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Reaction of chlorinated benzenes with Si(1 0 0)2×1: a theoretical study

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Abstract

Theoretical (HF + DFT) investigations of the adsorption of chlorobenzene (ClPh), 1,2- and 1,4-dichlorobenzene (1,2-diClPh and 1,4-diClPh) on a silicon (1 0 0) surface are reported for the first time, and are compared with one another and with benzene. Binding energies for various structures with the molecules attached on-top and in-between the surface dimer rows are correlated with the STM experimental data. Novel structures with the molecules linking two dimer rows, stabilised by detachment of Cl (or H)-atoms forming Cl–Si (or H–Si) bonds, are described. For 1,4 and 1,2 binding, these linking structures are predicted to attach the phenyl ring parallel or perpendicular to the Si surface, respectively, while preserving its aromaticity. The potential-energy barriers between several different structures are evaluated, and compared with available experimental evidence. For 1,4-diClPh it is shown that the potential-energy barrier for the second Cl transfer is significantly lower than for the first one in contrast to the gas-phase, and comparable to the barrier for lifting the Bz-ring into a vertical position and forming a singly bonded 'displaced' structure. The predicted barrier-heights are consistent with the experimentally observed relative occurrence of the on-top, linking, and displaced structures.

Keywords: Density functional calculations; Chemisorption; Surface chemical reaction; Silicon; Aromatics

1. Introduction

The highly ordered Si(1 0 0) surface composed of parallel rows of Si dimers with their chemically active dangling bonds, offers a natural base for arranging molecules. This regular structure should permit one to produce chains of molecules adsorbed on-top of the dimer rows. This could be of value in constructing molecular 'wires'. However, it would be advantageous also to be able to connect these chains, in order to create two-dimensional structures with extensions perpendicular to the dimer rows.

Previous experimental and theoretical studies of small molecules adsorbed on Si(1 0 0) have included, in particular, acetylene, ethylene, propylene, and benzene ([1–3] and references therein). The STM images showed adsorption on-top of the dimer rows. This accords with the small size of the

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molecules relative to the gap between the rows. Adsorption between (as well as on-top of) the rows has, however, been observed for larger molecules, e.g. pentacene, $C_{22}H_{14}$ [4,5]. This is the structural equivalent of a linear chain of five benzene rings fused together. (Hereafter we use Bz for benzene.) Such systems composed of connected Bz-rings offer convenient structural properties for developing extended networks. An understanding of how such big systems attach to the surface is facilitated by studies of their smaller counterparts.

An important building block is Bz. Such molecules attach to the dimers by opening one or more of their multiple bonds. Usually this takes place without breaking the carbon–hydrogen bonds. The aromaticity of the Bz-ring is then partially destroyed, and its associated electrical conductivity is diminished.

Replacement of one or two carbon atoms in the Bz-ring by nitrogens as in pyridine (C_5H_5N) and pyrazine ($C_4H_4N_2$) has been found [6] to lead to a different form of attachment via a single N–Si bond, with the ring perpendicular to the surface. Another way to bind a fully aromatic ring to a Si(1 0 0) surface is to use a Bz-ring with acetylene attached. The acetylene group binds to a dimer pair leaving the Bz perpendicular to the surface [7].

The Bz halo-derivatives are thought to offer new possibilities for attachment to the surface, since the carbon–halogen bonds are weaker than the C–H bonds and can provide additional channels for molecule-surface reaction. Recent STM experiments [8] (previous paper) have demonstrated that chlorobenzene (hereafter ClPh), 1,2- and 1,4-dichlorobenzene (1,2- and 1,4-diClPh) can attach in a novel fashion between the dimer rows. The efficiency with which this occurs is dependent on the parent molecule, being highest for 1,4-diClPh. The purpose of the present theoretical study is to interpret these results in terms of ab initio calculations.

The paper begins by considering the effect of dichlorination on the binding of the aromatic ring in the 'on-top' configurations, proceeds to a novel weakly bound cyclohexadiene 'linking' configuration between rows and then to a strongly bound fully aromatic 'linking' configuration with chlorines transferred to the surface.

2. Calculational procedure

The aim of this work has been to investigate many geometric configurations for large systems with dozens of Si-atoms, with a primary interest in energetics and structures. This necessitates a modest level of ab initio theory. Our approach combines Hartree–Fock method (RHF for singlets, UHF for higher multiplicities) with the 3-21G basis set for geometry optimisation and the DFT(B3LYP/6-31G) single-point evaluation of energies. Similar tactics was followed in earlier work [2,9]. Selected results have been verified by geometry reoptimisation at a higher level of theory (B3LYP/6-31G*). Some AM1 data are also presented for comparison. Calculations have been done using the Gaussian-98 package [10].

The surface has been represented, as is customary, by a finite cluster-fragment with its bonds to the bulk Si terminated with H-atoms. We have avoided using the standard cluster models developed for bare Si surface and unrestricted optimisation, since this could lead to unrealistic distortions when a molecule is adsorbed. The model adopted has been to use an average cluster with a few layers of Si-atoms, with the lowest layer of atoms fixed at their positions in the real crystal.

Atomic positions of the Si-dimers and of the next layer to which they are directly bonded have been fully optimised, while the third layer atoms to which the second layer atoms are directly bound have been frozen. Freezing of the bottom layer could result in deviations from true adsorption energies, opposite in sign to those for the free-cluster case. The clusters used consisted of 12, 19, and 26 Si-atoms for one, two and three dimers in the same row, respectively, and 22 atoms for two dimers in adjacent rows. Geometries of the adsorbed molecules have been fully optimised in all cases.

The predicted Si–Si separation for the one-dimer 12-atom cluster model is 2.24 and 2.25 Å at the HF/3-21G and B3LYP/6-31G* levels of theory, respectively. This compares favourably with the other computations, namely fully optimised results of 2.24 and 2.28 Å at the two-configuration-HF and GVB levels [11] for the standard 9-atom cluster model (the GVB value is

unchanged for a 66-atom cluster), and 2.23–2.26 Å at the LDA level for slab models [12–14]. Our result also falls within the experimental interval [15] of 2.26 ± 0.1 Å. The AM1 result is 2.19 or 2.09 Å for the present 12-atom or fully optimised standard 9-atom cluster models, respectively.

Transition states were evaluated by taking several intermediate values for the selected reaction coordinate. For these points all other variables (positions of ad- and second-layer atoms) were optimised. The DFT energies were then calculated for these intermediate geometries, and a cubic-spline interpolation was used to evaluate the energy and geometry at the top of the potential barrier.

