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Theoretical molecular design of hexasilabenzene analogues aiming for the thermodynamic and kinetic stabilization

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ABSTRACT

A variety of synthesis strategy of hexasilabenzene (HSB) - the silicon analogue of benzene - is suggested on the basis of ab initio molecular orbital and DFT calculations. To overcome the difficulty of the isolation and to increase the thermodynamic and kinetic stabilities of HSB, various ideas are proposed by making efficient use of the substituent effects - theoretical molecular designing. For the purpose, the stability of HSB (BE-type) relative to the well-known valence isomers such as hexasilabenzvalene (BV-type), hexasilaprismane (PR-type) and hexasila-Dewar-benzene (DB-type) and the mechanism of isomerization between them have been investigated and compared for the introduction of various substituents into the Si_6 skeleton. As a result, it was found that some substituents consisting of hydrogen-bonding and stacking interaction between the substituents have remarkable effect to make HSB exclusively stable compared to the other isomers. Furthermore, some crosslinking substituents were found to be highly effective to achieve both thermodynamic and kinetic stabilization. For the HSB analogues with crosslinking substituents, the promising synthesis strategy was also discussed to realize experimental synthesis and isolation.

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1. Introduction

According to the Hückel rule, planar cyclic $(4n + 2)$ π-electron systems have aromaticity which is considered to be the cause of the extremely large stabilization compared to the corresponding conjugated chain $(4n + 2)$ π-electron compounds. In contrast, planar cyclic $4n$ π-electron systems have anti-aromaticity and are less stable compared to the corresponding conjugated chain $4n$ π-electron compounds. Benzene is a typical aromatic compound which belongs to 6 π-electron $(n = 1)$ system and by far more stable than the valence isomers such as benzvalene, prismane and Dewar-benzene. In addition, the reactivity is completely different from ordinary alkenes; the electrophilic addition is hard to take place while the electrophilic substitution is rather common.

On the other hand, hexasilabenzene (HSB) in which all skeletal carbon atoms of benzene are substituted with silicon atoms has not been isolated yet, and it has been a challenging target for synthesis in the field of silicon chemistry [1]. In recent decades, the progress of the chemistry of unsaturated silicon compounds has been remarkable. Not only disilenes with Si-Si double bond but also disilynes with Si-Si triple bond, which had been thought to be impossible to exist, were synthesized successfully [2–5]. Nevertheless, HSBs still remain unknown experimentally though some innovative suggestions for the synthesis and properties have been reported recently [1,6–8]. On the other hand, quite a few theoretical studies are available for the unknown compound from relatively early stage which predict the chair type structure and other various properties such as the aromaticity, interconversions between the isomers and the synthesis strategy [9–18].

In the present study, the remarkable effect of a wide variety of substituents are shown in order to change the structure and relative stability toward some valence isomers of HSB by ab initio MO and DFT methods. Furthermore, some ideas to overcome the difficulty of the isolation and to get the thermodynamic and kinetic stabilities of HSB are suggested in terms of theoretical molecular designing using of the various substituents.

2. Computational methods

Geometry optimizations of the molecules in this study were performed at the Hartree-Fock (HF), B3LYP [19–22], the second order perturbation (MP2) [23] and Coupled Cluster (CCSD(T)) [24] levels of theory with the 6-31G(d), cc-pVDZ, aug-cc-pVDZ and cc-pVTZ basis sets [25,26]. In addition, CAM-B3LYP [27] corrected by Grimme's empirical dispersion (GD3) [28] level was used

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Table 1
The dihedral angle (<Si1-Si2-Si3-Si4/degrees) and Si—Si bond length (Å) of HSB at various levels of theory.

Calculation	Dihedral angle (<Si1-Si2-Si3-Si4)/degrees	Si—Si bond length/Å
HF/6-31G(d)	16.72	2.218
B3LYP/6-31G(d)	36.25	2.245
B3LYP/cc-pVDZ	37.15	2.250
MP2/6-31G(d)	35.25	2.234
MP2/cc-pVDZ	34.71	2.247
MP2/cc-pVTZ	31.59	2.230
MP2/cc-pVQZ	29.79	2.222
CCSD(T)/6-31G(d)	36.96	2.246

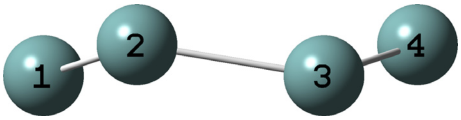

Fig. 1. Side view of the six-membered ring framework of HSB (Si_6H_6).

in the cases where the effect of dispersion force is not negligible. All optimized geometries were characterized as minima or transition states by normal mode analysis. In some case, Reaction plus program [29] based on the nudged elastic band (NEB) [30,31] method, was used for the preliminary search of transition-state structures. The IRC calculations have been carried out to confirm the connectivity of the transition state and two minima, the reactant and product, for each reaction. Furthermore, natural bond orbital (NBO) [32] analysis was applied to investigate the charge distribution and bond character. Also, the Wiberg bond index (WBI) [33] was used to estimate bond strength.

