Conversion between two binding states of benzene on Si(001)

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The adsorption and reaction of benzene (C_6H_6) on the Si(001) surface are investigated by first-principles density-functional calculations within the generalized gradient approximation. We find that the "tight-bridge" configuration in which C_6H_6 bonds across two adjacent Si dimers is more stable than the "butterfly" configuration in which C_6H_6 bonds on top of a single Si dimer. Upon C_6H_6 adsorption the latter configuration is initially formed but is converted to the former one with an energy barrier of 0.87 eV. As the coverage increases, such a conversion will be blocked if the butterfly configuration is formed at a single Si dimer site between two tight-bridge benzenes. Therefore we suggest that both the butterfly and tight-bridge configurations could coexist at saturation coverage, providing an explanation for recent high-resolution core-level photoelectron spectroscopy data.

The interaction of unsaturated hydrocarbon molecules with the Si(001) surface is of considerable interest because of the importance of silicon-carbide film formation as well as for possible technological applications ranging from molecular electronics to biosensors.[1,2] As the prototype systems, the adsorption of small organic molecules such as acetylene (C_2H_2),[3–7] ethylene (C_2H_4),[8–12] and benzene (C_6H_6)[13–25] on the Si(001) surface has been intensively studied by many experimental techniques and theoretical calculations. It is well established that the adsorption of C_2H_2 (C_2H_4) containing a C≡C triple (C═C double) bond takes place through the [2+2]-like cycloaddition reaction, where the π bond of the C≡C (C═C) bond interacts with the dangling bonds of the Si dimers, forming two new Si—C σ bonds. On the other hand, C_6H_6 containing a π-conjugated aromatic ring is known to interact with the Si(001) surface through the [4+2]-like cycloaddition reaction, forming the so-called "butterfly" configuration on top of a single Si dimer [see Fig. 1(a)]. However, whether it is a ground state or proceeds to convert to a lower-energy final state is still being debated.[13–25]

Using high-resolution electron-energy-loss spectroscopy, thermal-desorption spectroscopy, and auger electron spectroscopy, Taguchi *et al.*[13] observed two different binding states for C_6H_6 adsorption on Si(001) over a wide range of temperatures (i.e., 90 K and 300 K). They interpreted these two states as due to adsorption on terraces and at defects (or steps). On the other hand, the scanning tunneling microscopy (STM) studies of Wolkow and his co-workers[14–18] found that at low temperatures below 200 K C_6H_6 adsorption on Si(001) exhibits only one binding state which was assigned to the butterfly configuration, while at room temperature an additional binding state (not associated with defects or steps) appears at the surface. Wolkow and his co-workers[14–17] interpreted the latter state in terms of the "tight-bridge" configuration in which C_6H_6 adsorbs across two adjacent dimers in a bridging geometry [see Fig. 1(b)]. Moreover, they observed that upon C_6H_6 adsorption at room temperature the butterfly configuration was initially populated but was gradually converted to the tight-bridge configuration. Such a con-

version from the metastable state to the final state was also observed by the STM experiment of Borovsky *et al.*[19] Although Borovsky *et al.*'s interpretation[26] of the final state differs from that of Wolkow and his co-workers, the two STM studies drew the almost same conclusions: i.e., (i) the activation barrier for the conversion is 0.95 (Ref. 14) or 1 (Ref. 19) eV and (ii) the final state is more stable than the metastable state by 0.04 (Ref. 14) or 0.14 (Ref. 19) eV. Unlike these STM experiments, fully polarization-resolved near-edge x-ray absorption fine structure (NEXAFS) experiment observed only one binding state at room temperature, which was assigned to the butterfly configuration.[20] According to a recent high-resolution core-level photoelectron spectroscopy study of Kim *et al.*,[21] the adsorption structure of C_6H_6 on Si(001) varies depending on the coverage. They concluded that the tight-bridge configuration is favored at low coverage but the population of the butterfly configuration significantly increases as the coverage approaches the saturation value.

