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Pyrimidine and s-Triazine as Structural Motifs for Ordered Adsorption on Si(100): a First Principles Study

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Complete List of Authors:	Ng, Wilson; Chinese University of Hong Kong, Chemistry Liu, Jianwen; National Supercomputing Centre in Shenzhen, High Performance Computing Liu, Zhifeng; Chinese University of Hong Kong, Department of Chemistry and Centre for Scientific Modeling and Computation

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**Pyrimidine and s-Triazine as Structural Motifs
for Ordered Adsorption on Si(100):
a First Principles Study**

Wilson K.H. Ng¹, J.W. Liu², and Zhi-Feng Liu^{1,*}

¹Department of Chemistry

and

Centre for Scientific Modeling and Computation

Chinese University of Hong Kong

Shatin, Hong Kong, China

and

²National Supercomputing Center in Shenzhen

Shenzhen, China

*To whom correspondence should be addressed. Email: zfliu@cuhk.edu.hk fax: ++852-2603-

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Abstract:

The chemisorption of pyrimidine and s-triazine, two aromatic molecules with N atoms in the aromatic ring, is studied by first principles calculations to examine not only the chemisorption energy, but also the reaction barriers and the cooperative effects. Among the reaction paths at low coverage, the formation of a cross-bridge structure with two N—Si dative bonds is almost barrierless and should be dominant at low temperature. At higher coverage and low temperature, these cross-row structures should produce an ordered zig-zag pattern, even though it is not the energetically most stable arrangement. Upon heating, the zig-zag pattern could be transformed into lines along dimer rows. These two molecules also provide structural motifs that could facilitate the formation of ordered adsorption structures on Si(100). By symmetry, the complexity of tight-bridge structures could be greatly reduced, while the X-C-X motif, with X being an electronegative atom, could provide the building blocks for cross-row bridges.

1. Introduction

The growth of organic layers on silicon surfaces has been an active area of research.¹ By functionalizing and modifying such surfaces, it holds the potential to extend the current silicon technology and make new molecular electronic devices, especially when ordered layers could be produced by controlling the surface reactions. Aromatics are very useful building blocks for making organic materials, and the chemisorption of aromatic molecules on Si(100) surface has yielded a wide variety of structures, depending on the ring size, polarity, substituent groups, and the type of heteroatoms in the aromatic ring.² It offers both opportunities and challenges. With several double bonds in an aromatic ring, there are many possible channels for the chemisorption of an aromatic molecule. Even for the simplest aromatic molecule, benzene, several possible configurations are observed in previous studies.³⁻⁶ While such variations provide opportunities to explore novel surface structures, controlling these surface reactions to produce single or ordered monolayer on Si(100) is quite a challenge.^{1,2}

The presence of N atoms in the aromatic ring is expected to open up additional reaction channels for the chemisorption, notably for N-heteroaromatic six-member ring molecules pyridine⁷⁻¹⁷ and pyrazine¹⁸⁻²², on Si(100). In both cases, the first adsorption step can be easily identified as the formation of a dative bond between a N atom in the aromatic ring and the down Si atom in a surface dimer, labeled as the End-On structure in Figure 1. For the second and subsequent steps, there are many possibilities leading to a variety of structures. For pyridine, with only one N atom in the ring, the situation is found to be quite complex, in line with the expectation for such a molecule. In addition to the End-On structure, there are a number of possible Tight-Bridge (TB) structures, saturating two adjacent dimers in the same row. The relative abundance of these two types of structures has been studied by both experiments and theoretical calculations.^{7-14, 16, 17} Our recent computational study shows that the dominant configuration is determined by both reaction barriers and coverage.¹⁵ While the End-On structure is preferred both energetically and kinetically, the presence of an adsorption site could enhance further adsorptions either along or cross a dimer row, which is an important factor under high coverage and enhanced the presence of TB structures.

Unexpectedly, with a second *para* N in the aromatic ring, the pyrazine molecule is much simpler in its adsorption on Si(100), leading to well-ordered structures,²¹ which is quite rare on Si(100).^{23, 24} This is surprising, since pyrazine is of the same size as pyridine, and with one additional N atom, one would expect more reaction channels. As it turns out, the barrier for the formation of cross-row bridge (CRB) structure is lower than those for the other channels.²² More importantly, there is a

cooperative effect: when CRB structures are linked together into a line, there is a significant gain in adsorption energy. Elevated temperature opens up other reaction channels, but they facilitate the migration of adsorbed pyrazine, leading to the energy minimum of CRB lines. Pyrazine therefore provides a remarkable and exceptional example, in which the self-assembly of an organic molecule is achieved on the very reactive Si(100) surface.

In light of these results, it is interesting to explore the chemisorption of pyrimidine and s-triazine on Si(100), since they provide further variations for the nitrogen containing heteroaromatic six member ring. In both molecules, there is more than one N atom, sitting on *meta* positions. There are two types of CRB structures for them, either a (1,4)-CN-CRB, similar to that observed for pyridine, or a (1,3)-NN-CRB, similar to that observed for pyrazine, with two N atoms as bridgeheads and a shorter bridge length. For reactions along the same dimer row, their [2+2] and [4+2] addition products should be similar to pyridine, involving one N atom and one C atom. With the shifted positions of hetero atoms, variations in bonding properties are expected.

Unlike pyridine and pyrazine, there are only a limited number of studies on the adsorption of pyrimidine and s-triazine. For pyrimidine on silicon surface, there is one report of butterfly-like structure on Si(111), but no report on Si(100), to our best knowledge.²⁵ However, there is one report on Ge(100), in which well-defined zig-zag lines based on the NN-CRB structures are observed by scanning tunneling microscopy (STM).²⁶ For s-triazine, there is one report each for Si(111)²⁵ and Si(100)²⁷. On Si(111), butterfly-like structure are observed, similar to those in the case of pyrimidine. On Si(100), the adsorption products are not clearly assigned.

In this paper, we report first principles calculations on the adsorption of pyrimidine and s-triazine on Si(100). A systematic search is conducted for the possible reaction channels, which provides both the reaction energies and barriers. Furthermore, cooperative effects are also studied to understand the structural formation at high coverage. Our results show that while the adsorption of these two molecules is different from either pyridine or pyrazine, they offer interesting structural motifs that could be very useful for achieving ordered structures.

