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Isomers of Disilabenzene ($C_4Si_2H_6$): A Computational Study

U. Deva Priyakumar, D. Saravanan, and G. Narahari Sastry*

Department of Chemistry, Pondicherry University, Pondicherry 605 014, India

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Computational studies using density functional theory (B3LYP) and coupled cluster (CCSD(T)) method were performed on a large number of isomers of disilabenzene, $C_4Si_2H_4$. In all, 78 stationary points were identified, wherein 61 of them correspond to the minima on the $C_4Si_2H_6$ potential energy surface. Although the planar forms correspond to the most stable isomers, several unconventional structures are highly competitive in energy. While the framework is an important factor, the substitution pattern seems to be equally important in deciding the relative stabilities of the isomers of disilabenzenes. The relative energies of valence isomeric forms are compared with those of benzene, silabenzene, and diphosphabenzene isomers. The relative energy orderings of all the isomers are analyzed, and conclusions about the stability are drawn. Several H-bridged isomers were computed to be very stable. Several monocyclic six-membered ring structures, where the 6π-aromaticity is disturbed, also indicated the flatness of the potential energy surface of disilabenzene and their propensity toward high reactivity and facile rearrangements.

Introduction

The analogy between carbon and silicon appears to be straightforward, despite the substantial contrasts in the chemistry of hydrocarbons and their silicon-substituted counterparts.[1−4] The simplest silicon analogue of benzene—silabenzene—has been a subject of great interest for quite some time.[4−8] Although the parent compound of silabenzene remained an elusive species, the strategy of employing bulky groups attached to the Si center resulted in an unambiguous characterization of the substituted silabenzene.[5,6] Nonetheless, various spectroscopic studies on the identification of silabenzene and its isomerization to other products were known for quite some time.[7,8] The concept of silaaromaticity is one of the most intensely studied topics in the last three decades.[4−13] A large number of theoretical studies confess aromaticity on silabenzene, where one of the methine groups is replaced by SiH.[9−12] However, hexasilabenzene, $(SiH)_6$, is far from being aromatic.[13] Theoretical studies indicate that the most stable valence isomer of $(SiH)_6$ is the prismane analogue, and this is 9.5 kcal/mol more stable than the benzene analogue.[13d] In this context, it is interesting to explore how the relative energies of various valence and related isomers vary going from silabenzene to disilabenzene.

Experimental interest in mono- and disilaaromatic compounds has been very high.[5−8] The interplay between theory and experiments helped a great deal in discerning the novel contrasts between silaaromatics and their hydrocarbon analogues. Even though silabenzene was observed in an argon matrix quite a while ago, it was found to be unstable at room temperature due to its high reactivity.[7,8] Among the disilabenzene isomers, hexamethyl-substituted 1,4-disilabenzene (**3**) has been synthesized as early as 1987, and several photochemical reactions were studied.[14] Also, recent studies indicate the existence of silabenzene and 1,4-disilabenzene as ruthenium complexes.[15] Ando et al. have successfully

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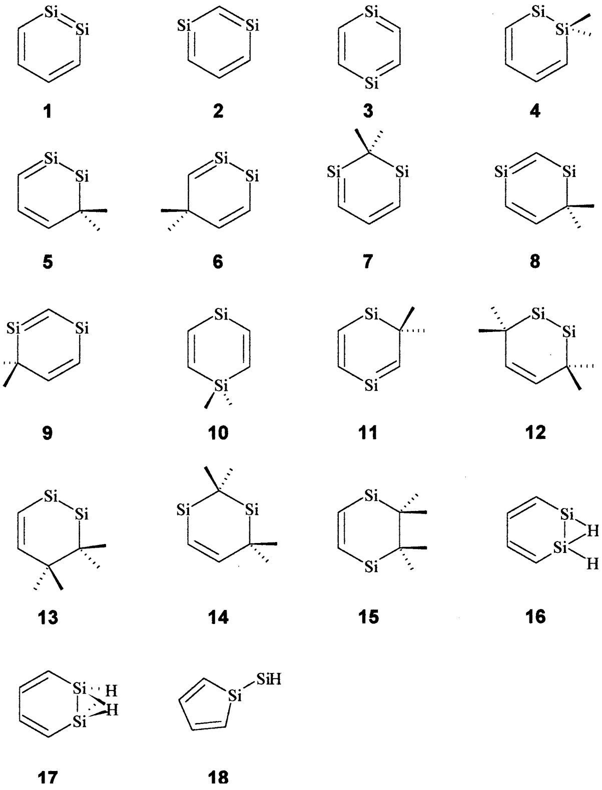
synthesized **40**, which yields **25** and **49** on heating, and proposed the possible common intermediate for both the conversions to be **42**.[16] Even though **37** and **46** are not valence isomers, we have considered them in this study, as their derivatives have been synthesized recently.[17]

Considering the experimental interest in the isomerization reactions among the various forms of disilabenzene, we ventured into a detailed theoretical study on disilabenzene isomers. Baldridge and Gordon reported theoretical studies on the three disilabenzenes **1**, **2**, and **3** using the HF method with the STO-3G basis set.[18] In 1985, Chandrasekhar and Schleyer have reported the HF/3-21G* energetics of **3**, **10**, **11**, and **25**.[19] Recently, Ando and co-workers used the HF method with the 6-31G* basis set to evaluate the energetics of **3**, **25**, **49**, **40**, and **42**.[16] Yoshizawa and co-workers reported a detailed computational study on the isomerization reaction between 1,4-disilabenzene (**3**) and 1,4-disila Dewar benzene (**25**) using the density functional B3LYP and CASSCF procedures employing a double-ζ basis set.[20] There has been a lot of interest in the isomerization reactions among the valence isomers of benzene and group V heterobenzenes in addition to that of silabenzene and disilabenzene.[21,22] We have reported computational studies on the valence isomers of benzene and group V heterobenzenes.[22] Recently, we reported theoretical calculations on the valence isomers of silabenzene, which identifies that 12 minima exist on the $(CH)_5SiH$ potential energy surface.[4] The experience with the study on monosilabenzene revealed that disilabenzene would be even more interesting. The computational studies done on these systems are limited in terms of number of isomers considered.

The present study reports B3LYP and CCSD(T) computed results of disilabenzene valence isomers and some related structures (Schemes 1−4). By no means have we considered all the possible isomers. For example, benzene has more than 200 isomers. Thus $C_4Si_2H_6$ will have well over 1000 isomers. But, in this study a systematic attempt is made to consider most of the stable isomeric forms. The structures considered are classified as (a) monocyclic, (b) bicyclic, (c) tricyclic, and (d) tetracyclic. The equilibrium geometries of all the stationary points located on the potential energy surface and their relative energies are discussed in the above order. Comparisons were made with the corresponding benzene, silabenzene, and diphosphabenzene valence isomers in some instances.

