Theoretical study of $[4 + 2]$ cycloadditions of some 6- and 5-member ring aromatic compounds on the Si(001)-2 $\times$ 1 surface: correlation between binding energy and resonance energy

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Received 14th May 2001, Accepted 18th June 2001
Published on the Web 21st June 2001

By means of first-principles density functional cluster model calculations, we demonstrate that the binding energies of the $[4 + 2]$ cycloaddition products of the 6- and 5-member ring aromatic compounds on the Si(001) surface depend strongly on their resonance energies.

Introduction

The interaction of $\pi$-conjugated aromatic compounds with silicon surfaces is not only of fundamental interest, but also of practical importance to the development of highly ordered thin-film of conducting polymers. 1,2 Growing efforts devoted to this topic include the experimental studies of the adsorption of benzene (C 6H 6),3 pyridine (C 5H 5N),4 furan (C 4H 4O),5 thiophene (C 4H 4S) 6,7 and pyrrole (C 4H 5N) 8 on the Si(111) surfaces and the adsorption of benzene 9 and pyrrole 10 on the Si(001)-2 $\times$ 1 surface, as well as the theoretical studies of benzene adsorption 9 on the Si(001)-2 $\times$ 1 surface. Of particular interest is that recent experimental and theoretical studies revealed the occurrence of $[4 + 2]$ cycloaddition (Diels-Alder reaction) of benzene onto the $\pi$-bonded, ethylene-like Si-Si dimer of the Si(001)-2 $\times$ 1 surface 9,10 and that the binding energy of the thus-formed di-$\sigma$ bonded, butterfly-like species is far lower than that of the analogous reaction of simple dienes e.g. 1,3-cyclohexadiene (C 6H 4) on the same surface. 7a,9b This intriguing phenomenon can be ascribed to the aromatic stabilization in benzene, and can easily be understood with the help of a simple energy decomposition scheme that correlates the binding energy of the $[4 + 2]$ cycloaddition product with the resonance energy (RE) of benzene, as shown in Scheme 1(a). We will show in this communication that this simple scheme is applicable to other 6-, and 5-member ring aromatic compounds and that the binding energies of the corresponding $[4 + 2]$ cycloaddition products on the Si(001)-2 $\times$ 1 surface would show strong dependence on the resonance energies of the aromatic compounds.

In Scheme 1(a), the $[4 + 2]$ cycloaddition process is divided into two ideal steps. First, the $\pi$-conjugated benzene is ideally localized into a nonaromatic analog, i.e., 1,3,5-cyclohexatriene. The energy cost ($\Delta E_1$) in this step should correspond to the so-called resonance energy (RE) 10 of benzene. Second, the nonaromatic analog undergoes $[4 + 2]$ cycloaddition onto a Si-$\sigma$Si dimer. This step is exothermic with a reaction heat ($\Delta E_2$) close to the heat of the analogous reaction of 1,3-cyclohexadiene on the same surface site. Therefore, the difference in binding energy between the $[4 + 2]$ cycloaddition products of benzene and 1,3-cyclohexadiene should have a value close to the difference in RE between benzene and 1,3-cyclohexadiene. This is indeed the case, as previous B3LYP/6-31G** cluster model calculations 9b did predict a difference of 32.6 kcal mol $^{-1}$ in binding energy between benzene and 1,3-cyclohexadiene, which is comparable to the difference (ca. 28.3 kcal mol $^{-1}$) 10,11 in RE between benzene and 1,3-cyclohexadiene.

Scheme 1(a) can be generalized to the cases of other 6-member ring, aromatic compounds containing one (or more) heteroatom(s) and to those of the 5-member ring, aromatic compounds depicted in Scheme 1(b). For example, for a series of 6-member ring compounds listed in Scheme 1(a), their nonaromatic analogs contain the same localized dienes as has the 1,3-cyclohexadiene and would have similar values of $\Delta E_2$ when undergoing $[4 + 2]$ addition on the Si(001) surface. Note that among them, benzene has the largest value of RE. 10b It is thus deducible that the $[4 + 2]$ cycloaddition reactions of the heterocyclic ones would be more exothermic than that of benzene and would follow such a trend that the compound having higher RE would give lower binding energy. A similar trend could also be expected for the 5-member ring compounds listed in Scheme 1(b).

