

Adsorption of protected and unprotected amino-cyclopentene at the Si(100) surface modeled with a hybrid quantum mechanical cluster technique

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Both 1-amino-3-cyclopentene (ACP) and its protected form *N*-1-*tert*-butyloxycarbonyl-amino-3-cyclopentene (BACP) were adsorbed at the depassivated Si(100) surface using a hybrid calculation method in a Si₁₉₇H₁₀₈ cluster. It was found that the ACP molecule can potentially adsorb in at least eight different modes to the surface. The most stable one connects through both its carbon-carbon double-bond and its amine group, forming a bridge-like structure between two dimers, and has an adsorption energy of -73.9 kcal mol⁻¹. In what concerns the BACP molecule, it was found that the *tert*-butyloxycarbonyl (tBOC) protecting group does indeed inhibit the reaction of the amine group without affecting energetically the adsorption through the double bond. Its adsorption energy is basically the same as the one for ACP when adsorbed by the same group with both of them having an adsorption energy within 1 kcal mol⁻¹.

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I. INTRODUCTION

Emerging technologies are revealing an ever-increasing interest in DNA chips.¹⁻³ One of the objectives involves the possibility to identify a person by its DNA characteristics or even identify specific types of genes in any individual, in an almost instant process. This requires the design of an electronic chip with DNA detection capacity, a DNA sensor chip.⁴ Whichever the technological solution used, it will always be necessary to attach DNA to the surface in an organized, durable, and predictable manner.^{2,4,5} For this reason, there is already some experimental work done in DNA attachment to surfaces, such as silicon^{6,7} and diamond.^{8,9} However, the silicon surface is the preferred one as this will facilitate the interface between the biological DNA layer and the electronic silicon one. One of the methodologies being investigated involves the attachment of a small portion of an oligonucleotide to the silicon surface, forming well-defined areas on the surface, that when exposed to a solution containing the complementary DNA sequence hybridizes, and changes the chemical and electronic characteristics of that area.¹⁰ Although the detection is currently made optically, by measurement of fluorescence intensity of the labeled DNA sequences that remain attached to the surface, the modification of the surface characteristics should be detectable by electronic means.¹⁰ If a chip containing a matrix of DNA areas with specific and relevant testing oligonucleotide sequences can be made to function in cooperation with a matrix of electronic detection circuitry, it could be used to determine almost instantly whether a given solution contains any of the relevant DNA sequences tested by that specific DNA chip.

Presently, one of the most used procedures in all of those works that have already been made with silicon, namely Si(100) and Si(111),⁶⁻⁹ consists of connecting initially a molecule to the surface to serve as a bridge between the surface itself and the thiol-modified oligonucleotide molecule. Usually, the whole process involves, as a first step, the function-

alization of the surface with amino groups. This functionalization can be attained by using many different molecules, but the usual ones have been those that contain a double bond at one end of a long aliphatic chain and a protected amino group at the other end. In 2002 though, Robert J. Hamers and co-workers⁷ suggested that the previously used long-chain bridge molecules could be unbeneficial due to molecular entanglement phenomena. They then proceeded by experimenting with the smallest bridge molecule possible, the 1-amino-3-cyclopentene (ACP). In that work, they found out that when this molecule is used unprotected it binds to the silicon surface either through its double bond or through its amine group. Therefore, trying to avoid adsorption through the amino group, they tried protecting the amino group with the *tert*-butyloxycarbonyl (tBOC) protecting group, commonly used in protein synthesis to protect the amino ends of polypeptides. The exact adsorption processes of both ACP and *N*-1-BOC-amino-3-cyclopentene (BACP) to the surface are not yet understood. It is only known that ACP adsorbs both through the amino group and the double bond, and that BACP only connects through its double bond. An improved understanding of this process is important in order to optimize the process in the future by designing new and better bridge molecules. Furthermore, the effect of the BOC protecting group in the adsorption process of BACP, which is known to avoid amine adsorption, is interesting in itself.