There have been many theoretical calculations for the adsorption of C_6H_6 on Si(001) using a variety of calculational methods. The semiempirical[22,23] method predicted an unrealistic structural model, while density-functional theory (DFT)
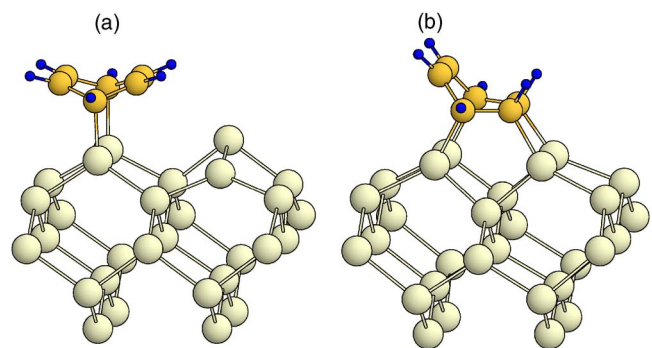

FIG. 1. (Color online) Optimized geometry of adsorbed C_6H_6 on Si(001): (a) the butterfly configuration and (b) the tight-bridge configuration. The large, medium, and small circles represent Si, C, and H atoms, respectively.

calculations[17,24] reported that the tight-bridge configuration is energetically favored over the butterfly one. In contrast, a recent *ab initio* cluster calculation[25] using multireference second-order perturbation theory obtained the reverse result where the butterfly configuration is the most stable among the existing structural models. For the reaction barrier (E_b) from the butterfly to tight-bridge configurations, the DFT calculation of Silvestrelli *et al.*[24] obtained ~0.5 eV, whereas the *ab initio* cluster calculation of Jung and Goldon[25] obtained 1.61 eV. The latter result implies that the conversion from butterfly to tight-bridge is kinetically prohibited at room temperature. These two theoretical results for E_b have not quantitatively or correctly explained the STM observation[14–17,19] where the butterfly configuration is converted to a lower-energy final state with $E_b=0.95$ or 1 eV.

In this paper, we study not only the binding energy of adsorbed C_6H_6 on Si(001), but also the energy profile along the reaction pathway from the butterfly to the tight-bridge configurations. We find that the initially formed butterfly configuration is converted to the more stabilized tight-bridge configuration with $E_b=0.87$ eV. This result agrees well with previous STM experiments[14–16,19] where E_b was estimated as 0.95 and 1 eV. As the coverage increases, a single Si dimer site between two tight-bridge benzene molecules may exist, effectively blocking the conversion from the butterfly to the tight-bridge configurations. Consequently, the two adsorption configurations could exist at saturation coverage, consistent with recent high-resolution core-level photoelectron spectroscopy experiment.[21]

The total-energy and force calculations were performed using DFT[27] within the generalized-gradient approximation (GGA).[28] The C (Si and H) atoms are described by ultrasoft[29] (norm-conserving[30]) pseudopotentials. The surface is modeled by a periodic slab geometry. Each slab contains five Si atomic layers plus adsorbed molecules and the bottom Si layer is passivated by two H atoms per Si atom.[31] The thickness of the vacuum region between these slabs is about 10 Å. A plane-wave basis set was used with 25 Ry cutoff, and the **k** space integration was done with meshes of four and two **k** points in the 2×2 and 4×2 surface Brillouin zones, respectively. All the atoms except the bottom Si layer were allowed to relax along the calculated Hellmann-Feynman forces until all the residual force components were less than 1 mRy/bohr.

We first determined the atomic structure of adsorbed benzene on Si(001) within the butterfly and tight-bridge configurations. Here, we used a 2×4 unit cell which involves four dimers along the dimer row. Each optimized structure is shown in Figs. 1(a) and 1(b), respectively. The calculated adsorption energies of the two configurations are given in Table I, together with previous DFT and cluster data.[15,17,24,25] We find that the tight-bridge configuration which has an adsorption energy (E_{ads}) of 0.91 eV is more stable than the butterfly configuration by $\Delta E_{ads}=0.07$ eV, in good agreement with the STM data[14] where ΔE_{ads} was estimated as 0.04 eV. Our result of the greater stability of the tight-bridge configuration is consistent with previous DFT[17,24] and cluster[15] calculations (see Table I). In contrast, a recent cluster calculation carried out by Jung and Gordon[25] obtained the reverse result with $\Delta E_{ads}=-0.10$ eV, favoring the butterfly configu-

TABLE I. Calculated adsorption energies of C_6H_6 on Si(001), in comparison with previous DFT and cluster calculations. Abbreviations in the parentheses represent the used GGA exchange and correlation functionals: BLYP (Ref. 32), PW91 (Ref. 33), and PBE (Ref. 28).