Computational method and model

To confirm the above inference, we have investigated the $[4 + 2]$ cycloaddition of five 6-member ring compounds,
including benzene, pyridine, silabenzene (C₅H₆Si), phosphabenzenes (C₆H₅P), pyrazine (C₆H₅N₂) and 1,3-cyclohexadiene, and four 5-member ring compounds, including pyrrole, thiophene, furan and cyclopentadiene (C₅H₆), onto a π-bonded Si–Si dimer site of the Si(001) surface modeled by a Si₆H₁₂ cluster. The hybrid B3LYP density functional method and the standard 6-31G* basis set were used in our calculations. Adsorption geometries were optimized at the B3LYP/6-31G* level of theory with no geometric constraint. All calculations were performed using the Gaussian94 program.  

### Results and discussion

The calculated key structural and energetic parameters for the [4 + 2] addition products of those 6- and 5-member ring compounds on the Si–Si dimer sites are listed in Table 1, together with the theoretical resonance energies reported by Dewar et al.  

The correlation equations, \( E_b / \text{RE/mol} \) for the \([4 + 2]\) cycloaddition products on the Si(001)-2 \( \times \) 1 surface, were performed using the Gaussian94 program.  

**Table 1** Key structural and energetic parameters for the products of \([4 + 2]\) cycloaddition of some 6- or 5-member ring compounds on the Si(001)-2 \( \times \) 1 surface (predicted at the B3LYP/6-31G* level). Resonance energies (RE) of the aromatic compounds extracted from ref. 10 are listed.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C–SiÅ</th>
<th>Si–SiÅ</th>
<th>( E_b / \text{RE/mol} )</th>
<th>6-Member ring</th>
<th>5-Member ring</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₆</td>
<td>1.976</td>
<td>1.979</td>
<td>1.977</td>
<td>1.978</td>
<td>1.965</td>
</tr>
<tr>
<td>C₆H₅P</td>
<td>1.976</td>
<td>1.954</td>
<td>1.973</td>
<td>1.958</td>
<td>1.965</td>
</tr>
<tr>
<td>C₆H₅N</td>
<td>96.2</td>
<td>97.2</td>
<td>95.6</td>
<td>98.3</td>
<td>94.8</td>
</tr>
<tr>
<td>C₆H₅Si</td>
<td>96.2</td>
<td>98.3</td>
<td>95.3</td>
<td>99.9</td>
<td>94.8</td>
</tr>
<tr>
<td>C₆H₅N₂</td>
<td>28.3</td>
<td>26.0</td>
<td>25.6</td>
<td>25.3</td>
<td>22.7</td>
</tr>
</tbody>
</table>

*Parameters relevant to the carbon atom neighboring the heteroatom.

In summary, we have demonstrated, by means of density functional cluster model calculations, that the binding energies of the \([4 + 2]\) cycloaddition products of some 6- and 5-member-ring, aromatic compounds on the Si(001) surface depend strongly on their resonance energies. We should note that other bonding configurations of those 6- and 5-member ring compounds on the Si(001)-2 \( \times \) 1 surface, e.g., the di–σ bonding configurations involving direct heteroatom-surface bond and the tetra–σ bonding configurations, have also been considered in our calculations. The results will be published elsewhere.

### Acknowledgements

This work is supported by National Science Foundation of China, the Ministry of Education of China, Xiamen University and Emory University through the Robert W. Woodruff professorship.

### References

7. (a) Y. Taguchi, M. Fujisawa, T. Takaoka, O. Kada and M.
This value is determined using the theoretical resonance energy given in ref. 10a and assuming that 1,3-cyclohexadiene and 1,3-butadiene have the same RE. Note the theoretical resonance energies given in ref.10a were derived with an implication that the RE of 1,3-butadiene is zero.