In order to compare to some extent our results with previous works, we have to rely on similarities between the adsorption of ACP, cyclopentene,¹¹⁻¹⁴ and amines¹⁵⁻¹⁸ on the Si(100) surface. ACP has got both a cyclopentene group and one amine; hence we expect to find comparable processes and energies when ACP connects only through one of them. However, there is the possibility for ACP to adsorb through both groups simultaneously and these should present completely new results for which there is no experimental energetic data or comparable theoretical work.

In this theoretical work, we investigate the structures and the energies involved in ACP and BACP adsorption to the

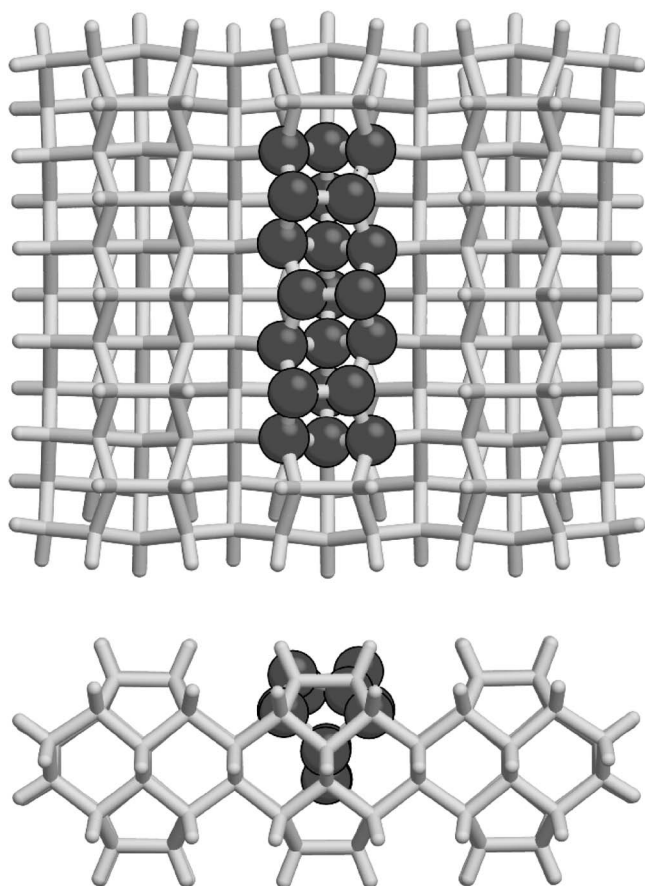


FIG. 1. Top and front views of the $\text{Si}_{197}\text{H}_{108}$ cluster used. Balls represent the high layer silicon atoms and sticks represent the whole silicon low layer with valence compensating hydrogen atoms.

$\text{Si}(100)$ surface. As we are interested in understanding the process involving only one molecule at the surface avoiding any coverage problems, we did not use any periodic slab method and proceeded by using a single cluster theoretical approach. Moreover, we tried to represent the silicon surface as realistically as possible and therefore we have used a large cluster. If only DFT (Ref. 19) type calculations were used, we would be very limited due to the computational limitations, so we have used a hybrid calculation approach that allowed us to concentrate the computational power in the more important areas, while still representing a large cluster.

II. METHODOLOGY

A cluster approach using a hybrid quantum-mechanical/quantum-mechanical method (QM/QM) was used. The whole concept has already been described previously,²⁰ and it consists of the use of the ONIOM hybrid method²¹ with one high-level layer (DFT/B3LYP)²² and one low-level layer (AM1 semi-empirical method).²³ This way we could use a large cluster containing 197 silicon atoms and 108 valence-compensating hydrogen atoms ($\text{Si}_{197}\text{H}_{108}$ cluster). Figure 1 illustrates the cluster showing both the top view, perpendicular to the surface plane, and the side view, showing the thickness and the upper and lower cluster surfaces. This cluster

