J. Org. Chem. **1983**, *48*, 3453–3457 3453

1102, 1070, 850, 775 cm^{-1}. Anal. Calcd for $C_{15}H_{13}F_3N_2$: C, 64.7; H, 4.68; N, 10.1. Found: C, 64.6; H, 4.92; N, 10.3.

Coated Quartz Disks. Four quartz disks (1.0 cm in diameter) were cleansed sequentially with distilled water, methanol, acetone, sulfuric acid, and distilled water and then air-dried. The disks were then soaked for 5 min in a 1% aqueous solution of [(3-methylamino)propyl]methoxysilane (MAP).[44] The disks were removed, washed with distilled water, dried under a stream of nitrogen, and placed in an oven overnight at 110 °C.

Helical Pitch Measurements. The pitch bands of the cholesteric liquid crystals were measured on a Cary 14 spectrophotometer. Samples containing $\leq 0.7\%$ (by weight) azobenzene were prepared and applied to the MAP coated disks, which were separated by a 0.025-nm Teflon spacer. Samples were heated in an aluminum thermostating block until they cleared and were then allowed to cool to an appropriate temperature. Pitches with λ_{max} of the reflectance band from 230 to 2600 nm were observable.

Kinetic Procedures. The syn isomer of each azobenzene was obtained by irradiation of the anti isomer in the reaction cells for ca. 5 min. Irradiation wavelengths were dictated by the absorption spectrum of the anti isomers but generally were 300–400 nm (Pyrex and Corning CS-754 filters). The change in optical density (OD) was monitored on either a Beckman Model DU or a Perkin-Elmer Model 552 recording spectrophotometer. When the Beckman DU was used for isotropic liquids, a cuvette was employed as the reaction cell. It was irradiated outside the sample compartment, placed in the cell compartment, and allowed to equilibrate thermally for 10–20 min. The OD was recorded as a function of time at a single wavelength at or near the λ_{max} of either the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transition of the anti isomer for at least 2 half-lives. The liquid–crystalline samples examined with the Beckman DU were housed in an aluminum cell holder containing spaces for both sample and reference. The whole thermostatted cell compartment was removed and irradiated as above to obtain the syn isomer. The cell compartment was replaced and thermally equilibrated (10–20 min), and the change in OD was monitored as before.

When the Perkin-Elmer 552 was used, sample cells were housed in specially made thermostated cell holders. The cell holders were removed from the cell compartment, irradiated, and replaced to obtain the syn isomer. Thermal equilibration required 10–20 min. The change in OD was monitored at a single wavelength as before.

Temperature measurements were made by using a calibrated thermistor and immersing its tip into the benzene or toluene sample. Since it was not possible to measure the temperature of the liquid crystal directly due to the design of the cell holder, the temperature was recorded by placing the thermistor tip agaiinst the cell window.

Concentrations of the various azobenzenes varied from 5×10^{-5} to 1×10^{-3} M in benzene, *n*-butyl stearate and toluene, depending on which absorption band was followed. Sample concentrations in of cholesteryl chloride/cholesteryl nonanoate (35/65 w/w) were <1% (w/w; $\lesssim 10^{-2}$ M) and depended on the azobenzene substituents, the spectroscopic properties, and the thickness of the spacer (usually 0.025 or 0.05 mm). Kinetic runs were performed at temperatures between 40 and 65 °C in benzene and *n*-butyl stearate, 55–80 °C in toluene, 40–70 °C in $(CCl/CN)_c$, and 76–90 °C in $(CCl/CN)_i$. At least 20 points were taken for each run, and correlation coefficients were always better than 0.99. The rate constants, temperatures, concentrations, etc. are included as supplementary material.

Acknowledgment. Dr. Jeanne M. Nerbonne is thanked for contributing her ideas and for aiding in the design of the problem. The National Science Foundation (Grant No. CHE-79-06572) is acknowledged for its financial support of this work. Dr. Valerie C. Anderson and two referees are thanked for their helpful suggestions.

Registry No. *syn*-**1**, 1080-16-6; *syn*-**2**, 15516-72-0; *syn*-**3**, 86885-32-7; *syn*-**4**, 6720-28-1; *syn*-**5**, 86885-33-8; *syn*-**6**, 6530-97-8; *syn*-**7**, 30926-02-4; *syn*-**8**, 82570-64-7; *syn*-**9**, 30926-04-6; *syn*-**10**, 86885-34-9; *syn*-**11**, 86885-35-0; *syn*-**12**, 86885-36-1; *syn*-**13**, 86885-37-2; *syn*-**14**, 86885-38-3; *syn*-**15**, 20488-60-2.

Supplementary Material Available: Tables of rate constants for syn → anti isomerizations in various solvents and at various temperatures (15 pages). Ordering information is given on any current masthead page.

