C=C or Si=Si double bonds of alkenes or disilylenes.[5] However, the π bond in Si(100) is rather weak, suggesting that a diradical description, each Si atom having an unpaired electron, could be more adequate.[6] In addition, it has been shown that the silicon−silicon dimers tilt on the surface, imparting a zwitterionic character which arises from a charge transfer from the "down" atom to the "up" atom.[7] The final reconstructed surface consists of rows of tilted silicon dimers and provides a uniform, ordered, and reactive template for surface chemistry.

The reactivity of these silicon dimers toward cycloaddition reactions with unsaturated bonds has been known for several years and has been exploited to form ordered organic monolayers.[8−11] Particularly studied is the reaction of simple alkenes[12−17] and alkynes[18−22] through [2 + 2] cycloaddition and that of conjugated dienes or aromatic molecules through [4 + 2] cyclo-addition,[23−27] both leading to the formation of two strong Si−C

σ bonds. The zwitterionic character of the surface silicon dimers has also opened the possibility of attaching molecules with electrophilic and nucleophilic groups such as BF$_3$,[28] alcohols,[29−31] and amines.[32−36] In particular, reactions of different organic amines on the silicon surface have recently been studied, showing that primary and secondary amines react with the silicon surface via N−H dissociation, whereas tertiary amines attach molecularly through a N→Si dative bond.

A challenging target in the surface chemistry field is constituted by the reactions with polyfunctional organic molecules, which allow creation of ordered arrays, ready for further functionalization, provided that at least one reactive group is kept unaltered.[37−39] However, the interaction of polyfunctional organic molecules with a semiconductor surface is often poorly understood using the most common surface techniques because of the manifold reactive channels existing on the surface. Theoretical investigations can then be very helpful to systematically explore the various configurations for the adsorption process, evidencing their thermodynamic stability and the kinetic factors controlling the selectivity of the reactive channels.
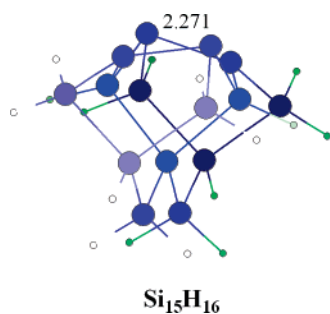
We recently investigated by density functional theory (DFT) the adsorption on the Si(100) surface of a bifunctional organic molecule, the 1-(dimethylamino)-2-propyne (DMAP),[40] with the aim of clarifying the experimental evidence of Yoshinobu and co-workers.[41] They suggested a temperature-dependent selective functionalization of the silicon surface by switching the adsorption linkage of DMAP from the amine to the alkyne group. High-resolution electron energy loss spectroscopy (HREELS) and scanning tunneling microscopy (STM) indicated that at low temperature (65−90 K) DMAP adsorbs on the Si(100) surface through a N→Si dative bond, leaving the −C≡CH unit intact, while, by annealing to 300−400 K, the adsorption linkage is switched to a more stable adsorption configuration, leaving the tertiary amino group free. Even if this configuration has been attributed to a Si−C di-σ-bonded alkene, the experimental data cannot univocally identify the final adsorption structure, and

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Density Functional Study of the Switching Adsorption Linkage

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CHART 1

Si₁₅H₁₆

some data still remain to be fully understood, such as a single-dimer depression in the STM image and an unexpected Si−H stretch in the HREELS, both attributed to the di-σ-bonded species.[41] Employing the one-dimer cluster, Si_9H_{12}, as a model for the silicon surface, we sketched, at a reduced computational cost, the main reaction pathways for the adsorption linkage switching of the dative bonded DMAP.[40] We outlined that only two pathways are kinetically competitive at 300−400 K, i.e., the cycloaddition of the alkyne group and the methylene C−H bond cleavage, thus ruling out the methyl C−H and the N−CH₃ bond cleavage. However, our preliminary work still provides evidence for some shortcomings, essentially due to the use of the one-dimer cluster model, urging for further investigations on the interaction of this bifunctional molecule on larger cluster models.

In the present work, we report the results of DFT calculations on the adsorption of DMAP on the Si(100) surface by employing a two-dimer cluster as a model for the silicon surface. This larger cluster model enables an exhaustive description of the potential energy surface of DMAP adsorbed on the silicon surface, allowing us to consider the adsorption of the bifunctional organic molecule onto two adjacent silicon dimers.

