

## Chemisorption of Barrelene on Si(100) from First Principles Calculations

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The chemisorption of  $C_8H_8$  bicyclo[2.2.2]-2,5,7-octatriene (barrelene) on the Si(100) surface is studied from first principles calculations. We find that, in the most stable configuration, barrelene is bonded to Si(100) through four Si–C bonds, with the C–C bonds which are orthogonal to the underlying Si dimers. The chemisorption reaction responsible for this structure is driven by the biradical nature of the Si–Si dimer bond. Two others, slightly less stable configurations, exist which are also characterized by four Si–C bonds but have a different orientation or location with respect to the Si(100) surface. The properties of these and other, less stable configurations have been investigated. For the most stable structures, the effect of different surface coverages has been also studied, showing a tendency to easily form complete monolayers of barrelene on the Si surface. On the basis of energetic and kinetic considerations, we expect that chemisorption of barrelene monolayers on the Si(100) surface will be characterized however by a certain amount of disorder. Finally, several possible reaction pathways, leading from one stable structure to another of lower energy or from a molecule in the gas phase to a chemisorbed configuration, have been investigated in detail and estimates of the relative energy barriers are given.

## I. Introduction

The relevance of semiconductor surfaces for the development of new electronic devices cannot be overemphasized. In particular, a great interest has recently arisen in the chemisorption processes of unsaturated organic molecules onto silicon surfaces,<sup>1,2</sup> with a special emphasis on the growth of thin organic films. Controlled combination of organic molecules with the existing, silicon-based technology is very promising but difficult: although the formation of ordered organic monolayers has been reported,<sup>3</sup> most organic films grow on silicon in a disordered way, i.e., lacking long-range positional order; this behavior often derives from the existence of multiple, almost isoenergetic adsorption configurations for a given organic molecule interacting with the Si surface.

Adsorption of unsaturated hydrocarbons on the Si(100) surface is mainly driven by the formation of bonds between the C atoms and the surface Si dimers; therefore these formed bonds are strongly oriented, so that the dimerized Si(100) surface acts as a template for propagating order throughout the chemisorbed organic film. In principle, also the packing of the molecules in the thin film could contribute to the ordered arrangement; in fact a monolayer might be well ordered, although an isolated molecule on the surface has not a unique, well-defined structure.

Of particular importance is the possibility of using the residual chemical functionality of the chemisorbed molecules as anchor points (“glue molecules”) to which other, more complex molecules can be attached<sup>4–7</sup> in specific orientations and at well-defined locations on the semiconductor surface. The interaction with the Si(100) surface of such a glue molecule, norbornadiene (NBE), has been studied recently both theoretically and experimentally (see ref 7 and further references quoted therein). NBE has two parallel C–C double bonds separated by a distance

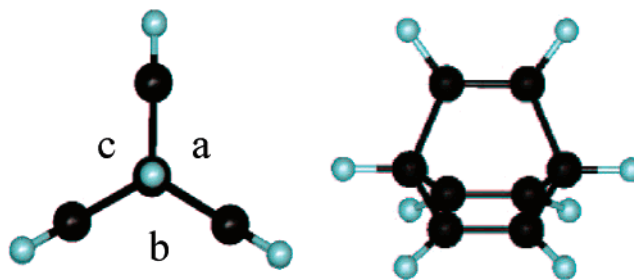


Figure 1. Isolated barrelene molecule in two different views.

close to that of two neighboring Si dimers on the same row, allowing in principle for both C–C bonds to react simultaneously with the two dimers, bridging them. Such a binding configuration would fix the orientation of the apical group not involved in the formation of the chemical bonds with the Si surface, allowing one in principle to produce a “functionalized” Si surface where the tethering of more complex organic molecules could proceed in a controlled manner.

