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RELATIVE STABILITIES OF 1,4-DISILABENZENE AND ITS VALENCE ISOMERS

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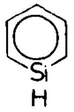
Summary

Ab initio calculations (3-21G(*)//STO-3G) indicate planar, aromatic 1,4-disilabenzene (**5**), its Dewar form (**6**), and a silylene isomer (**7**) to have rather similar thermodynamic stabilities. While the corresponding monosilabenzene isomers have larger energy differences, both sets of compounds illustrate the reduced aromaticity of the silabenzenes and the relative weakness of π-Si–C over π-C–C and σ-Si–Si bonds.

Introduction

The current widespread experimental [1] and theoretical [2] interest in organosilicon chemistry has brought to light several interesting features concerning multiply bonded silicon compounds. The preferred geometries as well as the relative energies of various isomers are found to be significantly different from those of the corresponding carbon analogs [1–4]. It would be of considerable interest to find if this pattern persists in aromatic organosilicon compounds, especially in view of recent successful characterization or trapping of silabenzene (**1**) [5], silatoluene [6], and hexamethyl-1,4-disilabenzene [7]. Ab initio calculations have revealed that the silylene isomers **3** and **4** are ca. 20 kcal/mol higher in energy than **1**, while the Dewar form, **2**, is less stable by a further 18 kcal/mol [8]. These energy differences



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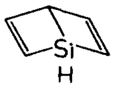

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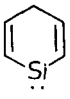

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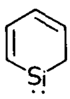

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represent a significant reduction compared to the relative energies of the corresponding valence isomers of benzene. The factors responsible for this reduction are likely to be even more effective in determining the relative stabilities of the isomers of 1,4-disilabenzene. We have explored this possibility using the same methods employed in the earlier study of monosilabenzene. Although 1,4-disilabenzene (**5**) has recently been calculated [9] to be a slightly less stable than the 1,2- and 1,3-isomers, the present study remains quite relevant. Not only is a derivative of 1,4-disilabenzene known experimentally [7], but also the isomers considered here may be accessible through simple rearrangements involving **5**. In fact, the potential involvement of the Dewar form **6** in a subsequent reaction has even been discussed [7], albeit inconclusively.

Results and discussion

The geometries of 1,4-disilabenzene (**5**), 1,4-disilabicyclo[2.2.0]hexa-2,5-diene (Dewar disilabenzene, **6**), and 1,4-disilacyclohexadienylidene (**7**) were optimized with the minimal STO-3G basis set under D_{2h}, C_{2v}, and C_{2v} symmetry constraints, respectively [10]. These geometries were employed in single-point calculations with the 3-21G(*) basis set, a split-valence basis including a set of d functions on silicon [11]. At this level, the Dewar form, **6**, is only 5.9 kcal/mol higher in energy than the planar structure, **5** (Table 1). Since larger basis sets and inclusion of electron correlation generally tend to favor bicyclic over monocyclic geometries [12] **5** and **6** may have quite similar energies; the stability order may even be reversed. This certainly represents a dramatic change from the 60 kcal/mol energy difference between Dewar benzene and benzene [13], and from the 38 kcal/mol difference calculated at the 3-21G(*)//STO-3G level for the corresponding monosilabenzene isomers [8].

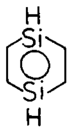
The reasons for the comparable stability of **5** and **6** are similar to those discussed in detail in our earlier work on monosilabenzene isomers [8]. First, the aromaticity in **5** is significantly less than that in benzene. Using bond separation energies calculated with the 3-21G basis, Baldridge and Gordon [9] find **5** to have only 62% of the resonance energy in benzene. Further, the replacement of two Si–C π-bonds (39 ± 5 kcal/mol each) [14] by the generally stronger C–C π-bond (65 kcal/mol) [15] and an Si–Si σ bond (74 kcal/mol) [16] leads to a further reduction in the energy difference between **5** and **6**. Finally, the ring strain in **6** may not be as severe as in Dewar benzene. Since silicon atoms generally form bonds with significant *p* character [3,17,18], it may be easier to accommodate silicon in a four membered ring

TABLE 1

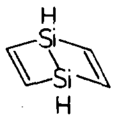
CALCULATED TOTAL AND RELATIVE ENERGIES OF DISILABENZENE ISOMERS

Molecule	Total energy [a]		Rel *E* [b]
	STO-3G	3-21G(*)	3-21G(*)
5, D_{2h}	−724.19133	−728.99227	0.0
6, C_{2v}	−724.20837	−728.98286	5.9
7, C_{2v}	−724.23139	−729.00805	−9.9
8, C_s	−724.15844		

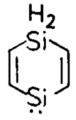
[a] In Hartrees; STO-3G geometries used. [b] In kcal/mol.