Computational Details

The Si(100) surface has been modeled by a two-dimer cluster model, $Si_{15}H_{16}$, where the top layer consists of four silicon atoms, representing two adjacent surface dimers in the same row of the reconstructed 2 × 1 surface, while all the remaining subsurface silicon atoms are saturated by hydrogen atoms to avoid dangling bond effects; see Chart 1. Although the terminating hydrogen atoms may create a chemical environment different from the actual Si(100)-2 × 1 surface at the cluster boundary, a recent study on cluster models of various sizes has shown that the error is insignificant.[42]

All of the electronic structure calculations in this work are based on DFT [43,44] implemented in Gaussian 03 program package.[45] The structures of the stationary points on the potential energy surface were calculated employing the B3LYP hybrid functional[46−48] for the exchange and correlation energies. B3LYP has been used extensively to calculate organic reactions on the Si(100)-2 × 1 surface with the cluster approximation,[49−52] leading to results generally in good agreement with experiments. All of the structures were optimized by imposing geometrical constraints at the third- and fourth-layer substrate atoms,[53] with an all-electron 6-31G(d,p) basis set. The nature of the stationary points (local minima or transition states) was checked through frequency calculations. Single-point energy calculations were performed on the optimized structures using the larger 6-311+G-(2d,p) basis set. All of the energies reported in the text are zero-point corrected.

Despite the biradicalic nature of the silicon dimers, the initial Si−N dative bond formed in the adsorption of DMAP on the

$Si_{15}H_{16}$ cluster bias the following reaction mechanisms to zwitterionic rather than radicalic character. To verify this statement, unrestricted single point energy calculations have been performed on the geometries optimized with restricted formalism. Indeed, the results have shown that restricted and unrestricted energy values are in agreement.

Results and Discussion

A bifunctional organic molecule as DMAP can give rise to many adsorption structures when approaching the Si(100) surface. The Si−N dative bonded adduct has been shown to be the kinetically favored product at low temperatures (65−90 K), while, by annealing to 300−400 K, the DMAP can evolve via a number of pathways, reaching thermodynamically more stable configurations, involving the formation of Si−C σ bonds. On the basis of the results gathered with the one-dimer cluster model,[40] in the present work we will focus on the kinetically competitive pathways at high temperatures, i.e., the formation of a di-σ bonded species through the addition of the alkyl unit and the methylene C−H bond cleavage, thus neglecting the methyl C−H and the N−CH₃ bond cleavage.

We found seven local minima on the potential energy surface for the adsorption of DMAP by considering the direct attack of the C≡C triple bond and the methylene C−H bond cleavage on the two-dimer cluster model, and they are shown in Figure 1, together with the main geometrical parameters and the binding energy values with respect to free reactants.

The first minimum, structure **1a** in Figure 1, corresponds to the N→Si dative bonded DMAP, which is formed without barrier when DMAP approaches the silicon cluster. Its optimized structure shows a Si−N bond length of 2.045 Å and an adsorption energy of 20.0 kcal mol⁻¹, a value in excellent agreement with that calculated in the previous work corrected for the zero-point energy (−20.2 kcal mol⁻¹),[40] thus confirming the validity of the one-dimer cluster model for the description of localized interactions. We also considered the rotation of DMAP on the Si−N bond, obtaining a second conformer, **1b** in Figure 1, lying only 2.9 kcal mol⁻¹ higher in energy than **1a**, where the C≡C triple bond is oriented above the adjacent silicon dimer, thus suitable placed to attack its dangling silicon atoms. On a real silicon surface the former conformer, **1a**, would correspond to an orientation of the C≡C triple bond between silicon dimer rows, while the latter, **1b**, would correspond to an orientation of the C≡C triple bond along a silicon dimer row. Due to the small energy differences, both conformers **1a** and **1b** are expected to be populated at the experimental temperature values of 300−400 K.