contains 15 surface dimers and is six layers thick. Out of the 197 silicon atoms, 21, shown as large dark spheres in Fig. 1, have been studied with the high-level method DFT/B3LYP with the SHC* basis-set²⁴ when performing the adsorption optimizations and 6-311+G(3df,2p) to calculate singlepoint energies of the optimized adsorbed geometries. The remaining cluster, shown as sticks in Fig. 1, is calculated with the AM1 semi-empirical method. This way, the three central dimers are contained in the DFT part while all around there is, at least, one low-level dimer neighbor. These three central dimers are de-passivated, while the remaining dimers are passivated. This was done in order to avoid the incorrect semi-empirical charges that are calculated for the de-passivated surface dimers, as well as being justifiable by the method used in experimental works where UV radiation is used to de-passivate the surface and allow the adsorption reactions to proceed. As large silicon clusters have a marked tendency to bend due to the tension created by the surface dimers, we also dimerized the lower cluster surface to compensate for that tension. This resulted quite well and the cluster remained perfectly planar throughout all calculations.

We have tested previously hybrid QM/QM clusters against other methodologies, such as Hartree-Fock only or DFT, with several different basis sets. The results of this study have been published elsewhere.²⁰ Basically we found that the hybrid AM1/DFT/SHC* methodology generates geometry representations with parameters very close to the experimental values.²⁰ Therefore, since it is known that the dimer tilts and is stabilized due to partial electron transfer from the lower Si atom to the upper Si atom,²⁵ if we get good geometrical results, then the electronic characteristics of the silicon dimer should be close to the correct representation.

The Gaussian03 and Gaussview software package²⁶ was used to perform all calculations and structure visualization.

III. RESULTS AND DISCUSSION

ACP has both a double bond and an amine group. As such, we would predict that ACP may adsorb by the double bond as the cyclopentene does and by the amine group like other primary amines do. Additionally, there is the possibility of adsorption by both groups simultaneously. As for the BACP, because its amine group is protected, there should be no chance of adsorption by this group, but the double bond adsorption should not be affected.

In the first adsorption study we started by placing each of the molecules, ACP or BACP, above the surface, at a distance of about 4.5 Å from the cluster's central surface dimer, and then optimizing without any restrictions. There was a major behavioral difference between both molecules. While the ACP molecule approached the surface and found a low-energy adsorption site, with no formal covalent bonds established, the BACP just got farther away from the surface. Even starting the calculation with BACP at a similar distance to that of the ACP first adsorption site, it still escaped the surface. This suggests that the protection group is somehow affecting the energy profile for the molecules approaching the surface, and where we previously found a local minimum for the ACP molecule we did not find a similar one for the

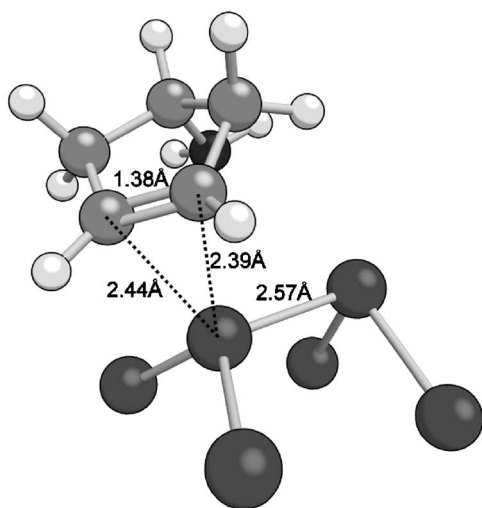


FIG. 2. First ACP adsorption site with $-7.1 \text{ kcal mol}^{-1}$ adsorption energy. Only relevant atoms are shown. Large dark spheres represent silicon atoms, medium-gray spheres represent carbon atoms, the very dark sphere represents a nitrogen atom, and small white spheres represent hydrogen atoms.

case of the BACP molecule. This ACP first adsorption state, shown in Fig. 2, has an energy of just $-7.1 \text{ kcal mol}^{-1}$. Geometrically, the depassivated silicon dimers are tilted and there is a displacement of one electron from the lower silicon atom to the upper silicon atom. The lower atom is turned into an electrophile that promptly attracts the double bond π electronic density of ACP. This slightly affects both the double bond length, which increases from 1.34 \AA in ACP to 1.38 \AA in this adsorbed ACP geometry, and also the silicon dimer bond length which increases from 2.43 to 2.57 \AA . The ACP carbons involved in the double bond remain at a distance of 2.44 and 2.39 \AA from the lower silicon atom.

