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Theoretical Study of Silabenzene and Its Valence Isomers

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Quantum mechanical calculations at the ab initio (MP2, CCSD(T)) and the hybrid density functional levels with an array of basis sets (6-31G*, 6-31G**, cc-pVDZ, 6-311+G**) were performed on 15 $(CH)_5SiH$ structures. Of the 15 structures considered on the $(CH)_5SiH$ potential energy surface, 12 structures were characterized as local minima. Two new valence isomeric forms of silabenzene, **V1a$_m$** and **V1b$_m$**, have been identified, which lie only about 20 kcal/mol higher than silabenzene (**B1**). **PY**, where Si is hexacoordinated, has been characterized as a stationary point, which lies only around 56 kcal/mol higher in energy than silabenzene. The relative energies are contrasted with those of the valence isomers of benzene. The lower magnitudes of the vibrational frequencies corresponding to the skeletal movements support the facile rearrangements witnessed in these compounds. The chemical hardness values were measured, and no direct correlation was obtained between the relative energy ordering and the chemical hardness values.

Introduction

Heteroanalogues of benzene are subjects of numerous experimental and theoretical studies and remain focal points in the molecular and electronic structural theory in the contemporary main group organometallic chemistry.[1−5] Although, the analogy between the carbon and silicon is obvious, the skeletal replacement by group V atoms leads to more stable heterobenzenes than silabenzene.[6,7] The concept of silaaromaticity is vividly debated and stimulated synthetic attempts toward silabenzenes.[6−10] The synthesis and characterization of substituted silabenzene was unambiguously achieved only recently, while the data on the other valence isomeric forms are scarce.[10] However, the infrared, electronic, and photoelectronic spectroscopic characterization of silabenzene and 1-methylsilabenzene in argon matrixes was reported quite a while ago.[11] The strategy of employing bulky substituents resulted in a flurry of synthetic accomplishments in the silaaromatics, which are otherwise elusive in their pristine form.[11,12] Maier and co-workers reported the photochemical isomerizations of silabenzene to Dewar silabenzene, in a matrix isolation study.[13] Ando and co-workers have reported intriguing isomerization reactions among the disilabenzene isomers.[14,15] In contrast to silabenzene, the chemistry of phosphinine isomers is very rich, and virtually all the valence isomers of phosphinine were synthesized and are found to display exciting isomerization reactions and novel binding modes to the transition metal frag-

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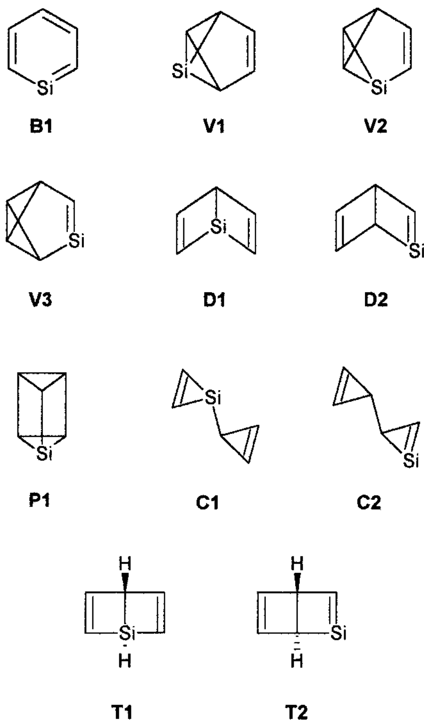
ments.[16,17] While the silabenzene was unambiguously characterized, the characterization of the isomerization product, benzvalene, was based only on the NMR data, which was not definitive, as acknowledged by the authors themselves, and this class of compounds is too reactive for elaborate experimental investigation using the conventional techniques such as X-ray diffraction.[10a]