2. Computational Details

Density functional theory (DFT) calculations reported here are performed by the VASP package,²⁸⁻³¹ with Perdew-Burke-Ernzerhof (PBE) gradient corrected functional^{32, 33} for the exchange-correlation energy and the projector-augmented-

wave type pseudopotential^{34,35} for the core region. The convergence threshold is set to 1×10^{-4} eV for the total energy in the electronic calculation, and 2×10^{-2} eV/Å for the residual forces in the optimization of atomic coordinates. There are 5 atomic layers in the slab model for silicon (100), with the bottom silicon layer passivated by hydrogen and fixed during geometry optimization to preserve bulk properties. The adsorption structures and reaction barriers are optimized with a 4×4 unit cell ($15.46 \times 15.46 \times 18.00$ Å³), while an 8×2 cell ($30.93 \times 7.73 \times 18.00$ Å³) or a 2×8 cell ($7.73 \times 30.93 \times 18.00$ Å³) is employed to study the high coverage effect. In all cases, there is a vacuum region between two adjacent periodic slab images with a distance around 12 Å. By Monkhorst-Pack scheme³⁶, the k-point sampling is performed with a $3 \times 3 \times 1$ mesh for the 4×4 unit cell, producing five irreducible k-points. For the two other cells, the same scheme, with $8 \times 2 \times 1$ or $2 \times 8 \times 1$ mesh respectively, produces eight irreducible k-points.

In our previous studies on the adsorption of pyridine¹⁵ and pyrazine²², we find that van der Waals correction is very important for both the adsorption energy and reaction barrier, when the aromatic ring is flat on the surface, as in the case of the TB and CRB structures. For the adsorption of benzene on Si(100)³⁷ and on a number of metal surfaces,³⁸ it has been shown that better agreement with experimental or higher level theoretical results is achieved by adding semi-empirical dispersion potentials to the DFT total energy, as in the DFT-D2 method devised by Grimme and co-workers.³⁹ This method is adopted in the current study, as well as in our previous studies.^{15,22} All the energy values and optimized geometric parameters reported are D2 corrected. All the minimum energy reaction pathways are mapped out by the nudge elastic band (NEB) method,⁴⁰ and the transition state is further refined by the climbing image NEB method proposed by Jonsson and co-workers.⁴¹

3. Results and Discussion

For both pyrimidine and s-triazine, the End-On structure is the starting point for all the subsequent adsorption paths. By a barrierless process, a dative bond is formed between an electronegative N atom and a down Si atom of a surface dimer, as in the cases of pyridine, pyrazine and other organic molecules containing electronegative atoms.⁴² For comparison, the calculated adsorption energy is 1.68 eV for pyrimidine and 1.53 eV for s-triazine, compared with 1.68 eV for pyrazine²² and 1.80 eV for pyridine¹⁵. As all four values are obtained by similar setups (PBE functional with D2 corrections), it indicates a trend of decreasing adsorption energy for the End-On structure as the number of N atoms increases in the aromatic ring.

a.) *the symmetry factors in [2+2] and [4+2] additions*

For pyrimidine, [2+2] addition starting from the End-On structure could take two different routes, either through the C atom between the two meta-N atoms, or through the C atom away from the other N atom. For the sake of discussion, we shall call the former as the cis route and the latter the trans route. Each route could be further divided into two paths, either by addition on one dimer, or by addition cross two adjacent dimers. These divisions are simply an example of the well-known complexity involved in the chemisorption of an aromatic molecule on Si(100). However, the case of pyrimidine provides the first indication that the symmetry of the molecule could reduce the complexity of its adsorption.

As shown in Figure 2a, the cis on-dimer addition leads to a tilted structure, cis-OD-TL. A further step of reaction, with almost no barrier, produces a structure labeled as TR, as the other N atom forms another dative bond with the surface. With two Si—N bonds around 1.91 Å and one covalent Si—C bond around 1.96 Å, TR is more stable than the EO structure by 0.1 eV. The cis addition could also take place cross two adjacent dimers, as shown in Figure 2b, leading first to an inter-dimer tilted product, labeled as cis-ID-TL, which is distinct from cis-OD-TL. However, the other N atom in cis-ID-TL could also form a dative bond with a surface Si atom, leading to the same TR structure as in Figure 2a.

There has always been a problem in the modification of silicon surface by the addition of an unsaturated double or triple bond: both on-dimer and inter-dimer additions are accessible, which produces different products. As the barriers for these two reactions are often not significantly different from each other, it is hard to control the adsorption process to make it selective. It is therefore interesting to notice in the case of pyrimidine, the on-dimer and inter-dimer paths for the cis route lead to the same intermediate, TR. Further reactions are possible for TR, by forming one more C—Si bond, which produce two tight bridge structures, TB_I and TB_{II}, as shown in Figure 2c. The two barriers are less than 0.3 eV, and equilibrium among TR, TB_I and TB_{II}, can be easily achieved.

Unfortunately, there is also a trans route for the [2+2] addition of pyrimidine, which complicates the adsorption process. As shown in Figure 3, the tight-bridge structures produced through the trans route are bound to the surface by one N—Si and three C—Si bonds for TB_{III} and TB_{IV}, unlike the structures TB_I and TB_{II} in Figure 2 with two N—Si and two C—Si bonds. In addition, there are also [4+2] addition paths, leading to a mixture of these tight-bridge structures, although the barriers for these reactions are significantly higher, as shown in the supporting information.

However, such complexities can be reduced in the case of s-triazine adsorption. With an additional N atom in the meta position, there is no difference between the cis

and trans routes, as shown in Figures 4. Furthermore, [4+2] additions also lead to the tight-bridge structures with two N—Si bonds and two C—Si bonds, as shown in Figure 5. What should be achieved by all these paths is an equilibrium between TR, TB_I and TB_{II}, as shown in Figure 4c, separated by barriers around 0.2 eV.

Symmetry is typically not an important factor in the adsorption of organic molecules on Si(100). The Woodward-Hoffman symmetry rule for addition reaction is violated on Si(100),⁴³ and the reaction usually takes place via π complexes or dative end-on structures. The symmetry of an organic molecule is incompatible with the symmetry of Si(100) surface, and cannot be preserved after chemisorption. But, s-triazine does provide an interesting example and structural model, for which the symmetry of the organic molecule dramatically reduces the number of possible configurations.

b.) *cross bridge structures*

There are two possible CRB structures for the adsorption of pyrimidine and s-triazine, respectively, as shown in Figures 6 and 7. The first one is a para-bridge, with one C—Si bond and one N—Si bond, which is similar to the case of pyridine and shall be labeled as CN-CRB. The second one is a meta-bridge, forming two N—Si bonds, which is similar to the case of pyrazine and shall be labeled as NN-CRB.

In terms of energy, the formation of CRB is exothermic in all four cases, in contrast to the cases of pyridine and pyrazine, in which the CRB structure is slightly less stable than the EO structure. Furthermore, the formation of CRB is also favored kinetically, as the reaction barriers are low. While the barrier for the formation of CN-CRB is around 0.2 eV, the formation of NN-CRB is practically barrierless. It is obvious that at very low temperature, the adsorption of pyrimidine or s-triazine shall be dominated by the formation of NN-CRB structures.