Barrelene (BRL) is a three-double-bond, completely symmetric molecule (see Figure 1), which has been intensively studied theoretically.<sup>8</sup> The basic difference between NBE ( $C_7H_8$ ) and BRL ( $C_8H_8$ ) is represented by the replacement of the “apical” C atom of NBE with a pair of double-bonded C atoms in BRL, resulting in a symmetric structure with three completely equivalent C=C double bonds (see Figure 1). Given the conformation of the molecule and of the Si(100) surface structure, one expects that a low energy chemisorbed structure may be realized where the BRL molecule sticks to the Si(100) surface through the interaction of two double C=C bonds with a pair of adjacent surface Si dimers, in the same way as in the case of NBE. Clearly, the attractive feature of BRL is that while two C–C double bonds are used for bonding to the Si surface, the third one remains available for subsequent chemical attachment. Complete coverage of the Si(100) surface through the ideal mechanism described above would result in an ordered

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array of reactive C–C double bonds, parallel to the surface and to one another, with a density which is 1/2 of the original density of Si surface dimers. Such a functionalized surface could be used for selective adsorption of other more complex molecular objects. As we will show in the following, the scenario for chemisorption of BRL on Si(100) is far more complex than this simple picture may suggest: in fact additional structures occur, which differ in the orientation of the chemisorbed molecule with respect to the Si surface and in the relative location of the two involved Si dimers (they can belong to the same Si dimer row or to adjacent rows).

Nanopatterning of the Si surface with barrelene is also possible in principle, in the same way as done with NBE on Si(100):<sup>9</sup> here the Si surface is first exposed to atomic hydrogen, resulting in the formation of a chemically inactive monohydride-terminated surface. Then hydrogen is selectively removed from such surface with a scanning tunneling microscopy (STM) tip, allowing one in principle to design nanometric domains of clean Si surface (immersed in an otherwise unreactive region) where chemisorption of NBE is possible. We suggest a similar procedure with BRL instead of NBE: the C–C double bond not involved in the binding with the substrate could provide an anchor point for additional chemisorption of molecules in a predefined way.

The goal of the present study is to investigate the chemisorption of BRL on the Si(100) surface as a possible candidate for the formation of ordered monolayers. We hope that our study will stimulate experimental studies of such system.<sup>10</sup>

## II. Method

We have carried out first principles calculations using the CPMD package<sup>11</sup> in the framework of the density functional theory and using gradient corrections in the PBE implementation:<sup>12</sup> gradient corrected functionals have been adopted in the most recent theoretical studies of adsorption of organic molecules on Si(100) because they are typically more accurate than the simple local density functional in describing chemical processes on this surface.<sup>13,14</sup> In particular, we adopted the PBE functional, because of its strong physical background and its reliability in a number of studied systems. The calculations have been carried out considering the  $\Gamma$  point only in the Brillouin zone (BZ) and using norm-conserving pseudopotentials,<sup>15</sup> with  $s$  and  $p$  nonlocality for C and Si. Wave functions were expanded in plane waves with an energy cutoff of 50 Ry. We have explicitly checked that, at this value of the energy cutoff, the structural and binding properties of our system are well converged. We used a slab model to simulate the Si surface in the  $(2 \times 2)$  reconstruction: the slab is made of 5 Si layers, plus a vacuum region, 6 Å wide, separating the repeated images of the slab. A monolayer of hydrogen atoms is used to saturate the dangling bonds on the lower surface of the slab. Most of our simulations have been performed using a supercell with a  $p(\sqrt{8} \times \sqrt{8})R45^\circ$  periodicity, i.e., with 4 Si surface dimers. On the basis of previous experience in simulations of similar systems,<sup>16</sup> we expect that, with such a supercell, a sampling of the BZ limited to the  $\Gamma$  point is adequate. A different, larger supercell characterized by a  $p(4 \times 4)$  periodicity, containing a slab of 6 Si layers (with 16 atoms for each layer, i.e., 8 Si surface dimers), has been used to check for finite-size effects and/or different surface coverages, as explained in the following. Structural relaxations of the ionic coordinates have been performed using the method of direct inversion in the iterative subspace.<sup>17</sup> During the ionic relaxations, the lowest Si layer and the saturation hydrogens were kept fixed. To better investigate

**TABLE 1: Bond Lengths (Å) and Angles (Degrees, see Figure 1) Computed for the Isolated BRL and NBE Molecules, Compared with Experimental Data (References 27 and 28) in Parentheses**

	C=C	C–C	$a = b = c$
BRL	1.34 (1.34)	1.54 (1.54)	105.6 (105.9)
NBE	1.35 (1.34)	1.54, 1.56 (1.54, 1.56)	

