Adsorption of benzene on Si(100) from first principles

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Adsorption of benzene on the Si(100) surface is studied from first principles. We find that the most stable configuration is a tetra-σ-bonded structure characterized by one C-C double bond and four C-Si bonds. A similar structure, obtained by rotating the benzene molecule by 90°, lies slightly higher in energy. However, rather narrow wells on the potential-energy surface characterize these adsorption configurations. A benzene molecule impinging on the Si surface is most likely to be adsorbed in one of three different di-σ-bonded, metastable structures, characterized by two C-Si bonds, and eventually converts into the lowest-energy configurations. These results are consistent with recent experiments.

Adsorption of benzene on the Si(100) surface is a topic of great current interest[1–9] both because it represents a prototype system for the study of molecular adsorption (and desorption) of hydrocarbons on semiconductor surfaces, and because it is considered a promising precursor for technologically relevant processes, such as the growth of Si-C and chemical vapor deposition diamond thin films on Si surfaces. However, despite many experimental and theoretical investigations, the adsorption mechanism is not yet well understood. In particular, at present there is no consensus about the lowest-energy structure of benzene on Si(100): results obtained from surface science experimental techniques, semiempirical methods, and first-principles approaches provide a number of different predictions.

Benzene is known from experiments to adsorb exclusively on top of the Si(100) surface dimer rows, thus avoiding energetically disfavored structures with unsaturated, isolated Si dangling bonds. Even so, since the size of the benzene molecule is comparable to the spacing between two adjacent dimers on the same row, many different bonding configurations are possible. Among the structures proposed in the literature as the lowest-energy configurations, the 1,4-cyclohexadiene-like (''butterfly'') configuration, in which the benzene molecule is di-σ-bonded to the two dangling bonds of the same Si surface dimer, is supported by thermal desorption and angle-resolved photoelectron spectroscopy,[5] scanning tunneling microscopy (STM),[7] vibrational infrared (IR) spectroscopy, and near-edge x-ray absorption fine-structure techniques,[9] and first-principles cluster calculations.[5] Instead, other STM experiments[6] suggest the 1,3-cyclohexadiene-like (''tilted'') structure. Finally, semiempirical calculations,[3,8] STM, and IR spectroscopy experiments[8] favor a tetra-σ-bonded configuration where benzene is bonded to two adjacent surface dimers.

Another open issue concerns the occurrence and nature of metastable adsorption states. In fact, the results of STM and IR spectroscopy[6,8] support the hypothesis that benzene is initially chemisorbed in a metastable, ''butterfly''-like state, and then slowly converts (within minutes) to a lower-energy final state, which is a ''tilted'' structure according to Ref. 6, or a tetra-σ-bonded one according to Ref. 8. Moreover, recent IR experiments[9] suggest that, at room temperature, benzene is predominantly adsorbed in the butterfly configuration, while the existence of a less stable structure, consistent with a tetra-σ-bonded configuration, is proposed.

Previous theoretical calculations on benzene on Si(100) have been restricted to semiempirical or *ab initio* cluster-model methods. In the latter approach the Si surface is modeled with a cluster of Si atoms, thus considerably reducing the cost of a first-principles calculation. However, the effects of such an approximation can be relevant. It is well known, for instance, that the characteristic buckling of the Si dimers on the clean Si(100) surface can only be obtained by using models with a slab geometry and periodic boundary conditions. As shown in the following, the details of the surface reconstruction (i.e., buckling and periodicity of the surface dimers) are crucial ingredients in determining the adsorption structure of benzene. Moreover, the convergence of different properties, such as the binding energies of adsorbed molecules, is rather slow as a function of the cluster size.

In order to overcome these limitations and to clarify the open issues discussed above, we have performed a full *ab initio* study of benzene adsorption on Si(100). Total-energy calculations and molecular-dynamics (MD) simulations have been carried out within the Car-Parrinello approach[10,11] in the framework of the density-functional theory, in the local spin-density approximation. Tests have been also performed using gradient corrections in the BLYP implementation[12]. The calculations have been carried out considering the Γ-point only of the Brillouin zone (BZ), and using norm-conserving pseudopotentials,[13] with s and p nonlocality for C and Si. Wave functions were expanded in plane waves with an energy cutoff of 35 Ry. We have explicitly checked that increasing the energy cutoff or using a better sampling of the BZ does not lead to substantial changes in our results.