---

(44) Kahn, F. J. *Appl. Phys. Lett.* **1973**, *22*, 386.

Structures and Relative Energies of Silabenzene Isomers

Jayaraman Chandrasekhar,*[1a,c] Paul von Ragué Schleyer,*[1a] R. O. W. Baumgärtner,[1b] and M. T. Reetz*[1b]

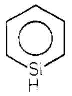
Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, D-8520 Erlangen, and Fachbereich Chemie der Philipps-Universität Marburg, D-3550 Marburg, Federal Republic of Germany

Received June 3, 1982

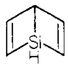
Ab initio molecular orbital calculations with the 3-21G$^{(*)}$ basis set (a split-valence basis which includes d functions on silicon) were carried out on silabenzene (1), Dewar silabenzene (2), 1-silacyclohexadienylidene (3), 2-silacyclohexadienylidene (4), and 4-silacyclohexadienylidene (5). Geometries optimized at the STO-3G level were used for 1–3 and 5, while the MNDO geometry was employed for 4. Planar 1 is the most stable isomer with an aromatic stabilization of ca. 20 kcal/mol. Isomers 3 and 4 are estimated to be only 20–25 kcal/mol higher in energy and may be suitable precursors for the synthesis of 1. The calculated relative energy of 38 kcal/mol for 2 represents an upper bound; inclusion of electron correlation is expected to reduce this value. The least stable isomer considered, 5, is the only structure indicated to have a triplet ground state. The reasons for the differences in the relative energies of C_6H_6 and C_5SiH_6 isomers are analyzed. On the basis of the calculated electronic structures and charge distributions, substituents which might be suitable for stabilizing the different isomers preferentially are suggested.

The recent matrix isolation and IR, UV, and PE spectral characterization of silabenzene (1) and silatoluene have heightened interest in group 4 heterobenzene molecules.[2–6] The possibility of valence isomerization in 1 assumes im-

0022-3263/83/1948-3453$01.50/0 © 1983 American Chemical Society



1



2

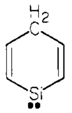
mediate significance. Benzene is by far the most stable C_6H_6 isomer, but some of the isomers of silabenzene may be as stable as the aromatic structure **1**. Of particular interest is 1-silabicyclo[2.2.0]hexa-2,5-diene (**2**) hereafter referred to as Dewar silabenzene. Although this structure lacks aromaticity, it contains no Si–C multiple bonds. In view of the relative instability generally associated with multiple bonds involving silicon,[6,7] **2** may be close to **1** in energy. Other structural candidates are based on the surprising conclusions of recent ab initio calculations, viz., that silicon may prefer divalency to multiply bonded structures.[8] The following calculated stability orders are illustrative:

$$CH_3SiH \geq CH_2SiH_2 > CHSiH_3{}^{8}$$

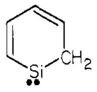
$$SiCH_3{}^+ > HSiCH_2{}^+ > H_2SiCH^+ > H_3SiC^{+\,8f}$$

Thus, we have considered 1-silacyclohexadienylidene (**3**) and 2-silacyclohexadienylidene (**4**) as well as 4-silacyclohexadienylidene (**5**) in singlet and triplet states.

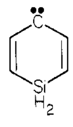
We report the geometries and relative energies of silabenzene isomers **1**–**5**, calculated by using ab initio molecular orbital theory. Previous theoretical studies on



3



4



5

C_5SiH_6 molecules include a minimal basis set investigation of **1** and **5**,[9] an FSGO calcualtion on **1**,[10] and a MINDO/3 study of **1**.[11] In addition to providing estimates for the relative energies of the various isomers, our calculations also suggest means of stabilizing the different structures preferentially.

Computational Details

Ab initio calculations were carried out by using the recently developed 3-21G$^{(*)}$ basis set[12] which is a split-valence basis augmented by a set of d functions on silicon. For **1** and **5**, the geometries optimized by Schlegel et al.[9] at the STO-3G level were used. We also optimized the geometries of **2** and **3** at the STO-3G level with C_s and C_{2v} symmetry constraints, respectively, using analytical gradients and efficient multiparameter searches.[13] For **4**, the geometry obtained from the semiempirical MNDO method[14] was taken. The unrestricted Hartree–Fock formalism[15] was employed in the ab initio calculations on triplets, while the MNDO examination of open shells used the half-electron method.[16] The calculated energies are presented in Table I. The relative energies obtained at the highest theoretical level used (3-21G$^{(*)}$) are also included in this table and will form the basis for all further discussion of the relative stabilities of the silabenzene isomers. The STO-3G- and MNDO-optimized geometries are given in Table II. In addition to the minimum number of parameters needed to fully specify the geometries of the isomers, several bond lengths and angles of interest in the optimized structures are also included in Table II. Charge distributions obtained from Mulliken population analyses[17] on the 3-21G$^{(*)}$ wave functions are given in Table III.