3. Results and discussion

3.1. Adsorption on-top of dimer rows

In this section we address the question of modification in the geometry and binding of chlorobenzene to Si(1 0 0) on-top of the dimer rows, as compared with the case of Bz. The example given is 1,4-diClPh. For consistency, the comparison is made with the Bz structures optimised using the same cluster models and ab initio theory.

As in the case of Bz [2,9,16] we obtain doubly and quadruply sigma-bound structures. They have geometries very similar to those formed by Bz. The number of possible doubly bound structures is greater for the present example, since the two Cl substituents can be attached at the C bound to the underlying Si, or away from it. This duality is illustrated in Fig. 1(a), 'butterfly' (1,4-BF), and Fig. 1(b), 'rotated butterfly' (2,5-BF) structures. We have not illustrated it for the isomer of the 2,3-bonded structure (Fig. 1(c)), which would have 1,2 binding to the surface. The quadruply bound structures are shown in Fig. 1(d) and (e); twisted, TwB, and tight bridge, TB, respectively. These also have 'rotated' forms (not shown) with the pair of Cl-atoms adjacent to the positions given in Fig. 1(d) and (e).

The effect of Cl substitution on the atom–atom distances and binding to the surface has been examined for the cases of 1,4-BF, 2,3-bonded, TwB and TB (Fig. 1(a)–(e)) and found to be small. This can be associated with the fact that the Cl-atoms are generally at a distance from the surface (in the structures studied) and therefore have relatively little effect. For 1,4-diClPh the Si–Si distances in the dimers increase, and the Si–C bonds shorten, by $\leqslant 0.01$ Å, while the distances between the Cl-carrying C-atom and its neighbours in the Bz-ring change by −0.02 to +0.01 Å. Other distances are perturbed even less. The binding energy is slightly larger for 1,4-diClPh (by <0.1 eV for 1,4-BF and by ≈0.2 eV for 2,3-bonded, TwB and TB). This slight increase in binding can be understood in terms of a larger charge pulled from the surface by 1,4-diClPh due to the electronegativity of chlorines, as confirmed by calculations. Consistent with this explanation, the effect of rotating the pair of Cl substituents by one C-atom is in general found to be negligible, $\leqslant 0.1$ eV.

The single case in which a significant contribution to the binding by the Cl-atoms has been found is the 'rotated butterfly' (2,5-BF) structure. In this configuration the binding of 1,4-diClPh to the surface is 0.5 eV greater than it is for the non-rotated, 1,4-BF and is the strongest found for the on-top structures (Table 2). This can be rationalised in terms of the proximity, in this case, of the two Cl-atoms to the underlying Si-atoms.

The binding energies for the above on-top structures of 1,4-diClPh range from 0.6 eV for 2,3-bonded to 1.5 eV for 2,5-BF (Table 2). The Hartree–Fock and AM1 calculations gave values which are close to one another and about two to four times larger than the DFT values. This reflects the effect of electron-correlation, which is apparently strong for the systems under study. The AM1 calculations produced two other isomers, with the molecule parallel and perpendicular to the surface, with the Cl-atoms above the centres of the Si-dimers. Both have turned out to be unstable configurations at the Hartree–Fock level. For Bz previous workers have also found additional isomers and different binding energies for AM1 as compared to DFT [9].

In our AM1 calculations, larger Si clusters with an additional dimer on each side of those bonded to the molecule and with two additional layers of

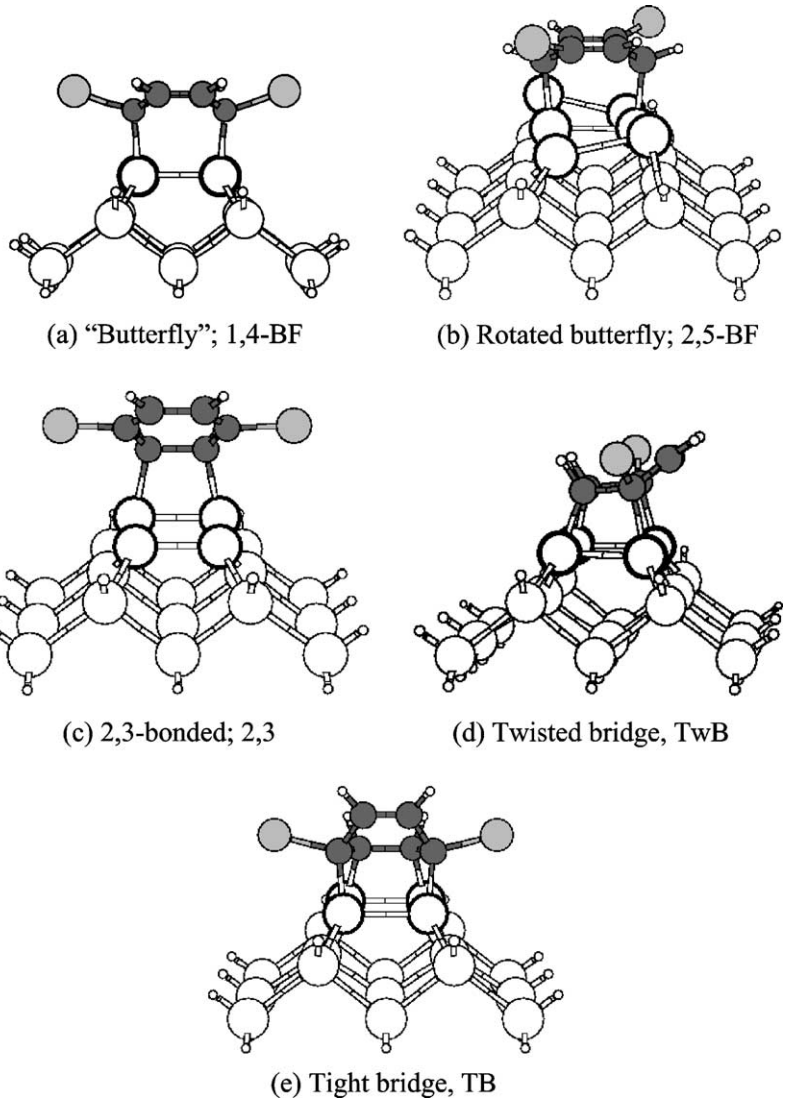

Fig. 1. Optimised structures of 1,4-diClPh/Si(1 0 0): attachment on-top of a dimer row. (a) 'Butterfly', 1,4-BF; (b) rotated 'butterfly', 2,5-BF; (c) 2,3-bonded, 2,3; (d) 'twisted bridge', TwB; and (e) 'tight bridge', TB. The surface dimers are highlighted.

atoms have also been used in all cases, and the corresponding structures fully optimised. The binding energies obtained decreased by only $\leqslant 0.15$ eV or $\leqslant 10\%$.