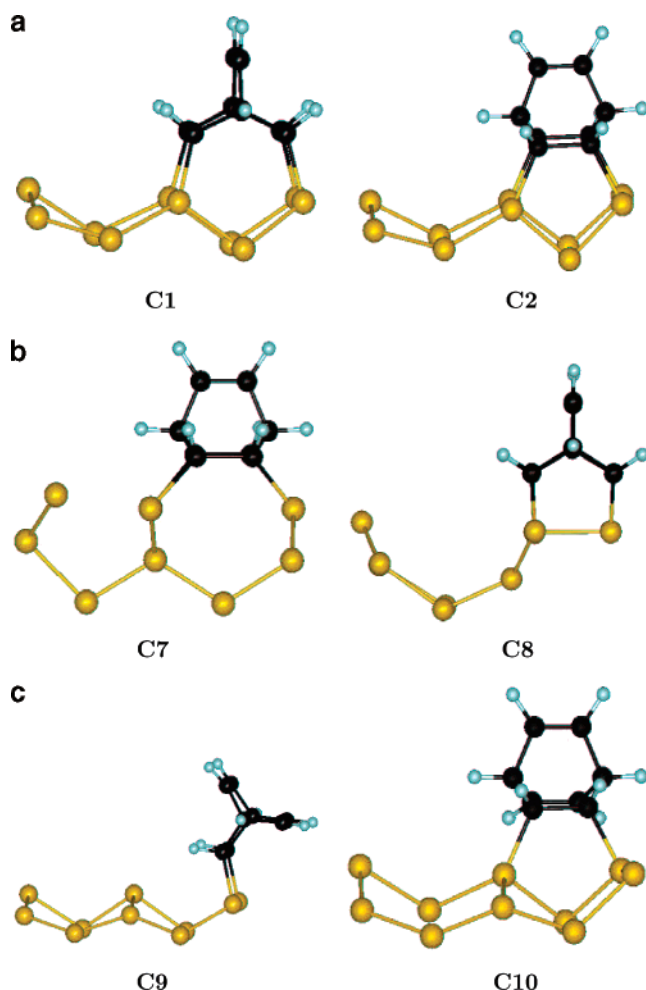
the complex potential-energy surface of this system, in some cases the optimization procedure was repeated using a simulated-annealing strategy and starting from different initial configurations. We verified that, by starting with the unreconstructed, clean Si(100) surface, the structural optimization procedure correctly produces asymmetric surface dimers, with a dimer bond length and buckling angle in good agreement with previous, highly converged ab initio calculations.<sup>18</sup> Accurate estimates of the pathways and energy barriers characterizing the different dissociation processes have been obtained from first principles by means of a recently proposed variant of the popular “nudged elastic band” method, i.e., the “climbing image nudged elastic band” (CI-NEB) method,<sup>19,20</sup> which has proven to be a very efficient technique to determine minimum energy paths in complex chemical reactions.

An extensive set of preliminary calculations have been performed using semiempirical potentials within classical molecular dynamics simulations.<sup>21,22</sup> This allowed us to rapidly explore a larger portion of the configurational space in order to search efficiently for stable chemisorbed structures, possible dissociation pathways, and dissociation products; then the resulting structures and pathways have been reinvestigated, using the more accurate ab initio approach described above. We find this procedure particularly effective in systems such as the one studied here, where a large number of possible structures and bonding geometries are possible: in fact an already good guess for the structures to be studied allows one to find more rapidly and with much less computational effort the correct equilibrium structures at the ab initio level.

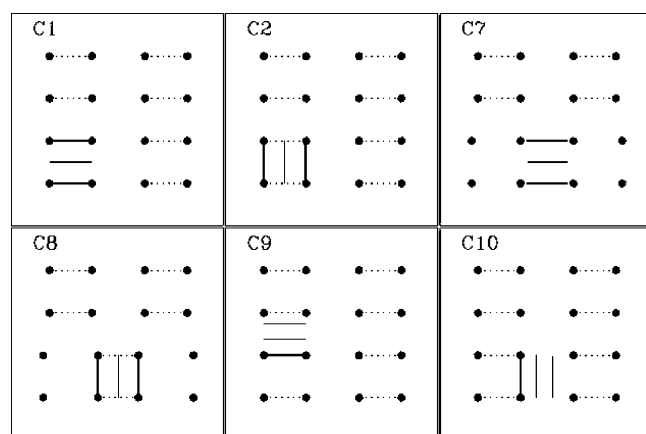
## III. Results

As a preliminary test, we have calculated, from first principles, the structural properties of isolated BRL and found a good agreement (see Table 1) with the experimental data. For comparison, we also show our calculated structural parameters for the NBE molecule. Given the structural similarities between NBE and BRL, a comparison with the existing experimental and theoretical results for NBE chemisorption on Si(100) will certainly be useful, as shown in the following.