Scheme 1



Computational Details

All the structures given in Scheme 1 were fully optimized within the symmetry constraints at the B3LYP level with the 6-31G* basis set. The stationary points obtained using the default gradient procedures were characterized on the basis of the frequency calculations. The normal modes corresponding to the imaginary frequencies of the transition states and higher order saddle points were followed, and the true minima were located. Single-point energy calculations at the B3LYP/cc-pVTZ level on the B3LYP/6-31G* optimized geometries were done to estimate the effect of basis set on the relative energies. Although the gradient-corrected hybrid density functional methods are well suited for describing the equilibrium geometries, these methods show a tendency to slightly overestimate the stability of delocalized structures compared to the nondelocalized structures.[23] The coupled cluster method was found to yield excellent energetics for this class of compounds.[21b] Therefore, we have performed CCSD(T) single-point calculations with the 6-31G* basis set on the B3LYP optimized geometries. To account for the inadequacy of the 6-31G* basis set at the CCSD(T) level, we have done basis set corrections using the density functional theory results as shown in the following equation. The best estimate, ΔE, given in following equation is expected to yield results similar to those at the CCSD(T)/cc-pVTZ level, even though the effect of an increase in the quality of the basis set is evaluated only at the B3LYP level. Similar equations provided energies that are in excellent quantitative agreement with those obtained at the G2 level of theory for the benzene valence isomers.[22,24]

$$\Delta E = \Delta E_{\mathrm{CCSD(T)}} + \Delta E_{(\mathrm{B3LYP/cc-pVTZ\ -\ B3LYP/6-31G^*})} + \Delta H \tag{1}$$

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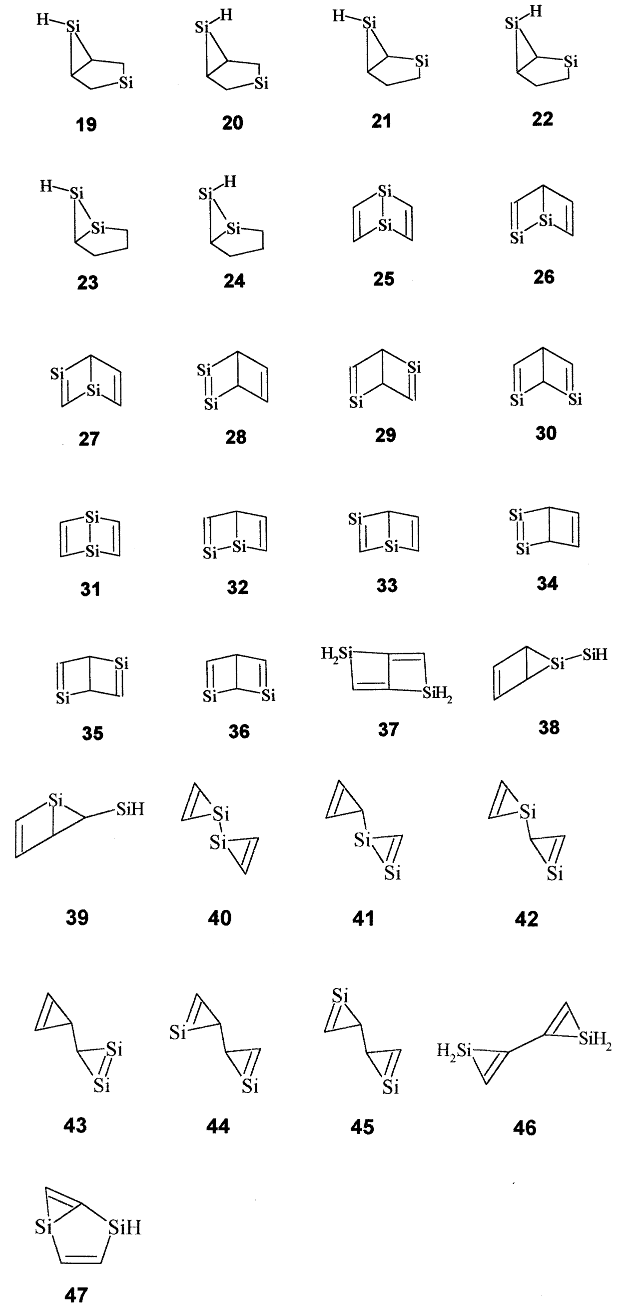
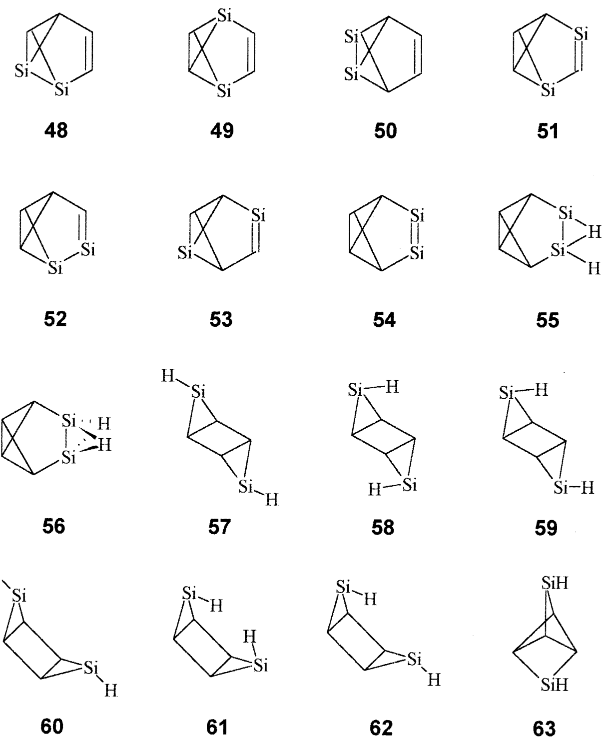
Scheme 2

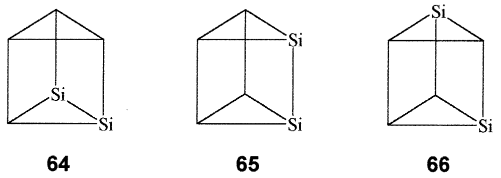


Enthalpy correction values (ΔH) are included from the frequency data obtained at the B3LYP/6-31G* level. All the theoretical methodologies employed are based on the single determinantal approach. Hence, we have performed CASSCF and CASPT2[25] calculations with 6-31G* and cc-pVDZ basis sets by including the π-system in the active space for **1**, **2**, and **3**. The coefficients of the major Slater determinant are found to be more than 0.92 in all the cases at the CASSCF level with either the 6-31G* or cc-pVDZ basis set. This indicates that nondynamic electron correlation is not decisive and single determinantal approaches adequately describe the electronic structure and bonding in this class of compounds. All density functional theory calculations were performed using the Jaguar 4.1 program package.[26] The Gaussian 98 suite of programs[27] was used to perform the CCSD(T), CASSCF, and CASPT2 calculations. The graphical interface program MOPLOT was used to examine the equilibrium geometries.[28]