The Si(100) surface is modeled with a periodically repeated slab of 5 Si layers and a vacuum region of 7 Å (tests have been also carried out with a vacuum region of 10 Å, without any significant change in the results). A monolayer of hydrogen atoms is used to saturate the dangling bonds on the lower surface of the slab. We have used a supercell with $p(\sqrt{8} \times \sqrt{8})R45°$ surface periodicity, corresponding to 8 Si atoms/layer; however, in order to check finite-size effects,
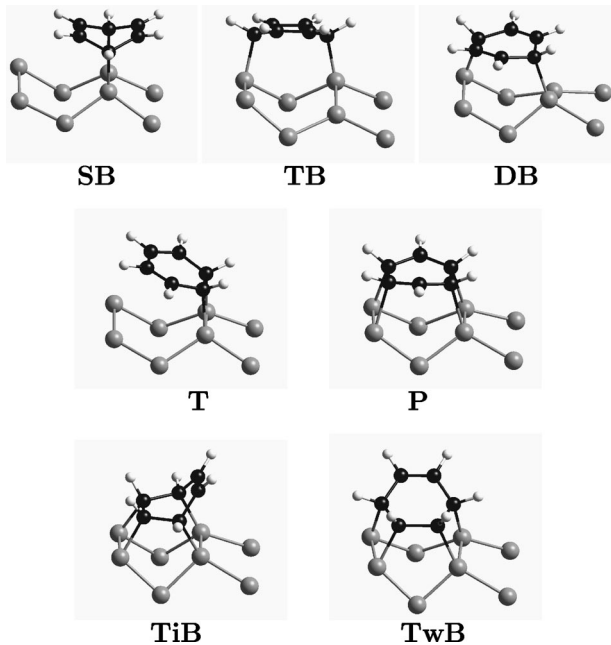
FIG. 1. The stable structures of benzene adsorbed on Si(100): SB=standard butterfly, TB=tilted-bridge butterfly, DB=diagonal-bridge butterfly, T=tilted, P=pedestal, TiB=tight bridge, and TwB =twisted bridge. For clarity only the four Si atoms of two dimers and four belonging to the second layer are shown.

TABLE I. Binding energies (in eV) of different configurations for benzene adsorbed on Si(100) in the (2×1) and $c(4\times2)$ reconstructions (the nomenclature is the same as in Fig. 1). The $p(\sqrt{8} \times \sqrt{8})R45°$ supercell was used; L denotes results obtained with the larger $p(4\times4)$ supercell and BLYP means application of BLYP gradient corrections (Ref. 12). A missing entry indicates that a stable configuration was not obtained by the optimization process.

Configuration	(2×1)	$(2\times1)\ L$	(2×1) BLYP	$c(4\times2)\ L$
SB	2.04	2.06	1.22	2.20
TB	2.10	2.08	1.12	1.99
DB	1.63	1.70	0.41	2.24
T	1.50	1.55	0.77	1.68
P	1.51	1.60		
TiB	2.68	2.77	1.53	2.65
TwB	2.47	2.53	1.31	2.38

the geometry optimizations have been repeated using a larger $p(4\times4)$ supercell with 16 atoms/layer.

Structural relaxations of the ionic coordinates are performed using the method of direct inversion in the iterative subspace.[14] During ionic relaxations and MD simulations, the lowest Si layer and the saturation hydrogens are kept fixed. 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.[15] We have considered different surface periodicities for the dimer reconstruction that may occur on the Si(100) surface, i.e., (2×1), $p(2\times2)$, and $c(4\times2)$. A single benzene molecule is added on top of the slab and the system is then fully relaxed towards the minimum-energy configuration. To better explore the complex potential-energy surface of this system, in most of the cases the optimization procedure was repeated using a simulated-annealing strategy and also starting from different initial configurations.

We find that the lowest-energy configurations are given by two tetra-σ-bonded structures, characterized by the presence of one C-C double bond, which we refer to as ''tight bridge'' (TiB) and ''twisted bridge'' (TwB) (see Fig. 1). TwB is similar to TiB but the benzene molecule is rotated by 90° with respect to the Si surface and is slightly higher in energy (see Table I). This result is in agreement with the findings of Ref. 8 and turns out to be independent of the size of the supercell used in the simulation and on the different reconstructions of the Si(100) surface. It remains true also using BLYP gradient corrections, as can be seen in Table I.

We also find, at somewhat higher energies, three different, *metastable* butterfly structures, characterized by two C-Si bonds, which are shown in Fig. 1. One of them [''stan-

dard butterfly'' (SB)] is the well-known configuration with the benzene molecule adsorbed on top of a single Si dimer. The others [''tilted-bridge butterfly'' (TB) and ''diagonal-bridge butterfly'' (DB)], which bridge two adjacent surface dimers, have not been reported in any previous study.