The TB structure with its four sigma-bonds is effectively a combination of the 1,4-BF and 2,3-bonded structures. The rather small increase in binding for the quadruply bound system relative to the doubly bound is due to increased strain in the former case. The increase in strain can be estimated as $1.0 + 0.6 - 1.2 = 0.4$ eV, i.e., the sum of the binding energies for the structures 1,4-BF and 2,3-bonded, minus that for TB.

The 1,4-BF and TB structures resemble one another, with 1,4-diClPh effectively turned around the dimer-axis from horizontal (for 1,4-BF) to the tilted (for TB) position. The barrier for such a transformation has been evaluated as function of

the turning angle (reaction coordinate). The barrier-height is predicted by DFT to be ≈1.7 eV from the 1,4-BF side (Fig. 2). This value can be compared with ≈1 eV barrier for a similar transformation of Bz, deduced from time sequences of images [2]. In a recent work 4 V pulses gave rise to the same transformation [8]. The transition state is found, by DFT, to occur when 1,4-diClPh tilts from the 1,4-BF structure by about 10° (Fig. 2).

3.2. Adsorption between dimer rows

3.2.1. Attachment between two dimers in adjacent rows

In this section a novel structure linking dimer rows is described. The distance of about 5.5 Å between the nearest Si-atoms in the adjacent dimer rows is more than twice as large as in the Si dimer on Si(1 0 0). However, the dimers can stretch when a molecule is attached to their atoms, due to breaking the Si–Si π-bond. Additionally, the Si dangling bonds are directed into the gap between the rows. Both factors could facilitate attachment between the dimers in the adjacent rows, even for such a small molecule as Bz.

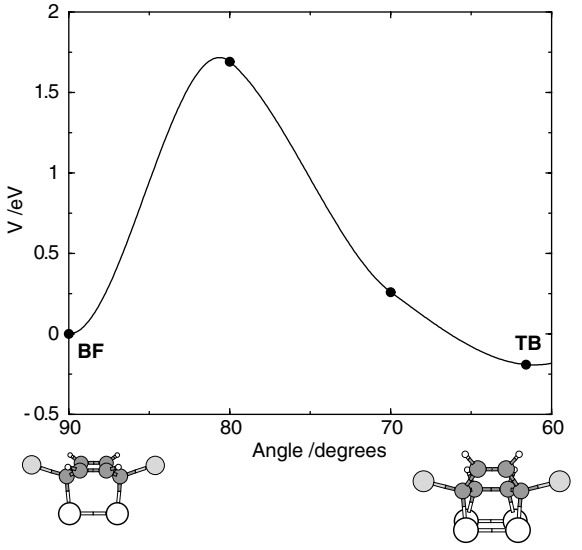

Fig. 2. Potential-energy barrier between the 1,4-BF and TB structures for 1,4-diClPh: turning the molecule around the dimer axis.

Such between-rows structures predicted for ClPh, 1,2- and 1,4-diClPh are shown in Fig. 3; their geometric parameters are given in Table 1. For the 1,4-diClPh case, this is a direct analogue of the 1,4-BF structure with one double-bond opened. The resulting cyclohexadiene structure linking the dimer rows is symbolised diene L. The distance between the C-bonded Si-atoms becomes 0.36 Å shorter on attachment of the molecule. The Bz-ring with the sp^3-hybridised 1,4-carbons fits the orientation of the Si dangling sp^3-bonds. As a result the Bz-ring lies flat, parallel to the surface.

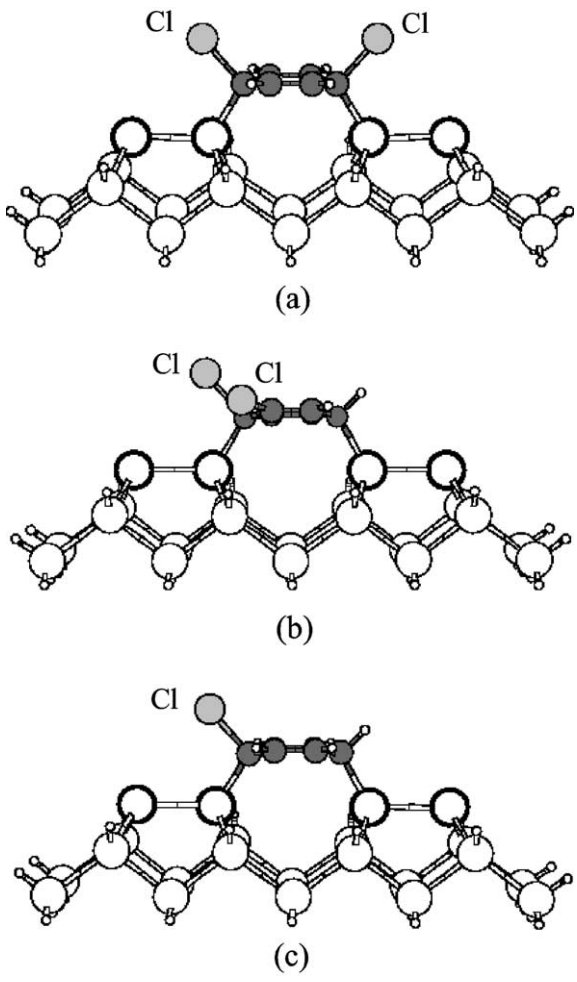

Fig. 3. Optimised structures of chlorobenzenes on Si(1 0 0): attachment between two dimers in the adjacent rows. (a) 1,4-diClPh, (b) 1,2-diClPh, and (c) ClPh.