The silicon–organic compounds have been favorite hunting grounds for theoretical and computational chemistry for more than three decades. Incredible contrasts have been observed between the silicon and the corresponding carbon compounds.[18] Chandresekhar and Schleyer have done calculations on **B1**, **D1**, and three other isomers of silabenzene.[19] Recent studies indicate that silabenzene is only slightly less aromatic than benzene.[8,12] Wakita et al. along with their experimental investigation on the isomerization of silabenzene to silabenzvalene reported B3LYP/6-31G* energetics on the five (**B1**, **V2**, **V3**, **D1**, **D2**) valence isomeric forms.[10a] It is surprising to note that to date there is no systematic theoretical study on the valence isomers of silabenzene despite considerable interest in this compound and its isomerization. A systematic computational study that identifies all the potential valence isomers of silabenzene and the characterization of all the minimum energy structures, assessing their relative stabilities and vibrational spectra, throws light on the chemistry of silabenzene and its potential skeletal rearrangements. Standard ab initio and DFT methods were used to obtain the equilibrium geometries, relative energies, harmonic frequencies, frontier orbital energies, and chemical hardness for all the isomers considered in the study. Comparison is made with the corresponding benzene isomers to ascertain the perturbation caused by Si substitution in the benzene skeleton.

Computational Details

All the geometries were fully optimized within the symmetry constraints at the B3LYP level[20] of theory with the 6-31G* basis set initially. The stationary points thus obtained were characterized on the basis of the frequency calculations. The geometries were further refined with the cc-pVDZ and 6-311+G** basis sets at the B3LYP level. The geometries were also evaluated at the MP2/6-31G** level. These were followed by single-point calculations at the MP2/6-311+G** and CCSD(T)/6-31G* levels on the MP2/6-31G** optimized geometries. However, the 6-31G* basis set is probably not adequate at the CCSD(T) level, and therefore we have considered a bigger basis set at the MP2 level. This scheme (eq 1) was quite impressive in giving good fits with the higher level calculations.[21,22]

Scheme 1



$$\Delta E = \Delta E_{\mathrm{CCSD(T)}} + \Delta E_{(\mathrm{MP2/6-311+G^{**}}\ -\ \mathrm{MP2/6-31G^{**}})} + \Delta H \quad (1)$$

ΔH is the enthalpy correction factor obtained by frequency calculations at the B3LYP/6-311+G** method. Harmonic frequencies were computed using 6-31G*, cc-pVDZ, and 6-311+G** basis sets at the B3LYP level and are listed in the Supporting Information. The differences in the computed harmonic frequencies obtained using various basis sets were very small. Thus the basis set employed to obtain the harmonic frequencies is adequate. Most of the B3LYP optimizations were carried out using the Jaguar 4.1 program package initially.[23] However, for the sake of uniformity all the reported calculations were done using the Gaussian 94 suite of programs.[24]

Results and Discussion

All the valence isomeric forms of silabenzene given in Scheme 1 were fully optimized within the symmetry constraints initially at the B3LYP level with the 6-31G* basis set. All the structures were characterized as minima, showing all real frequencies except for the benzvalene isomer, **V1**. Attempts to locate **V1** lead to