Scheme 3



Scheme 4



Results and Discussion

A total of 66 isomers were considered initially (Schemes 1−4). Upon geometry optimization and characterization of the nature of the stationary points of all the structures considered, 61 of them were confirmed as the true minima possessing all real harmonic frequencies. However, some are found to be transition states, some are higher order saddle points, and some do not correspond to a stationary point on the disilabenzene potential energy surface. The normal modes corresponding to the imaginary frequencies of the saddle points were followed in each case, and the minimum energy structures were

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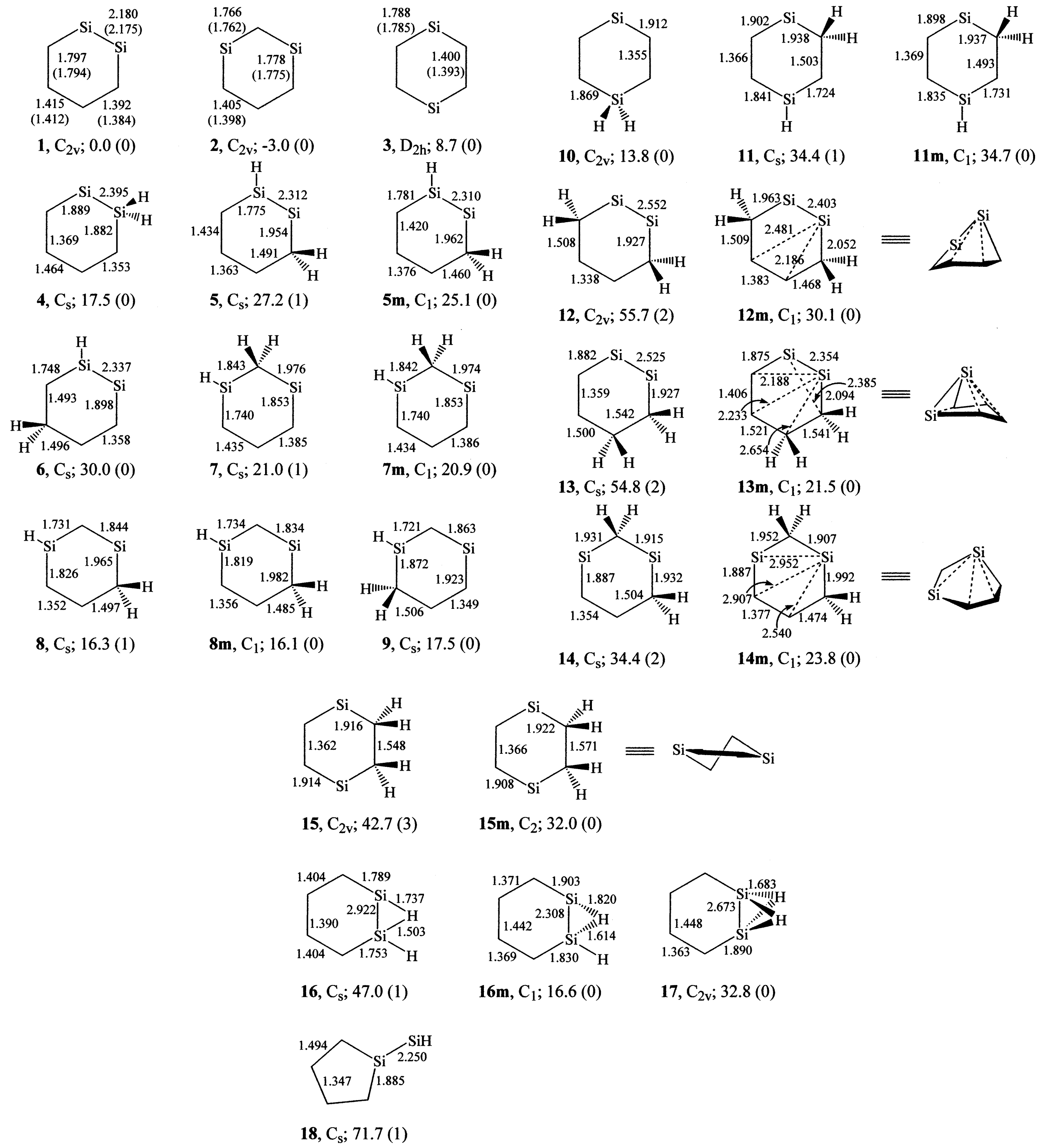

Figure 1. Principal geometric parameters of the monocyclic isomers obtained at the B3LYP/6-31G* level. Those obtained at B3LYP/cc-pVTZ are given in parentheses only for **1**, **2**, and **3**. All values are given in Å.

obtained, which increases the total number of stationary points to 78. Among them, 61 were characterized as minima, 12 as transition states, four as second-order saddle points, and one structure was found to be a third-order saddle point. The equilibrium geometries of the stationary points and their nature on the potential energy surface are discussed first. They are arranged in the following order: monocyclic, bicyclic, tricyclic, and tetracyclic isomers. Then, the relative energies of the various isomers are discussed. Various factors controlling the relative energy orderings are addressed briefly in general as well as in each group of the positional isomers.

Equilibrium Geometries: Monocyclic Isomers. Figure 1 depicts the important geometric parameters of the disilabenzenes and other monocyclic isomers obtained at the B3LYP/6-31G* level. For the disilabenzenes (**1**−**3**) the reported bond lengths obtained at the B3LYP/cc-pVTZ level are given in parentheses.[9] The geometric parameters obtained using the two basis sets are very similar, with a maximum deviation of 0.007 Å. A detailed study of skeletally disubstituted benzenes and the various factors that affect the relative stability ordering are analyzed by us and others elsewhere.[29,30]

We also have considered some monocyclic structures (**4**−**15**) where the π-delocalization in the three disilabenzenes is disrupted and concomitantly one or both the Si atoms become divalent. Among the monocyclic isomers with one divalent silicon (**4**−**11**), the planar forms of those structures where the divalent silicon is present adjacent to a CH_2 group are found to be transition states (**5**, **7**, **8**, and **11**). The corresponding minimum energy structures (**5m**, **7m**, **8m**, and **11m**) were then identified. Importantly, at the CCSD(T) level, **8m** and **11m** lie higher in energy compared to **8** and **11**, respectively. This reveals that the planar forms are very likely to be minima at the CCSD(T) level, indicating that the B3LYP method incorrectly designates the nature of the planar molecules. This indicates that the out-of-plane distortion may be traced to the limitation of the B3LYP method, and a similar observation was made earlier.[27b] All the molecules with two divalent silicon atoms are found to be higher order saddle points (**12**−**15**). The minimum energy structures **12m**, **13m**, and **14m** correspond to pyramidal like structures, with one of the Si atoms forming the apex of the pyramid. Unlike in the previous case, the planar forms lie much higher in energy compared to the nonplanar structure. **16**, where one of the hydrogens is bridged between the two Si atoms, is found to be a transition state. The Si−Si bond length is too long (2.922 Å), and the connection between the two may be traced mainly through the bridging hydrogen atom. The normal mode of the imaginary frequency corresponds to the puckering of the bridged hydrogen, which was then followed and **16m** was obtained. Therefore, **16** may be treated as a transition state interconnecting the two identical forms of **16m**. In **16**, all the C−C and C−Si bonds are almost comparable to the aromatic bond lengths, whereas in the minimum energy structure (**16m**) the bonds are localized. Similar to **16**, the Si−Si bond length in **17** is substantially elongated, with the bridging hydrogens strongly bound to both the silicon atoms. **18** is found to be a transition state and following the normal mode corresponding to the imaginary frequency yielded **48**.