The other minima, **2**−**7** in Figure 1, all refer to the adsorption of DMAP on the silicon surface through Si−C σ bonds and represent feasible adsorption products upon the switching adsorption linkage of DMAP at temperatures of 300−400 K. In particular, structures **2** and **3** show the di-σ addition of the alkyne group on two silicon atoms lying, respectively, between two adjacent dimers and on the top of the dimer adjacent the dative bonded one, while keeping the Si−N dative bond. These structures correspond, respectively, to the well-known end-bridge and on top di-σ configurations considered in previous studies of the adsorption of acetylene on the silicon surface.[19] On the other hand, structure **4** shows the methylene C−H bond cleavage, while structures **5**−**7** come from the nucleophilic attack of the alkyne unit on the adjacent Si−Si dimer in **4** after the C−H bond cleavage. Our calculations show that structures **2**−**7** are by far thermodynamically more stable than the dative bonded structure and, even if the number of Si−C σ bonds
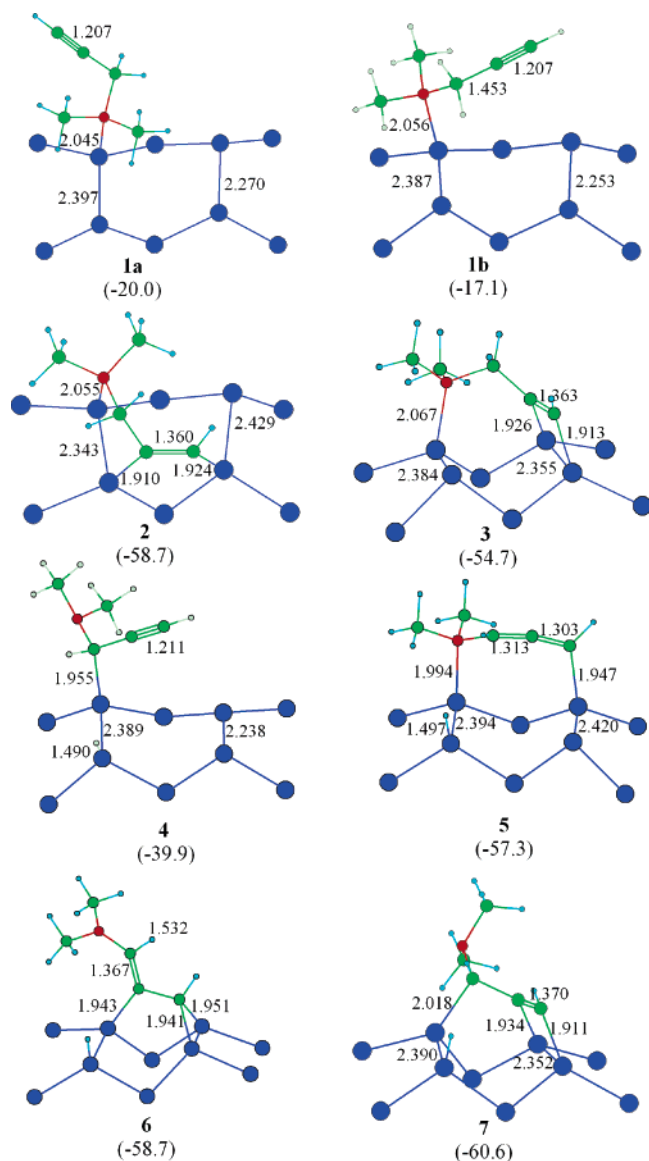
Figure 1. Optimized structures for the adsorption of DMAP on the two-dimer cluster model of Si(100). Only the first and second layers of silicon atoms are shown for clarity. Bond distances in angstroms and binding energies with respect to free reactants in kcal mol^{-1}.

formed range from one (structure **5**), to two (structures **2** and **3**) and to three (structures **6** and **7**), comparable binding energy values have been computed, equal to 58.7, 54.7, 57.3, 58.7, and 60.6 kcal mol^{-1}, respectively, for **2**, **3**, **5**, **6**, and **7**.

Chart 2 depicts the potential energy diagram for the alkyne addition pathway leading to product **2** and **3**, while Chart 3 sketches the potential energy surface for the methylene C—H bond cleavage. According to Chart 2, the C≡C triple bond of the dative bonded DMAP can attack the adjacent silicon dimer, leading to the transition state **TS1**, lying only 12.5 kcal mol^{-1} above **1b** (4.6 kcal mol^{-1} below the reactants). **TS1**, showing a slight lengthening of the C≡C triple bond of 0.03 Å and a Si—C bond distance of 2.307 and 3.105 Å, respectively, for the terminal and the inner carbon atom of the C≡C triple bond, is essentially an asymmetric π adduct of the alkyne unit with the buckled down silicon atom on the adjacent dimer. Notably, the interaction of the C≡C triple bond on the adjacent silicon dimer enhances the electrophilic character of the inner carbon atom of the alkyne group, thus favoring its attack on the buckled up silicon atom of the dative bonded dimer, with a formal charge of −1, because of the quaternary ammonia group. This reaction

pathway thus leads to the adsorption product **2**, with a binding energy of 58.7 kcal mol^{-1}, where two covalent Si—C bonds have formed on two adjacent dimers (1.910 and 1.924 Å), while the terminal C—C bond has lengthened to 1.360 Å (double bond) and the Si—N dative bond is kept unaltered (2.055 Å, see Figure 1). The analysis of the electronic structure shows that **2** is still a zwitterionic form, since the negative charge has moved from the dangling silicon atom of the dative bonded dimer on the adjacent dimer. It is remarkable that the energy barrier of 12.5 kcal mol^{-1} connecting **1b** to **2** is in good agreement with the observed switching of the adsorption linkage of DMAP at 300 K, so that **2** is a good candidate for the adsorption configurations of DMAP after annealing at high temperatures.[41]