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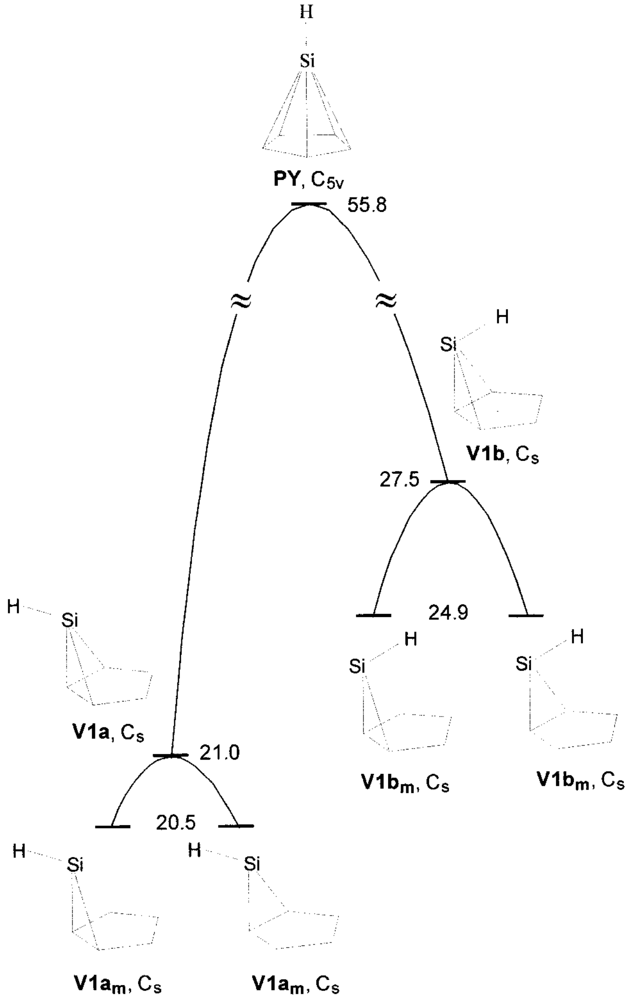
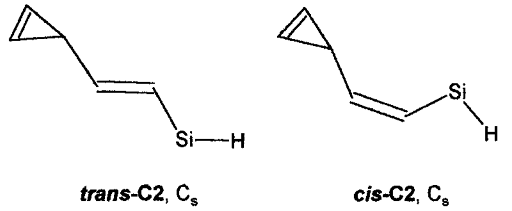
Scheme 2



one or the other stationary point, **V1a** and **V1b**, and both of them turned out to be first-order saddle points (Scheme 2). The normal modes corresponding to the imaginary frequencies are followed, and minimum energy structures, **V1a$_\mathbf{m}$** and **V1b$_\mathbf{m}$**, were obtained. The two new structures **V1a$_\mathbf{m}$** and **V1b$_\mathbf{m}$** are distinctly distorted when compared to benzvalene and correspond to bicyclic structures. Energetically, these two isomers lie closer to the benzenoid compound, **B1**, compared to the other isomers (vide infra). This prompted us to investigate the aesthetically appealing C_{5v} pyramidal structure, **PY**, where the Si is bound to all five carbons and a stationary point was located. The frequency calculation characterizes this as a second-order saddle point. Following one of the two imaginary frequencies led to the first-order saddle point, **V1a** and **V1b**, which further led to minima (**V1a$_\mathbf{m}$** and **V1b$_\mathbf{m}$**). Although, it is necessary to have two electrons less to stabilize such a nido system, the relatively low energy of **PY** and its connectivity to the novel minimum energy structures, **V1a$_\mathbf{m}$** and **V1b$_\mathbf{m}$**, prompted us to explore this part of the potential energy hypersurface in detail. The cyclopentadienyl moiety is virtually flat in all the cases, **PY**, **V1a**, **V1b**, **V1a$_\mathbf{m}$**, and **V1b$_\mathbf{m}$**, depicted in Scheme 2. While SiH is bound in η^5-fashion in **PY**, it is in η^3-fashion in **V1a** and **V1b** and η^2-fashion in **V1a$_\mathbf{m}$** and **V1b$_\mathbf{m}$**. Similarly, a closer examination of the optimized structure of **C2** reveals that the C−Si single bond was broken in the Si-containing three-membered ring, leading to an open structure, ***trans*-C2**, with a divalent Si (Scheme 3). The corresponding cis isomer, ***cis*-C2**, was located and characterized as a minimum on the potential energy surface. Several attempts to locate a stationary point corresponding to **T1** failed at both the B3LYP and MP2 levels, and the putative structures collapsed to **D1** upon optimization. Attempts were made to locate **T1** at the HF, B3LYP, and MP2 levels, and in each case all the putative structures converged to the *cis*-Dewar benzene, thus indicating that the **T1** structure does not correspond to a stationary point on the potential energy surface of (CH)$_5$SiH. Thus the present study identifies 15 important stationary points on the potential energy surface of silabenzene, where 12 are minima, two are transition states, and one structure is a second-order saddle point. All 15 structures were then reoptimized and recharacterized by frequency calculations at the B3LYP level using the cc-pVDZ and 6-311+G** basis sets. The geometry optimization was also carried out at the MP2/6-31G** level. The assignment of the stationary points with higher basis sets was found to be identical with the 6-31G* basis set. The equilibrium geometries are discussed first and then the relative energies, vibrational spectra, and the reactivity.