In NN-CRB, the molecule is bound to the surface by two N—Si bonds, with a distance around 2.00 Å. In CN-CRB, the N—Si distance is shortened to 1.83 Å. The aromatic ring is less disturbed in NN-CRB, as indicated by the N-C-C-C dihedral angle around only 2° for both molecules. In contrast, the corresponding dihedral angle in CN-CRB is around 13° for pyrimidine and 16° for s-triazine. Interestingly, the NN-CRB structure for pyrazine, with the two N—Si distances around 1.87 Å and two N-C-C-N angles around 16.4°, is similar to CN-CRB reported here, rather than NN-CRB, since for pyrazine the NN-CRB structure is also a para-bridge (as shown in the bottom of Figure 1). The near planar geometry for pyrimidine and s-triazine in the NN-CRB structure indicates that the formation of the two N—Si dative bonds produces little disturbance to the aromatic ring, as geometrically both pyrimidine and s-triazine are a nice fit for such a meta-bridge structure.

These results also suggest a useful structural motif, which would produce stable and easily formed cross row bridge hold by two dative bonds, in the general form of X-C-X, with X being an electronegative elements, such as N or O. Whether the C atom is sp^2 or sp^3 hybridized probably does not matter, since the molecule would be held by two X—Si dative bond.

c.) *high coverage*

As shown for both pyridine and pyrazine, cooperative effects are important at high coverage, and the adsorption energy could be enhanced as more molecules are lined up on the surface.^{15,22} In the case of pyrazine, it leads to the formation of 1D lines perpendicular to dimer rows, with the NN-CRB structure as its basic unit.²¹ With the other reaction channels providing the migration paths, pyrazine molecules can assemble by themselves into 1D lines upon heating.²² In the case of pyridine, there is only one N atom and the migration of an adsorbed molecule is more difficult. Nevertheless, it is still possible for pyridine molecules to form lines either perpendicular to dimer rows, with NC-CRB as the basic unit, or lines along dimer rows, with TB (tight-bridge) as the basic unit.¹⁵

Such effects can also been seen for the case of pyrimidine and s-triazine. Shown in Figure 8 is the energy change for the formation of an NC-CRB line, perpendicular to a dimer row. By the fourth step, the adsorption energy has increased by 0.5 eV for both s-triazine and pyrimidine. The formation of a TB line along a dimer row, as shown in Figure 9, is also energetically favorable, although the adsorption energy increases by only 0.2 eV for both s-triazine and pyrimidine. However, as discussed above, there is a barrier for the formation of NC-CRB structure (~ 0.2 eV), and an even larger barrier for (0.3~0.5 eV) for the formation of TB structures. At low temperature, the formation of NC-CRB or TB structure can be blocked.

Kinetically, NN-CRB structure is much more favorable than other structures. However, it cannot produce a line structure similar to that based on the CN-CRB structure. As shown in Figure 10 for s-triazine, the adsorption energy for the second NN-CRB along such a line decreases by 0.6 eV, and by the fourth molecule, the adsorption energy has decreased by 1.3 eV. In fact, there is a reaction barrier even for the formation of the first dative bond in the second step. (0.17eV for pyrimidine and 0.22eV for s-triazine, in a (4×4) unit cell, see supporting info.)

The reason is that the two N—Si bonds in the NN-CRB structure are dative, and as a result, the two bridgehead Si atoms (Si2 and Si3) in Figures 6 and 7 are both in the down position. Further formation of N—Si dative bond on either Si1 or Si4 is getting more difficult since they are both tilted up and do not interact favorably with the lone pair on N. This is in contrast to the NC-CRB structure, also shown in

Figures 6 and 7, in which the two dimers, Si1-Si2 and Si3-Si4, are tilted in the same direction, and a new N—Si4 bond could be easily formed for the growth of a NC-CRB line.

At high coverage of pyrimidine or s-triazine, the kinetically favorable adsorption pattern is the zig-zag structure based on NN-CRB, shown in Figure 11, rather than the line structure based on NC-CRB. The adsorption energy for each successive molecule actually decreases slightly for the four steps considered in our calculations. But the adsorption energy is still around 1.5 eV for triazine and 2.0 eV for pyrimidine. More importantly, there is almost no barrier for these reactions. In fact, this was exactly the structure observed for the adsorption of pyrimidine on Ge(100) in a previous experimental report.²⁶

It should be noted that the NN distance in NN-CRB is 2.4 Å, while the CN distance (2.7 Å) in CN-CRB. For future studies, it would be very interesting to vary the XX distance in the X-C-X structural motif suggested above, which could determine whether a 1D line or a zig-zag pattern is produced at high coverage.

It is also possible to transform such zig-zag structures, by raising the temperature after a zig-zag monolayer is formed by adsorption at low temperature. According to the calculated energy values, what should be favored are the CN-CRB lines, when the reaction barriers could be overcome. However, the migration path for pyrimidine or s-triazine is limited to moving the dative Si—N bond in an EO structure diagonally along a dimer row, by the TR structures shown in Figures 2 and 4. Once a zig-zag mono-layer as shown in step 8 of Figure 11 is formed, such migrations cannot bring a pyrimidine or s-triazine molecule to the right position for the formation of CN-CRB lines. The only other channel open is to transform the NN-CRB structure into a TB structure, leading to the formation of TB lines along a dimer row. This would be especially interesting for s-triazine, since its TB structure is an easily established equilibrium between TB_I, TR, and TB_{II}, as shown in Figure 4c. It could provide a potential method to make lines along dimer rows.

There is, nonetheless, one precaution. Similar to pyridine, the adsorbed pyrimidine and s-triazine could also undergo dissociation upon moderate heating. A number of such channels have been identified by our calculations (with details in supporting info). The lowest barrier identified is for the TB_I structure, with a value of 0.72 eV for pyrimidine and 0.65 eV for s-triazine. While they are higher than the chemisorption barriers, there is a limit to the degree of heating that could be tolerated.

4. Conclusion

The chemisorption of pyrimidine and s-triazine on Si(100) can lead to ordered structures. In both cases, the kinetically most favorable pathway is the formation of

NN-CRB structure, with almost no barrier, which should dominate at low temperature and low coverage. At higher coverage and low temperature, a zig-zag pattern should be formed by these NN-CRB structures, instead of the CRB lines observed before for pyrazine. This is again determined by the kinetics, in spite of the fact that the zig-zag pattern is not energetically the most stable. Upon heating, it is possible to transform such zig-zag patterns into TB lines along dimer rows.

The chemisorption of pyrimidine and s-triazine on Si(100) also provides two structural motifs that could be useful in choosing the right organic molecules to reduce the complexity of the adsorbed configurations. The first one is illustrated by s-triazine, with 3 N atoms in meta-positions. Due to its symmetry, there is not much difference between [2+2] and [4+2] addition, or between on-dimer and inter-dimer reaction paths. The overall chemisorption eventually reaches an equilibrium between two tight bridge structures. The second one is in the form of X-C-X, with X being an electronegative atom. With the right distance between the two X atoms, the structure can form a cross row bridge, with two X—Si dative bonds.

(More reaction and dissociation paths are provided in the Electronic Supplementary Information.)

