

# Microscopic detail provided for the adsorption of protected amino-cyclopentene on Si(100)

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## Abstract

We have studied the adsorption of the protected form of amino-cyclopentene on the Si(100) surface at several coverage densities, using a very large cluster of 21 silicon dimers and a hybrid QM/QM (ONIOM) methodology. We performed linear transit scans for the study, and have understood the process at a microscopic detail. The work has answered all doubts that remained from previous studies, including the fact that the stabilization provided by the carboxylic groups is not due to the formation of hydrogen bonds as previously hypothesized, but to dipole–dipole attractions.

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## 1. Introduction

The *N*-1-BOC-amino-3-cyclopentene (protected ACP) molecule has been used by Hamers et al. [1] to functionalize the Si(100) surface, as a first step in a process that aimed to attach single-stranded DNA (ssDNA) to the same surface for later use as a specific DNA sensor. However, microscopic detail of the adsorption process remains unclear. To have a comprehensible picture of the adsorption of protected ACP on the Si(100) surface at several coverage densities, it is mandatory to follow the whole process and carefully analyse the molecules behaviour and interactions with the surface and other adsorbed molecules. In this Letter, we present these observations and results.

Given that the typical adsorption process for carbon–carbon double bonds on the silicon (100) surface is a two-step process [2–11], we can analyse each of them separately. Fig. 1 shows the typical adsorption energy graph for this process. At a first stage the molecule is in a free state ('A' in Fig. 1) and approaches the surface. An intermediate state then forms by  $\pi$ -electronic density sharing between the unsaturated C=C bond and the electrophilic silicon

atom on the surface dimer (structure 'B'). This weakly bonded three-atom complex allows the system to break its symmetry and is mandatory to the adsorption process [10,11]. From this intermediate state and via a [2+2] cycloaddition, the molecule goes through a relatively low-energy transition-state ('TS'), the unsaturated bond breaks and two new carbon–silicon  $\sigma$ -bonds form. This, then, produces the final chemisorbed state ('C').

In order to find the adsorption energy diagrams, we performed three relaxed potential energy scans for each molecule (shown as dashed arrows in Fig. 1). One from the adsorbed state towards the transition-state ('C' to 'TS'), another from the intermediate state towards that same transition-state ('B' to 'TS') and, finally, one from the intermediate state towards the free-molecule state ('B' to 'A').

## 2. Methodology

We used a hybrid QM/QM (quantum-mechanical/quantum-mechanical) methodology (ONIOM) [12–14] with a large cluster containing 21 silicon dimers, arranged in three rows with seven dimers each [8,15–17]. From these 21 silicon dimers, the central five are treated with DFT [18–20] using the B3LYP hybrid functional [21] and SHC\* as the basis-set [22,23]. All the other dimers are treated in the

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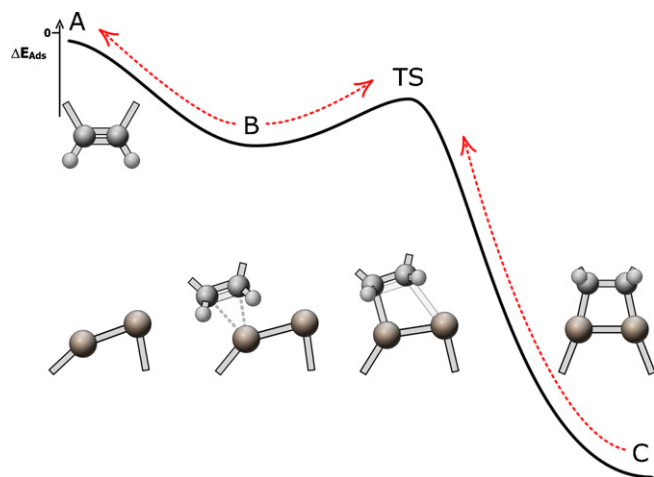


Fig. 1. Illustration showing the typical adsorption energy graphic (black line) and four molecular states for the adsorption of an unsaturated C=C bond on the Si(100) surface dimer. The dashed arrows indicate the directions of the three potential energy scans performed in this work. From left to right: 'A' is the non-adsorbed free-molecule state; 'B' is the intermediate state; 'TS' is the transition-state; 'C' is the chemisorbed structure.

semi-empirical AM1 formalism [24]. The protected ACP molecules are included in the QM/QM layers according to the dimers that they are attached or attaching to. All calculations were performed with the GAUSSIAN 03 software package [25].

In order to avoid unrealistic local distortions we added three hydrogen molecules, at a large enough distance from the cluster and at roughly orthogonal positions relatively to the central silicon dimer that could act as anchors for the distance constraints imposed in the adsorbing molecules. These hydrogen molecules, as well as some of the silicon atoms in the outer part of the cluster, were fixed in space and not allowed to move during all the calculations. This ensured that all atoms of interest were completely free to move with the sole exception of one of the carbon atoms from the desorbing unsaturated bond, which had a distance to one of the hydrogen molecules constrained. We performed the potential energy scans with these constraints. Furthermore, the trajectory of the ACP molecule is somehow complex. From A to B (Fig. 1), the molecule approaches the surface freely in a roughly perpendicular motion. From B to C, the molecule moves still freely but roughly parallel to the surface in the dimer bond direction.