Previous studies showed that the lowest energy arrangement for the adsorption of free acetylene on the silicon surface at low coverage is represented by the on top di-σ configuration, where the alkyne unit is added to the Si—Si dimer bond, that is also kinetically favored with respect to the end-bridge config-uration, where the alkyne unit is added across two adjacent silicon dimers.[54] Therefore, we also explored the reaction pathway leading from the dative bonded DMAP **1b** to the on top di-σ alkene product (structure **3** in Figure 1). Despite an accurate study of the potential energy surface of the investigated system, we could only find a transition state **TS2**, lying 2.1 kcal mol^{-1} above the reactants and correlating products **2** and **3**. This result implies that the formation of **3** would occur from **2** with an energy barrier of 60.8 kcal mol^{-1} above **2** and could be therefore ruled out. However, the complexity of the potential energy surface for the adsorption of DMAP on the silicon surface could hinder the determination of another transition state, connecting directly **1b** to **3** and maybe lying above a narrow channel on the potential energy surface. Actually, the presence of the Si—N dative bond does impose severe geometric constraints on the attack of the C≡C bond, hindering the formation of the more strained on top di-σ configuration **3**, and favoring the attack between two adjacent dimers, leading to the less strained end-bridge configuration **2**. This latter attack is also favored by the formal negative charge on the buckled-up silicon atom on the dative bonded dimer. It is therefore not unexpected that only the end-bridge product **2** is formed from the dative bonded configuration **1**. Of course, we cannot exclude the formation of the on top di-σ adsorption product **3** through a direct attack of the C≡C triple bond on the two-dimer cluster without the assistance of the amine group, but this would require the preliminary breaking of the Si—N dative bond and a further barrier of some kcal mol^{-1}, as discussed in previous studies,[21,54] implying a total energy barrier from **1** of more than 25 kcal mol^{-1}, much higher than the barrier leading to **2**. Once **2** is formed and the terminal alkyne carbon atom is bound on the adjacent dimer, the amine assisted formation of the di-σ on top product **3** is easier. Indeed, as reported in Chart 2, the optimized structure of **TS2** shows the bond cleavage of the Si—C bond on the inner alkyne carbon atom (3.344 Å), while keeping the Si—C bond on the terminal carbon atom (1.978 Å) and can proceed to structure **3** through the shift of the inner alkyne carbon atom to the dangling silicon atom on the dimer adjacent to the dative bonded one, forming a di-σ bonded species on this latter dimer.