From this first adsorption site, ACP can then react via a typical $[2+2]$ cycloaddition reaction with formation of two carbon-silicon bonds and rupture of the carbon-carbon double bond, much in the same way as was already known for the cyclopentene molecule.¹¹ Because the amine group can be in one or the other side of the cyclopentene ring, there are actually two possibilities for ACP to adsorb through its double bond—either the *cis*-C-adsorbed ACP is formed if the amine group is at the same side of the carbon-silicon surface, or the *trans*-C-adsorbed ACP is formed if the amine group is on the other side of the cyclopentene ring (farther from the surface). The *cis* form has an adsorption energy of $-36.9 \text{ kcal mol}^{-1}$ while the *trans* form has an energy of $-36.1 \text{ kcal mol}^{-1}$. While we could argue that the small difference in adsorption energy between the *cis* and *trans* forms of ACP could be due to a small positive interaction of the amine group nearest to the surface, in fact this effect is too small and too close to the error associated with the calculations. For comparison, we also adsorbed cyclopentene on the same surface and have obtained an adsorption energy of $-36.4 \text{ kcal mol}^{-1}$. One of the previous works concerning the adsorption of cyclopentene¹² found that its adsorption energy was $-36.9 \text{ kcal mol}^{-1}$ while using a periodic slab approach with DFT within the general gradient approximation (GGA)

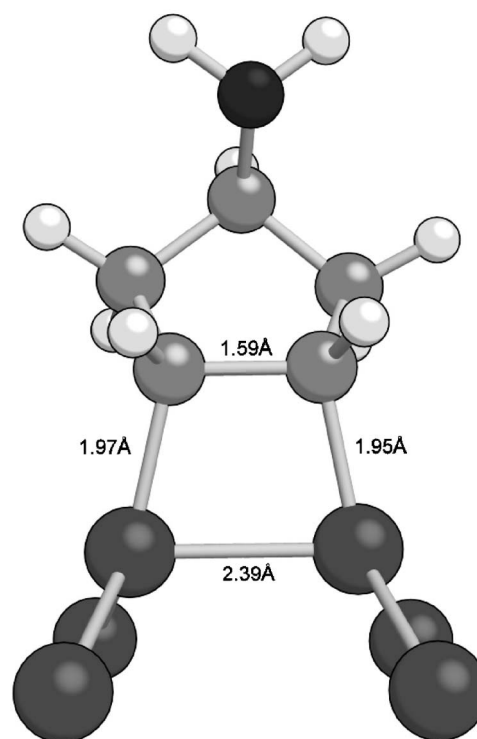


FIG. 3. *Trans*-C-adsorbed ACP geometry over a silicon dimer. This structure has an adsorption energy of $-36.1 \text{ kcal mol}^{-1}$. Only relevant atoms are shown. Large dark spheres represent silicon atoms, medium-gray spheres represent carbon atoms, the very dark sphere represents a nitrogen atom, and small white spheres represent hydrogen atoms.

for a surface coverage of 0.5 ML and $-27.0 \text{ kcal mol}^{-1}$ for a 1 ML surface coverage. Yet another theoretical work¹⁴ found that that adsorption energy was $-32.3 \text{ kcal mol}^{-1}$ within the local-density approximation (LDA) and $-13.8 \text{ kcal mol}^{-1}$ in the GGA, for a surface coverage of 1 ML . As we performed the adsorption of a single molecule at the surface, coverage effects are avoided. This means that the only value with which we can compare our values is the one found for a surface coverage of 0.5 ML as this is the one that is closer to eliminate any coverage problems. As such, our value of $-36.4 \text{ kcal mol}^{-1}$ found for cyclopentene is in good agreement with those more complex periodic slab methods. This makes us confident about all the other energetical values found with our methodology.