The Si(100) reconstruction crucially affects the occurrence and energetic ordering of the three butterfly structures. In fact, in the (2×1) reconstruction (with parallel buckled dimers), SB and TB are the most stable (almost isoenergetic) butterfly configurations, while DB is considerably less favored; in contrast, with reconstructions involving alternating buckled Si dimers, such as the $p(2\times2)$ and the $c(4\times2)$, SB and DB are the lowest-energy configurations, while the binding energy of TB is significantly smaller. This clearly happens because the two C-Si bonds of the TB structure are more easily created when the benzene molecule is adsorbed onto Si(100) (2×1), while the formation of the DB structure is favored by the presence of alternating buckled Si dimers.

The other configurations proposed in the literature, namely, the ''tilted'' (T) and the ''pedestal'' (P) ones, lie higher in energy for all the Si(100) reconstructions considered (see Table I). In particular, the P structure is only found to be stable in the (2×1) reconstruction; however, even in this case, an MD simulation performed at 300 K shows that the structure converts very rapidly (in less than 1 ps) into a DB structure. Although the P structure has four C-Si bonds, it is energetically disfavored because it involves the presence of two radical centers.

Inspection of the C-C distances for the various stable structures reveals the existence of two kind of bonds: a long one (''single'') and a short one (''double''), of length 1.49–1.59 and 1.34–1.36 Å, respectively. These values should be compared with the C-C bond length in the isolated benzene molecule, 1.39 Å . One double bond characterizes the TiB and TwB structures, while two double bonds are found in the butterfly structures. In contrast, in the P configuration all the C-C bonds are single ones. These conclusions are confirmed by a more quantitative analysis of the electronic orbitals, which we performed by using both the notion of Mayer bond order[16] and the method of the localized Wannier functions.[17] In the three butterfly configurations (SB, TB, DB), the bond angles (119°–122°) at the C atoms not involved in the Si-C bonds, are close to that (120°) of the isolated benzene mol-

ecule, while those $(103°–113°)$ at the four-fold coordinated C atom are closer to the ideal tetrahedron $(109.5°)$ angle. This clearly indicates sp^2 and sp^3 hybridization, respectively. After benzene chemisorption, although the Si-Si dimers are preserved, the Si dimer buckling angle is almost reduced to zero, with the exception of the TB and DB structures. In the lowest-energy TiB structure the angle between the double bond and the Si(100) surface is $45°$, in good agreement with the experimental estimate,[9] $\sim 43°$.

The structural parameters do not change appreciably when a larger $p(4 \times 4)$ surface supercell is used. Use of BLYP gradient corrections makes bond lengths about 1%–2% longer, while binding energies are significantly reduced (see Table I). Moreover, in the (2×1) reconstruction, the P configuration is no longer stable and, among the three butterfly structures, BLYP favors SB, while the binding energy of DB is even smaller than that of the T structure. Note, however, that TiB and TwB remain the lowest-energy configurations.

According to the results of some experiments and theoretical calculations,[8,9] adsorbed benzene predominantly forms a butterfly (SB) configuration, while the TiB one (and perhaps TwB) appears in detectable amounts on relatively long timescales only, thus indicating the existence of an energy barrier between the two structures.

In order to identify possible metastable states, occurring in the early stages of adsorption, we have tried to find, in the simplest way, the most probable structure of a benzene molecule impinging on the Si(100) surface. If we place the molecule at some distance from the surface we observe that, regardless of the initial position and orientation of the molecule, after full relaxation the final structure is almost invariably one of the three butterfly configurations. This happens because the dimers are tilted, favoring the formation of the di-bonded butterfly structures rather than the tetra-bonded ones. The specific butterfly configuration that is actually formed depends critically on the type of reconstruction of the Si surface that is considered, as already discussed above. On the contrary, there are only very few initial positions that lead to the low-energy TiB and TwB configurations.

We have tried to characterize the energy barrier that must be overcome to relax from the butterfly configurations to the lower-energy TiB and TwB structures. To this aim we started with the benzene molecule in the SB configuration. Let C_d be one of the C atoms involved in the Si-C bonds. Many calculations have been performed in which the ionic coordinates of both the molecule and the substrate were optimized under the constraint that the x,y coordinates of the two C_d atoms are held fixed. A particular pathway, connecting the SB to the DB structure, is shown in Fig. 2, where the reaction coordinate is defined as the distance between the C_d-C_d axis of the initial configuration and that of the displaced structure. The pronounced energy minimum corresponds to the occurrence, during the transformation, of the lowest-energy TiB structure. Note however that this is characterized by a very narrow well. From Fig. 2 a lower bound of ~ 0.5 eV can be inferred for the energy barrier, to be compared with the experimental estimates,[6,8] ~ 0.9–1.0 eV. A similar calculation for the TB$\rightarrow$TwB transition gives a
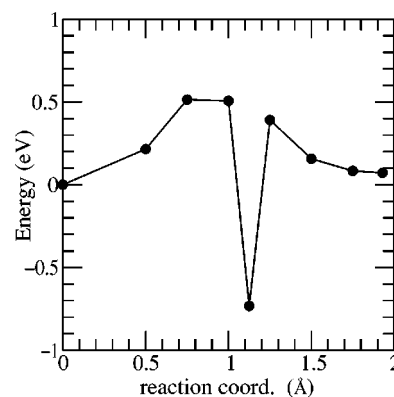