Chart 3 reports the potential energy diagram for the dissocia-tive adsorption of DMAP on the silicon cluster, involving the methylene C—H bond cleavage. Once in the dative bonded well, the adsorbed DMAP can undergo the abstraction of one hydrogen atom from the methylene group to the buckled up silicon atom on the dative bonded dimer, passing through the
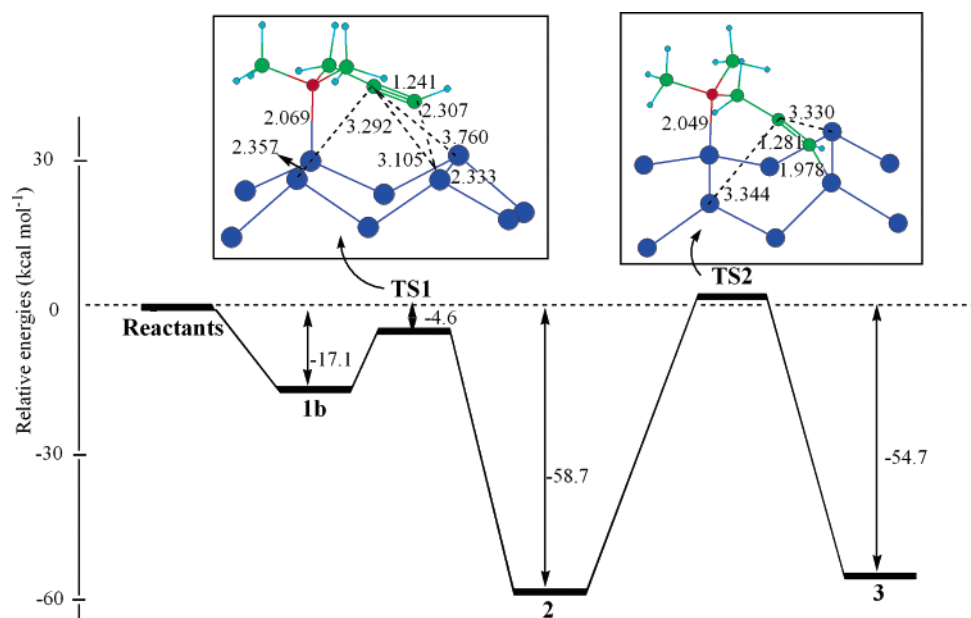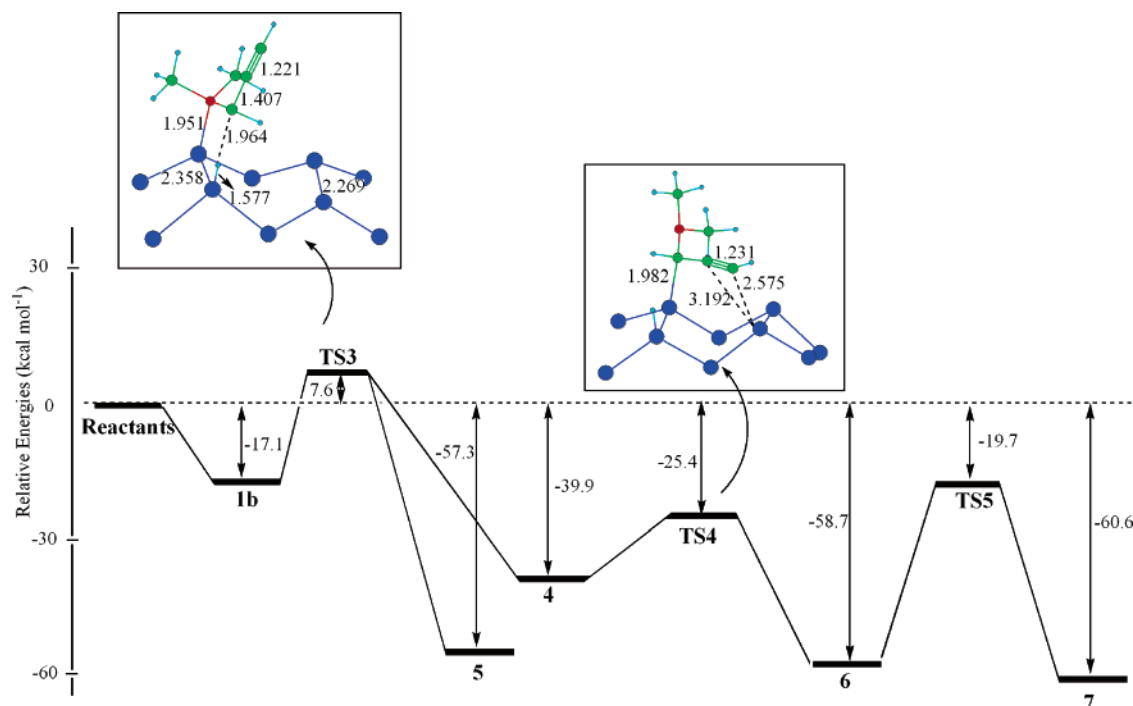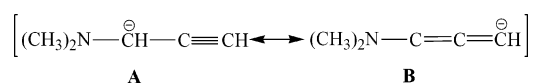
CHART 2

CHART 3

transition state **TS3**, lying 24.7 kcal mol^{-1} above **1b** (7.6 kcal mol^{-1} above reactants). The optimized structure of **TS3** shows a lengthened C−H bond (1.964 Å) and an almost formed Si−H bond (1.577 Å), while the Si−N bond is strengthened (1.951 Å), assuming mostly a covalent character. Our calculations on a one-dimer cluster model[40] showed that the energy barrier for the abstraction of the hydrogen atom from the −CH$_2$ group in α to the C≡C triple bond lies even 15.1 kcal mol^{-1} lower in energy than that for the abstraction of the hydrogen atom from the −CH$_3$ group. This difference in energy can be due to the proximity of the C≡C triple bond, allowing for a delocalization of the negative charge along the C−C−C skeleton and consequently for a large stabilization in energy of the transition state structure. Indeed, the analysis of the Mulliken atomic charges on **TS3** demonstrates that a positive charge is mainly

localized on the silicon atom of the Si−N bond, while a negative charge is delocalized on the methylenic and the terminal alkyne carbon atoms, so that they assume a nucleophilic character and are both ready for an electrophilic attack. According to Chart 3, **TS3** can evolve along two main reaction pathways. In the first one the methylene carbon atom with a carbanionic character attacks the positively charged dative bonded silicon atom, thus causing the displacement of the amino group with the formation of a Si−C (1.954 Å) and a Si−H bond (1.492 Å) and leading to the adsorption product **4**. This reaction pathway, where a Si−H and a Si−C bond are formed, respectively, upon the C−H bond cleavage and the displacement of the dative bond, is well-known for the adsorption of methyl-, dimethyl-, and trimethylamines.[36] In the second pathway, the terminal alkyne carbon atom attacks the silicon dangling atom on the adjacent dimer,