Scheme 3



Equilibrium Geometries. Figure 1 depicts the principal optimized geometric parameters of all the structures considered in the study at the B3LYP/6-31G*, B3LYP/cc-pVDZ, B3LYP/6-311+G**, and MP2/6-31G** levels of theory. In general, the geometries obtained at the B3LYP and MP2 levels are in good agreement with each other. However, the B3LYP method consistently overestimates the C−Si single bond lengths with all the basis sets compared to the MP2 level. The geometric parameters obtained using the 6-31G* and the 6-311+G** basis sets are essentially identical, and therefore, 6-31G* quality basis set may be assumed to be quite adequate for the geometries. The discussion on the equilibrium geometries from here throughout the rest of the text will be based on those obtained at the MP2/6-31G** level.

The C−C bond lengths in silabenzene **B1** are equal, and the C−Si bond length is found to lie between the C−Si single and double bond lengths, which is in agreement with the previous studies.[3b,8,10] In **V1a** and **V1b**, the five-membered ring formed by the carbon atoms is found to be virtually planar. All the C−C bond lengths are closer to the aromatic bond lengths, whereas the C−Si bonds are substantially elongated. It occurred to us that the situation might correspond to the one where a cyclopentadienyl anion is coordinated in a η^3-fashion with a SiH$^+$ cap. Indeed, the natural population analysis at the HF/6-31G*//MP2/6-31G** indicates that there is a charge polarization of +0.4546 in **V1a** and +0.4678 in **V1b** on the SiH group, indicating that the