In Figure 2a–c we show the lowest-energy chemisorption structures (a schematic of the top view is shown in Figure 3 where, for clarity, additional Si dimers are drawn) of BRL on Si(100) obtained by ab initio geometry optimizations and using the  $p(\sqrt{8} \times \sqrt{8})R45^\circ$  supercell: such a supercell contains four surface Si dimers, so that, if we assume that a full, 1.0 monolayer (ML) coverage is obtained when a BRL molecule is present per each pair of Si dimers (see Figure 4), then chemisorption of a single BRL molecule in this supercell corresponds to a 0.5 ML coverage. The binding energies and the geometrical data characterizing these structures are reported in Tables 2 and 3, respectively. Given the analogy with the case of chemisorption of NBE onto Si(100), we adopt here a nomenclature similar to that used in the paper of Bilić et al.:<sup>7</sup> in particular, the *odd-numbered* structures have their reactive C–C bonds *parallel* to the underlying Si dimers, while the *even-numbered* ones have them *perpendicular*.

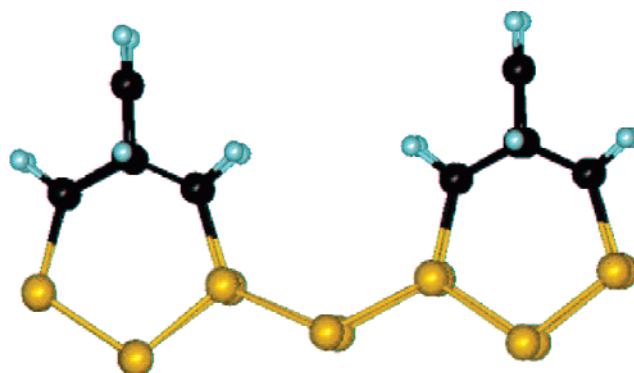


**Figure 2.** (a–c) Stable configurations for chemisorption of BRL on Si(100), obtained using the  $p(\sqrt{8} \times \sqrt{8})R45^\circ$  supercell, at 0.5 ML coverage. Light blue, black, and yellow balls indicate H, C, and Si atoms, respectively. For clarity, only a few surface Si atoms are shown and the configurations of panel b have been rotated by  $90^\circ$  with respect to the other structures.



**Figure 3.** Schematic of the top view of the stable chemisorbed structures shown in Figure 2a–c. Solid circles indicate the positions of the surface Si dimers, dotted segments denote surface Si–Si dimers, and solid segments represent C–C bonds (thicker segments indicate the bonds between C atoms which form Si–C bonds with the substrate).

In principle, the reaction of a carbon–carbon double bond with the surface Si dimers can occur through different mechanisms: if one assumes that the surface Si dimers are symmetric and have a genuine double-bond character, then a true [2+2]



**Figure 4.** Complete monolayer (1.0 ML, saturation coverage) of BRL chemisorbed on Si(100), in the C1 configuration.

**TABLE 2: Binding Energies (in eV/Molecule) of BRL Chemisorbed on Si(100) Computed Using the  $p(\sqrt{8} \times \sqrt{8})R45^\circ$  Supercell, at 0.5 ML Surface Coverage; Data in Parentheses Have Been Obtained with the  $p(4 \times 4)$  Supercell at 0.25 ML Surface Coverage<sup>a</sup>**

configuration	$E_{\text{bind}}$	configuration	$E_{\text{bind}}$
C1	3.05 (3.25)	C8	3.18 (3.45)
C2	3.37 (3.74)	C9	1.60
C7	(1.39)	C10	1.44

<sup>a</sup> The missing entry (for the C7 configuration with the  $p(\sqrt{8} \times \sqrt{8})R45^\circ$  supercell) means that the structure is unstable; see the text.