All calculations were performed with the Gaussian 09 program [34].

3. Results and discussion

3.1. Structure and frontier MOs of HSB (Si_6H_6) in comparison with benzene (C_6H_6)

First, let us summarize the difference of benzene and hexasilabenzene (HSB) in the geometry and frontier molecular orbitals on the ground electronic state. Contrary to benzene with a planar D_{6h} structure, as mentioned in the introduction, it has been known that HSB has a *nonplanar* D_{3d} structure without bond-alternation by theoretical calculations [10]. In Table 1 summarized are the dihedral angle (<Si1-Si2-Si3-Si4, see Fig. 1) and Si—Si bond length of HSB, obtained at various levels of calculation. The bond length is almost constant but the non-planarity of HSB seems to be enhanced by the electron correlation effect and flexible basis sets. On the other hand, as Table 2 shows, the Si—Si bond length of the six-membered ring skeleton is between a single bond and a double bond length both for benzene and HSB. Therefore, benzene and HSB is similar in the geometrical character except for the planarity of the six-membered ring framework.

In Fig. 2 depicted are the HOMO and LUMO of both molecules. They seem to be basically the same except for the energy levels. Table 3 shows a comparison of the HOMO-LUMO energy gap. As the B3LYP level of calculations tend to underestimate a HOMO-LUMO energy gap, the comparison was also made at the MP2 level. The HOMO-LUMO gap of HSB is about half of that of benzene. Therefore, HSB is expected to have much higher reactivity than benzene at least from the small HOMO-LUMO energy gap.

3.2. Isomerization of HSB (Si_6H_6) in comparison with benzene (C_6H_6)

Among the huge number of isomers of benzene [35], benzvalene (BV), prismane (PR), and Dewar-benzene (DB) are well known as major valence isomers of benzene. And the reaction mechanisms for the isomerization from benzene have extensively been investigated for many years by molecular orbital method. Recently, the existence of great many isomers of HSB (Si_6H_6) has

Table 2
The C—C and Si—SiSi—Si bond lengths (Å) in each three types of molecule at the MP2/cc-pVTZ level.

	C-C bond length / Å	symmetry		Si-Si bond length / Å	symmetry
ethane	1.524	D_{3d}	disilane	2.351	D_{3d}
ethylene	1.332	D_{2h}	disilene	2.156	C_{2h}
benzene	1.394	D_{6h}	HSB	2.230	D_{3d}

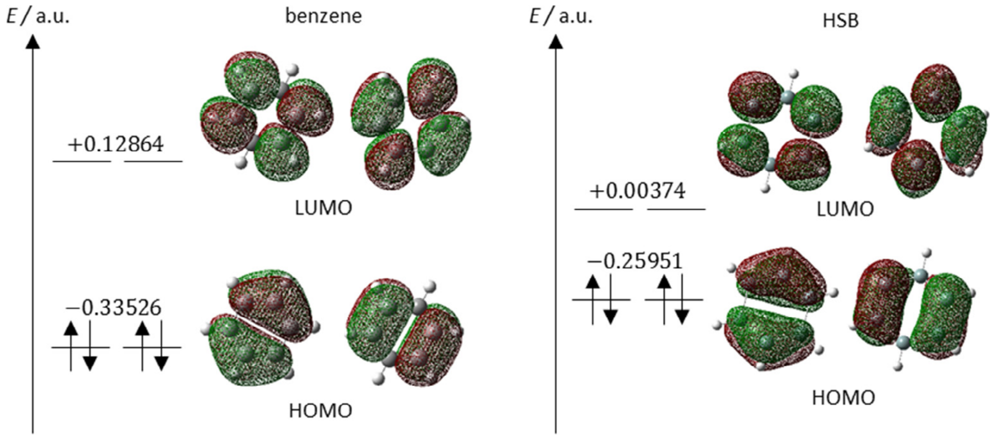

Fig. 2. HOMO and LUMO with the energy level (a.u.) of benzene and HSB at the MP2/cc-pVTZ level.

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