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Stabilisation of the [6]-prismane structure by silicon substitution[†]

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Abstract. Using the second-order Møller–Plesset perturbation (MP2) theoretic method and the cc-pVDZ basis set, it is shown that with an increase in the number of carbon atoms substituted by silicon, the [6]-prismane structure becomes increasingly more stable, relative to the two isolated benzene (like) structures. A similar trend is observed for germanium substituted prismanes as well. Extending this investigation, the stability of benzene-capped fullerene (C₆₀ fused with benzene) is also investigated.

Keywords. [6]-Prismane; silabenzene; germanobenzene; benzene-capped fullerene.

1. Introduction

Benzene is known to be highly stable. The interaction of two benzene molecules has been investigated over the years, and the parallel displaced and T-shaped geometries have been shown to be comparable in stability from a theoretical point of view.^{1–4} However, experimental evidence obtained thus far indicates the benzene dimer to be T-shaped.^{5–7}

While benzene is known to interact strongly with cations and to form sandwich complexes with them,^{8–10} the fused dimer in which two benzene moieties form covalent bonds in a face-to-face configuration is energetically unstable.¹¹

The present paper reports on the effect of silicon substitution on the stability of fused benzene dimer configuration, known as [6]-prismane.

Prismanes are a class of hydrocarbons consisting of a series of fused cyclobutane rings with a generic chemical formula (C₂H₂)_n, where *n* is the number of cyclobutane rings.^{12,13} The simplest member, triprismane or [3]-prismane, (C₆H₆) is considered an isomer of benzene.¹⁴ Many *ab initio* quantum chemical investigations have been carried out to examine the structural and thermodynamical properties of [n]-prismane along with the effect of substitution on its mechanical properties.^{15–21} While the synthesis of lower prismanes (*n* < 6) was

readily achieved,^{22–25} synthesis of [6]-prismane remained a challenge until Mehta and Padma^{26,27} came up with a novel idea to synthesize it using Diels-Alder addition and photocatalysis. [6]-Prismane has the structure of a regular hexagonal prism wherein two parallel 6-membered rings are co-joined face-to-face resulting in the formation of six cyclobutane rings (Figure 1). Alonso *et al.*,²⁸ have studied the thermally forbidden [6+6] cycloaddition of two aromatic benzene rings and examined the aromaticity profile along the reaction coordinate. In general, any [n]-prismane can be considered as a dimer of an n-membered conjugated ring.

The present work focuses primarily on the feasibility of [6]-prismane formation. Many synthesized as well as theoretically predicted benzene dimers have been reported in the literature [see above]. Rogachev *et al.*,¹¹ have investigated twelve different forms of benzene dimers, of which four were reported theoretically for the first time. Their calculations at the MP2/cc-pVTZ level of theory for the new benzene dimers featuring one or more cyclohexadiene rings emphasized a destabilisation energy of 50–99 kcal/mol, relative to the two isolated benzene molecules. [6]-Prismane differs from the other benzene dimers due to the absence of cyclohexadiene rings. *Ab initio* calculations suggest the *D*_{6h} symmetry to be the lowest energy arrangement with an interaction energy of +115 kcal/mol relative to the two isolated benzene molecules, indicating that [6]-prismane is an unstable benzene dimer.

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[†]Dedicated to the memory of the late Professor Charusita Chakravarty.

Although carbon and silicon belong to the same group in the periodic table, there is a distinct difference in their bonding abilities. Innumerable unsaturated carbon compounds exist, but unsaturated silicon compounds are rare as silicon prefers an sp^3 bonding environment over sp^2 .^{29–32} For the same reason, compounds containing Si = Si bonds transform readily into their saturated form. Mohan and Dutta³³ studied theoretically the structural properties of a series of silicon substituted benzene ($C_nSi_{(6-n)}H_6$, $0 \leq n \leq 6$) molecules and the stability of their complexes with elemental chromium. These silicon substituted benzene moieties have Si = Si bonds and they exhibit a pseudo-Jahn-Teller (PJT) distortion owing to the interaction between the close lying highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).^{34,35} Due to PJT distortion, three Si atoms in conjugation undergo puckering or buckling to attain the favourable sp^3 hybridization. Buckling leads to stabilization of the σ backbone and a simultaneous destabilization of the π backbone. Jose and Dutta have elucidated puckering in silicenes in great detail elsewhere.^{36,37}