Bicyclic Isomers. The equilibrium geometries of the bicyclic isomers (Scheme 2) considered in the present study are discussed in this section. Figure 2 gives the principal geometric parameters of the bicyclic isomers obtained at the B3LYP/6-31G* level. In our previous study on the silabenzene valence isomers, we identified two bicyclic structures where a SiH unit is bound to a cyclopentadienyl species in a η^2 fashion.[4] These unusual structures were found to be the next stable species to silabenzene on the $(CH)_5SiH$ potential energy surface. We have considered similar structures, **19**−**24** (Scheme 2), out of which stationary points corresponding to **19**, **20**, **22**, and **24** could be located and were found to be minima. Initial structures of **21** and **23** upon optimization collapsed to **48**, indicating that these are not stationary points on the potential energy surface. In **24**, the C−Si bond with the η^2-bound SiH moiety seems to be too long, and in contrast the Si−Si bond length is quite normal, indicating that its connectivity is close to that found in **18**. The greater stabilization in **24** compared to **18** may be traced to the higher delocalization in the five-membered ring in the former.

The stationary points corresponding to the six Dewar benzene isomers (**25**−**30**) were obtained, and the frequency calculations indicate that all the Dewar benzene isomers are minima except **28**. In all the cases except in **25**, the bridging bond is longer compared to the corresponding standard bond lengths, a feature that is observed in the parent Dewar benzene itself.[22c] The Si−Si distance in **27** is computed to be too short. However, the bond order calculated using Atoms in Molecules (AIM)[31] at the B3LYP/6-31G* level of theory is only 0.04, suggesting that a bond between the two Si atoms does not exist. The normal mode of the imaginary frequency in **28** corresponds to the out-of-plane distortion of the hydrogen atoms connected to the two Si atoms. The minimum energy structure corresponding to **28** is obtained following the direction of the imaginary frequency normal mode. **28m** is found to have a twisted double bond, where the hydrogens connected to the Si atoms stay out-of-plane. This is similar to the situation in the silicon analogue of ethylene, where the D_{2h} form of $H_2Si{=}SiH_2$ is a transition state; the corresponding minimum energy structure involves substantial pyramidalization at the Si center.[32] Thus there seems to an inherent tendency for the Si=Si to have a puckered geometry, but considering the fact that the planar 1,2-disilabenzene (**1**) corresponds to minima, this puckering could be prevented when a stronger symmetrizing force is operative. All of our attempts to locate a stationary point corresponding to **32** were futile; upon geometry optimization, the initial structures collapsed to **48**. The frequency calculations designate the five stationary points for the *trans*-Dewar benzenes as minima on the potential energy surface. In all the isomers except in **33**, the bridging bond is short compared to that in the corresponding *cis* compound. Most of the computed peripheral bond lengths in the *trans*-Dewar benzene isomers are longer compared to those in the *cis* isomers, which is indicative of higher strain in the *trans* isomers. Similar to **27**, despite the Si−Si interatomic distance of 2.476 Å in **33**, the bond order calculation does not support any bond between the Si atoms.

Among the bicyclopropenyl isomers (**40**−**45**), **43** is computed to be a transition state. The normal mode of the imaginary frequency corresponds to the out-of-plane distortion of two hydrogens connected to the Si atoms. Optimizing **43** with the two hydrogen atoms out-of-plane lead to ***t*-43m**, where one of the C−Si bonds becomes too long to give a monocyclic compound, with only one three-membered ring. In the process, the sp^3 carbon has become an sp^2 carbon and one of the Si atoms becomes