Table 1
Equilibrium bondlengths (in Å) of ClPh, 1,2- and 1,4-diClPh/Si(1 0 0)

	Structure	r (Si–Si)	r (Si–C_{Si})	r (C_{Si}–C_{Si})	r (C_{Si}–C)	r (C–C)
1,4-diClPh	1,4-BF	2.48	1.95	–	1.51	1.32
	2,3-bonded	2.41	1.99	1.60	1.48	1.31, 1.47
	TwB	2.40	1.97, 2.03	1.58, 1.61	1.48	1.32
	TB	2.43, 2.40	1.98, 2.01	1.58, 1.61	1.50	1.32
	diene-L	2.55	1.98	–	1.50	1.32
	diene-L•	2.53, 2.56	2.00, 1.91	–	1.49, 1.43	1.37
	L	2.51	1.92	–	1.39	1.38
	D	2.53	1.91	–	1.39	1.37, 1.38
ClPh	diene-L	2.55, 2.56	1.97, 1.98	–	1.50	1.32
	diene-L•	2.57, 2.55	1.91, 2.01	–	1.43, 1.50	1.37
	L	2.51	1.92	–	1.39	1.38
	D	2.54	1.90	–	1.39	1.38
1,2-diClPh	diene-L	2.55, 2.56	1.98, 1.99	–	1.49, 1.50	1.31, 1.32
	diene-L•	2.57, 2.55	1.92, 2.01	–	1.43, 1.50	1.36, 1.37
	L′	2.78	1.99	1.45	1.40	1.39, 1.37
	D	2.54	1.92	–	1.38, 1.40	1.38
	D•	2.53	1.90	–	1.41, 1.39	1.40, 1.39
	D″	2.50	1.95	1.43	1.39	1.39, 1.38

The distances are given for bonded pairs of atoms.
C_{Si} is the C-atom bonded to the Si-atom.
For pairs of numbers, the first number refers to the bond involving the Cl-carrying C, or to the Si-atom bonded to such a C-atom.

The Cl-atoms protrude upwards at a larger angle than for 1,4-BF, at 50° versus 20° to the surface. The reduced strain leads to a binding energy higher by 0.5 eV relative to the 1,4-BF structure (Table 2), i.e. the same value as for 2,5-BF. For 1,2-diClPh and ClPh, the binding energy is the same, to within 0.04 eV, and geometries remain almost the same, indicating only a weak influence from the Cl-atoms. The AM1 and HF binding energies are more than twice as large as those from DFT. For the geometry of the diene-L structure reoptimised at the more accurate, B3LYP/6-31G* level, the DFT binding energy is reduced by 20%, to 1.2 eV.

Table 2
Binding energies (in eV) of 1,4-diClPh/Si(1 0 0)

Structure	AM1	HF/3-21G	DFT (B3LYP/6-31G)
1,4-BF	1.8	2.4	1.0
2,5-BF	2.9	3.3	1.5
2,3-bonded	2.3	1.5	0.6
1,2-bonded	2.2	1.8	0.6
TwB	3.3	3.1	1.1
2,5-TwB	3.6	2.8	1.1
TB	2.9	3.4	1.2
2,5-TB		3.1	1.2
diene-L	3.2	3.6	1.5
2,5-diene-L		3.4	1.4
diene-L•			2.8
L	6.6	6.4	5.1
D			3.6

All the above results are given for a triplet electronic state of the diene-L linking structure, consistent with two dangling bonds at its ends, which do not overlap. The corresponding singlet state is strained and hence less stable, with a minimal binding energy of about 0.2 eV (at the B3LYP/6-31G* level).

It should be noted that AM1 calculations predict, in addition, a spurious bound structure with the molecule attached to the two dimers in the adjacent rows via its Cl-atoms acting in a di- or trivalent fashion. The chlorines are slightly shifted from the positions above the centres of the dimers, both C–Cl bonds being bent down from the Bz-ring, with the ring located between the rows. The AM1 binding energy is 1.2 eV. No such structure exists at the HF level of theory, however.

The potential-energy barrier for formation of the diene-L structure from 1,4-BF has been eval-

uated for a simple reaction path along the dimer axis (reaction coordinate). This barrier, separating the singlet (1,4-BF) and triplet states, is evaluated in terms of minimal energies for both multiplicities at every point. The shift of 1,4-diClPh in this direction, pictured in (Fig. 4) is found to preserve the molecule intact. The barrier to diene-L formation is found to be 3.7 eV, starting from 1,4-BF (Fig. 4). This value is consistent with the fact that the 5 V pulses are observed [8] to shift the adsorbed molecules from the on-top to between-rows (BF $\rightarrow$ diene L) position. In the transition state, the dimers are tilted (buckled) towards one another and the dimer initially bonded to the molecule is pulled towards the other dimer. The C–Si bonds are 2.1 Å long in the transition state, and the molecule is tilted while keeping its 'butterfly' shape.

For the corresponding 'rotated' (2,5-diene-L) structure, the molecules are bonded to the Si-atoms via the 2,5 carbons, with the C–Cl bonds almost parallel to the surface. The associated binding energy for 1,4-diClPh is found by DFT to be only 0.1 eV smaller than the unrotated diene-L (Table 2).

3.2.2. Stabilisation of the between-rows structure by detachment of Cl-atoms

3.2.2.1. 1,4-diClPh. For the diene-L structure of 1,4-diClPh, the Cl-atoms point in the directions of the outer Si-atoms of the dimers to which the molecule is bound. It appears probable that the chlorines can be transferred to the silicons in a molecule-surface reaction. The corresponding structures are shown in Fig. 5 and are described in Table 1. When a Cl-atom leaves the Bz-ring and forms a bond with the nearest Si-atom, the ring tilts in the direction in which the Cl-atom moved (Fig. 5(b)). The tilt is due to the increased sp^2 character of the carbon atom. The associated C–Si distance shortens by $\approx$0.1 Å and bond-angles are close to 120°, characteristic of the sp^2 hybridisation. The separations between the C bonded to the surface and its nearest and next-nearest neighbours in the Bz-ring become 1.4 ± 0.03 Å, indicating a partial restoration of the aromaticity in

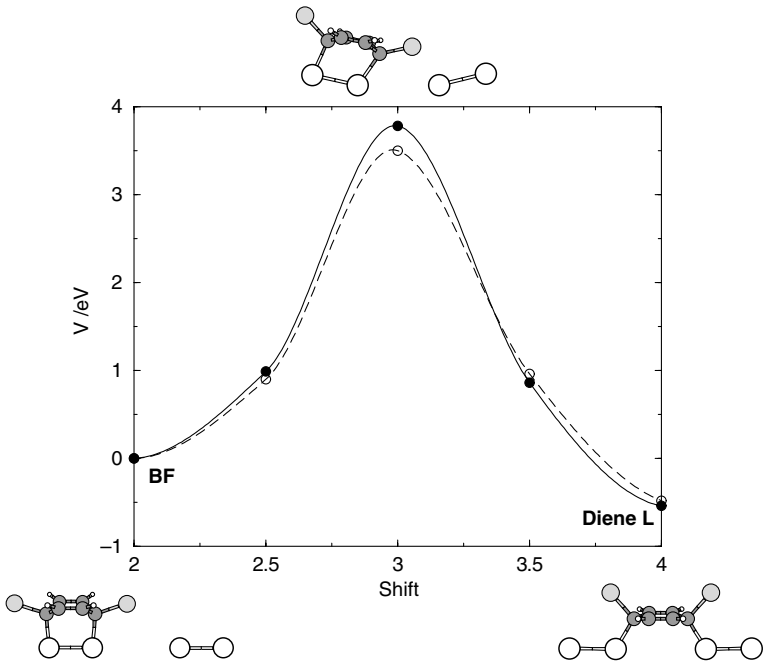

Fig. 4. Potential-energy barrier between the 1,4-BF and diene-L structures: transition of 1,4-diClPh (—) and Bz (- - -) from on-top to between-rows position.