By a detailed analysis of the vibronic interactions in two or more benzene molecules stacked on top of each other, Boltrushko *et al.*,³⁸ have shown that Jahn-Teller effect could account for a lowering of the barrier for di-benzene formation (although such a dimer is energetically less stable than the separated benzene molecules). However, when three or more benzene moieties were stacked on top of each other, the PJT effect led to buckling within each ring.

There is substantial experimental evidence³⁹ for the formation of silicon/germanium analogs of tetrahedrane, [3]-prismane and [4]-prismane (cubane), but none so far for the Si/Ge analogs of [6]-prismane. Hopefully, our results would spur new experimental efforts to make Si/Ge analogs of [6]-prismane.

Our theoretical investigations show that [6]-prismane made up of silicon substituted benzene moieties are stable with respect to their silicene monomers (see below).

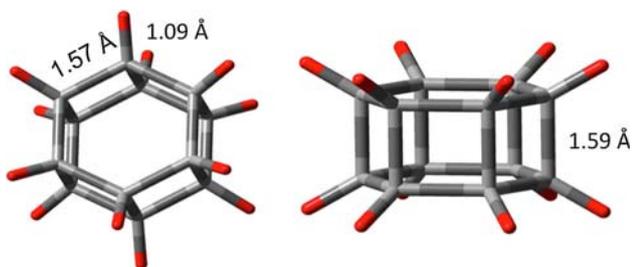


Figure 1. Structure of [6]-prismane, *top* and *side* view.

To obtain a detailed understanding of the enhanced stability of the dimer of hexasilabenzene (Si_6H_6)₂ over [6]-prismane formed by two benzene units, we have investigated systematically the stability of sequentially substituted silabenzene dimers.

2. Computational details

All electronic structure calculations were carried out using the Gaussian 09 suite of programs.⁴⁰ Although initial geometry optimization for the different prismanes and capped fullerene was done using the Hartree-Fock (HF) method and the 6-311G basis set, additional calculations were at the second-order Møller–Plesset perturbation (MP2) theoretic level using the Dunning’s correlation consistent double zeta (cc-pVDZ) basis set. Frequency calculations were carried out to ensure that all the optimized geometries obtained corresponded to true minima. The stabilization or the interaction energy (ΔE) for the dimer was computed as,

$$\Delta E = E_{\text{dimer}} - 2E_{\text{monomer}} \quad (1)$$

for both Si- and Ge- substituted prismanes. For the benzene capped fullerene,

$$\Delta E = E_{\text{capped-fullerene}} - E_{\text{benzene}} - E_{\text{fullerene}}. \quad (2)$$

Negative values of ΔE indicate stabilisation of the dimer or the capped fullerene.

3. Results and Discussion

The face-to-face dimer ([6]-prismane) formed by the covalent interaction between two benzene rings is unstable relative to the two benzene monomers by an energy (ΔE) of 125 kcal/mol at the MP2/cc-pVDZ level of theory. Such an instability can be accounted for by the loss of aromaticity (each benzene moiety has a resonance energy of 36 kcal/mol) and the formation of six highly strained cyclobutane rings. These two factors severely negate the stability gained by the formation of σ bonds between the monomers even though the newly formed σ bonds are significantly stronger than the previously present π bonds. In the case of singly substituted silabenzene, dimerization is energetically unfavourable by 42.9 kcal/mol. The Si-Si bond in the dimer provides the Si atoms with their favourable sp^3 bonding environment. Additionally, the number of cyclobutane rings formed on dimerization is reduced to 4 due to the presence of one Si atom in place of C when compared to 6 in benzene dimer. The longer Si-Si bond length lowers the angular strain in the remaining 2 rings.