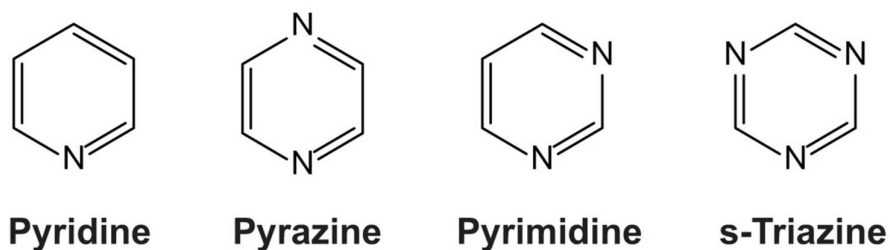
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Typical Adsorption Structures:

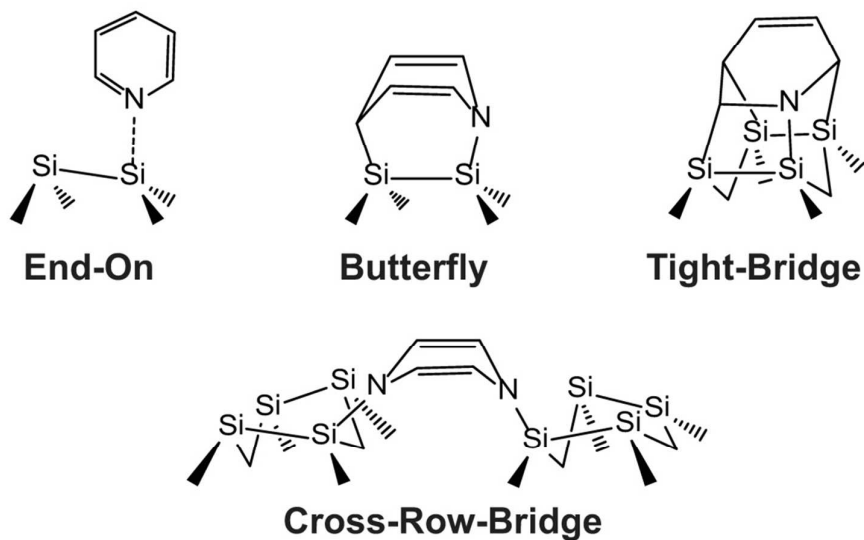


Figure 1: The structure for pyridine, pyrazine, pyrimidine and s-triazine, and their typical chemisorption structures on Si(100).

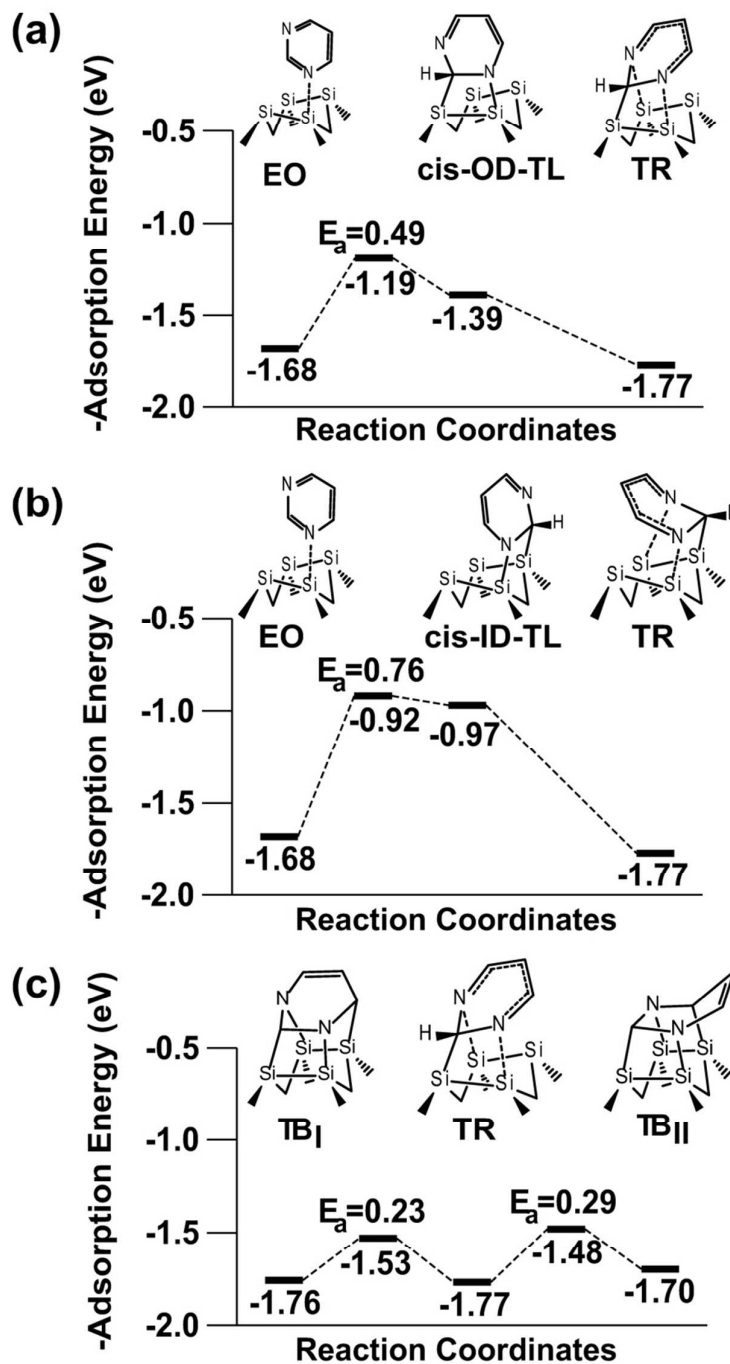


Figure 2: Cis [2+2] addition of pyrimidine on Si(100), starting from the EO (end-on) structure. The on-dimer and the inter-dimer additions produce the same intermediate structure, TR.