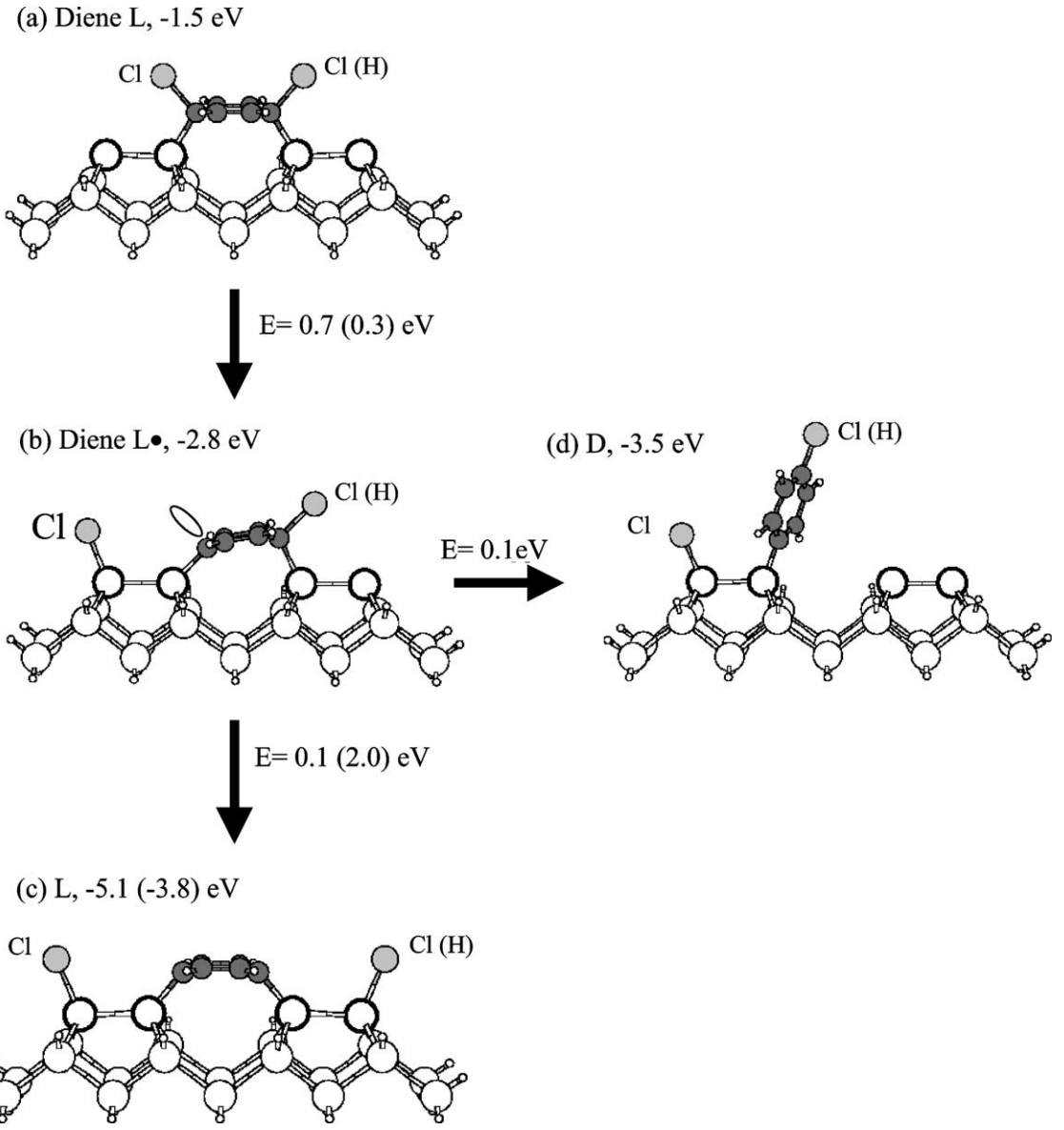

Fig. 5. Optimised structures of 1,4-diClPh/Si(1 0 0): detachment of Cl-atoms. (a) The initial diene-L structure, (b) the diene-L• structure with one Cl transferred, (c) the L-structure with both Cl transferred, and (d) the D-structure with the Bz-ring lifted. The numbers in brackets refer to the case of ClPh.

the previously hexadiene ring. As a result of the increased aromaticity the energy of the system decreases by 1.3 eV for this diene-L• free-radical structure. The adsorption energy, i.e. the energy of the system relative to the surface plus intact molecule at infinite separation, becomes $E_{ad} = 2.8$ eV.

Similar transfer of the other Cl-atom to the opposite silicon produces a symmetric row-linking structure (L) with the Bz-ring parallel to the surface (Fig. 5(c)). The bond-angle between the C bonded to the surface and its neighbours is close to 120°, indicating sp^2 hybridisation of the ring

atoms. All C–C distances are almost equal (1.4 ± 0.01 Å), indicating almost fully restored aromaticity of the Bz-ring. Accordingly, the system is stabilised further by 2.3 eV and reaches the substantial value of $E_{ad} = 5.1$ eV. The AM1 and HF methods give values which are larger by about 1.5 eV (or 25–30%). For the L-structure geometry reoptimised at the B3LYP/6-31G* level, the E_{ad} value becomes 5.4 eV.

These highly stable L-structures are thought to be the molecules found in the experiments to adsorb symmetrically between adjacent dimer rows [8]. The energy barriers for transfer of the Cl-atoms have been evaluated. Sequential C–Cl rupture was compared with simultaneous transfer of both Cl-atoms (Fig. 6(a)). As would be expected, the breaking of two C–Cl bonds simultaneously required a greater energy, viz., 1.5 eV, and was therefore less likely. However, this is significantly smaller than 3.2 eV required to remove the Cl-atoms from the adsorbed 1,4-diClPh to the gas-phase, and smaller than 7.2 eV for the removal of two Cl in the isolated molecule.