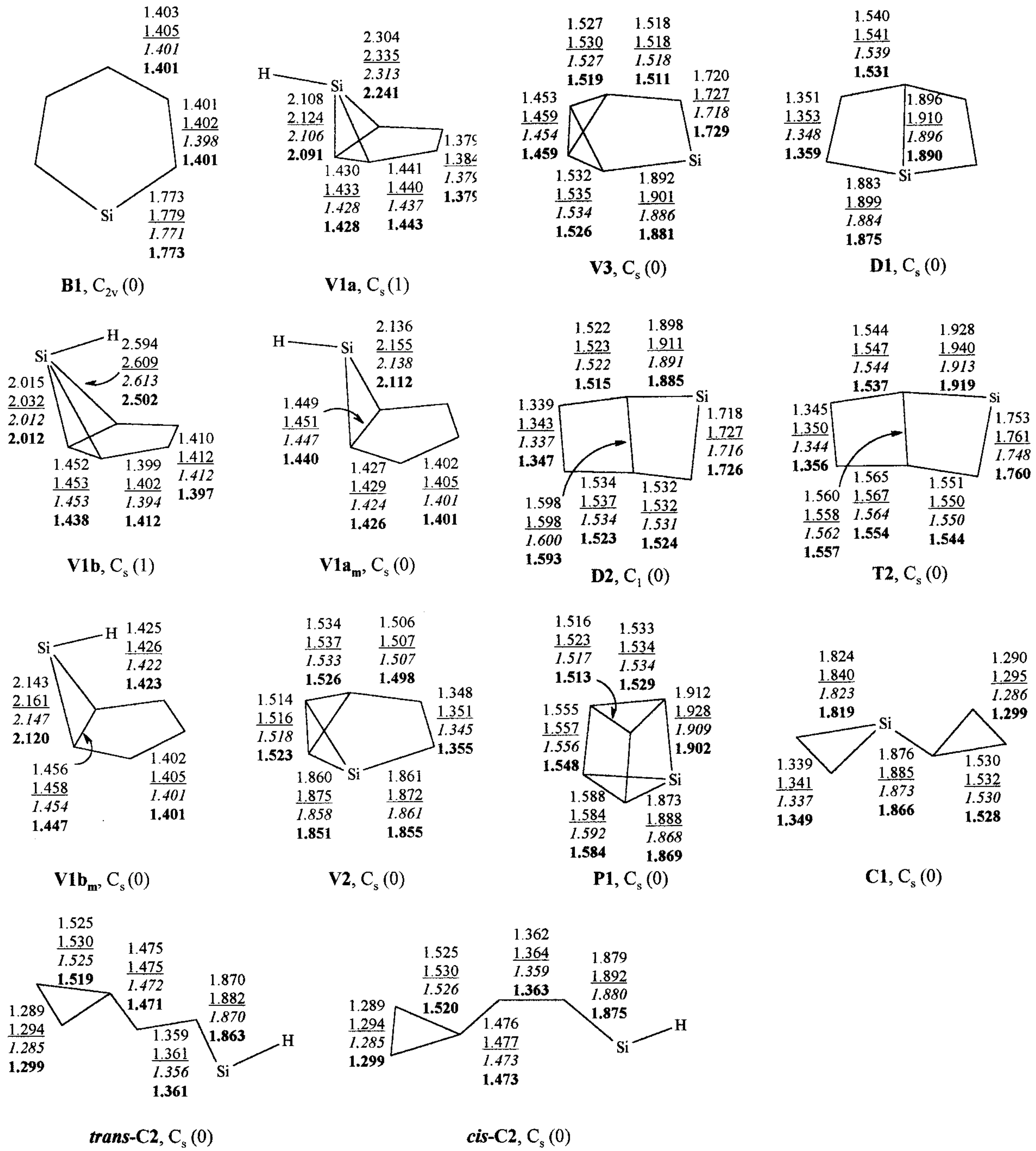

B1, C_{2v} (0); **V1a**, C_s (1); **V3**, C_s (0); **D1**, C_s (0); **V1b**, C_s (1); **V1a$_m$**, C_s (0); **D2**, C_1 (0); **T2**, C_s (0); **V1b$_m$**, C_s (0); **V2**, C_s (0); **P1**, C_s (0); **C1**, C_s (0); ***trans*-C2**, C_s (0); ***cis*-C2**, C_s (0)

Figure 1. Principal geometric parameters in the valence isomers of silabenzene obtained at the B3LYP level using 6-31G* (normal), cc-pVDZ (underlined), and 6-311+G** (italics) basis sets and the MP2/6-31G** level (bold). All values are given in Å. The number of imaginary frequencies is given in parentheses; the point group is also given.

five-membered ring has substantial aromatic stabilization. However, among the benzvalene isomers, only **V2** and **V3** retain the skeleton, and **V1** does not correspond to a stationary point and spontaneously collapses to **V1a** and **V1b**. This is in contrast with the valence isomers of pyridine, phosphinine, and arsabenzene, where all three benzvalene isomers were characterized as minima.[21] These two structures are transition states; the five-membered ring formed by the carbon atoms in the corresponding minimum energy structures, **V1a$_m$** and **V1b$_m$**, exhibits similar properties. It is interesting to note that the SiH unit is coordinated to only two carbon atoms. The bridging C−C bond of the bicyclobutane moiety in **V2** is 1.523 Å, which is elongated compared to 1.453 Å in the pristine compound at the same level of theory. This may be due to the release of strain caused by the presence of Si in the bicyclobutane moiety in **V2**. The comparable bond length in **V3** with the corresponding C−C bond length in pristine benzvalene confirms this.

In **C1**, ***trans*-C2**, and ***cis*-C2**, the bond lengths in the three-membered rings are shorter when compared to the corresponding standard bond lengths. The bridging C−C bond in **T2** is substantially shrunk compared to the C−C bond in the cis isomer, **D2**, whereas all other bonds are elongated.