**TABLE 3: Structural Parameters (Bond Lengths in Å, Angles in Degrees) of BRL Chemisorbed on Si(100) Computed Using the  $p(\sqrt{8} \times \sqrt{8})R45^\circ$  Supercell, at 0.5 ML Surface Coverage<sup>a</sup>**

confign	Si <sub>b</sub> –Si <sub>b</sub>	Si–Si	C <sub>b</sub> –C <sub>b</sub>	C–C	Si <sub>b</sub> –C <sub>b</sub>	<i>a</i>	<i>b</i>	<i>c</i>
C1	2.37	2.30	1.58	1.35	1.97	103.6	116.7	103.6
C2	2.39	2.29	1.59	1.35	1.98	109.1	108.4	109.1
C7		2.33	1.63	1.35	2.02	105.9	117.2	105.9
C8	2.39	2.31	1.58	1.34	1.95	107.8	108.8	108.4
C9	2.37	2.31	1.56	1.35	1.95	109.4	107.6	101.0
C10		2.33	1.59	1.35	1.98	108.7	107.0	105.1

<sup>a</sup> C<sub>b</sub> and Si<sub>b</sub> indicate atoms which form Si–C bonds; *a*, *b*, and *c* denote the angles shown in Figure 1.

“cycloaddition” reaction could occur; however this process is symmetry forbidden. A similar reaction (R1) is instead possible if the surface Si dimers (as has been observed in our simulations and in many other theoretical studies; see, for instance, ref 7) are asymmetric and cannot be described in terms of a double bond but have instead a “zwitterionic” character,<sup>23</sup> with the reactive electrons which correspond to the nonbonding orbitals of each Si atom; an alternative bonding mechanism (R2) is active when the two C atoms stick to Si atoms belonging to different, adjacent Si dimers. Mechanism R1 leads to a C–C bond vertically aligned above a dimer row and parallel to the underlying Si–Si dimer bonds: the configurations C1 and C9 are examples of such a mechanism. Mechanism R2 can occur in two ways: either with the reacting Si atoms located in the same dimer row, so that the C–C bonds of the chemisorbed BRL molecule are aligned in a perpendicular way with respect to the Si dimer bonds (see configurations C2, C8, and C10), or with the reacting Si atoms located in different dimer rows, so that the C–C bonds are parallel to the Si dimer bonds (see configuration C7). Note that the C8 structure is obtained by breaking two surface Si dimers and forming two new Si bonds between Si atoms originally located in different dimers. Interestingly, in the C7 configuration, differently from what was



reported for the corresponding structure of NBE on Si(100),<sup>7</sup> the Si dimers, to which the BRL molecule bonds, are broken, without the formation of new Si–Si bonds, thus explaining the relatively low binding energy computed for this structure.

The different chemisorbed structures can also be classified according to the number of formed Si–C bonds: the configurations C1, C2, C7, and C8 are characterized by the formation of four Si–C bonds (two C=C double bonds react with the Si surface), while C9 and C10 are obtained through the reaction of just one C=C double bond with the formation of only two Si–C bonds. As expected, the C atoms involved in C–Si bonds have their hybridization changed from  $sp^2$  to  $sp^3$ .

In strict analogy with the case of NBE,<sup>7</sup> many other chemisorbed structures are possible and have been investigated in our study; however they are unstable or characterized by a relatively smaller binding energy and therefore are not discussed here. As expected, the value of the binding energy is mainly determined by the number of formed Si–C bonds (see Table 2), although also configurations characterized by the same number of Si–C bonds exhibit different binding energies due to other effects such as the different strain of the Si surface. As can be seen from inspection of Table 2, the configurations C1, C2, and C8 are the most stable ones. C2 differs from C1 only by a rotation of 90° with respect to the Si surface; a possible reason for the difference in their binding energies could be related to different deformations that the BRL molecule undergoes: in fact, as can be seen in Table 3, the  $b$  angle (see Figure 1) is closer to the value (105°) assumed in the isolated BRL molecule when the system has the C2 structure (108°) than in the C1 configuration (117°). This result might also support the conclusion that the reaction mechanism R2 is, at least energetically, more favorable than R1. Interestingly, the fact that C2 is more stable than C1 is a result similar to that obtained for chemisorption of acetylene ( $C_2H_2$ ) on Si(100), where it has been found<sup>24</sup> that a “paired end-bridge” configuration, with the C–C bonds perpendicular to the Si dimers, is slightly favored with respect to the structure realized with the C–C bonds parallel to the dimers; the stability of the “paired end-bridge” configuration of acetylene on Si(100) was previously proposed by Sorescu and Jordan<sup>13</sup> and by Morikawa.<sup>25</sup> Configuration C8 can be obtained from the C2 one by shifting the BRL molecule from a location above the dimer row to one above a “trough” between dimer rows; as discussed above this structure is characterized by the formation of two new surface Si dimers and (see Table 2) is slightly less stable than C2.