In Fig. 3 the *trans*-C-adsorbed ACP structure is shown with geometrical data. The other two structures, the *cis* form and cyclopentene, have exactly the same geometries. The broken carbon-carbon double bond has a length of 1.59 \AA , slightly longer than a typical 1.54 \AA single bond, and the silicon-silicon bond has a length of 2.39 \AA , also slightly longer than the typical 2.34 \AA . These differences, although small, may be caused by the geometrical constraints of the newly formed four-member ring. As for the carbon-silicon bond lengths, they were always 1.97 and 1.95 \AA . They were never equal to each other and this asymmetry was always found in all the C-adsorbed molecules. This is a direct effect of the neighbor dimers (not shown in Fig. 3) that remain tilted, with the upper silicon atoms being closer to the 1.97 \AA

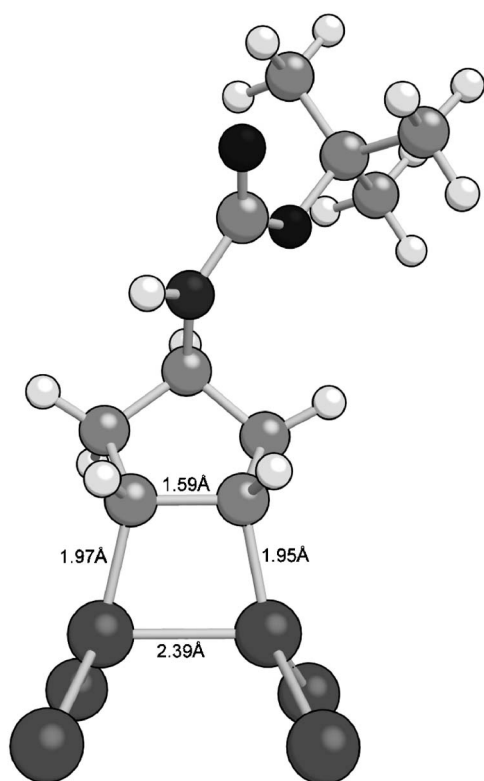


FIG. 4. *Trans*-C-adsorbed BACP geometry over a silicon dimer. This structure has an adsorption energy of $-36.8 \text{ kcal mol}^{-1}$. Only relevant atoms are shown. Large dark spheres represent silicon atoms, medium-gray spheres represent carbon atoms, the very dark sphere represents a nitrogen atom, the two black spheres represent oxygen atoms, and small white spheres represent hydrogen atoms.

bond and the lower silicon atoms being closer to the 1.95 \AA bond.

The adsorption of BACP followed the same steps as the adsorption of ACP. Once again, the protected amine group can be either *cis* or *trans* relative to the carbon-silicon bonds and their adsorption energy was found to be -35.9 and $-36.8 \text{ kcal mol}^{-1}$, respectively. Figure 4 shows the *trans*-C-adsorbed BACP. Geometrically, the distances found in the C-adsorbed BACP structure are identical to the ACP ones, with differences only in the third decimal place and outside the methodology accuracy.

Therefore, these five forms, *cis*-C-adsorbed ACP, *trans*-C-adsorbed ACP, cyclopentene, *cis*-C-adsorbed BACP, and *trans*-C-adsorbed BACP, all have very similar adsorption energies, with a maximum difference of 1 kcal mol^{-1} . However, we can see the inexistence of the first approaching structure for the BACP case as compared to the ACP suggests that the protecting groups might be affecting the adsorption kinetics by modifying the approximation energetic profile. In the end, though, the final adsorption energy difference mean that the substituting groups at the cyclopentene ring are not significantly affecting the final existing adsorption states.

As formerly said, ACP can also adsorb by the amine group and the adsorption energy for the N-adsorbed ACP at the Si(100) surface is $-30.0 \text{ kcal mol}^{-1}$. This state is typical