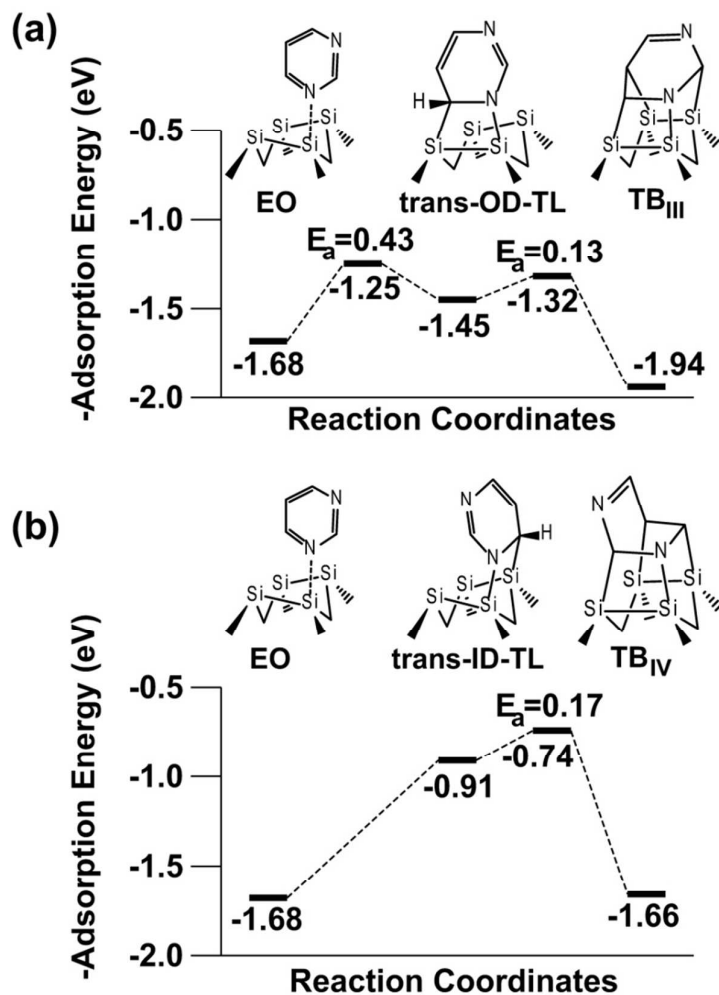


Figure 3: Trans [2+2] addition of pyrimidine on Si(100), starting from EO and leading to tight bridge structures different from the cis [2+2] products.

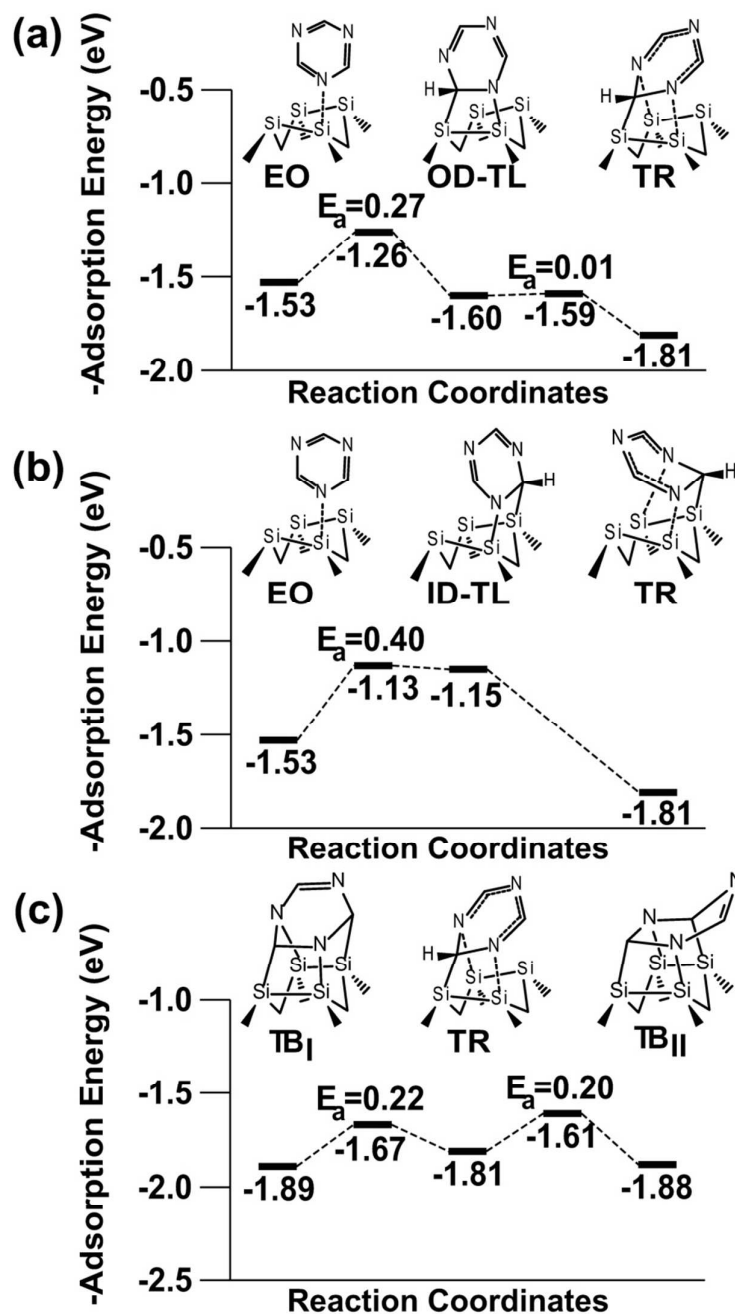


Figure 4: The [2+2] addition of s-triazine on Si(100), starting from EO. Due to the symmetry of s-triazine, the products are the same for on-dimer and inter-dimer additions. There are only two possible tight-bridge structures, TB_I and TB_{II}, which are separated by barriers around 0.2 eV.

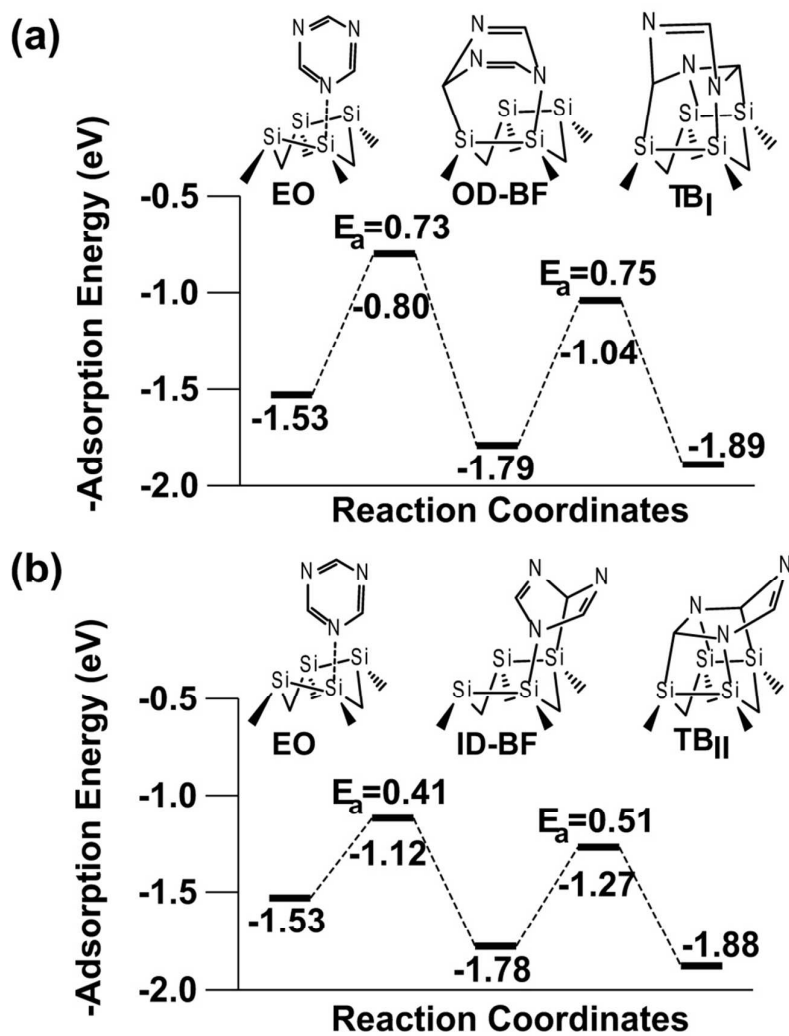


Figure 5: The [4+2] addition of s-triazine on Si(100), starting from EO. The products are the same as the [2+2] addition, due to the symmetry of s-triazine.