For multi-Si-substituted benzene, the stability of the dimer depends on the position of Si atoms in the ring. In the case of doubly substituted benzene ring, the dimer formed by 1,2-disilabenzene is slightly unstable ($\Delta E = +0.5$ kcal/mol) as it leads to the formation of three cyclobutane rings, whereas those formed by 1,3-disilabenzene ($\Delta E = -10.6$ kcal/mol) and 1,4-disilabenzene ($\Delta E = -21.8$ kcal/mol) are stable as they lead to the formation of only two cyclobutane rings. Among these two dimers of doubly substituted benzene, 1,4-disilabenzene is more stable as the two cyclobutane rings are separated from each other. However, in 1,3-disilabenzene, the cyclobutane rings are juxtaposed to each other. For the triply substituted benzene, three Si-Si σ bonds are formed and hence the stability of the dimer is more compared to the dimer of doubly substituted benzene. Among different isomers of tri-substituted benzene dimers, 1,2,3-trisilabenzene dimer is the least stable ($\Delta E = -38.8$ kcal/mol) as it has two cyclobutane rings and 1,3,5-trisilabenzene dimer is more stable ($\Delta E = -48.5$ kcal/mol) as no cyclobutane ring is formed. However, 1,2,4-trisilabenzene dimer is the most stable ($\Delta E = -54.4$ kcal/mol). The stability of the dimer is further enhanced in the case of the tetrasubstituted benzene dimer. 1,2,4,5-Tetrasilabenzene dimer is the most stable ($\Delta E = -88.4$ kcal/mol) as it has no cyclobutane ring and there are four Si-Si σ bonds. 1,2,3,4-Tetrasilabenzene dimer is the least stable ($\Delta E = -79.3$ kcal/mol) as it has one cyclobutane ring. 1,2,3,5-Tetrasilabenzene dimer has an intermediate stability ($\Delta E = -84$ kcal/mol).

Pentasubstituted silabenzene forms a stable dimer with a stabilization energy of -112.6 kcal/mol. Hexasilabenzene forms the most stable dimer/prismane, with $\Delta E = -134.8$ kcal/mol. The molecule belongs to the D_{6h} point group, with six covalent Si-Si σ bonds between the rings. Figure 2 shows the optimized geometry of different dimers of Si-substituted benzene, while Figure 3 reveals the relative stability of the dimers formed as a function of the number of carbon atoms substituted. The Si-Si bond length in the optimized geometry of the dimers of Si-substituted benzene varies from 2.28 Å to 2.45 Å, whereas the C-C bond length in the substituted benzene ring varies from 1.5 Å to 1.65 Å. Natural bond orbital analysis revealed a higher p character in the Si-Si bond formed between monomer layers compared to the planar Si-Si bond. The C-Si bonds are polarized with the C atom having more than 70% share of the electrons. Likewise, the Si-H bond is also slightly polar with the H atom being more electronegative and having a share of about 60% of the bond electrons. A summary of the stabilisation energy

values for Si-substituted benzene dimers is given in Table 1.

Since Ge belongs to the same group as Si and C in the periodic table, we were curious to know the stability of Ge-substituted benzene and its dimer. We repeated the calculations for Ge-substituted benzene. It was found that planar Ge_6H_6 with D_{6h} point group symmetry is not a minimum energy structure, but a second order saddle point. Ge_6H_6 exists in a puckered form like Si_6H_6 and this can be attributed to the PJT effect as explained by Jose and Dutta³⁶ in the case of Si_6H_6 . The HOMO of Ge_6H_6 is doubly degenerate and the LUMO is non-degenerate, similar to the case of Si_6H_6 . But the HOMO-LUMO energy gap in Ge_6H_6 is smaller by 6.5 kcal/mol than that in Si_6H_6 . This smaller HOMO-LUMO energy gap leads to a larger PJT effect and hence a larger distortion in the structure of Ge_6H_6 . This is reflected in an enhancement in the puckering angle, from 34.65° in Si_6H_6 to 46.64° in the case of Ge_6H_6 . The Ge-Ge bond length is slightly longer than the Si-Si bond length in the optimized geometry of the dimers of substituted benzene. The Ge-Ge bond length varies from 2.4 Å to 2.5 Å and the C-C bond length falls in the range 1.5 – 1.6 Å in the germanium substituted benzene dimer. A natural bond orbital analysis shows similar features for Ge substituted benzene as observed for Si substituted benzene.