Ab initio calculations were also carried out with the STO-3G* and the 3-21G basis sets, which are intermediate in size to the minimal STO-3G and the extended 3-21G$^{(*)}$ basis sets.[12] The calculated relative energies of **1**–**5** show significant basis set and method dependence, since widely differing structural types are involved. The results are, however, quite consistent with basis set effects found in smaller model systems.[8q] The effects of d functions on silicon and of extending the basis set on the calculated relative energies are found to be quite additive. Thus, the

---

(1) (a) Universität Erlangen-Nürnberg. (b) Universität Marburg; (c) Present address: Department of Chemistry, Purdue Unviersity, West Lafayette, IN 47907.

(2) Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem.* **1980**, *92*, 58; *Angew. Chem., Intl. Ed. Engl.* **1980**, *19*, 52. Solouki, B.; Rosmus, P.; Bock, H.; Maier, G. *Angew. Chem.* **1980**, *92*, 57; *Angew. Chem., Intl. Ed. Engl.* **1980**, *19*, 51. Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1978**, *100*, 5246.

(3) Silatoluene: Kreil, C. L.; Chapman, O. L.; Burns, G. T. Barton, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 841. Bock, H.; Bowling, R. A.; Solouki, B.; Barton, T. J.; Burns, G. T. *Ibid.* **1980**, *102*, 429.

(4) Germabenzene: Märkl, G.; Rudnick, D. *Tetrahedron Lett.* **1980**, *21*, 1405.

(5) Several group 5 heterobenezenes are well characterized. Review: Ashe, A. J., III. *Acc. Chem. Res.* **1978**, *11*, 153. *Top. Curr. Chem.* **1982**, *105*, 125. Ashe, A. J., III; Diephouse, T. R.; El-Sheik, M. Y. *J. Am. Chem. Soc.* **1982**, *104*, 5693.

(6) Reviews: Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. *Acc. Chem. Res.* **1975**, *5*, 18. Jutzi, P. *Angew. Chem.* **1975**, *87*, 269. Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. Bertrand, G.; Trinquier, G.; Mazerolles, P. *Organomet. Chem. Rev.* **1981**, *12*, 1. Coleman, B.; Jones, M., Jr. *Rev. Chem. Intermed.* **1981**, *4*, 297.

(7) For spectroscopic characterizations of compounds containing Si–C multiple bonds, see for example: Mahaffy, P. G.; Gutowsky, R.; Montgomery, L. K. *J. Am. Chem. Soc.* **1980**, *100*, 2854. Koenig, T.; McKenna, W. *Ibid.* **1981**, *103*, 1212. Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheik, M. *Ibid.* **1979**, *101*, 83. Brook, A. G.; Nyburg, S. C.; Reynolds, W. F.; Poon, Y. C.; Chang, Y. -M.; Lee, J. S.; Picard, J. -P. *Ibid.* **1979**, *101*, 6750. Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R. *J. Chem. Soc., Chem. Commun.* **1981**, 191. Brook, A. G.; Kallury, R. K. M. R.; Poon, Y. C. *Organometallics* **1982**, *1*, 987. Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Plavac, N. *Ibid.* **1982**, *1*, 994. Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y. -M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

(8) (a) Blustin, P. H. *J. Organomet. Chem.* **1976**, *105*, 161. (b) Murrell, J. N.; Kroto, H. W.; Guest, M. F. *J. Chem. Soc., Chem. Commun.* **1977**, 619. (c) Gordon, M. S. *Chem. Phys. Lett.* **1978**, *54*, 9. (d) Barthelat, J.-C.; Trinquier, G.; Bertrand, G. *J. Am. Chem. Soc.* **1979**, *101*, 3785. (e) Snyder, L. C.; Wasserman, Z. R. *Ibid.* **1979**, *101*, 5222. (f) Hopkinson, A. C.; Lien, M. H. *J. Chem. Soc., Chem. Commun.* **1980**, 107. (g) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163. (h) Goddard, J. D.; Yoshioka, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1980**, *102*, 7644. (i) Gordon, M. S.; Koob, R. D. *Ibid.* **1981**, *103*, 2939. (j) Gordon, M. S.; Pople, J. A. *Ibid.* **1981**, *103*, 2945. (k) Trinquier, G.; Malrieu, J. -P. *Ibid.* **1981**, *103*, 6317. (l) Poirier, R. A.; Goddard, J. D. *Chem. Phys. Lett.* **1981**, *80*, 37. (m) Lien, M. H.; Hopkinson, A. C. *Ibid.* **1981**, *80*, 114. (n) Gordon, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 4352. (o) Kohler, H. J.; Lischka, H. *Ibid.* **1982**, *104*, 5884. (p) Verwoerd, W. S. *J. Comput. Chem.* **1982**, *3*, 445. (q) Krogh-Jespersen, M. -B.; Chandrasekhar, J.; Schleyer, P. v. R.; Pople, J. A.; Gordon, M. S., to be submitted for publication.