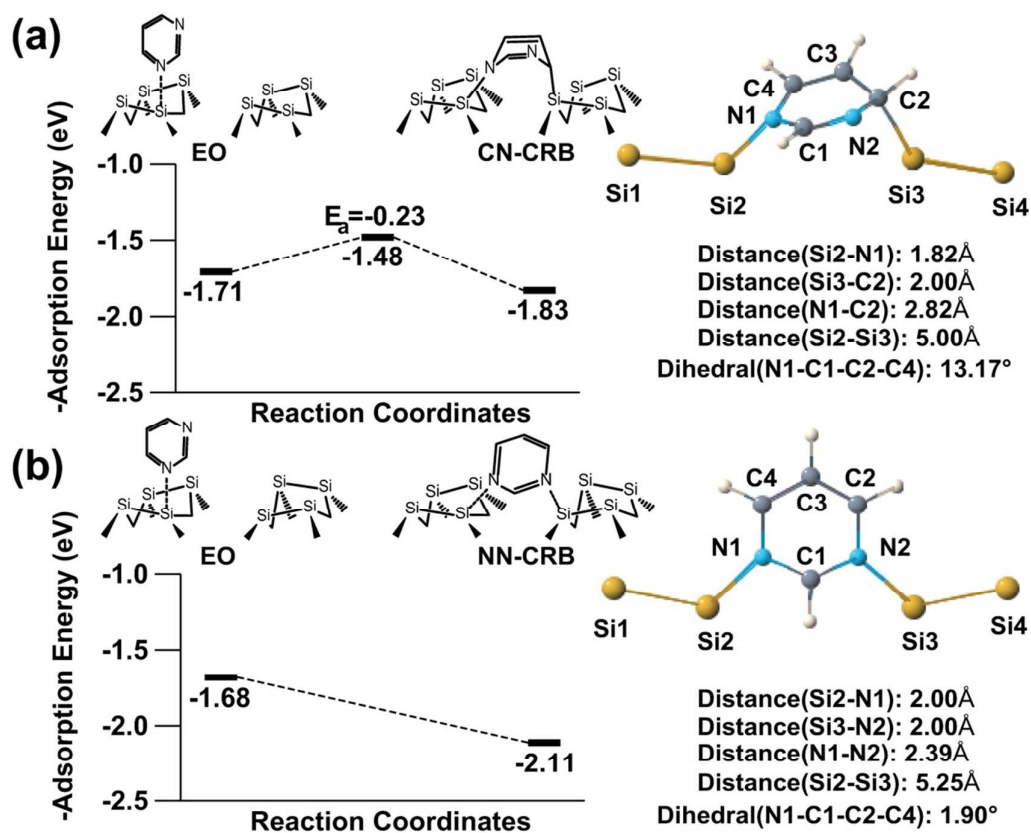


Figure 6: Formation of cross-row bridge structures for pyrimidine: (a) CN-CRB; (b) NN-CRB. The small difference in the energy for EO between (a) and (b) is due to the change in the tilt of the neighboring dimer row.

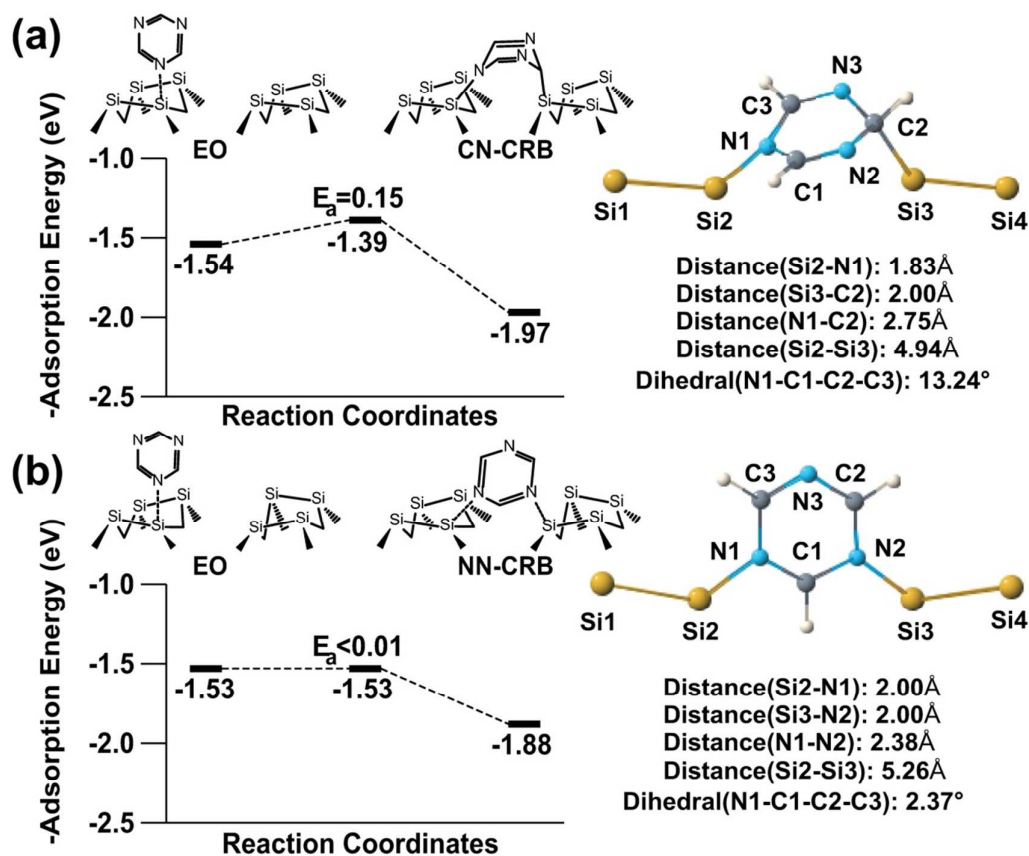


Figure 7: Formation of the cross-row bridge structures for s-triazine: (a) CN-CRB; (b) NN-CRB. The small energy difference for EO between (a) and (b) is due to the change in the tilt of the neighboring dimer row.