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CHART 4

$$\left[(CH_3)_2N\!-\!\overset{\ominus}{C}H\!-\!C\!\equiv\!CH \longleftrightarrow (CH_3)_2N\!-\!C\!=\!C\!=\!\overset{\ominus}{C}H \right]$$

A **B**

thus forming a Si–C bond of 1.947 Å and leading to the adsorption product **5**. This nucleophilic attack of the terminal alkyne carbon atom is favored by its carbanionic nature, due to the allenic resonance form **B** of the incipient carbanion formed after the C–H rupture; see Chart 4. The adsorption structure **5**, although mono-σ-bonded, shows an adsorption energy of 57.3 kcal mol^{-1}, comparable to those of the di-σ (**2** and **3**) and three-σ (**6** and **7**) adducts; this is probably due to the presence of the allenic C=C=C moiety on the carbon skeleton, with C–C bond distance values of 1.303 and 1.313 Å, that highly stabilizes this structure.

The adsorption product **4** can still evolve through the nucleophilic attack of the C≡C triple bond to the buckled down silicon atom on the adjacent dimer; this occurs via the transition state **TS4**, with an energy barrier of 14.5 kcal mol^{-1} above **4**, i.e., 25.4 kcal mol^{-1} below reactants. **TS4**, having Si–C bond distances of 2.575 and 3.192 Å, respectively, for the terminal and the inner alkyne carbon atom, resembles quite well the asymmetric π adduct structure of **TS1** in Chart 2, except for the assistance of a covalent Si–C bond instead of the Si–N dative bond and the presence of a Si–H bond saturating the dangling silicon atom and hindering an end-bridge product. By performing an IRC calculation, we found that **TS4** proceeds with the nucleophilic attack of the terminal carbon atom of the alkyne unit on the dangling silicon atom and ends up with the adsorption product **6**, with a binding energy of 58.7 kcal mol^{-1}. As shown in Figure 1, in structure **6** the alkyne unit has become a single C–C bond of 1.532 Å, since the terminal carbon is coordinated to two silicon atoms of the adjacent dimer (1.941 and 1.951 Å) and the inner carbon has replaced the Si–C bond of the methylenic unit (1.982 Å), while a double C=C bond has formed between the methylenic carbon atom and the adjacent one (1.367 Å). This unusual tri-σ bonded coordination reminds the well-known r-bridge configuration considered in previous studies of the adsorption of acetylene on the silicon surface[19] except that its tetra-σ bonding configuration is not achieved due to the saturation of the fourth silicon atom by a hydrogen atom.

Structure **6** can further evolve to the adsorption product **7**, lying only 1.9 kcal mol^{-1} below **6** and evidencing an on top di-σ configuration for the alkyne unit, with Si–C bond distances of 1.911 and 1.934 Å, plus a third Si–C bond on the methylenic carbon atom (2.018 Å, see Figure 1). However, the formation of **7** would occur from **6** through **TS5**, crossing an energy barrier of 39.0 kcal mol^{-1} above **6**, so that we can conclude that **6** is the final adsorption product of this reaction pathway.

Chart 3 shows that the rate-determining step for the methylenic C–H bond cleavage is determined by **TS3**, the highest energy barrier along the path, and therefore, with an energy of 24.7 kcal mol^{-1} above the dative bonded adduct **1b**, this reaction could compete only at temperatures above 300 K with the reaction pathway of the alkyne addition on two adjacent dimers, leading to product **2**, for which an energy barrier of only 12.5 kcal mol^{-1} has been calculated (see above). Chart 3 also shows that two adsorption products, **5** and **6**, having almost the same thermodynamic stability, can be regarded as final products of the methylenic C–H bond cleavage. It is remarkable that the EELS spectra[41] show a peak assigned to the Si–H stretch, which results enhanced upon annealing at 400K, thus strengthening

our suggestion on the competitiveness of the methylenic C–H bond cleavage pathway.

In the previous study on a single-dimer cluster,[40] we also explored the methyl C–H and the N–CH$_3$ bond cleavage pathways, computing, respectively, an energy barrier of 48.4 and 49.1 kcal mol^{-1}, i.e., 15.1 and 15.8 kcal mol^{-1}, respectively, higher in energy than that of the methylenic C–H bond cleavage pathway. We therefore concluded that the reaction pathways involving the methyl C–H and the N–CH$_3$ bond cleavages on the dative bonded DMAP are not kinetically competitive, and they have been ruled out in the present work.