	Coverage	Butterfly	Tight-bridge
Cluster[a]		1.02	1.64
Cluster[b]		1.26	1.16
DFT (BLYP)[c]	0.5 ML	1.22	1.53
DFT (PW91)[d]	0.5 ML	1.12	1.47
Presnt DFT (PBE)	0.25 ML	0.84	0.91
	0.5 ML	0.82	1.05

[a]Reference 15.
[b]Reference 25.
[c]Reference 24.
[d]Reference 17.

ration over the tight-bridge configuration. This cluster result supports the NEXAFS experiment[20] where the adsorption structure of C_6H_6 on Si(001) was assigned to the butterfly configuration, but contradicts with the STM results[14–17,19] which showed the conversion from the metastable (i.e., butterfly) to the final states.

From previous theoretical[17,24] and experimental[14,15,18] studies, benzene is known to initially interact with a single Si dimer through the [4+2]-like cycloaddition reaction, forming the butterfly configuration. To examine the conversion from such an initially formed butterfly configuration to the tight-bridge configuration, we calculate the energy profile for the reaction pathway. We optimize the structure by using the gradient projection method[34,35] where the two distances (i.e., d_1 and d_2 in Fig. 2) between the C_2 and C_3 atoms and their bonded (in the tight-bridge configuration) Si atoms are con-
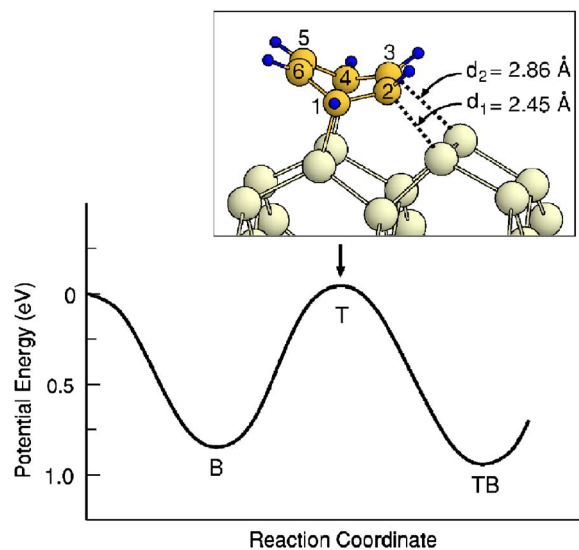

FIG. 2. (Color online) Calculated energy profile for the conversion from the butterfly (*B*) to the tight-bridge (*TB*) configurations. Atomic geometry of the transition (*T*) state is given. The numbers denote the the six different C atoms.
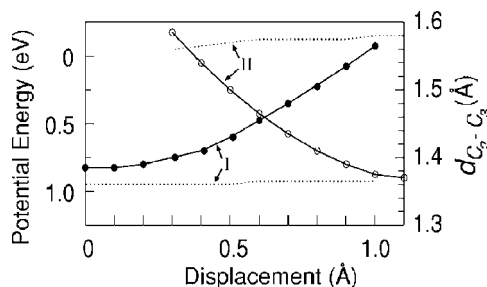
FIG. 3. Calculated energy profile and $d_{C_2-C_3}$ along the constrained reaction pathway I and II (see text). The solid (open) circles represent the energies of the S_1 (S_2) state. The dotted lines represent the bond length $d_{C_2-C_3}$, corresponding to the S_1 and S_2 states.