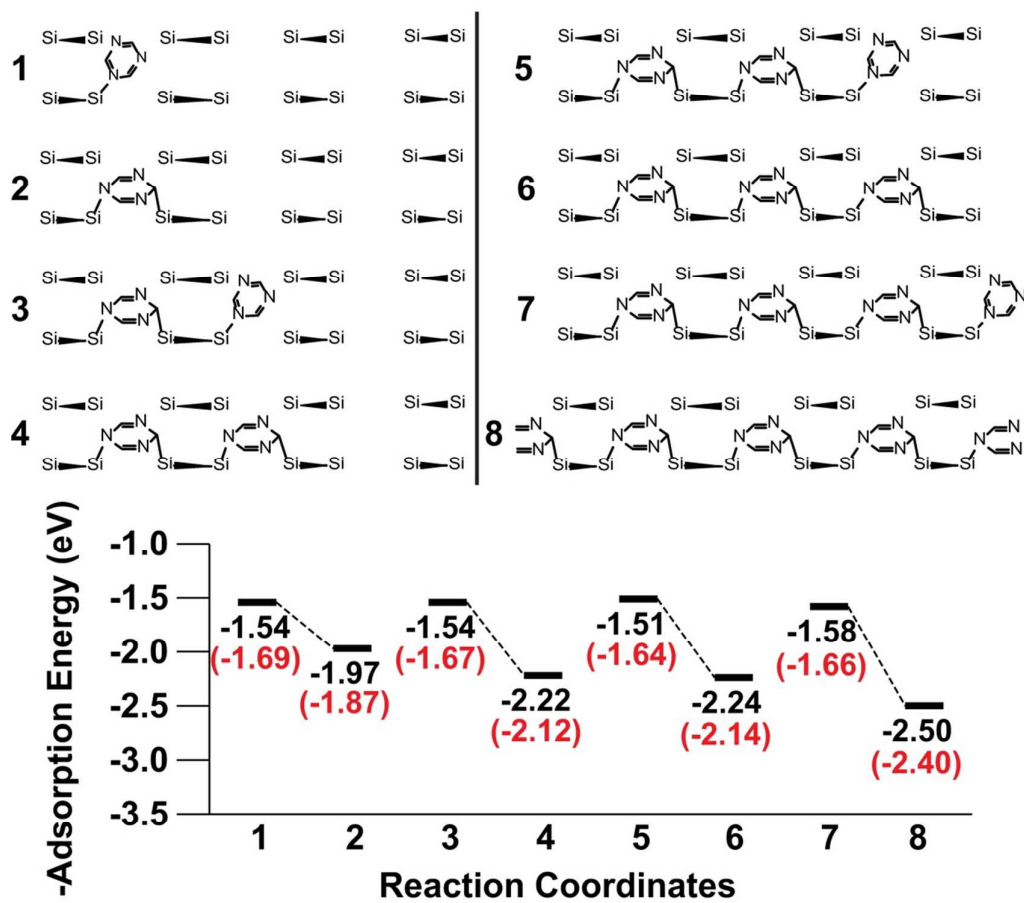


Figure 8: Stepwise energy change during the formation of a CN-CRB line. The values for s-triazine are listed in black, and for pyrimidine in red and parenthesis.

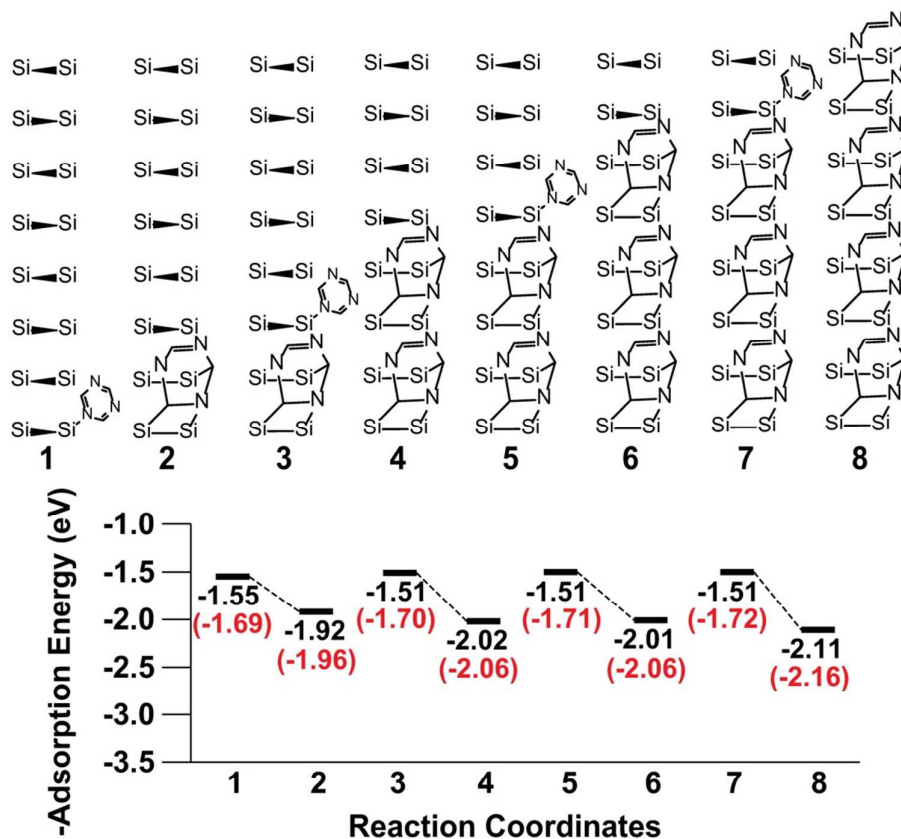


Figure 9: Stepwise energy change during the formation of a TB line along a dimer row. The values for s-triazazine are listed in black, and for pyrimidine in red and parenthesis.