Transfer of only the first Cl-atom to the surface has a 0.7 eV barrier, while the second Cl-atom is found to detach spontaneously, with only a negligible energy-barrier (≈0.1 eV). It appears likely that the first chlorine could supply enough energy for detachment of the second via a recoil of the Bz-ring. The ease of transfer of two Cl-atoms from 1,4-diClPh to form the L-structure is consistent with the explanation presented here for the observed large number of bright features in-between Si dimer rows [8].

The Bz-ring linking the dimer rows in the L-structure is calculated to be bonded to the surface by 5.1 eV. By chance, it is the same as the total binding, $E_{ad} = 5.1$ eV, given in Fig. 5(c). This is a consequence of the thermoneutrality of the two Cl-atom transfer from the 1,4-diClPh to the surface. The question arises as to the effect of the two adjacent chlorines on the binding energy of the Bz-ring in its linking, L, structure. Calculation shows that the presence of these two Cl-atoms decreases the binding energy of the Bz-ring by 0.4 eV. This is due to the fact that both the Bz-ring and Cl withdraw charge from the surface, and both are negative.

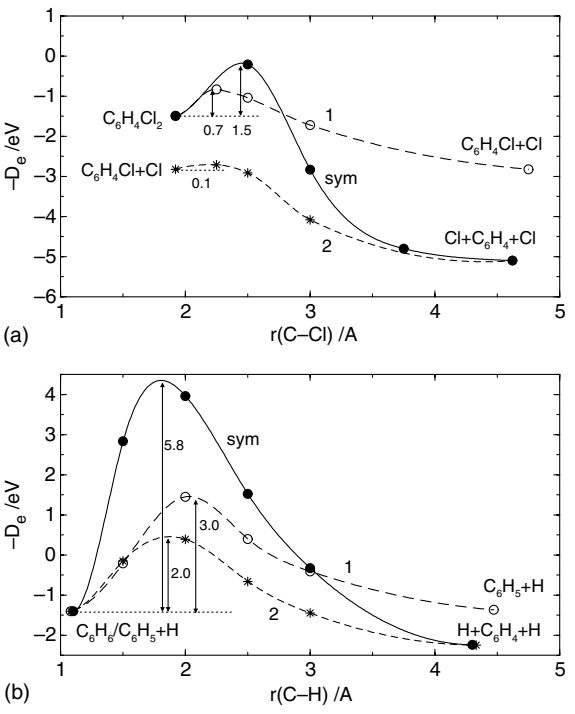

Fig. 6. Potential-energy barriers between the diene-L, diene-L•, and L-structures of (a) 1,4-diClPh: transfer of Cl-atoms to the surface and (b) Bz: transfer of H-atoms. Solid and dashed curves refer to the simultaneous (marked sym) and sequential (marked 1 and 2) atom-transfer, respectively.

It is significant that for Bz the experiments showed no bright features between rows even with up to 6 V pulses being applied [8]. Failure to form the L-structure is readily understood in terms of the energy-barriers shown in Figs. 4 and 6. The barrier to formation of the aromatic L-structure from diene-L, by sequential transfer of two Cl-atoms from 1,4-diClPh to the surface, is only 0.7 eV followed by 0.1 eV (Fig. 6(a)) whereas that for transfer of two H-atoms from Bz to the surface is ≈3 eV followed by ≈2 eV. This increase in barrier-height for C–H rupture correlates with the increase in bond dissociation energy in going from C–Cl to C–H. The stabilisation for Bz is accordingly smaller than for 1,4-diClPh, namely zero and 0.9 eV for the first and second H transfer, respectively, resulting in $E_{ad} = 2.3$ eV.

Together with the ≈3.5 eV barrier for the BF → diene-L transition of Bz (Fig. 4), these two

H transfers add up to an energy of ≈8.5 eV. This value significantly exceeds the energy of 6 V pulses (unlike in the 1,4-diClPh case). However we may consider a two- or even three-electron process in which the BF → diene-L transition is followed by a simultaneous or sequential breaking of two C–H bonds. This would have a diminished cross-section. Moreover, the effect of a delayed breaking of the second C–H bond would be likely to result in the formation of an alternative outcome, D, with the Bz-ring vertical (see below). Once the Bz-ring is in the vertical position, the second H will not be transferred to the surface.

As was just noted, there is an alternative process competing with the formation of the L structure of 1,4-diClPh. After the first Cl-atom is gone the Bz-ring can break the C–Si bond on the opposite side and lift from the surface to form structure D (Fig. 5(d) and Table 1). This is a likely process since the potential-energy barrier for lifting is found to be only 0.1 eV. The transition state occurs very early during the lifting, when the associated C–Si bond (reaction coordinate) is stretched only by 0.02 Å. The energy increases slightly from the diene-L• structure and drops sharply when the transition state is passed. This lifting fully restores the aromaticity of the ring, with the other Cl-atom remaining attached. The system is stabilised by 0.8 eV in this transformation (to $E_{ad} = 3.6$ eV). As in the case of the L-structure, this value determines also the C–Si bond strength and hence the binding energy of the C_6H_5 radical to the surface, since the C–Cl bond in the intact molecule has the same energy as the Si–Cl bond. The Bz-ring is turned at an angle of ≈40° to the dimer row due to repulsive electrostatic interaction between the H on the ring and the nearest Si-atom in the adjacent row, both being positively charged. A comparable structure, but with the ring perpendicular to the row, has been proposed for pyridine and pyrazine [6].

This lifted structure can be associated with the bright feature, D, observed experimentally for ClPh and diClPh, displaced to the side of the centre-point between dimer rows [8]. It is apparent in Fig. 5(d) that the Bz-ring for structure D is displaced to the side of the inter-row gap. By contrast the Bz-ring in the L-structure of Fig. 5(c) is centrally placed.

Experimentally the D-structure is observed with a probability of only ≈10% as compared with ≈50% for the L-structure. This is despite the fact that the D and L structures are calculated to have the same barrier for formation from their precursor diene-L• (Fig. 5(b)). The more probable formation of the L-structure rather than D may be due to recoil of the Bz-ring following exoergic detachment of the first Cl, bringing the second Cl close to the Si-atom with which it then bonds.

3.2.2.2. ClPh and 1,2-diClPh. Theory shows similar transfers of Cl (and H) -atoms to the substrate to be possible for ClPh and 1,2-diClPh, forming linking, L, and displaced, D, structures. The diene-L• structure comparable to Fig. 5(b) resulting from the initial transfer of a Cl-atom is formed. The adsorption energies are almost the same for all molecules to within 0.1 eV. The barrier to diene-L• formation is found to be low in all cases, namely 0.3 eV for ClPh and 0.8 eV for 1,2-diClPh (cf. 0.7 eV for 1,4-diClPh). The transition state occurs in every case at a C–Cl distance (reaction coordinate) stretched by ≈0.5 Å.