As a consequence of the chemisorption process, the BRL molecule is substantially deformed as can be seen by looking at Table 1 and 3: for instance, in the case of configuration C2, the length of the two C–C bonds, involving the four C atoms bonded to Si atoms, goes from the 1.33 Å value of the free BRL molecule (a typical value of a C=C double bond) to 1.59 Å, which is even longer than typical C–C single bond lengths (1.50–1.55 Å). Concerning the Si surface structure, the most noticeable change is represented by the fact that the Si dimers completely saturated by C atoms become essentially flat (the “buckling” angle characteristic of the Si dimers of the clean surface is reduced to zero); instead the bond lengths of the Si dimers to which the BRL molecule is bonded undergo only marginal changes, thus confirming that a genuine [2+2] cycloaddition reaction (assuming Si–Si double bonds) is not realized. Interestingly, in the case of configurations C1 and C2, we find a substantial reduction of the distance between adjacent Si dimers saturated by C atoms (from 3.9 Å for the clean surface to 3.3–3.6 Å); this suggests that the Si surface undergoes a

**TABLE 4: Comparison of the Binding Energy (in eV/Molecule) of BRL and NBE on Si(100) in Different, Stable Chemisorbed Configurations, Computed Using the  $p(4 \times 4)$  Supercell, at 0.25 ML Coverage; Data from Reference 7, at the Same Coverage, Are Reported in Parentheses**

configuration	BRL	NBE	configuration	BRL	NBE
C1	3.25	3.12 (3.51)	C7	1.39	1.94 (3.12)
C2	3.74	3.73 (4.16)	C8	3.45	3.88 (3.69)

**TABLE 5: Energy Barriers (in eV) Relative to Selected Minimum Energy Paths of BRL on Si(100), Computed Using the  $p(\sqrt{8} \times \sqrt{8})R45^\circ$  Supercell<sup>a</sup>**

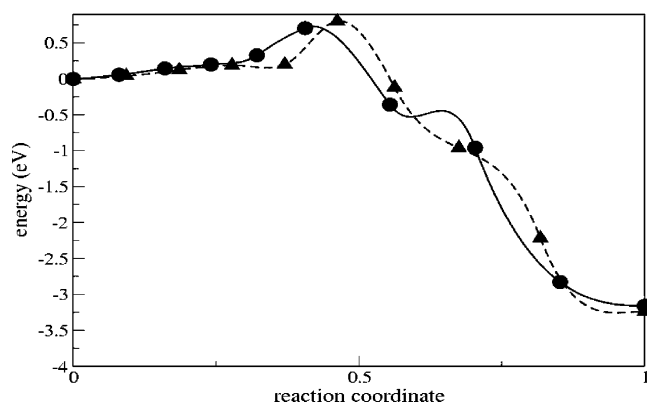
reaction path	energy barrier	reaction path	energy barrier
P–C1	0.7 (0.7)	P–C8	4.0
P–C2	0.4	C9–C1	0.5

<sup>a</sup> P indicates a generic physisorbed state in which the BRL molecule is relatively far from the Si(100) surface. The energy barrier for a reaction path of NBE on Si(100) is reported in parenthesis.

significant strain. The calculations relative to some of the structures studied, particularly those in which incompletely saturated Si dimers are involved, have been repeated by taking spin polarization into account to check whether unpaired electrons play a significant role; however no noticeable differences have been observed in the basic physical quantities investigated.