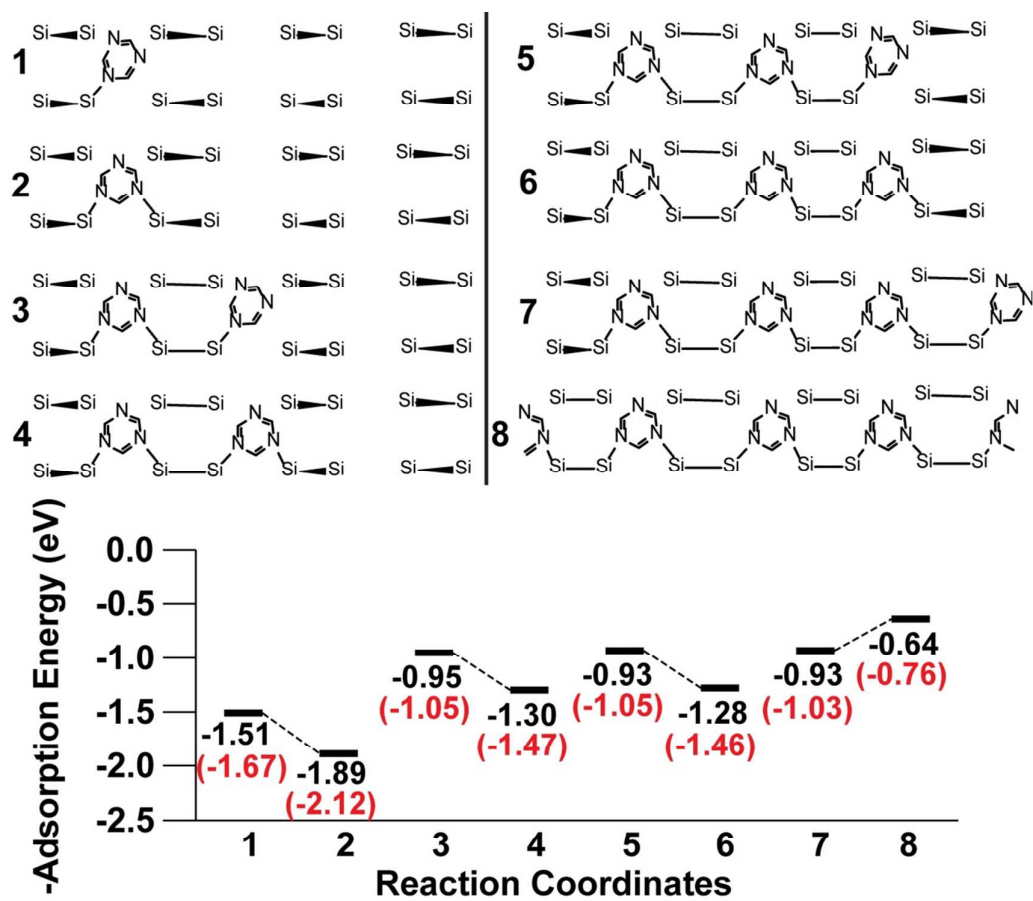


Figure 10: Stepwise energy change during the formation of a NN-CRB line. The values for s-triazine are listed in black, and for pyrimidine in red and parenthesis.

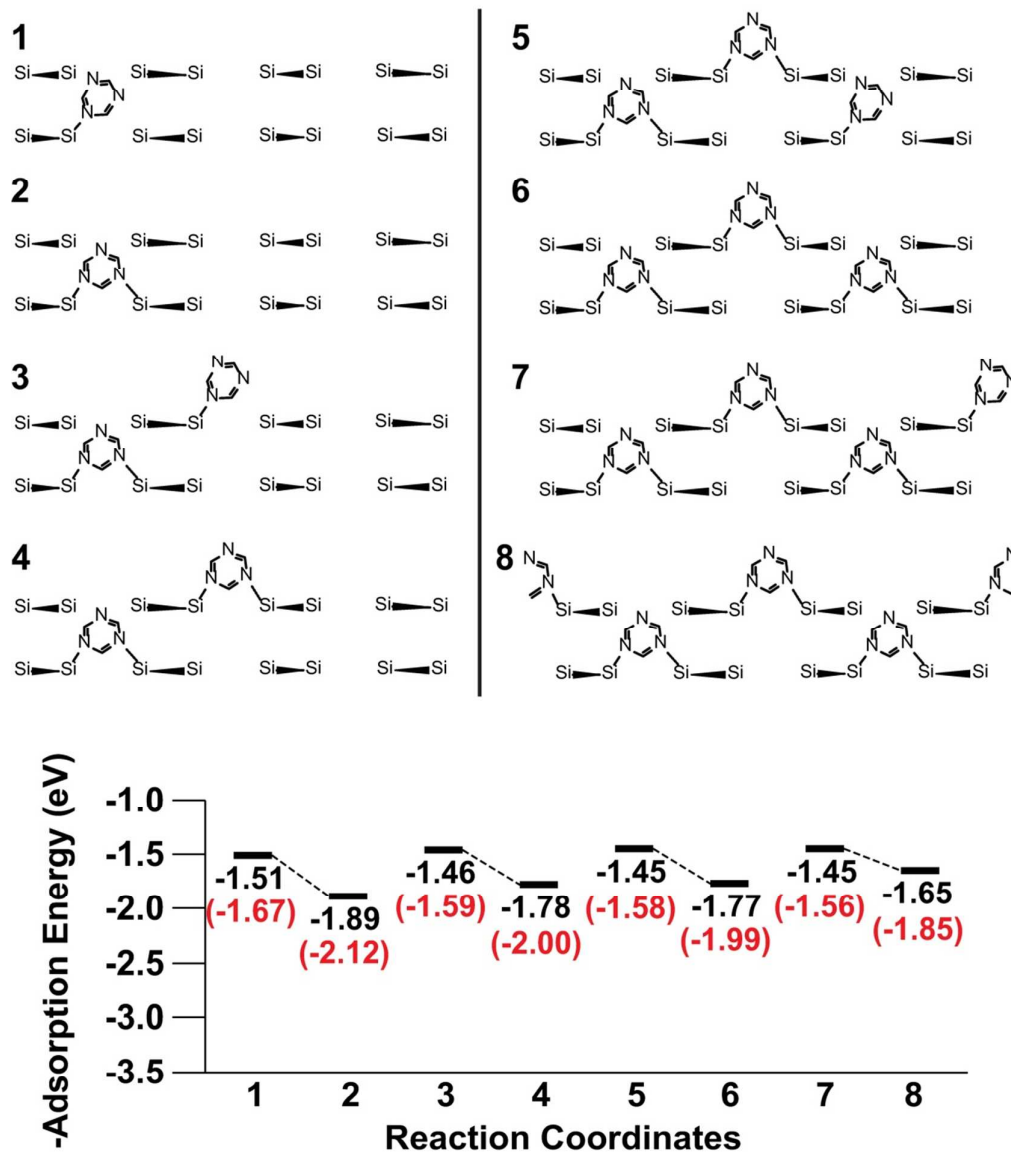
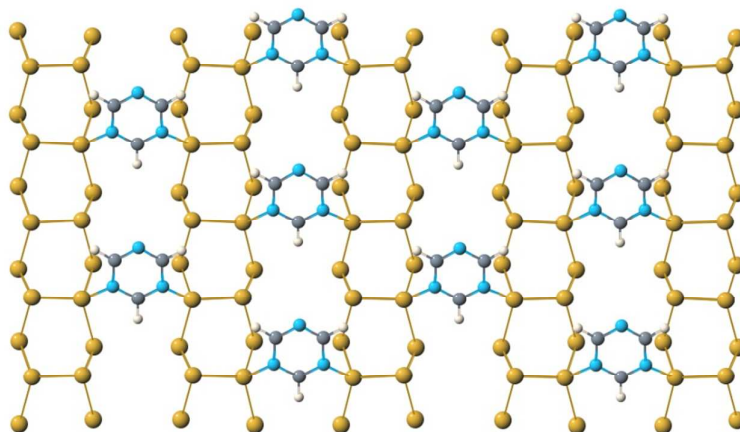


Figure 11: Stepwise energy change during the formation of a NN-CRB based zig-zag structure. The values for s-triazine are listed in black, and for pyrimidine in red and parenthesis.

Table of Contents Entry

Graphics:



Texts:

Kinetically controlled chemisorption of *s*-triazine on Si(100) at low temperature would produce ordered zigzag pattern, according to DFT calculations.