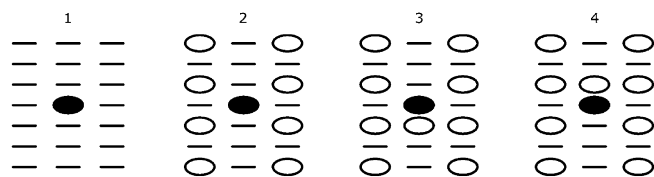


Fig. 2. Schematic representation of the four coverage scenarios used in this work. Lines represent free silicon dimers, filled black ellipses represent the adsorbing molecule and unfilled ellipses represent molecules adsorbed on the surface.

Working with those constraints we have allowed for the realistic and complex motions of the whole adsorbing molecule as well as those from the relevant silicon surface atoms. In this way both the adsorbing molecule and the surface can be in their lowest energy positions and geometries at specific relative distances.

To test different surface coverage situations we devised four scenarios in which a molecule could adsorb. A schematic representation of these four scenarios is shown in Fig. 2. The first one, from left to right, mimics a completely clean surface. The second recreates a situation where a molecule adsorbs in a clean row, in between rows filled with adsorbed molecules at 0.5 ML coverage. Finally, the third and fourth scenarios are based on the second, and only add an extra adsorbed molecule at the front and at the back of the adsorbing one. Comparing the results for the first scenario with the ones obtained for the second we can test how the adsorbing molecule is affected by adsorbed molecules on the lateral surface rows, while comparing the second scenario with the third and fourth scenarios, we can see how the adsorption process is affected when a molecule adsorbs right next to another molecule. We have to notice that since the adsorbed structures are not symmetric, adsorption at the back or at the front is not equivalent, hence the distinction between these last two cases.

### 3. Results and discussion

Fig. 3 shows the calculation results compiled in four adsorption energy diagrams. Each of the curves is labelled with the corresponding scenario number as previously defined in Fig. 2.

We shall compare all results to those that we have obtained in curve 1, which describes reality with the desired accuracy according to recent papers on olefinic adsorption on Si(100) [2–11,26–29].

Comparing curves 1 and 2, which represent adsorption on the free surface and adsorption in between 0.5 ML coverage filled lateral rows, respectively, (see Fig. 2) we can see that from the adsorbed state until near the transition-state the behaviour is identical for both scenarios. Fig. 4 shows

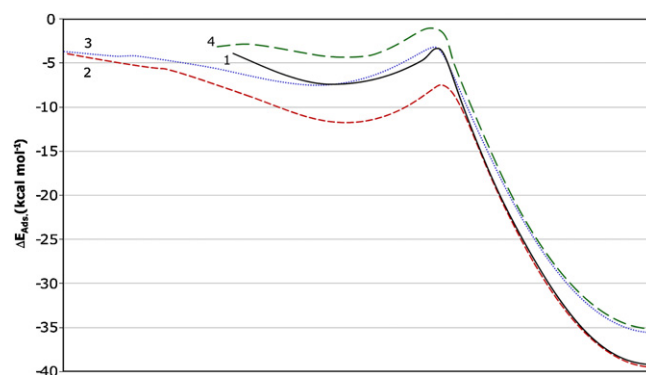


Fig. 3. Adsorption energy diagrams for the four studied scenarios. Each curve is numbered with the respective scenario number as defined in Fig. 2.

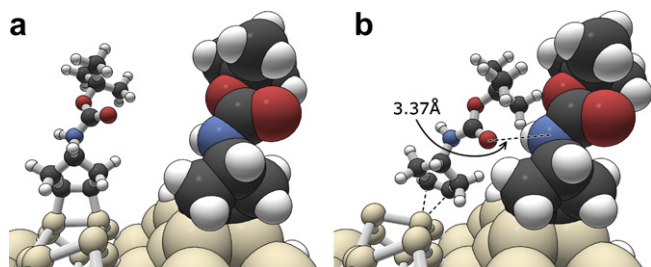


Fig. 4. Detail of part of scenario 2 in the adsorbed state (a) and in the intermediate state (b). Spheres represent the low-level layer and ball and stick model represents the high-level layer.

part of the scenario 2 system in both the adsorbed state (a) and in the intermediate state (b). Analysis of these structures shows that the upright position of the adsorbed molecule keeps the protecting group apart from the lateral rows (Fig. 4a). This prevents any interaction between the adsorbing molecule and those adsorbed on the lateral rows. However, when approaching the transition-state, the molecule becomes angled relatively to the surface and this allows the protecting group to approach the molecules adsorbed on the lateral rows and interact with them (Fig. 4b). Considering the difference between curves 1 and 2, we see that this interaction accounts for about  $4 \text{ kcal mol}^{-1}$  of stabilisation in the intermediate state. Effectively, we can observe from the structures that a dipole–dipole interaction must be formed between the adsorbing molecule and the one in the lateral row. In Fig. 4b, we can see the relatively small distance between the molecules and the  $3.37 \text{ \AA}$  that separate the carboxylic oxygen and nitrogen atom from the amino group. This distance is too high to be considered a hydrogen bond and it looks as if its formation is being hindered by the clash between the bulky *tert*-butyl groups. This interaction, however, although not as strong as a hydrogen bond, persists along part of the remaining adsorption process as can be observed from the almost constant distance between curves 1 and 2 around the intermediate state. This means that the existence of adsorbed molecules on the surface can boost the adsorption process in a significant way.