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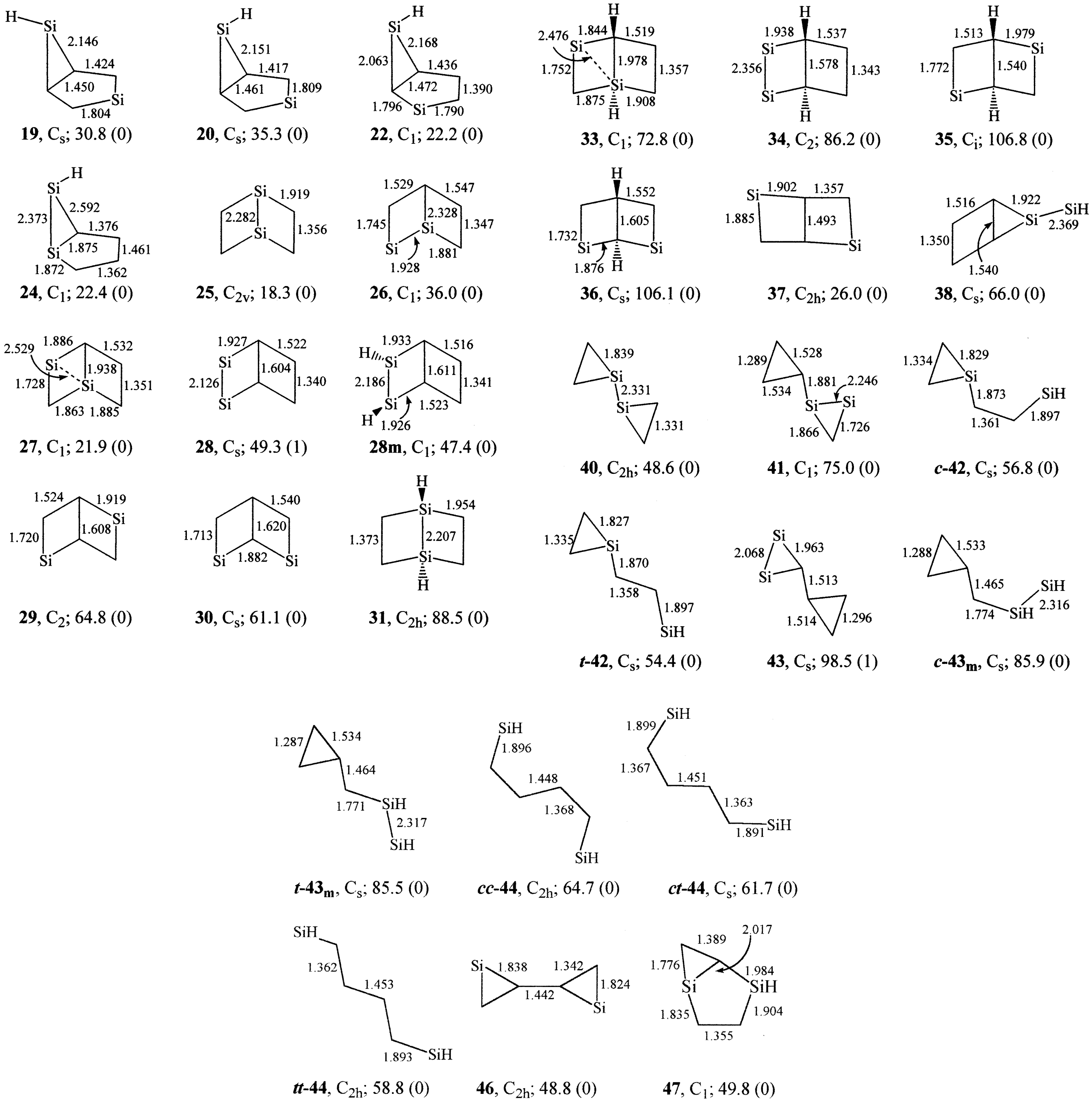
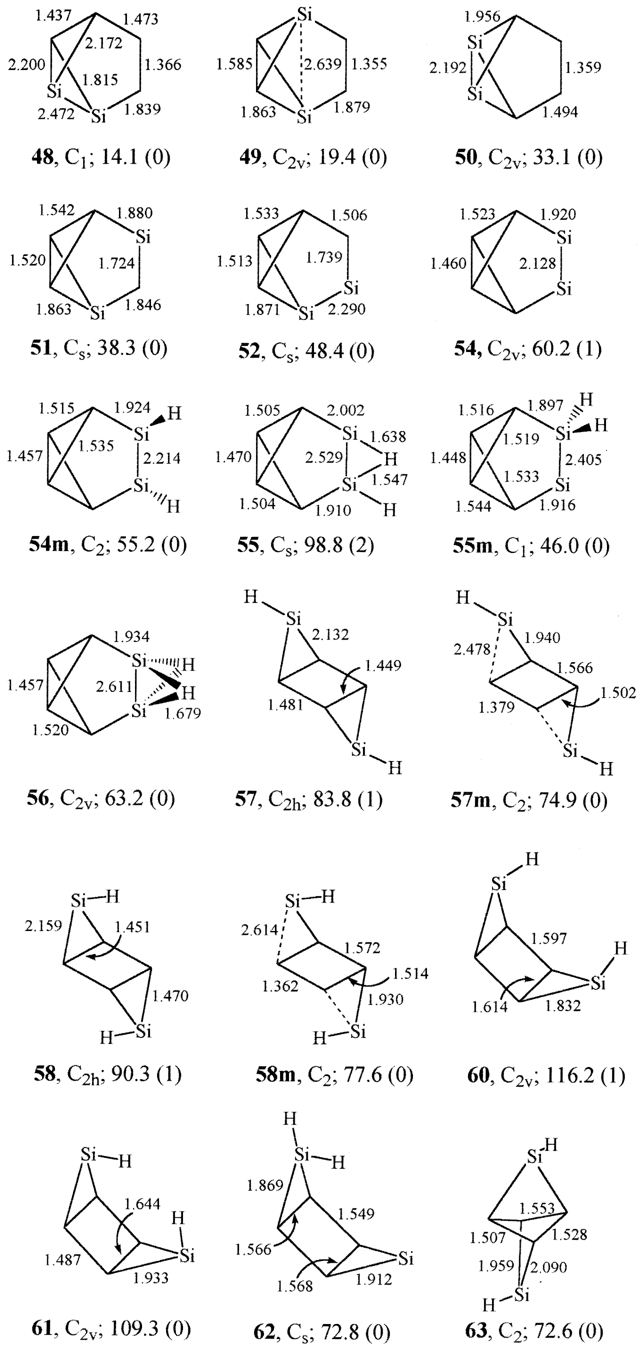


Figure 2. Principal geometric parameters of the bicyclic isomers obtained at the B3LYP/6-31G* level. All values are given in Å.

divalent. The corresponding *cis* isomer, ***c*-43m**, was also optimized and was characterized as a minimum. Similarly, **42** on optimization leads to a monocyclic compound, ***t*-42**, with one divalent silicon; the *cis* compound ***c*-42** was also then identified. Both **44** and **45** upon optimization collapse to an acyclic compound, ***tt*-44**, with two divalent silicon atoms; the corresponding *cis*–*trans* isomers (***cc*-44** and ***ct*-44**) were then characterized as minima on the disilabenzene potential energy surface. The opening of the ring containing a tricoordinated Si is similar to our observation made in one of the monosilabicyclopropenyl isomers.[4] This contrast with the parent bicyclopropenyl can be explained on the basis of the instability of the divalent carbene compared to the divalent Si. The propensity of three-membered rings containing a tricoordinated Si for ring opening may be understood on the basis of the following points: (1) it relieves strain in the three-membered ring, (2) one C–Si π-bond is replaced by a C–C π-bond, (3) it leads to divalent Si.

Isomers **37** and **46**, where all the hydrogens are replaced by tertiary butyl groups, have been synthesized recently, and a photochemical rearrangement reaction has been observed between these two compounds.[17] In both cases, especially in **46**, the Si–C single bond lengths are slightly shortened compared to the standard bond length. **38** is computed to be minima, while its positional isomer, **39**, is a transition state. Following the normal mode corresponding to the imaginary frequency and optimizing, this collapsed to **22**.



48, C_1; 14.1 (0) **49**, C_{2v}; 19.4 (0) **50**, C_{2v}; 33.1 (0)

51, C_s; 38.3 (0) **52**, C_s; 48.4 (0) **54**, C_{2v}; 60.2 (1)

54m, C_2; 55.2 (0) **55**, C_s; 98.8 (2) **55m**, C_1; 46.0 (0)

56, C_{2v}; 63.2 (0) **57**, C_{2h}; 83.8 (1) **57m**, C_2; 74.9 (0)

58, C_{2h}; 90.3 (1) **58m**, C_2; 77.6 (0) **60**, C_{2v}; 116.2 (1)

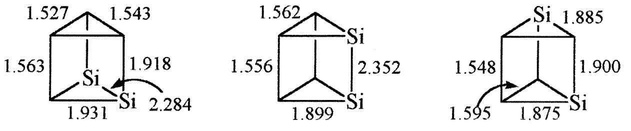
61, C_{2v}; 109.3 (0) **62**, C_s; 72.8 (0) **63**, C_2; 72.6 (0)

Figure 3. Principal geometric parameters of the tricyclic isomers obtained at the B3LYP/6-31G* level. All values are given in Å.