Dimerization energy values for Ge-substituted benzene were calculated the way they were calculated for silicon substituted benzene. A trend similar to that observed for Si was observed for Ge as well. That is, on increasing the number of Ge atoms in the benzene ring, the stability of the dimer increased. For single Ge substituted benzene, the dimer formation is energetically unfavorable by 35 kcal/mol. For multi-Ge substituted benzene, the stability of the dimer, like for multi-Si substituted benzene, depends on the position of the Ge atom in the benzene ring. Vibrational frequency calculations show that 1,2-digermanium benzene, 1,2,3-trigermanium benzene, 1,2,4-trigermanium benzene and 1,2,3,4-tetragermanium benzene are not minimum energy configurations, but are saddle points. The calculations, however, show the dimers to be relatively stable, with respect to the monomers. The dimers of 1,3-digermanium benzene and 1,4-digermanium benzene are stable by about -30 kcal/mol. The dimer formed by 1,3,5-trigermanium benzene is more stable, with a stabilization energy of -80 kcal/mol. The stabilization energy due to dimerization in tetra-Ge-substituted benzene is -107 kcal/mol and in the case of penta-Ge-substituted benzene, it becomes -120 kcal/mol. Hexa-Ge-benzene dimer is the most stable

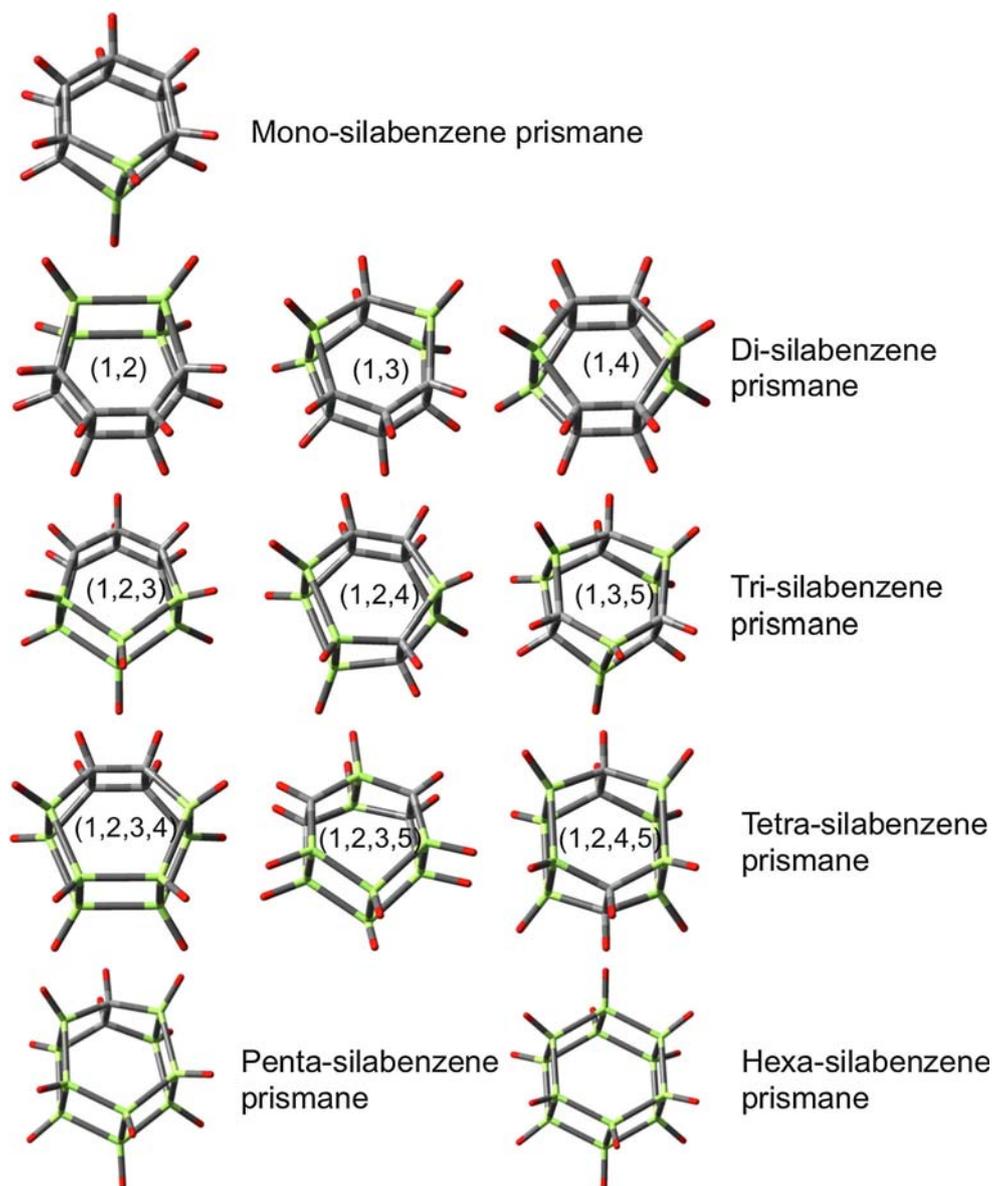


Figure 2. Optimized geometry of different silicon-substituted prismane structures obtained at the MP2/cc-pVDZ level of theory. The *light green color* in the ring indicates silicon atoms.