of amines¹⁶ and is characterized by the formation of a dative bond from the nitrogen atom to the lower, electron-deficient, silicon atom. However, it is known that primary amines promptly dissociate, transferring one of its hydrogen atoms to the other silicon atom of the dimer. We found the adsorption energy for this H-dissociated N-adsorbed ACP to be $-49.6 \text{ kcal mol}^{-1}$. Moreover, there is a probability, although a small one, that the amine dissociation may happen not at the N—H bond but at the N—C bond. This situation would leave an amine adsorbed to one silicon atom and a cyclopentenil group adsorbed to the other dimer atom. The adsorption energy for this situation is $-63.4 \text{ kcal mol}^{-1}$. A previous study, adsorbing not ACP but methylamine¹⁸ at a concentration of 0.5 ML with DFT-GGA and a periodic slab, found an amine adsorption energy of $-32.5 \text{ kcal mol}^{-1}$ for the undissociated state, $-47.0 \text{ kcal mol}^{-1}$ for the H-dissociated state, and $-60.2 \text{ kcal mol}^{-1}$ for the C-dissociated state. We can see that the behavior of ACP when adsorbing through the amine group is basically similar to the one found for other amines. This makes us predict that although the cyclopentene-dissociated N-adsorbed ACP may have the highest adsorption energy, it must be very unlikely as it involves the breaking of a nitrogen-carbon bond which correlates to a very high energy transition state, while the H-dissociated form only involves a proton transfer between the amine and a silicon atom.^{16,18} For other amines, the energy of the transition state involved in a C-dissociation was always above the energy of the free reagents by a prohibitive amount, hence, observing the conservative behavior of ACP, it is fair to assume that C-dissociation is nearly impossible. The three N-adsorbed structures are shown in Fig. 5 with geometrical data. In the upper structure, showing the non-dissociated N-adsorbed ACP, we can see that the nitrogen atom stays at 2.01 \AA from the silicon atom, compatible with the formation of the dative bond. This electronic sharing also slightly affects the nitrogen-carbon bond which increases from 1.47 \AA in the free ACP to 1.52 \AA . The dimer bond also gets longer, from 2.43 to 2.53 \AA , which concurs with the fact that part of this bond's stability is due to the partial electronic transference from the lower silicon atom to the upper one.²⁷ The dissociation at the amine group eliminates this dative bond. One proton transfers to the upper silicon atom passivating its dangling bond, the dative bond turns into a full single bond, and the completely passivated dimer becomes parallel to the silicon surface. The carbon-nitrogen bond gets back to the free amine value of 1.47 \AA , the nitrogen-silicon bond stays at 1.75 \AA , the dimer bond stays at a typical fully passivated bond length of 2.49 \AA , and the hydrogen-silicon distance continues to be 1.51 \AA . As for the bottom structure in Fig. 5, the cyclopentene-dissociated N-adsorbed ACP, there are no significant differences in the nitrogen-silicon and dimer bond lengths, and in the carbon-silicon distance of 1.52 \AA .

The BACP molecule has no way of adsorbing through its amine group as the protecting group completely eliminates the possibility of approximation of the nitrogen atom to the silicon surface. The protecting group is simply too large and collides with the silicon surface upon approximation. These observations concur with the experimental findings, where ACP connects to silicon through nitrogen and carbon atoms, while BACP only connects to silicon through carbon atoms.