Tricyclic Isomers. The principal geometric parameters of all the tricyclic isomers obtained at the B3LYP/6-31G* level are given in Figure 3. Initially, efforts were made to locate the stationary points for the seven possible disilabenzvalene isomers (**48**−**54**) depicted in Scheme 3. However, exhaustive attempts could not yield a stationary point corresponding to **53**. All the putative structures of **53**, upon optimization, relaxed to **48**. Thus, the computations imply that **53** is not a stationary point on the disilabenzene potential energy surface. All other stationary points were characterized as minima, except **54**, which was characterized as a transition state. Seven disilabenzvalenes were located, out of which six were characterized as minima. In **48** the Si atom, which is in the bridgehead of the bicyclobutane moiety, is weakly bound to two carbon atoms and the other silicon. However, this isomer is the one that is energetically more stable, compared to the other benzvalene isomers. The five-membered ring formed by one of the Si atoms and the four carbon atoms is virtually planar, and the bond distances are substantially short compared to the corresponding standard single bond lengths. This situation is very similar to that observed in the monosilabenzene isomer, where the most stable silabenzvalene isomer is aptly described as an SiH^+ ion bound to the cyclopentadiene anion in η^3 fashion.[4] Thus, **48** may be considered as an SiH^+ ion bound to the silacyclopentadienyl species in an η^3 fashion to the CCSi portion. The computed bond lengths in **49**, **51**, and **52** exhibit normal bond distances except for the bridging bond of the bicyclobutane moiety in **49**, which is slightly elongated. In **49**, the Si−Si distance is computed to be only 2.639 Å. In **50**, the computed Si−Si and C−C single bond lengths are shorter compared to the normal bond lengths. The frequency calculation characterizes **54** as a transition state and the imaginary frequency normal mode corresponding to out-of-plane distortion of the hydrogens attached to the Si═Si, similar to the situation in **28** and **43**. Following this normal mode, the minimum energy structure **54m** is reached, where the silicon center is pyramidal. In both **54** and **54m**, the bridging bond of the bicyclobutane moiety is found to be very short compared to the corresponding C−C bond in other isomers.

Benzvalene isomer **54**, with one hydrogen bridging between the two Si atoms (**55**), was computed to be a second-order saddle point. Following the normal modes of the imaginary frequencies, the structure **55m** was obtained, which has a tetravalent and a divalent Si. However, similar structure **56**, with two bridging hydrogens, was computed to be a minimum energy structure. In **56**, the Si−Si bond length is too long compared to the normal Si−Si single bond distance. Similar to the structures **19**−**24**, we have considered **57**−**63**, where two SiH units are bound to a cyclobutadiene moiety in various possible modes. Among these structures, **61** and **63** are minima; **57**, **58**, and **60** are computed to be transition states. Many attempts to locate a stationary point corresponding to **59** failed, and all the initial geometries collapsed to **20** upon optimization. **57m** and **58m** correspond to distorted forms of **57** and **58**, respectively, where two C−Si bonds are significantly elongated. These compounds can be viewed as cyclobutenes, where two hydrogens connected to sp^3 carbon atoms are substituted by SiH units. Distorting the skeleton of **60** following the normal mode of the imaginary frequency and optimizing lead to **20**. Initial structures of **62** on optimization lead to a molecule where one of the Si is tetravalent with two hydrogens connected and the other is divalent Si (Figure 3).

Tetracyclic Isomers. All the three structures were located and characterized as minima on the potential energy surface. The important geometric parameters of the three prismane isomers obtained at the B3LYP/6-31G* level are depicted in Figure 4. In all three isomers, the strain due to the replacement of two Si atoms in the parent prismane moiety is reflected in the bond angles and dihedral angles and not in the bond lengths.



64, C_s; 56.3 (0) **65**, C_{2v}; 67.0 (0) **66**, C_2; 56.0 (0)

Figure 4. Principal geometric parameters of the tetracyclic isomers obtained at the B3LYP/6-31G* level. All values are given in Å.

Table 1. Relative Energies of 2 and 3 with Respect to 1 Obtained at Various Levels of Theory (all values are given in kcal/mol)

method	2	3
HF/6-31G*	−2.6	13.4
HF/cc-pVDZ[b]	−1.9	14.2
B3LYP/6-31G*[a]	0.0	10.5
B3LYP/cc-pVDZ[b]	1.2	9.8
CASSCF/6-31G*[e]	2.2	12.5
CASSCF/cc-pVDZ[e]	4.0	14.5
CASSCF/cc-pVDZ	4.2	14.7
MP2/6-31G**[c]	−0.7	9.8
CASPT2/6-31G*[e]	−6.7	9.2
CASPT2/cc-pVDZ[e]	−5.5	10.7
MP3/6-31G*[c,d]	0.7	11.3
MP4SDQ/6-31G*[c,d]	0.0	10.9
CCSD/6-31G*[c,d]	−0.3	11.0
CCSD(T)/6-31G*[c,d]	0.0	10.6
B3LYP/cc-pVTZ[a,e]	−3.1	8.5
B3LYP/cc-pVTZ[b]	−3.0	8.3
MP2/6-311+G**[c,d]	−4.6	7.1
MP2/cc-pVTZ[b]	−3.2	8.7
CCSD(T)/cc-pVTZ[b,f]	−3.3	8.9

[a] This work. [b] Taken from ref 9. [c] Taken from ref 27b. [d] Single-point calculations on the MP2/6-31G** optimized geometries. [e] Single-point calculations on the B3LYP/6-31G* optimized geometries. [f] Single-point calculations on the B3LYP/cc-pVTZ optimized geometries.

However, all the C−Si bond lengths are slightly elongated, indicative of the strain present in the prismane.

Relative Energies. The relative energies of the three disilabenzenes have been studied extensively by theoretical calculations of various sophistication, the results of which are given in Table 1.[9,29b] The complexities in choosing the reliable computational procedures for silabenzenes were thoroughly investigated by Baldridge et al., and their systematic and elaborate calculations on a series of silabenzenes inferred that the B3LYP level with a cc-pVTZ quality basis set is a reliable approach for getting the correct energetics compared to the conventional HF or MP2 methodologies.[9] The B3LYP/cc-pVTZ method, which was shown to yield results comparable to that of the CCSD(T)/cc-pVTZ level, is chosen as the method of choice in this study to model the other nonplanar isomers considered. Considering the lack of multideterminantal nature of the wave functions, the CASSCF and CASPT2 approaches do not seem to be appropriate for this class of compounds. Table 1 reflects that the qualitative agreement of MP2 and B3LYP is much better with higher level calculations compared to that of CASPT2. The B3LYP/6-31G*, B3LYP/cc-pVTZ, and CCSD(T)/6-31G* relative energies and the best estimates of the relative energies obtained using eq 1 are given in Table 2. The B3LYP level computed relative energies using the 6-31G* and the cc-pVTZ basis sets are in close agreement with each other, with a maximum deviation of 3.5 kcal/mol. The qualitative trend of the relative stabilities obtained at all the levels of theory employed is essentially the same. The discussion on the energetics will be based on the best estimates of the relative stabilities unless otherwise stated.