(9) Schlegel, H. B.; Coleman, B.; Jones, M.; Jr. *J. Am. Chem. Soc.* **1978**, *100*, 6499. See also; Gordon, M. S.; Boudjouk, P.; Anwari, F. *Ibid.* **1983**, *105*, 4972.

(10) Blustin, P. H. *J. Organomet. Chem.* **1979**, *21*, 166.

(11) Dewar, M. J. S.; Lo, D. H.; Ramsden, C. A, *J. Am. Chem. Soc.* **1975**, *97*, 1311.

(12) All ab initio calculations were carried out by using the Gaussian 76 series of programs, modified to perform geometry optimizations using analytical gradients:[13] Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1978**, *11*, 368. 3-21G$^{(*)}$: Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039. STO-3G: Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. Hehre, W. J.; Ditchfield, R.; Stewart, R.; Pople, J. A. *Ibid.* **1970**, *52*, 2769. STO-3G*: Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *Ibid.* **1976**, *64*, 5142. 3-21G: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(13) Schlegel, H. B.; Wolfe, S.; Bernardi, F. *J. Chem. Phys.* **1975**, *63*, 3632. Davidon, W. C. *Comput. J.* **1968**, *10*, 406. Fletcher, R.; Powell, M. J. D. *Ibid.* **1963**, *6*, 163.

(14) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

(15) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.

(16) Dewar, M. J. S.; Hashmall, J. A.; Venier, C. G. *J. Am. Chem. Soc.* **1968**, *90*, 1953.

(17) Mulliken, R. S. *J. Chem. Phys.* **1952**, *23*, 1833, 1841, 2338, 2343.

Table I. Calculated Total and Relative Energies of Silabenzene Isomers

molecule	total energy			rel E[c] for 3-21G(*)
	MNDO[a]	STO-3G[b]	3-21G(*)[b]	
1	26.7	−476.043 20	−479.206 42	0.0
2	40.3	−475.995 60	−479.145 19	38.4
3	2.2	−476.027 84	−479.177 75	18.0
4	1.8	−476.019 05[d]	−479.168 90[d]	23.5
5, singlet	91.1	−475.938 78	−479.090 94	72.5
5, triplet	67.5	−476.021 26[e]	−479.147 06[e]	37.2

[a] Heat of formation in kcal/mol. MNDO geometries used. [b] In Hartrees. STO-3G geometries used, unless noted otherwise. [c] In kcal/mole. [d] Using MNDO geometry. [e] Using the singlet geometry.

Table II. STO-3G- and MNDO-Optimized Geometries of Silabenzene Isomers[a]