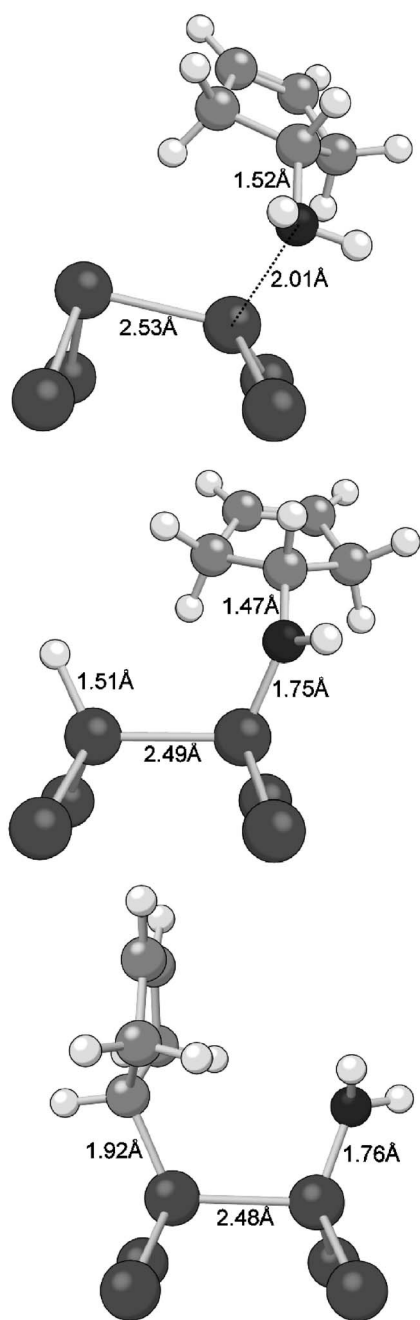


FIG. 5. Nondissociated, H-dissociated, and cyclopentene-dissociated N-adsorbed ACP structures. These have adsorption energies of -30.0 , -49.6 , and -63.4 kcal mol $^{-1}$, respectively. Only relevant atoms are shown. Large dark spheres represent silicon atoms, medium-gray spheres represent carbon atoms, the very dark sphere represents a nitrogen atom, and small white spheres represent hydrogen atoms.

There is a third adsorption possibility for the ACP molecule at the silicon surface. While adsorbed through the double bond, the amine group of the *cis* isomer may approximate the surface and form a bond with another silicon atom of the adjacent silicon dimer. In this adsorption position, ACP connects to the silicon surface by two carbon-silicon bonds and one nitrogen-silicon bond, a CN-adsorbed ACP structure. Once again, the amine group can dissociate and a

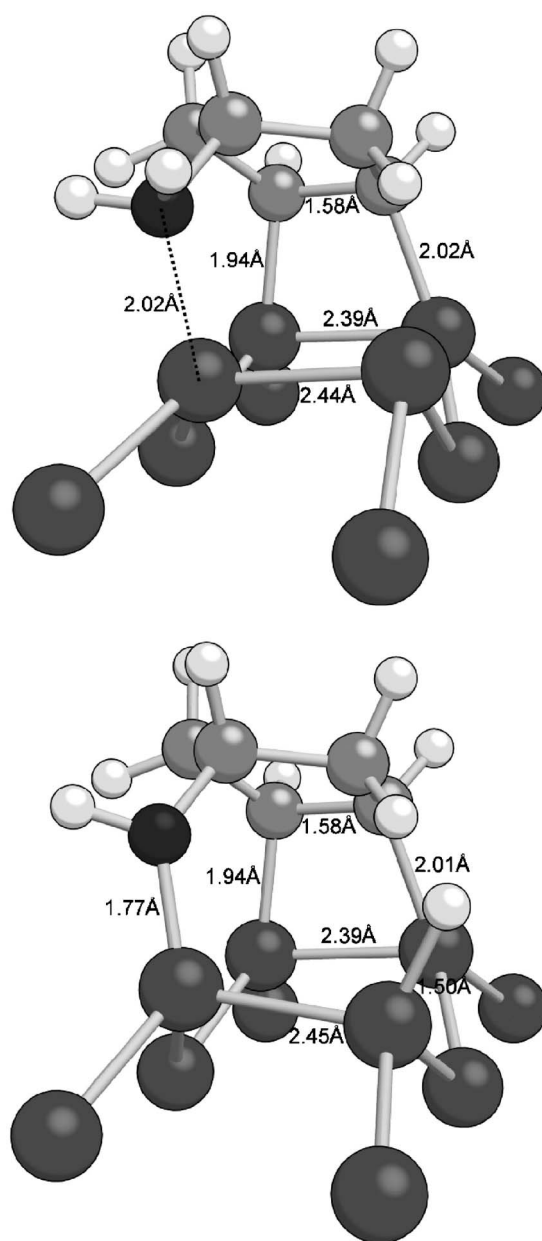


FIG. 6. Nondissociated and H-dissociated CN-adsorbed ACP structures. These have adsorption energies of -47.5 and -73.9 kcal mol $^{-1}$, respectively. Only relevant atoms are shown. Large dark spheres represent silicon atoms, medium-gray spheres represent carbon atoms, the very dark sphere represents a nitrogen atom, and small white spheres represent hydrogen atoms.