FIG. 2. Total energy along the pathway obtained by shifting the benzene molecule along a dimer row from the SB (at the origin) to the DB configuration, going through the lowest-energy TiB configuration (on the bottom of the narrow well). A $p(\sqrt{8} \times \sqrt{8})R45°$ supercell with a $p(2 \times 2)$ surface reconstruction has been used. Data are represented by symbols, while the line is just a guide for the eye. The energies are relative to the SB structure.

smaller value of ~ 0.4 eV. As a consequence the conversion from TB to TwB is expected to be somewhat faster than that from SB to TiB.

A large fraction of experiments on benzene on Si(100) is based on STM techniques. However, different interpretations of similar STM images led to contradictory conclusions[6–8] about the adsorption sites and geometry of the adsorbed molecules. For each of the structures reported in Table I we have produced ''theoretical'' STM images to be compared with the experimental ones, following the recipe of Ref. 18. Charge density iso-surfaces have been obtained by including electron states in an energy range down to ~ 2 eV below the highest occupied state, which corresponds to typical STM bias voltages. The simulated images are obtained by viewing these iso-surfaces at typical tip-surface distances (a few Å above the benzene molecule).

Our computed STM image for the TiB structure exhibits a density maximum above one of the two Si dimers involved in bonding with benzene, while the TwB configuration produces a similar image but rotated by $90°$. These images resemble those obtained by Lopinski et al.[8] The theoretical STM image for the SB structure is characterized by a bright two-lobe protrusion centered symmetrically above a single Si dimer unit and oriented orthogonal to the dimer axis, in qualitative agreement with the experimental findings.[6–8] Instead, the STM images of the TB and DB structures are quite different from that of SB. In fact the TB image is qualitatively similar to that of TwB (and the experimental STM resolution could be insufficient to distinguish between the two configurations), while DB gives rise to a much fainter feature, bridging in diagonal two Si dimers, which is probably hardly visible in experiments. These observations could explain why the DB and TB structures have not been detected in STM experiments. The T configuration produces an asymmetric (with respect to Si dimers) image, appearing as a bright region (placed between two Si dimers) adjacent to a dark region. Finally the P structure is characterized by two spots corresponding to the dangling bonds of benzene; this result supports the conjecture[7] that rules out the presence of a significant fraction of benzene molecules adsorbed in the P

structure because of the absence of such spots in the STM images.

We have also computed the vibrational spectra for a representative butterfly structure, SB, and for the lowest-energy TiB configuration, by performing Car-Parrinello MD simulations at room temperature. Our results for TiB show a slightly more quantitative agreement with the experimental results[1,9] than those for the SB structure, although the main features of the spectra are similar in the two structures. Let C'' (C') denote a C atom which shares a double (single) bond with another C atom. The C'-H and C''-H frequencies (2880 and 3010 cm^{-1}) are in agreement with the sp^3 and sp^2 stretching modes observed in recent IR spectroscopy experiments[9] (2945 and 3044 cm^{-1}), and semiempirical cluster calculations[8]. Note that the C-H vibrations for the isolated benzene molecule are characterized by a single IR-active frequency of 3063 cm^{-1}. For the C'-C'' and C''-C'' frequencies we find 1230 and 1520 cm^{-1}, respectively, to be compared with the electron-energy-loss spectroscopy experimental values,[1] 1170 and 1625 cm^{-1}. The C-H bending modes are found at 900 and 1100 cm^{-1}, whereas experimentally[1] they are at 910 and 1075 cm^{-1}.

In conclusion, using state-of-the-art *ab initio* simulations, we have shown that a tetra-σ bonded structure is the most stable configuration for benzene adsorbed on Si(100). However, this structure and a very similar one, lying only slightly higher in energy, correspond to very narrow wells in the potential-energy surface for a benzene molecule impinging on the surface. Therefore it is more likely for the molecule to be adsorbed into one of three different, metastable butterfly configurations, and eventually convert into the lowest-energy structures. Our paper provides detailed information about structural, electronic, and vibrational properties of the system, and allows a critical comparison with results obtained from different experimental techniques and previous theoretical calculations.

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