molecule	parameter
1, C_{2v}[b]	$SiC_1 = 1.722\ (1.715)$; $C_1C_2 = 1.381\ (1.395)$ $C_2C_3 = 1.395\ (1.407)$; $SiH = 1.419\ (1.435)$ $C_1H = 1.079\ (1.087)$; $C_2H = 1.086\ (1.096)$ $C_3H = 1.080\ (1.093)$; $C_1SiC_5 = 110.3\ (111.7)$ $SiC_1C_2 = 117.4\ (117.1)$; $C_1C_2C_3 = 125.1\ (124.7)$ $C_2C_3C_4 = 124.6\ (124.9)$; $C_2C_1H = 118.2\ (118.0)$ $C_1C_2H = 118.4\ (119.5)$
2, C_s	$SiC_1 = 1.845\ (1.828)$; $SiC_3 = 1.851\ (1.878)$ $C_1C_2 = 1.320\ (1.355)$; $C_2C_3 = 1.549\ (1.524)$ $SiH = 1.425\ (1.435)$; $C_1H = 1.079\ (1.076)$ $C_2H = 1.086\ (1.083)$; $C_3H = 1.083\ (1.091)$ $C_3SiH = 131.5\ (130.0)$; $SiC_3H = 131.8\ (137.3)$ $HSiC_1 = 123.5\ (122.6)$; $SiC_1C_2 = 92.8\ (90.5)$ $C_1C_2C_3 = 105.3\ (107.9)$; $SiC_3C_2 = 85.6\ (83.7)$ $C_2C_3H = 117.5\ (116.3)$; $HC_1C_2 = 127.9\ (129.5)$ $C_1C_2H = 129.0\ (129.4)$; $HC_1Si = 139.1\ (140.0)$ $HC_2C_3 = 125.7\ (122.7)$; $C_1SiC_3 = 76.3\ (77.9)$ $\phi(SiC_1C_2C_3) = -0.9\ (-0.3)$[c] $\phi(C_1SiC_3C_4) = 113.6\ (114.9)$[c] $\phi(HC_1C_2C_3) = -176.6\ (-179.3)$[c] $\phi(HC_2C_1Si) = 176.8\ (179.5)$[c]
3, C_{2v}	$SiC_1 = 1.866\ (1.792)$; $C_1C_2 = 1.316\ (1.346)$ $C_2C_3 = 1.522\ (1.506)$; $C_1H = 1.084\ (1.096)$ $C_2H = 1.088\ (1.096)$; $C_3H = 1.093\ (1.117)$ $C_1SiC_5 = 97.3\ (99.9)$; $SiC_1C_2 = 127.3\ (126.2)$ $C_1C_2C_3 = 126.3\ (125.5)$; $C_2C_3C_4 = 116.3\ (116.7)$ $C_2C_1H = 115.4\ (117.9)$; $C_1C_2H = 121.1\ (121.2)$ $HC_3H = 105.4\ (106.2)$
4, C_s	$SiC_1 = (1.833)$; $C_1C_2 = (1.489)$ $C_2C_3 = (1.355)$; $C_3C_4 = (1.463)$ $C_4C_5 = (1.352)$; $SiC_5 = (1.782)$ $C_1H = (1.116)$; $C_2H = (1.095)$ $C_3H = (1.094)$; $C_4H = (1.096)$ $C_5H = (1.095)$; $SiC_1C_2 = (119.9)$ $C_1C_2C_3 = (124.4)$; $C_2C_3C_4 = (124.6)$ $C_4C_5Si = (123.8)$; $HC_1Si = (106.0)$ $HC_2C_1 = (116.0)$; $HC_3C_2 = (119.7)$ $HC_4C_3 = (115.1)$; $HC_5C_4 = (118.1)$ $\phi(HC_1SiC_5) = (124.0)$[c]
5, C_{2v}[b]	$SiC_1 = 1.844\ (1.814)$; $C_1C_2 = 1.323\ (1.355)$ $C_2C_3 = 1.511\ (1.441)$; $SiH = 1.425\ (1.440)$ $C_1H = 1.086\ (1.090)$; $C_2H = 1.086\ (1.096)$ $C_1SiC_5 = 102.6\ (105.8)$; $SiC_1C_2 = 121.7\ (120.1)$ $C_1C_2C_3 = 129.4\ (124.2)$; $C_2C_3C_4 = 115.3\ (125.6)$ $C_2C_1H = 118.4\ (120.8)$; $C_1C_2H = 117.5\ (120.5)$ $HSiH = 109.3\ (109.4)$

[a] Bond lengths are in angstroms and angles in degrees. MNDO values are in parentheses. [b] STO-3G values from ref 9. [c] Dihedral angle. Sign of $\phi(ABCD)$ is positive if D is clockwise from A when looking through B toward C.

relative energies projected from the STO-3G, STO-3G*, and 3-21G values compare favorably with the 3-21G$^{(*)}$ values in all cases, with the exception of 2. The calculated total and relative energies at the lower levels of theory are included as supplementary material and may prove useful in investigations on larger derivatives of silabenzene for which high-level calculations are prohibitively expensive.

Results and Discussion

Relative Energies. As expected, the most stable C_5SiH_6 isomer is calculated to be the planar, aromatic form 1 (Table I). However, the silylene isomer 3 is computed to be only 18 kcal/mol higher in energy at the 3-21G$^{(*)}$ level (Table I). The alternative silylene, 4, is also likely to be comparably stable. (The calculated energy difference of 5.5 kcal/mol between 3 and 4 may be influenced by the use of MNDO- rather than the STO-3G-optimized geometry for the latter.)

The energies given in Table I do not include the effects of electron correlation. Corrections can be estimated from the detailed results available for simpler model systems. For example, the energy difference between methylsilylene (6) and silaethylene (7) is shifted by 5 kcal/mol in favor

$$\underset{6}{\mathrm{H_3C{-}\ddot{Si}H}} \qquad \underset{7}{\mathrm{H_2C{=}SiH_2}}$$

of the latter by inclusion of electron correlation.[8h] On the assumption of a similar correction for the C_5SiH_6 isomers, 3 and 4 probably are ca. 20–25 kcal/mol higher than 1 in energy.