proton can transfer to a fourth silicon atom. The adsorption energies are -47.5 and -73.9 kcal mol $^{-1}$ respectively, for the non-dissociated and for the dissociated CN-adsorbed ACP molecules. The latter energy is by far the highest adsorption energy of all and it is so easy to reach that it must be the predominant form of adsorbed ACP on the silicon surface. It only involves a [2+2] cycloaddition and a dissociative chemisorption, both known to occur promptly and without any large energy barriers,^{12,14,16-18} while forming four covalent bonds and eliminating four dangling bonds at the silicon surface. Interestingly, geometrically the ACP molecule fits

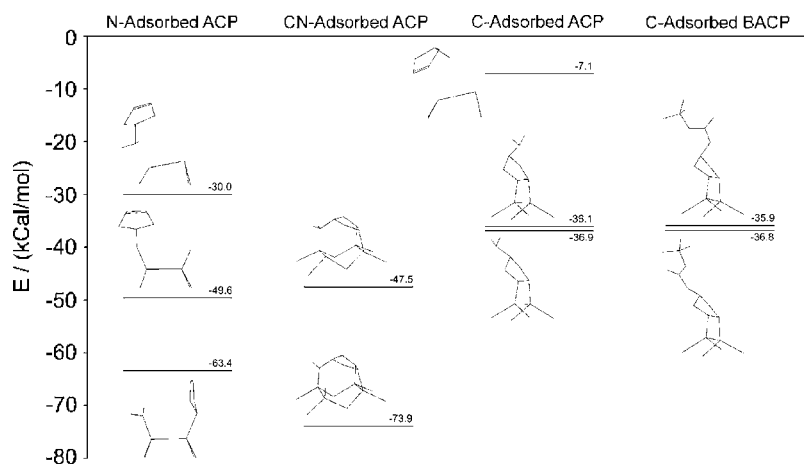


FIG. 7. Schematic description of the ten structures that are discussed in this paper with corresponding adsorption energies. The four columns show different structure types, from left to right; the N-adsorbed ACP structures, CN-adsorbed ACP, C-adsorbed ACP, and C-adsorbed BACP. Only relevant hydrogen atoms are represented.

exactly as a bridge between two dimers. This can be viewed in Fig. 6 where dissociated and non-dissociated forms are shown, once again with geometrical data. The bond lengths are very similar to the previous adsorptions, with only small variations due to some geometrical constraints and with no remarkable differences.

IV. CONCLUSION

This paper gives a detailed description of the adsorption of ACP and BACP onto silicon. Figure 7 schematically resumes the structures and energies found in this work. Some of the ten structures found confirm that ACP and BACP obey some general rules previously established for both the adsorption of alkenes and amines to the Si(100) surface. This shows that the amine group and the double bond are not perturbed by each other and with no significant effects of their coexistence in the same molecule.

Two of the structures, namely the CN-adsorbed structures, have no experimental or theoretical counterpart. Their existence is a possibility because of the distance between the two reacting groups in this specific molecule, which is nearly perfect for the adsorption at two neighbor silicon dimers simultaneously.

The energetic relations between the adsorption states were also established. From these, we can conclude that the H-dissociated CN-adsorbed state must be the most abundant one when adsorption of ACP is performed in the Si(100) surface, followed by the H-dissociated N-adsorbed ACP and both isomeric forms of the C-adsorbed ACP. However, in the end, kinetic effects can have some influence on the abundance of each of these structures. Although the cyclopentene-dissociated N-adsorbed state is energetically favorable, the energetic barriers must be quite high and so this adsorption form should be quite rare at the surface. As for the BACP molecule, only the two isomeric forms of the C-adsorbed state were found with energies very similar to the ACP corresponding structures. This is in agreement with experimental findings which stated that BACP could not react by its amine group. Moreover, the fact that the adsorption energies are basically the same as those of ACP shows that the t-BOC protecting group is doing exactly what it was meant to do: avoid one of the reaction pathways without affecting the other.

The hybrid calculation method applied to the Si(100) surface also showed that it can reliably present results comparable to the more time-consuming periodic slab DFT-GGA calculations. This makes it possible to try to adsorb larger molecules in less time than it was previously attainable.

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