To arrive at the linking structure for ClPh, an H-atom must be transferred to the surface. The resulting structure comparable to Fig. 5(c), with H in place of Cl, is stabilised by about 1 eV relative to diene-L•, with $E_{ad} = 3.8$ eV. Due to stronger C–H bond than C–Cl, such a transfer requires a higher activation energy than for Cl transfer, as expected from the Bz case above. The barrier to H-atom transfer is much higher, namely 2 eV, compared to 0.1 eV for Cl-atom transfer. Formation of the D-structure comparable to Fig. 5(d) from diene-L• for ClPh involves only a 0.05 eV barrier, hence theory predicts that this will be the preferred pathway as against detachment of H and formation of L.

The description of L and D formation given above for ClPh is not materially different for the case of 1,2-diClPh. The 1,2-diClPh has a Cl substituent directly adjacent to the C–Cl bond that breaks in forming diene-L•, but this does not change the ergoergicities or barrier heights significantly. The lower barrier for formation of D compared with L appears to be reflected in their

relative yields for both ClPh and 1,2-diClPh, namely ≈20% D and <10% L.

In the foregoing we have examined the case of single and double Cl-atom transfer for 1,4-diClPh, and single Cl-atom transfer for ClPh and 1,2-diClPh. It remains to consider the case of double Cl-atom transfer for 1,2-diClPh. Fig. 7 pictures three possible pathways, all originating in the product of single chlorination, to yield (b), (c), and (e) for transfer of the second Cl-atom to the Si surface. The most symmetric outcome, corresponding to the linking structure, L, discussed for 1,4-diClPh, is structure L′ (Fig. 7(c)). The adsorption energy of $E_{ad} = 5.3$ eV for L′, essentially the same

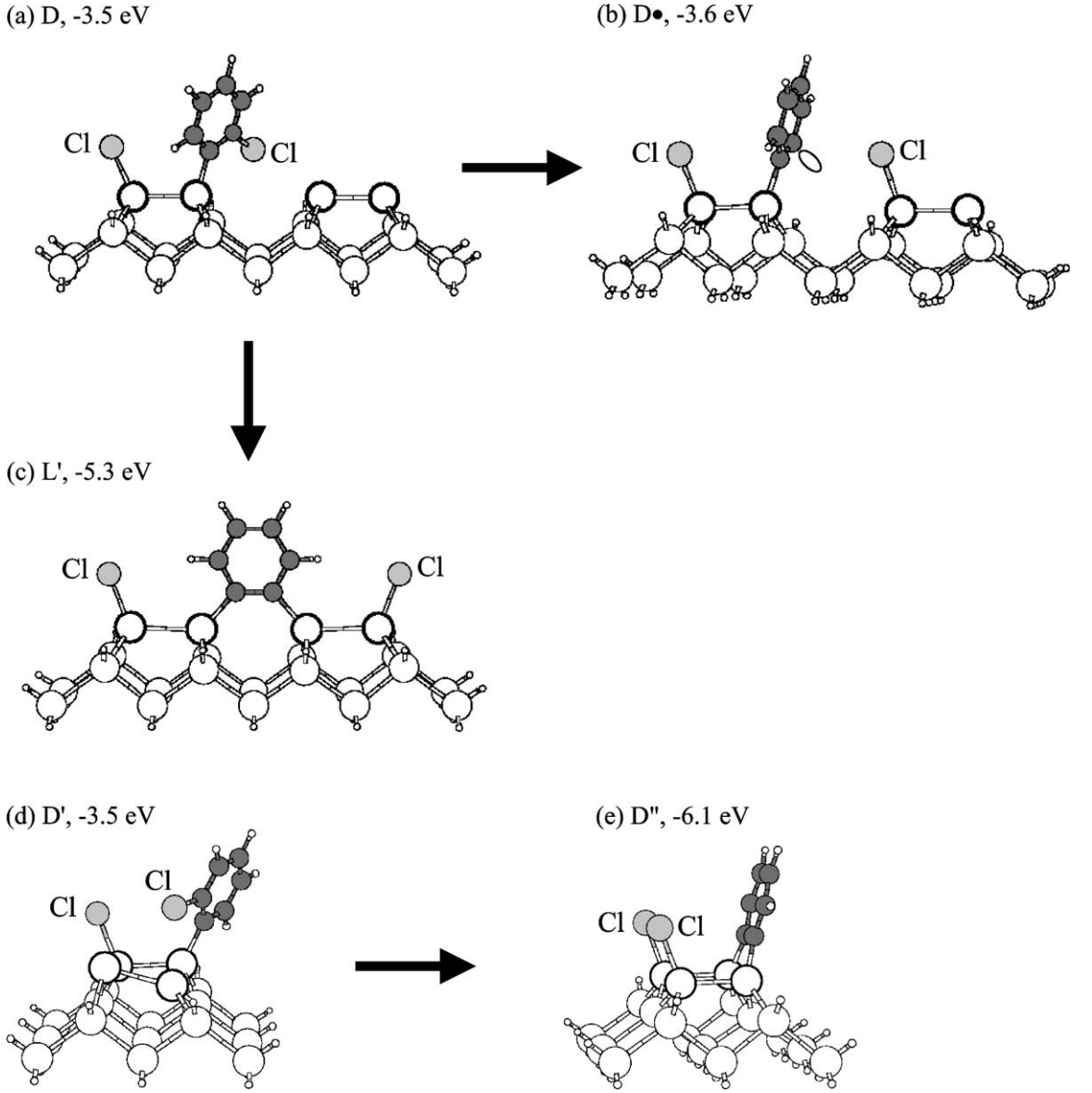

Fig. 7. Optimised structures of 1,2-diClPh/Si(1 0 0): detachment of the Cl-atoms. (a and d) The D and D′ structures with the Bz-ring lifted, and (b and c) D• and D″ structures with both Cl transferred.

as for 1,4-diClPh, is unchanged with reoptimisation at the B3LYP/6-31G* level. The most significant change in the nature of this row-linking structure L′ is the fact that the aromatic Bz-ring stands up with its plane perpendicular to the surface (and to the long axis of the dimer row). This is in contrast to the horizontal Bz-ring in the L-structure for 1,4-diClPh.