strained. Hellmann-Feynman forces aid in the relaxation of all the atomic positions for each of several values of d_1 and d_2. The calculated energy profile together with the atomic geometry of the transition state is displayed in Fig. 2. For this transition state we obtain $E_{ads}=-0.03$ eV which is 0.87 eV smaller than that ($E_{ads}=0.84$ eV) of the butterfly configuration, yielding $E_b=0.87$ eV from the butterfly to the tight-bridge configurations. Thus, our results for E_b as well as the energy difference ($\Delta E_{ads}=0.07$ eV) between the butterfly and tight-bridge configurations agree well with the STM data ($E_b=0.95$ eV and $\Delta E_{ads}=0.04$ eV) obtained by Wolkow and his co-workers.[14] We note that the previous DFT[24] (cluster[25]) result of $E_b=0.50(1.61)$ eV is seriously underestimated (overestimated) compared with previous STM and our DFT results. In their DFT calculation, Silvestrelli *et al.*[24] used a rather unrealistic reaction coordinate during the butterfly to tight-bridge conversion, where the C_1 and C_4 atoms (see Fig. 2) are constrained to have an identical position along the dimer row. With the same constraint, we optimized the structure at several discrete configurations along the reaction pathway I (II), in which the C_1 and C_4 atoms are displaced from the butterfly (tight-bridge) to the tight-bridge (butterfly) configurations in discrete steps along the dimer row. We find the presence of two states S_1 and S_2 along the reaction pathway I and II, respectively (see Fig. 3). These two states are characterized by the bond length ($d_{C_2-C_3}$) between the C_2 and C_3 atoms. As shown in Fig. 3, the S_1 state has a shorter $d_{C_2-C_3} \approx 1.36$ Å compared with that ($d_{C_2-C_3} \approx 1.58$ Å) of the S_2 state, indicating that the S_1 (S_2) state has double (single) bond character. We note that in S_1 the neighboring Si dimer is buckled (i.e., unreacted with C_2 and C_3), whereas in S_2 it becomes symmetric by formation of the C_2—Si and C_3—Si σ bonds. In Fig, 3 the energy curves of the S_1 and S_2 states are crossed to each other at point 0.38 eV above the adsorption energy of the butterfly configuration. This crossing energy is close to $E_b=0.50$ eV obtained by the previous DFT calculation of Silvestrelli *et al.*[24] However, the transition between the S_1 and S_2 states is symmetry forbidden because their orbital symmetry characteristics differ from each other.[36]

It is interesting to note that the geometry of our transition state differs from that in the previous cluster calculation of Jung and Gordon.[25] As shown in Fig. 2, our transition
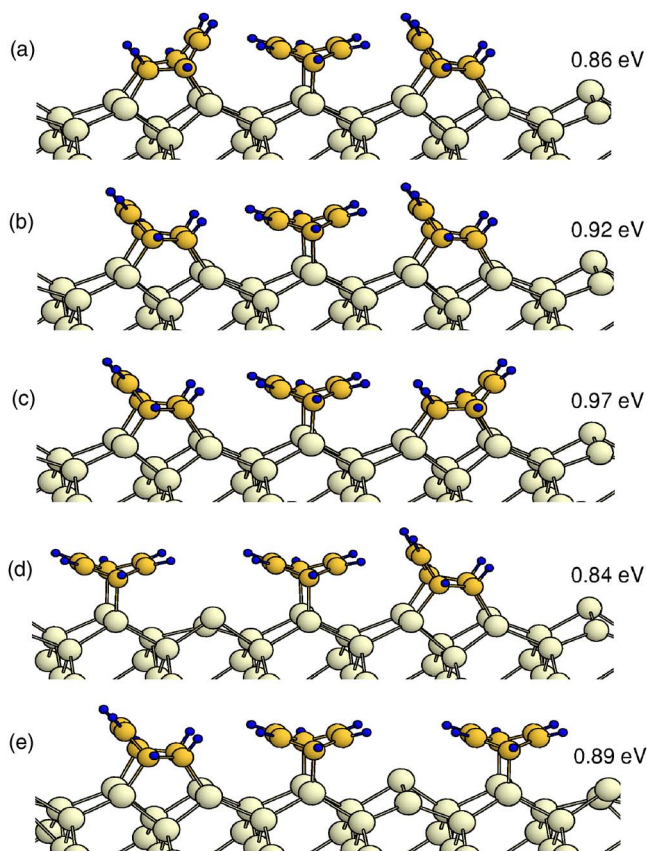