Relative Energies. Table 1 gives the relative energies obtained at various levels of theory, including the

Table 1. Relative Energies Obtained at Various Levels of Theory and the Best Estimates of the Relative Energies of the Valence Isomers of Silabenzene; All Values Are Given in kcal/mol

structure	B3LYP/6-31G*	B3LYP/cc-pVDZ	B3LYP/6-311+G**	MP2/6-31G**	MP2/6-311+G**[a]	CCSD(T)/6-31G*[a]	best estimate[b,c]
B1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
V1a	25.2	24.0	26.8	20.5	20.2	22.2	21.0
V1b	30.5	29.0	31.5	28.0	27.5	28.9	27.5
$\mathbf{V1a_m}$	23.4	22.2	25.0	20.1	19.9	21.2	20.5
$\mathbf{V1b_m}$	27.6	26.5	29.1	24.4	24.2	25.4	24.9
V2	48.0	49.6	49.0	41.9	40.4	43.2	40.4
V3	78.0	78.4	79.3	69.5	68.9	71.1	68.8
D1	42.7	44.9	43.4	39.2	38.5	37.5	35.5
D2	72.1	72.9	72.9	65.9	64.9	64.8	62.4
P1	89.1	90.2	91.3	83.1	81.5	84.8	81.3
C1	85.4	87.9	84.0	84.2	82.9	82.2	78.2
***trans*-C2**	85.1	84.6	85.1	89.0	89.6	83.4	82.1
***cis*-C2**	88.0	87.4	88.0	91.9	92.4	86.0	84.6
T2	132.3	131.8	132.3	128.0	125.3	124.8	120.3
PY	61.2	59.0	61.9	59.4	56.3	61.7	55.8

[a] Single-point calculations on MP2/6-31G** optimized geometries. [b] The best estimates are calculated using eq 1. [c] The enthalpy correction obtained at the B3LYP/6-311+G** level, scaled with a factor of 0.98.

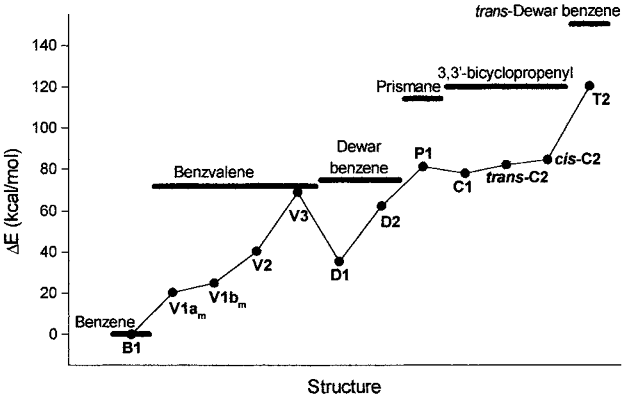


Figure 2. Correlation of the best estimates of relative energies of the valence isomers of silabenzene. The relative energies of corresponding benzene valence isomers are given for comparison.

best estimates calculated using eq 1. The trends obtained at various levels of theory are essentially identical with minor quantitative differences. The pure and hybrid density functional methods, including B3LYP, have inherent tendencies to overestimate the stabilization due to π-electron delocalization, and there are limitations in comparing the energies of localized and π-delocalized structures. This tendency is reflected in the present case also.[25] The discussion on the relative energies will be based on the best estimates throughout the paper unless otherwise specified. The scheme of best estimates employed in the paper, which includes CCSD(T)/6-31G* single-point calculation with basis set correction, was shown to be in good agreement with experimental and high-level theory on the valence isomers of benzene.[21]