The estimated energy difference between 1 and the divalent structures 3 and 4 is quite small compared to the relative energies of their C_6H_6 analogues. However, smaller differences are expected for silicon compounds.[8] In fact, the energy gap is unusually large compared to other multiply bonded silicon systems. High-level theoretical calculations predict nearly identical stabilities for 6 and 7.[8h] A further example is the experimentally demonstrated small energy gap between dimethylsilylene and methylsilaethylene.[18] The stability of 1 relative to 3 and 4 can be attributed to the aromaticity in silabenzene. While some π delocalization is possible in the silylenes 3 and 4 by interaction of the diene fragment with the empty p_π orbital on silicon, the resulting stabilization is far less effective than the aromaticity in 1. Indeed, the 20–25 kcal/mol energy difference is a measure of the aromaticity in the planar C_5Si ring. This value agrees with an independent estimate of 22 kcal/mol obtained by other means.[9]

The stability of 1 relative to 3 and 4 suggests a synthetic route for silabenzene. Starting from a suitable precursor of 3 or 4, 1 might be obtained by hydrogen migration. Although high-level theory predicts a high barrier for the intramolecular intercoversion of 6 and 7,[8h,19] alternative mechanisms are conceivable for such reactions. Indeed, several silylene to silene rearrangements have experimentally been observed even at low temperatures.[18,20] A

---

(18) Conlin, R. T.; Wood, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 1843. Drahnak, T. J.; Michl, J.; West, R. *Ibid.* **1981**, *103*, 1845. Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem.* **1981**, *93*, 615; *Angew. Chem. Intl. Ed. Engl.* **1981**, *20*, 597. Reisenauer, H. P.; Mihm, G.; Maier, G. *Angew. Chem.* **1982**, *94*, 864; *Angew. Chem., Intl. Ed. Engl.* **1982**, *11*, 854; *Angew. Chem. Suppl.* **1982**, *1785*.

(19) Schaefer, H. F. *Acc. Chem. Res.* **1982**, *15*, 283.

Table III. Calculated Charge Distributions in Silabenzene Isomers[a]

molecule	Si	C_1	C_2	C_3	C_4	C_5
1, σ	0.772	−0.396	−0.281	−0.208		
π	0.201	−0.120	0.084	−0.103		
total	0.973	−0.516	−0.197	−0.311		
2	1.419	−0.474	−0.203	−0.582		
3	0.733	−0.517	−0.160	−0.533		
4	0.728	−0.771	−0.160	−0.281	−0.192	−0.506
5, singlet	1.182	−0.431	−0.383	0.085		
5, triplet	1.188	−0.476	−0.278	0.031		

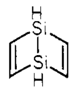
[a] Obtained from 3-21G$^{(*)}$ wave functions.

similar reaction of **4** or **3** to **1** is therefore likely to be equally facile in condensed phases.

Dewar silabenzene (**2**) is calculated to be less stable than the silylene isomers **3** and **4**. However, electron correlation is expected to influence the calculated relative energy of **2** significantly. Since bicyclic structures generally profit much more than monocyclic ones from electron correlation,[21] the 38 kcal/mol energy difference between **1** and **2** represents an upper limit. This value is still much smaller than the experimental energy difference of 60 kcal/mol between benzene and Dewar benzene.[22]

Three factors determine the relative stability of the mono- and bicyclic structures considered here. Aromaticity in the planar ring and the strain in the bicyclic isomer both result in a substantial energy difference between the two structures. However, the replacement of a π bond of the planar form by a generally stronger σ bond in the Dewar structure stabilizes the latter somewhat. The replacement of carbon by silicon reduces the energy gap by influencing all three factors. The aromaticity in silabenzene is estimated to be only two-thirds of that in benzene.[9] The strain in Dewar silabenzene is also relatively less. Second row elements often adopt angles close to 90°, while the first row elements prefer essentially tetrahedral angles.[23] Hence, it may be easier to accommodate a silicon atom in a four-membered ring compared to carbon.[24] A parallel is provided by the smaller estimated ring strain in thiacyclobutane (19.4 kcal/mol) compared to that in oxacyclobutane (26.4 kcal/mol) and in cyclobutane (26.2 kcal/mol).[25] Furthermore, the Si=C bond energy is low; the calculated rotational barrier in silaethylene (46 kcal/mol)[26] is much less than that in ethylene (65 kcal/mol).[26,27] The experimental rotational barriers in substituted silaethylenes (28–42 kcal/mol)[28] suggest an even weaker π bond. The lack of Si–C double bonds in Dewar silabenzene (**2**) is therefore a favorable feature. Our calculations indicate the feasibility of a valence isomerization of **1** to **2**. It is tempting to attribute the disappearance of the UV bands of **1** after even brief irradiation to the photochemical rearrangement of **1** to **2**.[2] A more detailed study of the photochemistry of **1** might be rewarding.