FIG. 4. (Color online) Atomic geometry of several mixed structures containing the butterfly and tight-bridge configurations. The numbers denote the adsorption energy of each structure.

state has a shorter $d_1=2.45$ Å between the C_2 atom and the down atom of the neighboring Si dimer compared with $d_2=2.86$ Å between the C_3 atom and the up atom. On the other hand, Jung and Gordon's cluster calculation obtained the reverse result ($d_1=3.11$ Å and $d_2=2.43$ Å). Considering the fact that the buckled Si dimer accompanies a charge transfer from the down atom to the up atom,[37] the π bonding state of the C_2 and C_3 atoms is possibly attracted to the empty dangling-bond state of the down atom of the neighboring Si dimer. In this sense, our transition state showing a shorter d_1 compared with d_2 is more reasonable than the transition state obtained by Jung and Gordon. It is likely that Jung and Gordon's transition state would be on a higher-energy pathway compared with the present reaction pathway, thereby resulting in the overestimation of $E_b=1.61$ eV.

According to the recent high-resolution core-level photoelectron spectroscopy data of Kim *et al.*,[21] the intensity ratio of two resolved C 1s peaks (represented by C_π/C_σ) increases from 0.5 at extremely low coverage to 2 at nearly saturation coverage. Here, the peak C_σ is caused by C atoms bonding to the Si dimer, whereas C_π is due to other C atoms involving a π bond. Noting in the butterfly (tight-bridge) configuration that the number of the former C atoms is half (double) that of the latter ones, the observed intensity ratio of C_π/C_σ led Kim *et al.*[21] to conclude that at low coverage benzene occupies the tight-bridge configuration but, as the coverage approaches the saturation value, the occupied tight-bridge con-

figuration is transformed into the butterfly configuration. As Kim *et al.* suggested, this transformation may take place because of the repulsive intermolecular interaction between adsorbed tight-bridge benzenes. In order to examine this possibility at saturation coverage, we calculate the adsorption energies of the butterfly and tight-bridge configurations for the coverage of $\theta=0.5$ ML, where one C_6H_6 molecule is adsorbed within the 2×2 unit cell. Our calculations show that at $\theta=0.5$ ML the tight-bridge configuration ($E_{ads}=1.05$ eV) is still more favored over the butterfly configuration ($E_{ads}=0.82$ eV). Interestingly, the energy difference between the butterfly and tight-bridge configurations becomes greater at $\theta=0.5$ ML compared with that at $\theta=0.25$ ML (see Table I). Thus, our calculated energetics of the butterfly and tight-bridge configurations cannot account for the transformation from the tight-bridge to the butterfly configurations with increasing coverage. However, we have to speculate that, as the coverage increases, a single Si dimer between two neighboring tight-bridge benzene molecules may remain unreacted. The presence of such an empty Si dimer site allows the formation of the butterfly configuration. Our calculations for several mixed structures containing both the butterfly and tight-bridge configurations (see Fig. 4) show that all of them are thermodynamically more stable than the butterfly configuration with $\theta=0.5$ ML. If we assume that every tight-bridge benzene is separated by a single Si dimer, the butterfly (tight-bridge) population will be 50 (50)% at saturation coverage, which can be its upper (lower) bound. From the STM measurements of Lopinski *et al.*[14] and Naumkin *et al.*[38] at submonolayer coverage, the butterfly (tight-bridge) population was estimated as ~15 (85)%. This STM data and our speculation for formation of the butterfly configuration may be consistent with the core-level photoelectron spectroscopy data of Kim *et al.*,[21] where the butterfly population significantly increases with increasing coverage, but do not support their conclusion that at saturation coverage most of adsorbed C_6H_6 molecules occupy the butterfly configuration.

In summary, our first-principles density-functional calculations for the energetics and energy barrier for the reaction of benzene on Si(001) showed that the butterfly configuration is converted to the tight-bridge configuration with an energy barrier of 0.87 eV, in good agreement with the STM experiments.[14–17,19] Unlike a recent cluster calculation,[25] our DFT calculation favors the tight-bridge configuration over the butterfly configuration. We suggested that the population of the butterfly configuration possibly increases with increasing coverage, partly consistent with recent high-resolution core-level photoelectron spectroscopy data.[21]

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