If comparison is made with the binding energies computed for NBE (see Table 4 and ref 7), our results exhibit some similarities: in fact, also for BRL on Si(100) the structures C1, C2, C7, and C8 turn out to be the favored ones, with C2 being the most stable; moreover C8 is slightly more stable than C1; however C7 and C8 are considerably less stable than the corresponding structures with BRL replaced by NBE. In particular, configuration C7 deserves a specific comment: as can be seen in Table 2, C7 is unstable using the  $p(\sqrt{8} \times \sqrt{8})R45^\circ$  supercell (that is, the total energy of the BRL/Si(100) system is not lower than the energy of the separated BRL and Si(100) subsystems), so that this is a case in which the use of the larger  $p(4 \times 4)$  supercell is mandatory. Although our calculations show that the binding energy of NBE interacting with Si(100) in the C7 structure is significantly larger than that of BRL, nonetheless it is much lower than that reported in ref 7 (for the other configurations a qualitative agreement is instead found): we presume that the discrepancy is due to the fact that in ref 7 configuration C7 is characterized by the reformation of the underlying Si dimers, while, as discussed above, this is not the case in our simulations (we have done specific tests starting from reformed Si dimers, but they invariably tend to break); possibly the different behavior can be ascribed to our use of a gradient-corrected functional (PBE) different from that (PW91) adopted in ref 7 or to differences in other technical details.

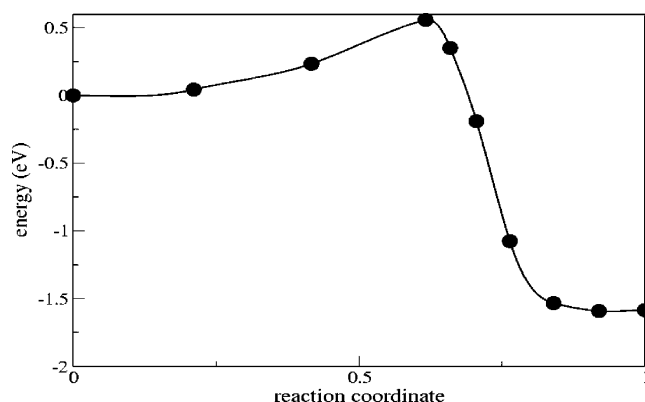
To predict the probability of a possible chemisorption configuration, it is important not only to estimate its energetic stability (i.e., the binding energy of the system in a given configuration) but also to take kinetic effects into account by evaluating the energy barrier (if any) that the system must overcome to arrive at this configuration and in some cases to go to another, stable configuration. Therefore we have estimated the energy barriers relative to different chemisorption mechanisms by using the CI-NEB method (see Method). The main results of many different reaction paths investigated are summarized in Table 5: since these calculations are much more computationally demanding than simple geometry optimization, all the reaction paths have been studied using the  $p(\sqrt{8} \times \sqrt{8})R45^\circ$  supercell, at 0.5 ML coverage.



**Figure 5.** Reaction paths of BRL (circles) and NBE (triangles) from a physisorbed state to the C1 configuration.

If we consider the reaction process leading from a BRL molecule in the gas phase (far from the Si surface) to a chemisorbed structure C1 or C2, we find energy barriers of 0.7 and 0.4 eV, respectively; this result suggests that C2 is favored with respect to C1 not only from an energetic point of view but also kinetically. Interestingly, the starting point of the reaction path leading to the C2 configuration turns out to be a weakly bonded, physisorbed state characterized by a binding energy of only 0.2 eV; the BRL molecule is therefore expected to approach the Si surface by going through this metastable state and then to undergo chemisorption by forming real, covalent C–Si bonds. Note that such a physisorbed state, in which the structure of the BRL molecule and that of the Si(100) surface remain almost identical to those of the separated, noninteracting systems, has been also detected<sup>7</sup> in the case of NBE on Si(100); from an experimental point of view, low concentrations of physisorbed molecules have in fact been observed on Si(100) surfaces exposed to alkenes.<sup>26</sup> Since the energy barrier for chemisorption into the C1 or C2 structure is small but not negligible, we predict that experimental observation of some physisorbed BRL molecules on Si(100) should be possible. As can be seen in Figure 5, where chemisorption into the C1 structure is considered, the reaction process for BRL interacting with the Si(100) surface is very similar to that which applies to NBE. In ref 7 the energy barrier for chemisorption of NBE on Si(100), starting from the physisorbed state, is found to be of the order of 0.1 eV, which is a value considerably lower than ours; a possible reason for such a discrepancy could be the fact that Bilić et al. have estimated the energy barriers by adopting the standard NEB approach while we have used the more sophisticated CI-NEB version which is expected to better reproduce the minimum-energy path in the vicinity of the energy maximum.