of all Ge-substituted-benzene dimers, with $\Delta E = -132$ kcal/mol. It is evident that the trends observed for Ge substituted benzene are similar to those observed for Si substituted benzene and thus can be explained in a similar manner.

3.1 Formation of benzene-capped fullerene

The hexagonal rings of C_{60} fullerene⁴¹ have unsaturated carbon atoms, but are less aromatic than the benzene ring due to less planarity. It seemed worthwhile to investigate the covalent interaction between an aromatic benzene and the less aromatic C_{60} fullerene molecule. We found

the face-to-face fusion of the benzene moiety with a six-membered ring of fullerene, *i.e.*, capped fullerene as the most favourable geometry as illustrated in Figure 4. This structure belongs to the C_{3v} point group. The C-C bond connecting the fullerene cage and the benzene ring is 1.56 Å long, while the C-C bond in the cap has a length of 1.55 Å. This capped fullerene structure is unstable by 101.3 kcal/mol, with respect to isolated benzene and fullerene moieties, at the HF/cc-pVDZ level of theory. It should be noted that this is lower than the destabilization energy of two benzene molecules forming [6]-prismane, which is 138 kcal/mol (HF/cc-pVDZ level).

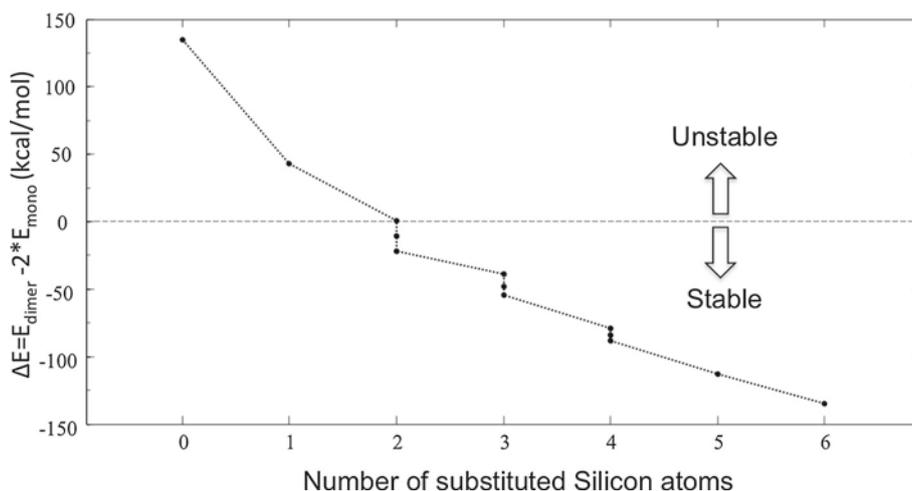


Figure 3. Relative stability of the dimers with respect to the two asymptotically separated monomers of benzene and different Si-substituted benzene moieties at the MP2/cc-pVDZ level of theory.