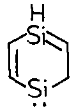
5, D_{2h}



6, C_{2v}



7, C_{2v}



8, C_s

compared to carbon. All these factors reinforce each other and result in **5** and **6** having similar thermodynamic stabilities. On the basis of the present calculations, the proposed involvement of the Dewar structure in the reaction of the precursor of hexamethyldisilabenzene is entirely feasible [7].

The silylene isomer, **7**, is calculated to be 9.9 kcal/mol more stable than the planar, aromatic form, **5** (Table 1). The true energy difference probably is somewhat small: when calibrated against the highest level calculations available on silaethylene and methylsilylene, the 3-21G(*) basis is found to overestimate the stability of divalent silicon relative to multiply bonded silicon by ca. 5 kcal/mol [3].

The present results may be compared with the earlier data on monosilabenzenes: silylene isomers **3** and **4** were estimated to be ca. 20 kcal/mol higher in energy than **1** [8]. The corresponding carbene isomer of benzene is even less stable, preferring a triplet ground state [8].

The remarkably similar thermodynamic stabilities of **5** and **7** can be rationalized by considering the features that distinguish the two isomers. Thus, **7** is derived from **5** by replacing two Si–C double bonds by a divalent silicon and a localized C–C double bond. The 6π aromaticity is lost as well. As is known from numerous theoretical and experimental studies [1–4], the energy change involved in the replacement of an Si–C π-bond by a silylene is very small. However, a C–C π-bond is at least about 25 kcal/mol stronger than an Si–C π-bond [14,15] and can easily compensate for the ca. 23 kcal/mol aromatic stabilization (estimated for 1,4-disilabenzene) [9] lost on going from **5** to **7**. Therefore, the calculated stability order for **5** and **7** is quite reasonable.

We also examined another silylene isomer, **8**, at the STO-3G level. Since the structure retains an Si–C π-bond, but without the aromaticity of **5**, **8** is calculated to be 21 kcal/mol less stable than **5**. Since the STO-3G basis significantly overestimates the stability of silylenes relative to multiply bonded silicon isomers, **8** is likely to be even higher in energy than **5** and was therefore not considered further.

The calculated geometries of **5**–**7** (Table 2) follow expected patterns. The Si–C bond lengths in **6** and **7** range from 1.85–1.88 Å and correspond to essentially single bonds. The Si–C bond length of 1.73 Å in **5** is significantly shorter and is similar to that found in **1**. Electron delocalization in **5** is evident since the Si–C bond length in silaethylene is calculated to be only 1.64 Å at the STO-3G level. The calculated C–C bond lengths also reflect the degree of conjugation in **5**. While values around 1.32 Å are found in **6** and **7**, the C–C bond lengths in **5** are 1.38 Å, typical of delocalized systems.

Mulliken population analyses consistently yield large positive charge on silicon and negative charges on carbon atoms bonded to silicon. This is due principally to the electropositive nature of silicon and the consequent polarization of the σ framework. The π charge distribution in **5** is fairly uniform with the silicon atoms possessing a modest positive charge (0.08 with the 3-21G(*) wave function).

TABLE 2

STO-3G OPTIMIZED GEOMETRIES OF DISILABENZENE ISOMERS [a]

5, D_{2h}	SiC	1.734[b]	CC	1.379
	SiH	1.417[b]	CH	1.083
	CSiC	114.8	SiCC	122.6
	HCSi	120.1	HSiC	122.6
6, C_{2v}	SiC	1.875	CC	1.322
	SiSi	2.182	SiH	1.424
	CH	1.084	SiCC	103.3
	CSiSi	76.8	HSiSi	143.0
	HCC	124.7	CSiC	104.9
	ϕ HCCSi	174.7[c]	a	109.0[d]
7, C_{2v}	Si_1C_2	1.883	C_2C_3	1.318
	Si_4C_3	1.847	C_2H	1.087
	C_3H	1.086	Si_4H	1.425
	HSi_4H	107.8	HC_2Si_1	113.3
	HC_3C_2	118.8	$C_2Si_1C_6$	101.0
	$Si_1C_2C_3$	131.1	$C_2C_3Si_4$	124.7
	$C_3Si_4C_5$	107.5		

[a] Bond lengths in Å, angles in degrees. [b] These values differ significantly from Gordon's STO-2G results [9]. [c] Dihedral angle. [d] Angle between the two four-membered rings.

Conclusions

Planar, aromatic 1,4-disilabenzene (**5**), its Dewar form (**6**) and a silylene isomer (**7**) are all calculated to have comparable thermodynamic stabilities. This remarkable result is due to the reduced aromaticity in **5**, and to the greater strength of Si–Si σ- and C–C π-bonds compared to Si–C π-bonds. Derivatives of **6** and **7** may serve as reaction intermediates.

Acknowledgments

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