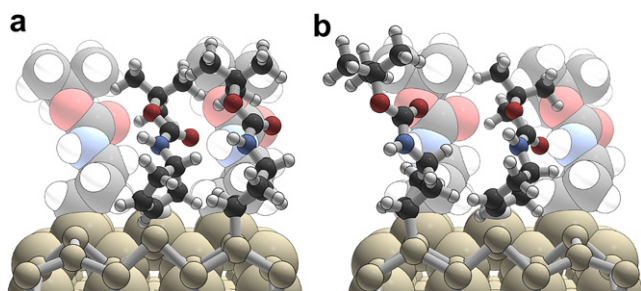


Fig. 5. Detail of part of scenario 3 (a) and of scenario 4 (b) both in the intermediate state. The adsorbing molecule is the one right below the identifying letters. Spheres represent the low-level layer and ball and stick model represents the high-level layer.

Curves 3 and 4 are always higher than curve 2. The difference seen in these curves is due to the repulsion that exists between the adsorbing molecule and the one already adsorbed on the same silicon dimer row. In this case, even in the adsorbed state, the repulsion effect is felt both on scenarios 3 and 4 and accounts for nearly  $5 \text{ kcal mol}^{-1}$ . This similarity between cases 3 and 4 is expected since the final state is, in fact, the same. However, when proceeding towards the transition-state, that difference reduces until it almost disappears near it. Looking at the structures we can see that when the molecule starts moving towards the transition-state it gets a slightly higher mobility and can get farther apart from the adsorbed molecule. As a result, this slightly reduces the repulsions between the molecules. However, once the molecule gets to the transition-state and goes on to form the three-atom complex of the intermediate state, it is forced to get closer to that molecule and the repulsions are again felt. In this case, these repulsions are not equivalent in cases 3 and 4. Fig. 5 shows the intermediate states for scenarios 3 and 4 and, although subtle, there are geometric differences between each other. In both scenarios, the geometries of the adsorbing molecule are very similar to the one seen previously in case 2; however, their positions and angle relative to the surface appear slightly offset. There are also visible differences in the geometries of the previously adsorbed molecules. While the one in Fig. 5a is roughly in the same position as it would be if no other molecule was adsorbed right next to it, in Fig. 5b the molecule is much more distorted and displaced from its normal position. Therefore, the geometries of the systems show, as already could be deduced from the adsorption energy curves, that adsorption of the protected ACP molecule next to another one is more difficult on one side comparatively to the other. This can potentially lead to some directionality on the monolayer formation.

The scans shown in Fig. 3 were taken to different extents. In scenario 1, it made no sense to continue the scan since there was nothing else to interact with the protected ACP molecule from that point onwards; the energy curve will simply increase steadily towards zero. Curves 2 and 3 were extended farther because the existence of protected ACP molecules adsorbed in the surface take the interaction farther from the surface. This is felt in the difference in the slope between curve 1 and the others. In those curves, some slight changes in slope occur caused by interactions with the adsorbed molecules. In curve 4, the energy actually comes down a little bit as the adsorbing molecule gets some mobility and gets farther from the adsorbed molecule thus reducing their repulsions. In the end, curves 3 and 4 must converge into curve 2 when the adsorbing molecules are at some distance from the surface and from the molecules adsorbed on it. The important point though, is that surface approximation is accomplished by the protected ACP molecules with no significant obstacles in all these scenarios and that the presence of adsorbed molecules on the surface can in fact decrease the approximation energy at higher distances.

#### 4. Conclusion

In conclusion, contrary to previous hypothesis [17], this work shows that there is no formation of hydrogen bonds when a protected ACP molecule is adsorbing in an already occupied surface. Although we found previously that these molecules could form a hydrogen bond when adsorbing right next to another in the same row [17], we have also ascertained that the distortion implied in that formation would totally defeat the stabilization energy of the hydrogen bond. In this work, we did see that the carboxylic groups get close to the amino groups preferentially in lateral rows but there is no formation of hydrogen bonds due to clashing of the bulky protecting groups. There is, however, a stabilization of around  $4 \text{ kcal mol}^{-1}$  due to dipole–dipole interactions between those groups. This stabilization improves the adsorption energy profile and can help speeding the adsorption process. Moreover, due to this stabilization, adsorption right next to another molecule can actually be very similar energetically to the adsorption on a clean surface. This should increase the probability of finding groups of two molecules adsorbed in the same row right next to each other and, consequently, allow for a higher surface coverage.

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