Figure 2 illustrates the variation of the relative energies of the various isomers considered in the study. The best estimates of the relative energies for the corresponding valence isomers of benzene were also given in the same figure for comparison. The two transition states (**V1a** and **V1b**) and the pyramidal structure (**PY**) are excluded, as they do not correspond to minima on the potential energy surface. However, all silabenzene isomers lie closer to the reference compound, silabenzene indicating that the substitution reduces the energy gap among the various valence isomers. Thus, the transition state structures **V1a** and **V1b** lie just 21.0 and 27.5 kcal/mol high energetically above the most stable silabenzene, **B1**. It is to be noted that the corresponding energy difference between benzene and benzvalene is as high as 71.7 kcal/mol.[21] The two corresponding nonclassical valence isomeric minimum energy structures, $\mathbf{V1a_m}$ and $\mathbf{V1b_m}$, are less stable than silabenzene only by around 20 and 25 kcal/mol, respectively. The nonclassical nature of $\mathbf{V1a_m}$ and $\mathbf{V1b_m}$ coupled with their proximity to the silabenzene warrants experimental attempts toward them. **V3** is found to be thermodynamically less stable than the other benzvalene isomers, the reason being the weak π-bonding ability of Si with C.[26] The framework seems to broadly decide the relative energies to a greater extent compared to the substitution pattern. Thus the relative energy ordering is quite similar to those observed in the valence isomers of benzene. There is a striking differentiation in the stabilization of the positional isomer, depending on the nature of the replacement site; thus replacement by Si at the saturated site is overwhelmingly preferred compared to the unsaturated sites. Thus, although the skeletal replacement by Si causes substantial stabilization among the valence isomers of silabenzene in general, the stabilization is marginal in the isomers containing C═Si. Similarly the weak C═Si bond in **D2** makes it energetically above **D1**. **C1**, which has two strained three-membered rings, is expected to be less stable than ***trans*-C2** and ***cis*-C2**, both having only one three-membered ring. But, **C1** is observed to lie below both the **C2** isomers, which may be due to the presence of divalent silicon in the latter. The C═Si present in the *trans*-Dewar benzene isomer, **T2**, renders it as a least stable isomer and is computed to lie about 120 kcal/mol with respect to silabenzene. Interestingly, **PY**, which is a higher order saddle point, was computed to lie only 55.8 kcal/mol higher and becomes more stable than many other valence isomers of silabenzene. This adds to the amazing list of contrasts that were wit-

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Table 2. Frontier Orbital Energies along with the Mulliken Symbols and the Absolute Chemical Hardness (η) of the Valence Isomers of Silabenzene Obtained at the B3LYP/6-311+G Level; All Values Are Given in eV**

structure	ϵ_{HOMO}	ϵ_{LUMO}	$\eta = (\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}})/2$
B1	−6.02 (B_1)	−1.14 (B_1)	2.44
V1a$_{\mathbf{m}}$	−6.24 (A′)	−2.16 (A″)	2.04
V1b$_{\mathbf{m}}$	−5.70 (A′)	−2.36 (A″)	1.67
V2	−6.58 (A″)	−0.75 (A″)	2.91
V3	−5.23 (A″)	−1.10 (A″)	2.07
D1	−6.80 (A′)	−1.32 (A′)	2.74
D2	−5.81 (A)	−1.35 (A)	2.23
P1	−5.87 (A″)	−0.30 (A′)	2.78
C1	−6.78 (A′)	−0.78 (A″)	3.00
***trans*-C2**	−5.88 (A′)	−2.62 (A″)	1.63
***cis*-C2**	−5.81 (A′)	−2.74 (A″)	1.54
T2	−5.32 (A)	−1.83 (A)	1.75

nessed in the chemistries of organic and silaorganic compounds. In all cases, there is a significant destabilization in the isomers where the C═Si exists, a result in agreement with the classical double bond rule.

Vibrational Frequencies. In most of the rearrangement reactions it will be possible to obtain only some spectroscopic data, and these data do not facilitate unambiguous assignment. Thus computations have an important role in assisting the characterization of the short-lived intermediates. The vibrational data obtained at the B3LYP level with the 6-31G*, 6-311+G**, and cc-pVDZ basis sets are provided in the Supporting Information. The magnitudes and intensities are very similar at these three levels, and therefore the vibrational data provided in the table is expected to provide reliable reference data. Our study reveals that **V1a$_{\mathbf{m}}$** and **V1b$_{\mathbf{m}}$** are only about 20 and 25 kcal/mol higher in energy than the global minima, respectively. Interestingly, these structures are very stable compared to the Dewar benzene and other valence isomeric forms. Listing of the computed vibrational frequencies would enable the experimentalists to assign the stable species as well as reactive intermediates on the potential energy hypersurface of silabenzene. The magnitudes of the frequency corresponding to the first few normal modes, which correspond to skeletal rearrangement, are substantially lower when compared to benzene isomers. Thus, the skeletal rearrangements are expected to be more facile among the silabenzene isomers compared to the benzene valence isomers.