Conclusions

The reaction of the bifunctional organic molecule 1-(dimethylamino)-2-propyne (DMAP) on the Si(100) surface has been investigated by means of density functional calculations on a two-dimer cluster model. We found that the amine unit adsorbs without barrier through a N→Si dative bond on the buckled-down silicon atom, with a binding energy of 20.0 kcal mol^{-1} (**1a**). We have then considered the attack of the C≡C triple bond to the buckled-up silicon atom on the dimer adjacent to the dative bonded one, leading to the di-σ alkyne addition product **2**, with a binding energy of 58.7 kcal mol^{-1}. Interestingly, the optimized structure of **2** shows two covalent Si–C bonds across the two adjacent dimers, while keeping the Si–N dative bond. An energy barrier of only 12.5 kcal mol^{-1} has been computed for the transition state **TS1**, connecting **1b** to **2**. This value is in good agreement with the observed switching of the adsorption linkage of DMAP at 300 K, such that **2** may represent one of the adsorption configurations of DMAP, involving Si–C di-σ bonds, more stable at high temperatures. The formation of the on top di-σ bonded configuration **3** requires the detachment of the dative bonded amine group involving a higher energy barrier, of at least 25 kcal mol^{-1}, and can be therefore ruled out. We have also explored the dissociative pathway involving the methylene C–H bond cleavage of the dative bonded DMAP, leading to two adsorption products, structures **5** and **6**, showing, respectively, one and three Si–C σ bonds on the two-dimer cluster and having almost the same thermodynamic stability. The rate-determining step for this overall reaction pathway has an energy barrier of 24.7 kcal mol^{-1} above the dative bonded adduct **1b** (7.6 kcal mol^{-1} above reactants) and may therefore compete at temperatures above 300 K with the reaction pathway of the alkyne addition on two adjacent dimers, leading to product **2**. It is remarkable that the EELS spectra[41] show a small peak assigned to the Si–H stretch that results enhanced upon annealing at 400 K.

In conclusion, our results give evidence of two reaction pathways consistent with the experimental results for the switching of the adsorption linkage of DMAP on the silicon surface, i.e., the addition of the alkyl unit and the methylenic C–H bond cleavage. The former is kinetically favored at 300 K and leads to the adsorption product **2**, where the alkyne unit has an end-bridge bonding configuration, while the latter should require slightly higher temperatures (400 K) and can lead to the formation of two adsorption products, structures **5** and **6,** with almost the same thermodynamic stability. However, we still cannot further discriminate between products **5** and **6**, since the experimental data do not supply any information on the nature of the C–C bond, i.e., the FT-IR spectra do not show the stretching frequencies of a double C=C bond or an allenic C=C=C moiety. Even if our theoretical study have pointed out the possibility of adsorption structures that were not considered in the previous experimental paper of Yoshinobu,[41] further

experimental investigations are required in order to clarify which adsorption products can be obtained by the temperature-dependent functionalization of the Si(100) with the DMAP molecule.

References and Notes

(1) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271.

(2) Bent, S. F. *Surf. Sci.* **2002**, *500*, 351.

(3) Hamers, R. J. *Nature* **2001**, *412*, 489.

(4) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413.

(5) Appelbaum, J. A.; Baraff, G. A.; Hamann, D. R. *Phys. Rev.* **1976**, *14*, 588.

(6) Redondo, E.; Goddard, W. A. *J. Vac. Sci. Technol.* **1982**, *21*, 344.

(7) Jung, Y.; Shao Y, Gordon, M. S.; Doren, D. J.; Head-Gordon, M. *J. Chem. Phys.* **2003**, *119*, 10917.

(8) Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlie, C. M.; Russel, J. N., Jr. *Acc. Chem. Res.* **2000**, *33*, 617.

(9) Schwartz, M. P.; Ellison, M. D.; Coulter, S. K.; Hovis, J. S.; Hamers, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 8529.

(10) Fang, J.; Liu, J.; Coulter, S. K.; Cao, X.; Schwartz, M. P.; Hacker, C.; Hamers, R. J. *Surf. Sci.* **2002**, *514*, 362.

(11) Liu, H.; Hamers, R. J. *Surf. Sci.* **1998**, *416*, 354.

(12) Li, X. *J. Am. Chem. Soc.* **2003**, *125*, 6384.

(13) Lee, H. S.; Choi, C. H.; Gordon, M. S. *J. Phys. Chem. B* **2005**.

(14) Liu, H.; Hamers, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 7593.