Table 1. Stabilization energy (ΔE) values for dimers of different silicon substituted benzene moieties at the MP2/cc-pVDZ level of theory

Monomer: $C_nSi_{(6-n)}H_6$	ΔE (kcal/mol)	Number of cyclobutane rings
C_6H_6	125.0	6
C_5SiH_6	42.9	4
1, 2- $C_4Si_2H_6$	0.5	3
1, 3- $C_4Si_2H_6$	-10.6	2
1, 4- $C_4Si_2H_6$	-21.8	2
1, 2, 3- $C_3Si_3H_6$	-38.8	2
1, 2, 4- $C_3Si_3H_6$	-54.4	1
1, 3, 5- $C_3Si_3H_6$	-48.5	0
1, 2, 3, 4- $C_2Si_4H_6$	-79.3	1
1, 2, 3, 5- $C_2Si_4H_6$	-84.0	0
1, 2, 4, 5- $C_2Si_4H_6$	-88.4	0
CSi_5H_6	-112.6	0
Si_6H_6	-134.8	0

Similar calculations were carried out for spherical Si_{60} capped with hexasilabenzene. It was found that the capped silicon-fullerene was stable with respect to isolated Si_{60} and Si_6H_6 with $\Delta E = -134$ kcal/mol. It should be mentioned that icosahedral Si_{60} is not an energy minimum but a first order saddle point. It would be worth deciphering the properties of capped fullerenes, as it may extend the scope of possible applications of this class of molecules.

4. Conclusions

MP2 calculations using the cc-pVDZ basis set showed that the stability of [6]-prismane increased with an

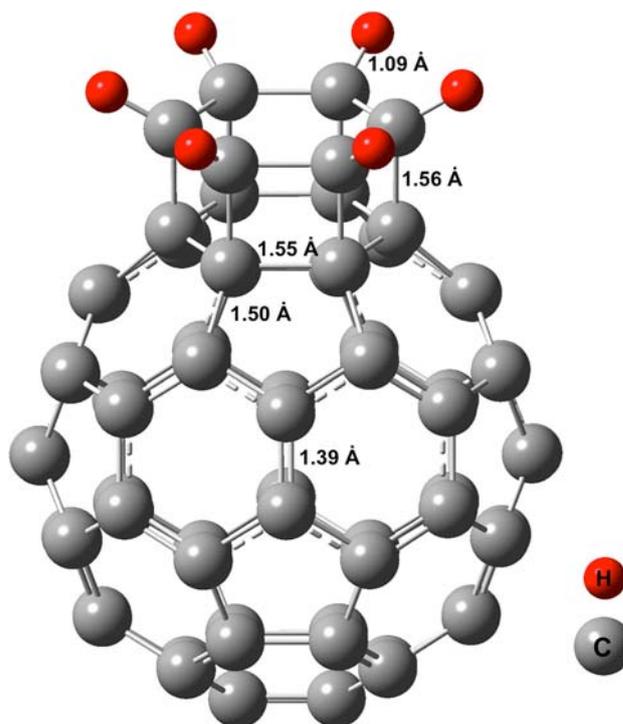


Figure 4. Optimized geometry of benzene-capped fullerene at the HF/cc-pVDZ level of theory.

increase in the number of Si atoms in each benzene ring, owing to the favourable sp^3 bonding environment for Si and a decrease in the strain energy of the ring due to a reduction in the number of cyclobutane rings formed. A similar trend was observed for Ge substituted [6]-prismane also. It was found that the six membered ring of fullerene and benzene can interact covalently leading to a capped fullerene. The stabilization energy, ΔE , indicates that the interaction between fullerene and

benzene is more favourable than the dimerization of two benzene molecules.

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