To better understand the whole adsorption process, one should also investigate possible processes which could make surface migration and/or rearrangement possible; in general, once the BRL is chemisorbed into one of the structures shown in Figure 2a–c, we find that it is extremely difficult for it to undergo a transformation into a different structure. A noticeable exception is represented by the C9–C1 transition: in Figure 6 we show the minimum energy path for the transformation going from C9 to C1; this process, in which the C–Si bonds increase from two to four, is characterized by an energy barrier of only 0.5 eV. As has already been discussed above, configurations C7 and C8 involve a significant reorganization of the Si dimers; therefore one can expect that these structures, although energetically stable, are not kinetically favored. In fact we find that the



**Figure 6.** Reaction path for the transformation from the C9 to the C1 structure.

**TABLE 6: Binding Energies (in eV/Molecule) of BRL Chemisorbed on Si(100) in the C1 and C2 Configurations, at Different Surface Coverages, Computed Using the  $p(4 \times 4)$  Supercell; Data in Parentheses Have Been Obtained with the Smaller  $p(\sqrt{8} \times \sqrt{8})R45^\circ$  Supercell**

coverage (ML)	C1	C2
0.25	3.25	3.74
0.50	3.00 (3.05)	3.71 (3.37)
1.00	2.91 (3.10)	3.63 (3.46)

energy barriers that the BRL molecule must overcome to assume these configurations are relatively large (of the order of 4 eV).

To shed some light on the possibility of functionalizing the Si(100) surface by means of BRL molecules, we have investigated the configurations obtained by taking as a reference the most stable C1 and C2 structures and considering different surface coverages, namely, 0.25, 0.50, and 1.00 ML (saturation coverage). To this aim, the calculations have been performed using the larger  $p(4 \times 4)$  supercell and simulating the chemisorption process of 1, 2, and 4 BRL molecules, respectively; the corresponding binding energies (per BRL molecule) are reported in Table 6. For the sake of estimating finite-size effects, calculations have been carried out, considering both the C1 and C2 configuration, using also the smaller  $p(\sqrt{8} \times \sqrt{8})R45^\circ$  supercell; of course, in this latter case it is possible to realize only the 0.50 and 1.00 ML coverages (by adsorption of 1 or 2 BRL molecules). The basic conclusion that can be drawn from Table 6 is that, apart from slight differences, which can be ascribed to the different supercell used, the binding energy per BRL molecule turns out to not depend strongly (at least for the C1 and C2 configuration) on the surface coverage; this supports the idea that intermolecular repulsive interactions (of steric or purely electronic nature) are not effective or, at most, are not so important to prevent the formation of a full monolayer of BRL on Si(100). This is directly seen in the case of the 0.50 ML coverage; in fact, using the  $p(4 \times 4)$  supercell this coverage can be realized either with nonadjacent or with adjacent (closer) BRL molecules: the difference in the computed binding energy per molecule is smaller than 0.01 eV. Interestingly, the C2 configuration seems to be favored over the C1 one at all the surface coverages.

#### IV. Conclusions

In conclusion, our ab initio calculations indicate that two chemisorption configurations for BRL on Si(100) appear to be both energetically and kinetically favored; these structures are characterized by the formation of four Si–C bonds and are energetically favored at all the surface coverages investigated.

In the most stable structure, the C–C bonds are orthogonal to the underlying Si dimers, similarly to what occurs in the case of NBE chemisorption on Si(100). The result that the binding energy per BRL molecule does not significantly change as a function of the surface coverage suggests that complete monolayers of BRL on Si(100) can easily be realized, although a certain amount of disorder is expected. In the lowest energy structure, a reactive C–C double bond is left for each chemisorbed molecule, which could act as an anchor point for selective chemisorption of different molecular species.

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## References and Notes

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