(15) Liu, X.; Zhu, M.; Wang, X. *J. Phys. Chem. B*, **2004**, *108*, 7359.

(16) Liu, X.; Zhu, M. *Chem. Phys. Lett.* **2004**, *393*, 124.

(17) Festa, G.; Cossi, M.; Barone, V.; Cantele, G.; Ninno, D.; Iadonisi, G. *J. Chem. Phys.* **2005**, *122*, 184714.

(18) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 4082.

(19) Rintelman, J. M.; Gordon, M. S. *Phys. Chem. B* **2004**, *108*, 7820.

(20) Sorescu, D. C.; Jordan, K. D. *J. Phys. Chem. B* **2000**, *104*, 8259.

(21) Taylor, P. A.; Wallce, R. M.; Cheng, C. C.; Weinberg, W. H.; Dresser, M. J.; Choyke, W. J.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 6754.

(22) Sorescu, D. C.; Jordan, K. D. *J. Phys. Chem. B.* **2000**, *104*, 8259.

(23) Choi, C. H.; Gordon M. S. *J. Am. Chem. Soc.* **1999**, *121*, 11311.

(24) Minary, P.; Tuckerman, M. E. *J. Am. Chem. Soc.* **2004**, *126*, 13920.

(25) Konecny, R.; Doren, D. J. *J. Am. Chem. Soc.* **1997** *119*, 11098.

(26) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. *J. Am. Chem. Soc.* **1997**, *119*, 11100.

(27) Minary, P.; Tuckerman, M. E. *J. Am. Chem. Soc.* **2005**, *127*, 1110.

(28) Cao, X.; Hamers, R. J. *J. Phys. Chem. B* **2002**, *106*, 1840.

(29) Miotto, R.; Srivastava, G. P.; Ferraz, A. C. *Surf. Sci.* **2005**, *575*, 287.

(30) Zhang, L.; Carman, A. J.; Casey S. M. *J. Phys. Chem. B* **2003**, *107*, 8424.

(31) Silvestrelli, P. L. *Surf. Sci.* **2004**, *552*, 17.

(32) Mui, C.; Wang, G. T.; Bent, S. F., Musgrave, C. *J. Chem. Phys.* **2001**, *114*, 10170.

(33) Cao, X.; Hamers, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 10988.

(34) Mui, C.; Han, J. H.; Wang, G. T.; Musgrave, C. B.; Bent S. F. *J. Am. Chem. Soc.* **2002**, *124*, 4027.

(35) Hossain, M. Z.; Machida, S.; Yamashita, Y.; Mukai, K.; Yoshinobu, J. *J. Am. Chem. Soc.* **2003**, *125*, 9252.

(36) Carman, A. J.; Zhang, L.; Liswood, J. L.; Casey, A. M. *J. Phys. Chem. B* **2003**, *107*, 5491.

(37) Hwang, H.; Baik, J. Y.; An, K.; Lee, S. S.; Kim, Y.; Hwang, C. C.; Kim, B. *J. Phys. Chem. B* **2004**, *108*, 8379.

(38) Kim, K.; Song, B.; Jeong, S.; Kang, H. *J. Phys. Chem. B* **2003**, *107*, 11987.

(39) Filler, M. A.; Bent, S. F. *Prog. Surf. Sci.* **2003**, *73*, 1.

(40) Nunzi, F.; Sgamellotti, A.; Re, N. *Chem. Phys. Lett.* **2005**, *413*, 473.

(41) Hossain, M. Z.; Yamashita, Y.; Mukai, K.; Yoshinobu, J. *Chem. Phys. Lett.* **2004**, *388*, 27.

(42) Widjaja, Y.; Musgrave, C. B. *Surf. Sci.* **2000**, *469*, 9.

(43) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864.

(44) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.

(45) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Oritz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 03*; Gaussian Inc.: Pittsburgh, PA, 1998.

(46) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(47) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(48) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(49) Mui, C.; Bent, S. F.; Musgrave, C. B. *J. Phys. Chem. A* **2000**, *104*, 2457.

(50) Barriocanal, J. A.; Doren, D. J. *J. Phys. Chem. B* **2000**, *104*, 12269.

(51) Widjaja, Y.; Mysinger, M. M.; Musgrave, C. B. *J. Phys. Chem. B* **2000**, *104*, 2527.

(52) Nunzi, F.; Sgamellotti, A.; Re, N. *J. Phys. Chem. B* **2004**, *108*, 10881.

(53) Lu, X.; Zhu, M. *Chem. Phys. Lett.* **2004**, *393*, 124 and references therein.

(54) Cho, J.; Kleinman, L. *Phys. Rev. B* **2004**, *69*, 075303.