Frontier Orbital Energies and Chemical Hardness. Absolute chemical hardness (η) has been used as a measure of kinetic stability or the reactivity of organic compounds.[27] Within Koopman's approximation, hardness (η) is defined as half of the magnitude of the energy difference between the HOMO and the LUMO.[28]

$$\eta = (\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}})/2$$

The frontier orbital energies and the chemical hardness computed at the B3LYP/6-311+G** level are given in Table 2. While the thermodynamic stabilities of the compounds under study are controlled by the skeleton of their structure, the kinetic stability seems to be dictated by the bonding type of the Si atom. **C1**, **V2**, **P1**, and **D1**, where the Si occupies the sp^3 center, are kinetically more stable than the other isomers. Whereas **B1**, **D2**, **V3**, **V1a$_{\mathbf{m}}$**, **T2**, and **V2b$_{\mathbf{m}}$** are more reactive, in all these cases Si is tricoordinated. Compounds containing divalent Si, ***trans*-C2** and ***cis*-C2**, are found to be the least stable. So the kinetic stability exactly follows the following order: isomers containing tetracoordinated Si > isomers containing tricoordinated Si > isomers containing dicoordinated Si. The relative stabilities and the hardness values do not have a linear relationship. Thus, quite a few valence isomers (**V2**, **D1**, **P1**, and **C1**) have much higher hardness values than the benzvalene isomers, **V1a$_{\mathbf{m}}$** and **V1b$_{\mathbf{m}}$**, which are very stable energetically, according to the hardness criteria correspond to least stable compounds.

Conclusions

The present study provides equilibrium geometries, relative stabilities, and vibrational spectra of all the possible valence isomeric forms of silabenzene using the standard post SCF ab initio and the hybrid density functional methodologies. Out of the 15 isomers considered, 12 of them were characterized as minima on the potential energy surface, two of them were transition states, and one as a second-order saddle point. The spread of the relative energies of various silabenzene isomers is substantially smaller compared to the corresponding benzene valence isomers. Interestingly, while benzene is more stable than any other isomer by about 70 kcal/mol, **V1a$_{\mathbf{m}}$** is only about 20 kcal/mol higher in energy than the most stable silabenzene (**B1**). However, the relative energy ordering in silabenzene valence isomers is very similar to that in benzene valence isomers in general, barring some exception such as one of the bicyclopropenyl isomers, **C1**, is more stable than the prismane isomer, **P1**. The smaller magnitudes for the harmonic frequencies corresponding to skeletal reorganizations, compared to benzene, indicate that skeletal rearrangements among the valence isomers of silabenzene are more facile compared to the parent benzene. Thus, the energy gaps between the various valence isomers of silabenzene are smaller compared to the benzene valence isomers, indicating the smoother rearrangements. This smaller energy difference and lowering also account for the higher reactivity of silabenzene valence isomers toward isomerization reactions. The hardness (η) values taken as a measure of reactivity indicate that compounds having sp^3 Si atoms are less reactive compared to those having tri- and dicoordinated Si. The apparent disparity in energetic and hardness criteria in determining the stability and the high reactivity of this class of compounds is indicative of intricacies involved in making predictions. We feel that the present study and the recent advances in synthesis of bulky group protected silaaromatics should enthuse the experimentalists to explore the rich potential of the rearrangement reactions of silabenzene.

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Supporting Information Available: Tables of Cartesian coordinates of the B3LYP and MP2 optimized structures, total

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energies obtained at various levels, and the computed harmonic frequencies along with the intensities obtained at the B3LYP/6-31G*, B3LYP/cc-pVDZ, and B3LYP/6-311+G** levels of all the compounds considered in the study. The structure of **PY** is also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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