The realization of the Dewar structure is even more likely in the case of disilabenzene isomers $C_4Si_2H_6$. Two silicon atoms present in the planar benzene-like form are expected to reduce aromaticity further. On the other hand, the bicyclic structure containing only singly bonded silicon atoms should have enhanced stability. Thus, Dewar disilabenzene (**8**) represents an attractive synthetic target,



8

especially since derivatives of 1,4-disilacyclohexa-2,5-dienes have already been synthesized.[29]

The carbene isomer **5** has been the focus of both experimental[30] and theoretical studies.[9] By analogy to a reaction involving C_6H_6 isomers, an attempt was made to obtain **1** from **5** via hydrogen transfer. Dimerization occurred instead.[30] The previous STO-3G calculations[9] and our additional computations indicate **5** to be the least stable C_5SiH_6 isomer considered. This is not surprising. In the model $CSiH_4$ system, silylcarbene is much less stable than either methylsilylene or silaethylene.[8] In the present case, the loss of aromaticity leads to a further destabilization of **5** relative to **1**. Like most carbenes, **5** is also likely to have a triplet ground state (vide infra).

The stability of silylene structures **3** and **4** relative to **1** and the instability of **5** are partly due to the weakness of Si–H bonds relative to C–H bonds.[31] Therefore, substitution at silicon is likely to alter the relative energies significantly. Methyl substitution at silicon has been calculated to favor multiply bonded silicon structures relative to silylenes by nearly 20 kcal/mol.[32] Thus, structures similar to **3** and **4** are likely to be inaccessible from silatoluene. The reverse reaction, viz., the rearrangement of silylene derivatives to substituted silabenzenes, should be correspondingly more favorable.

Geometries. The MNDO- and STO-3G-optimized geometries are quite similar (Table II). The only major discrepancies are the bond lengths involving the silylene group in **3** and the carbene center in **5**, which are calculated to be shorter at the MNDO level. The bond angles calculated by the two methods are in pleasing agreement.

The calculated structural parameters show no unexpected features. The Si–C bond length in silabenzene, 1.72

---

(20) (a) Barton, T. J.; Burns, S. A.; Burns, G. T. *Organometallics* **1982**, *1*, 210. (b) Barton, T. J.; Burns, G. T.; Goure, W. F.; Wulff, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 1149. (c) Burns, S. A.; Burns, G. T.; Barton, T. J. *Ibid.* **1982**, *104*, 6140.

(21) Whiteside, R. A.; Krishnan, R.; DeFrees, D. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1981**, *78*, 538. Andrade, J. G.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comp. Chem.* **1981**, *2*, 207.

(22) Cardillo, M. J.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 2399.

(23) Wells, A. F. "Structural Inorganic Chemistry"; Oxford University Press: London, 1962.

(24) Silacyclobutanes are well-known. See for example, ref 20c.

(25) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; O'neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

(26) Ahlrichs, R.; Heinzmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7452.

(27) Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315. Mulliken, R. S.; Merer, A. *Chem. Rev.* **1969**, *69*, 639.

(28) Pietro, W. J.; Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 7126. Walsh, R. *J. Organomet. Chem.* **1972**, *38*, 245. Gusel'nikov, L. E.; Nametkin, N. S. *Ibid.* **1979**, *169*, 155.

(29) Halevi, E. A.; West, R. *J. Organomet. Chem.* **1982**, *240*, 129. Chandrasekhar, J.; Schleyer, P. v. R., unpublished calculations. See also: Rich, J. D.; West, R. *J. Am. Chem. Soc.* **1982**, *104*, 6884.

(30) Coleman, B.; Jones, M., Jr. *J. Organomet. Chem.* **1979**, *168*, 393. Barton, T. J.; Banasiak, D. S. *Ibid.* **1978**, *157*, 255.

(31) The C–H and Si–H bond dissociation energies are 105 (in CH_4) and 90 (in SiH_4) kcal/mol, respectively. The C–C and Si–C bond dissociation energies are about the same (in CH_3–SiH_3 and CH_3–CH_3). Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. Bell, T. N.; Perkins, K. A.; Perkins, P. G. *J. Chem. Soc. Faraday Trans. 1* **1981**, *77*, 1779; *J. Phys. Chem.* **1982**, *86*, 3922.

(32) Hanamura, M.; Nagase, S.; Morokuma, K. *Tetrahedron Lett.* **1981**, *22*, 1813.

Å, is longer than a true Si–C double bond (1.64 Å for silaethylene at the STO-3G level)[8q] but is considerably shorter than the Si–C single bond length (1.86 Å in silaethane, STO-3G).[33] This reflects the expected partial double bond character in 1. The Si–C bond lengths in 2–5 are not significantly different from single bond lengths. The Si–C bond between the bridgehead atoms in 2 is calculated to be 0.05 Å longer than the other Si–C bonds at the MNDO level, but the difference is much smaller in the STO-3G-optimized geometry. The bond angles are consistently shorter at silicon than at carbon atoms. Thus, in 1 the STO-3G internal angle at Si is 110°, while the corresponding angles at the carbon atoms are 117° and 125°. Again, in the four-membered rings of 2, the angle of 76° at Si is the smallest. The CSiC angle in 3 (97°) is slightly more than the CSiH angle in methylsilylene (93°).[8h] The angle at the carbene center in 5 is much larger (115°). The calculated bond angles reflect the tendency of second row elements to adopt angles closer to 90° more easily than their first row counterparts.