Monocyclic Isomers. Among the three disilabenzenes (Figure 1), only the derivative of 1,4-disilabenzene, **3**, is experimentally known, and rearrangement reactions have been studied.[14−16] Interestingly, this is the least stable isomer among the three disilabenzenes. 1,3-Disilabenzene (**2**) is found to be more stable than 1,2-disilabenzene (**1**) by about 3 kcal/mol. This is in contrast to the situation in diphosphabenzenes, where 1,2-diphosphinine was found to be the global minimum.[21a] The relative stability ordering of the skeletally substituted benzenes has been one of the most intriguing aspects, and several mutually independent factors were found to be responsible. We have addressed this topic by invoking several factors such as sum of bond strengths, topological charge stabilization, electrostatic repulsion, out-of-plane distortivity, and hardness.[29]

Among the monocyclic isomers, where the π-delocalization is disrupted (**4**−**15**), **10** is found to be the most stable one and is found to lie only about 5 kcal/mol above its aromatic counterpart, **3**, whereas **4** is less stable than its disilabenzene counterpart, **1**, by about 17 kcal/mol. This indicates that it is more expensive to disrupt the π-delocalization in **1** than in **3**. Among those structures, where one of the silicon is divalent and the other Si is tricoordinated (**5**−**9**, **11**), **7m**, **8m**, and **9** are more stable than the rest. The origin may be traced to the preference of the Si atom to occupy the 1,3 positions for electrostatic reasons. Among the planar forms of the compounds containing two divalent silicon atoms (**12**−**15**), **14** is the most stable one, where the two Si atoms occupy the 1,3 positions. These structures were computed to be higher order saddle points. Among the nonplanar isomers, **13m** is the most stable, where one of the Si atoms is bound to the other Si and three carbon atoms. **16m** is less stable than **1** by 16 kcal/mol even though they possess equivalent skeletons. This may be due to the fact that the bridging brings in localization in the benzene skeleton, which is reflected in the geometries. This effect is furthered in the dibridged structure **17**, which lies around 32 kcal/mol higher than **1**.

Bicyclic Isomers. In addition to the classical valence isomeric analogues, Dewar benzene and bicyclopropenyl, several other isomers were considered in this category. Similar to the case in a monosilabenzene isomer, where SiH is coordinated to the cyclopentadienyl moiety in a η^2 fashion,[4] **22** and **24** lie only about 25 kcal/mol higher than the global minima. The charge analysis indicates that the five-membered ring formed by one Si and the four carbon atoms is negatively charged and the SiH possesses positive charge. The high stability of this class of compounds may be attributed to the aromatic stabilization of the five-membered ring, an observation made in our previous study on the silabenzene potential energy surface.[4]

Among the Dewar benzene isomers (**25**−**30**), **25** is the most stable isomer and lies only about 21 kcal/mol higher than the global minima. In this isomer, both the silicon atoms are tetracoordinated. It is to be noted that the parent Dewar benzene is less stable than benzene by about 75 kcal/mol. **27** and **26**, where one of the Si is

Table 2. Relative Energies (kcal/mol) of the Isomers of Disilabenzene Obtained at the B3LYP and CCSD(T) Levels and the Best Estimates of Relative Energies (number of imaginary frequencies (NIMG) obtained at B3LYP/6-31G* is also given)

structure	NIMG	B3LYP/ 6-31G*	B3LYP/ cc-pVTZ[a]	CCSD(T)/ 6-31G*[a]	best estimate[b]	structure	NIMG	B3LYP/ 6-31G*	B3LYP/ cc-pVTZ[a]	CCSD(T)/ 6-31G*[a]	best estimate[b]
1	0	0.0	0.0	0.0	0.0	**33**	0	81.2	78.6	77.5	72.8
2	0	0.0	−2.4	0.1	−3.0	**34**	0	93.7	94.9	86.4	86.2
3	0	10.5	9.5	10.7	8.7	**35**	0	118.2	118.1	109.5	106.9
4	0	16.9	18.5	16.1	17.5	**36**	0	117.1	115.1	110.2	106.1
5	1	24.7	26.6	24.4	27.2	**37**	0	31.1	30.7	30.3	26.0
5m	0	22.8	23.9	23.1	25.1	**38**	0	69.4	70.7	66.2	66.0
6	0	29.1	30.9	27.0	30.0	**40**	0	53.6	51.8	52.7	48.6
7	1	21.1	20.5	21.2	21.0	**41**	0	84.0	81.7	79.9	75.0
7m	0	21.0	20.5	21.2	20.9	***c*-42**	0	61.0	60.1	59.9	56.8
8	1	18.1	17.4	16.4	16.3	***t*-42**	0	58.2	57.3	57.3	54.4
8m	0	18.1	17.0	16.7	16.1	**43**	1	106.2	105.9	100.9	98.5
9	0	20.9	19.9	17.9	17.5	***c*-43m**	0	86.9	88.2	86.9	85.9
10	0	17.8	17.8	14.7	13.8	***t*-43m**	0	86.6	87.7	86.5	85.5
11	1	37.1	37.3	34.4	34.4	***cc*-45**	0	63.9	65.4	64.4	64.7
11m	0	37.1	37.0	35.0	34.7	***ct*-45**	0	61.2	62.6	61.4	61.7
12	2	54.2	55.5	52.3	55.7	***tt*-45**	0	58.3	59.7	58.6	58.8
12m	0	30.5	32.2	25.5	30.1	**46**	0	53.2	53.1	53.3	48.8
13	2	50.9	53.4	50.2	54.8	**47**	0	53.4	52.0	53.3	49.8
13m	0	22.5	24.9	16.0	21.5	**48**	0	18.2	18.1	14.9	14.1
14	2	36.5	36.7	32.9	34.4	**49**	0	27.8	25.8	23.2	19.4
14m	0	25.3	25.9	20.8	23.8	**50**	0	39.6	38.7	35.5	33.1
15	3	43.6	44.6	40.1	42.7	**51**	0	46.9	45.2	41.7	38.3
15m	0	35.9	36.0	29.9	32.0	**52**	0	54.6	55.6	48.7	48.4
16	1	46.3	44.2	49.7	47.0	**54**	1	66.3	68.3	59.3	60.2
16m	0	17.8	17.1	17.7	16.6	**54m**	0	62.7	65.2	53.9	55.2
17	0	32.9	31.6	34.5	32.8	**55**	2	107.1	105.8	101.3	98.8
18	1	74.8	73.3	74.0	71.7	**55m**	0	49.1	52.1	43.7	46.0
19	0	34.3	35.0	31.5	30.8	**56**	0	66.9	67.5	63.4	63.2
20	0	38.0	39.0	35.3	35.3	**57**	1	85.3	87.9	83.4	83.8
22	0	25.6	25.3	23.1	22.2	**57m**	0	78.3	80.6	74.4	74.9
24	0	24.4	25.1	22.5	22.4	**58**	1	91.5	94.5	89.2	90.3
25	0	24.7	23.5	20.8	18.3	**58m**	0	80.6	83.2	76.7	77.6
26	0	43.3	43.6	36.9	36.0	**60**	1	148.9	149.9	118.7	116.2
27	0	30.3	28.6	25.1	21.9	**61**	0	109.9	113.1	108.6	109.3
28	1	56.1	56.8	49.4	49.3	**62**	0	78.9	80.2	73.2	72.8
28m	0	54.7	56.0	47.2	47.4	**63**	0	73.4	76.9	70.5	72.6
29	0	74.0	74.4	66.1	64.8	**64**	0	62.2	62.4	57.8	56.3
30	0	71.5	71.5	62.7	61.1	**65**	0	72.0	73.0	67.9	67.0
31	0	93.6	93.6	91.1	88.5	**66**	0	63.2	62.3	58.9	56.0