Formation of the row-linking structure L′ for 1,2-diClPh can readily be prevented by transfer of the second Cl-atom to the nearby Si atom to which Bz-ring in the linking structure would be attached. This is the outcome of the D → D• process, as shown in Fig. 7(a) and (b). Transfer of the second Cl to the surface leaves a free radical, C_6H_4, attached to the surface via a single bond. The system stability remains almost unchanged in such a reaction. Such a blockage of formation of L′ appears to be reflected in the experimental data [8] giving equal probabilities of the between-rows features (attributed to the row-linking structures) for ClPh and 1,2-diClPh.

The third outcome of dichlorination is pictured in Fig. 7(e). Once more the second Cl-atom has been transferred to the nearby Si-atom. The difference from the case just discussed (Fig. 7(a) and (b)) is that the initial structure is D′ shown in Fig. 7(d), an equally stable alternative configuration (produced from diene-L•), with the Bz-ring rotated by about 180° from its orientation in D (Fig. 7(a)). With the second Cl pointing inward toward the same dimer row, the stable outcome is the structure D″ shown in Fig. 7(e), with the second Cl attached adjacent to the first. Concurrently the Bz-ring has attached its newly formed dangling bond to the Si-atom adjacent to its original point of attachment. (It is worth noting that transfer of the second Cl-atom to this nearest Si-atom does not occur, since such a configuration is calculated to be unstable with respect to the initial structure D′.) As a result, the system stabilises by 2.5 eV relative to D′, with $E_{ad} = 6.1$ eV, the largest value so far.

Just as the removal of two Cl-atoms for 1,4- and 1,2-diClPh facilitated the formation of a doubly sigma-bound Bz-ring in a row-linking configuration, in Fig. 7(e) it has facilitated formation of a doubly sigma-bound Bz-ring linking two Si-atoms of one-dimer row. The plane of the Bz-ring is, as noted, vertical in L′ and close to vertical but turned through 90° (hence parallel to the dimer row) in D″. Since two (weak) C–Cl bonds were severed in forming the linking structures, the aromaticity of the ring has been retained in all of them. We note that the free radical, C_6H_4, present in structure D•, with a dangling bond in the two position from the point of attachment should be able to stabilise by attaching to an adjacent Si atom of the same row, yielding an analogue of D″ structure in Fig. 7(e) with a differently placed Cl. The limited model-size precludes this. Similar stabilisation could take place if starting from the D-structure the second Cl were transferred elsewhere, e.g., to another Si-atom in the adjacent row. The high stability of the (displaced) structure D″ is consistent with the observed prevalence of displaced bright features in the case of 1,2-diClPh [8].

4. Conclusions

Molecular adsorption on and reactions with the Si(1 0 0) surface have been studied theoretically for a set of benzene halo-derivatives, ClPh, 1,2- and 1,4-diClPh. Results for the small-cluster models have been verified by calculations for larger Si subsystems at the AM1 level of theory.

Many configurations were investigated for the molecules attached on-top of one-dimer row for the case of 1,4-diClPh. Configurations with the molecules between two adjacent dimer rows were computed for all molecules. This was required in order to interpret experimental data showing both 'on-top' and 'between-rows' adsorption. The calculations showed that the presence of Cl-atoms in 1,4-diClPh only weakly affected the binding energies and geometries as compared with the Bz case. This was thought to be due to the upward tilt of the chlorines, away from the surface, as a result of the sp^3 hybridisation of the Si-bonded carbons. The position of the Cl substituents significantly affected the binding energy only in the case of the 'rotated butterfly', 2,5-BF, structure with the chlorines closer to the surface than in the 1,4-BF structure. The binding energy of this 2,5-BF is 1.5 eV, about 0.5 eV greater than for 1,4-BF. The 2,5-

BF structure is the most stable of the 'on-top' structures.

This paper is particularly concerned with a new category of benzene derivative structures that link dimer rows. Two types of such structures have been investigated. In the first, a double bond of the Bz-ring opens and the resulting dienyl ring bonds between two adjacent dimer rows. In all the cases examined, namely Bz, ClPh, 1,2- and 1,4-diClPh, these diene-L (linking) structures have ≈1.5 eV binding energy to the surface, comparable to that for the BF (on-top) structure. These diene-L structures have been noted in the companion paper to this [8] and are described in detail, for the first time, here. In order to obtain this diene-L structure by theory the electronic state of the system must be permitted to change from singlet to triplet, as has been done here.

In the second type of linking structure considered here, L, attachment to adjacent dimer rows is by way of dangling bonds resulting from the breaking of two C–Cl bonds (or one C–Cl and one C–H bond for ClPh and 1,2-diClPh). In contrast to diene-L, in the L structure the Bz-ring retains full aromaticity. This is the principal type of linking structure believed to be formed from ClPh, 1,2- and 1,4-diClPh adsorbed on Si(1 0 0). These molecules readily react with breaking of their C–Cl bonds. The C–Cl bond rupture is implicated in the formation of the L structure, since no such structure forms from unhalogenated Bz, even with substantial electron-impact energies. According to our calculations, formation of L from diene-L shall readily occur.

In principle the L-structure can also be formed from Bz, by the breaking of two C–H bonds, one at either end of the molecule. In practice these bonds are so strong that the formation of L from Bz has a prohibitively high energy-barrier, calculated here to be ≈5 eV starting from diene-L. The energy barrier for the corresponding process involving rupture of the two C–Cl bonds in 1,4-diClPh requires only ≈1 eV.

In our previous paper the L-structure has been postulated to be the explanation of very bright features observed midway between dimer rows, in experiments involving ClPh, 1,2-diClPh and, especially, 1,4-diClPh. The linking structures are computed to be bound to the surface by ≈5 eV in all cases. This strong binding should be compared with the weak 1.5 eV binding in the diene-L linking structure. The much greater stability of L as compared with diene-L is due to the presence of the full resonance energy of the intact Bz-ring of L. The intact Bz-ring has its plane parallel to the surface when L is formed by attachment at the 1,4 position, and perpendicular to the surface when the attachment is at 1,2 (the so-called L′ structure for 1,2-diClPh).

After the first Cl transfer from the diene-L structure, unless the second transfer occurs rapidly, there will be a competing process of lifting the Bz-ring into a vertical position to form a 'displaced' D-structure. The D-structure is bound by one C–Si bond and has a binding energy of ≈3.5 eV. This lifted structure, with the Bz-ring tilted away from the dimer is thought to explain the experimentally observed features between rows but displaced from the centre of the inter-row gap. The height of the barrier for lifting the Bz-ring into the singly bonded D-structure, namely ≈0.1 eV, is comparable to that for the second Cl-transfer to the surface.

The predicted energy-barriers and binding energies are consistent with the relative yields of the on-top, linking and displaced structures observed experimentally. The results of the HF + DFT calculations thus provide a basis for interpretation of the STM experiments.

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