[a] Single-point calculations on B3LYP/6-31G* optimized geometries. [b] Obtained using eq 1.

tetracoordinated and the other is tricoordinated, lie energetically higher compared to **25**. The least stable isomers are the ones where both the Si atoms are tricoordinated. However, **27** is energetically competitive to **25**, although one of the Si atoms is tricoordinated. In the case of diphosphabenzenes, all the Dewar benzene isomers lie very close to each other (44.8−52.4 kcal/mol),[21a] whereas Dewar disilabenzenes span a wide range of stabilities from 18.3 to 64.8 kcal/mol. As observed in the case of the valence isomers of benzene, silabenzene and group V heterobenzenes, *trans*-Dewar benzenes are the ones that are least stable among the valence isomers.[4,22] However, one of the *trans*-Dewar benzene isomers, **33**, lies below few bicyclopropenyl isomers (**41**, **43**, ***c*-43m**, and ***t*-43m**). Among the *trans*-Dewar benzene isomers (**31**−**36**), **33** is the most stable isomer and is found to be less stable than the global minima by only 76 kcal/mol, whereas the parent *trans*-Dewar benzene lies as high as 150 kcal/mol above benzene.

As observed in the Dewar benzene isomers, the environment in which the Si atom is present seems to control the relative stabilities of the bicyclopropenyl isomers. One might expect that ***tt*-45**, which does not have even a single three-membered ring, would be more stable than the other isomers having one or two strained three-membered rings. However, ***tt*-45** is found to be less stable than **40**, which has two three-membered rings. The relative stability ordering seems to be controlled by the position of the Si atoms. This indicates that the substitution pattern plays an important role in deciding the relative stability of the isomers in this class of compounds in addition to the strain in the skeleton. This is in contrast to the diphosphinine isomers, since the most stable bicyclopropenyl isomer is the one where both the phosphorus atoms occupy sp^2 centers and the least stable isomer is the one where the P atoms are present in sp^3 centers.[21a] **37** and **46**, whose derivatives were synthesized recently, are less stable than the global minima by only 29 and 52 kcal/mol, respectively. Both of them have two strained four- and three-membered rings, respectively, but are energetically competitive with the other isomers.

Tricyclic Isomers. In this section, the relative stabilities of benzvalene isomers and some other tricyclic nonclassical structures are discussed. As observed in the Dewar benzene and bicyclopropenyl isomers, molecules having two tetracoordinated Si atoms are stable compared to those containing tricoordinated Si atoms. This can be attributed to the weak π-bonding ability of Si either with C or with another Si. **48**, where one of the Si atoms is bound to the five-membered ring formed by the other silicon atom and the four carbon atoms in a η^3 fashion, is computed to be the most stable isomer among the benzvalene isomers. **55m**, where one of the Si is tetravalent and the other is divalent, is more stable than **54m**, where both the Si atoms are tricoordinated, otherwise sharing an equivalent skeleton, by 9.2 kcal/mol. This indicates that Si atoms are more stable when in tetravalent and divalent form compared to those in two tricoordinated form. The dibridged structure **56** lies 8 kcal/mol higher in energy than the corresponding nonbridged isomer, **54m**. Among the two SiH unit capped cyclobutadienyl systems (**57**−**63**), the *trans* compounds, **57** and **58**, are more stable than the corresponding *cis* compounds **60** and **61**. The isomer where the two SiH units are coordinated from either side to the opposite corners of the butadienyl species, **63**, is found to be the most stable among these isomers.

Tetracyclic Isomers. **64** and **66** lie close to each other, with **65** lying about 10 kcal mol^{-1} lower compared to the other two. Thus, the relative energy ordering of the prismane isomers is as follows: **66** ≈ **64** < **65**.

Conclusions

The present study provides a systematic computational analysis of the disilabenzene potential energy surface, where 66 structures were considered, which includes $(CH)_4(SiH)_2$ valence isomers and many other related isomers. Overall, 78 stationary points were located and their nature was characterized by frequency calculations. Out of the 78 stationary points, 61 were characterized as minimum energy structures, 12 as transition states, four as second-order saddle points, and one as a third-order saddle point. The environment in which the Si atoms are present and the strain in the skeleton are some guiding factors in explaining the observed stabilities. In most of the cases, the isomer where both the silicon atoms are tetracoordinated is found to be the most stable among the positional isomers. Thus, the silicon atom has an inherent preference to be tetracoordinated compared to tricoordinated, which is attributed to the weak π-bonding ability of Si with C or with another Si. In all the minimum energy structures of the bicyclopropenyl isomers where a tricoordinated Si atom is connected to an sp^3 carbon, the three-membered ring opens up to yield monocyclic or acyclic isomers. In Dewar benzene, benzvalene, and bicyclopropenyl isomers, those compounds with an Si=Si bond, where the hydrogens connected to them are in-plane, are computed to be transition states. Comparison of the relative energies of the valence isomers of disilabenzene and diphosphabenzene reveals that the positional isomers in disilabenzene span a wide range of relative stabilities compared to the diphosphabenzene isomers. This study highlights the richness of $C_4Si_2H_6$ isomers and importantly indicates how close these isomers are to each other energetically. This leads to a situation where facile rearrangement occurs among various isomeric forms owing to the high reactivity of this class of compounds. This theoretical study may be a guiding tool to understand the nature, reactivity, and potential energy landscape of $C_4Si_2H_6$ isomers and aid experimental research in this interesting area.

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Supporting Information Available: Tables of Cartesian coordinates of the B3LYP optimized structures and the total energies obtained at B3LYP with both 6-31G* and cc-pVTZ basis sets and CCSD(T) levels of all the molecules considered in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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