Charge Distributions. Mulliken population analyses on the 3-21G$^{(*)}$ wave functions yield the charges (in atomic units) in Table III. As with all extended basis sets, the calculated absolute charges are quite high. Only major trends in these values are of significance.

The electropositive nature of silicon is evident in the charge distributions. The positive charge at silicon is seen to increase with increasing number of carbon neighbors. Thus, the calculated values follow the trend 2 > 5 > 1 > 3, 4. The inductive effect of silicon falls off smoothly with distance. For example, the σ charges of the carbon atoms in 1 vary as ortho (–0.40) < meta (–0.28) < para (–0.21). The carbon atoms directly bound to silicon bear a much higher negative charge in all the other isomers as well (Table III). However, the π electron density in 1 is polarized differently. The ortho and para carbons gain more than 0.1 electron in their p_π orbitals, while the corresponding orbitals in silicon and the meta carbon are depleted of 0.20 and 0.08 electron, respectively. These results can be rationalized on the basis of perturbation theory by considering the effect of an electropositive element on the energies and coefficients of the familiar π MOs of benzene.[34]

The calculated charge distributions can be used for a qualitative prediction of substituent effects. For example, the stability of silabenzene may be increased by σ acceptor groups at ortho and meta positions, by π acceptors at ortho and para carbons, and by π donors at silicon. Comparison of the calculated charges of 1 and 2 suggests a suitable substituent for providing a thermodynamic driving force for the valence isomerization of 1 to 2. σ acceptors at the para position in 1 should be effective in this regard, since the bridgehead carbon in 2 would benefit far more than the para carbon in 1 from a σ withdrawing group.

Triplet States. A triplet of silabenzene has previously been calculated at the UHF/STO-3G level to be 107 kcal/mol less stable than the singlet.[9] The nonconjugated diene 2 is unlikely to have a low-lying triplet state. Silylenes are also known usually to prefer singlet ground states.[8h,35] This was confirmed by a preliminary MNDO examination of 3; the triplet was calculated to be 60 kcal/mol higher in energy than the singlet.[36] Hence, the triplets of 1–4 were not investigated at the 3-21G$^{(*)}$ level. However, carbene 5 shows a clear preference for the triplet state. Unfortunately, a quantitative prediction of singlet–triplet energy difference is a formidable computational problem. The UHF procedure generally overestimates the stability of open-shell systems. The error is about 20 kcal/mol for methylene.[37] Assuming a similar error in the present system, triplet 5 should be about 15 kcal/mol more stable than the corresponding singlet. A similar singlet–triplet energy difference has also been calculated for silylcarbene.[38]

Conclusions

Several C_5SiH_6 isomers lie close in energy to the planar aromatic structure. Silabenzene (1) is the most stable isomer, but the silylene derivatives 3 and 4 are only 20–25 kcal/mol higher in energy. Dewar silabenzene (2) comes next in the order of stability, while the carbene 5 with a triplet ground state is ca. 60 kcal/mol less stable than 1. The relative energies are the result of (i) ca. 20 kcal/mol aromaticity in 1, (ii) reduced strain in Dewar silabenzene compared to that in Dewar benzene, (iii) the weakness of π bonds involving Si–C relative to σ bonds, and (iv) the preference of silicon to adopt divalent structures instead of forming multiple bonds. Synthesis of 1 via hydrogen migration from 3 or 4 appears to be an attractive possibility. π donor substituents at silicon should provide an additional thermodynamic driving force. The photochemical valence isomerization of 1 to 2 seems feasible and is likely to be facilitated by σ acceptor groups at the bridgehead carbon. Silabenzene can be stabilized by π acceptor groups at ortho and para carbons, by σ acceptor substituents at all carbon atoms, and by π donor groups at silicon. Relative to benzene, heterobenzenes with electropositive elements should undergo a greater variety of rearrangement reactions under both thermal and photochemical conditions.

Acknowledgment. We thank Professor G. Maier for his interest and H. B. Schlegel for performing initial computations. The Fonds der Chemischen Industrie provided support.

Registry No. 1, 289-77-0; 2, 86646-24-4; 3, 86646-25-5; 4, 86646-26-6; 5, 68299-93-4.

Supplementary Material Available: Calculated STO-3G* and 3-21G total energies (Table IV) and relative energies at the MNDO, STO-3G, STO-3G*, 3-21G, and 3-21G$^{(*)}$ levels (Table V) for the silabenzene isomers 1–5 (2 pages). Ordering information is given on any current masthead page.

---

(33) Although the bond lengths in the model systems are available at higher levels,[8] the STO-3G values are used in order to keep the comparisons with the present results consistent.

(34) Bock, H. *Angew. Chem.* **1977**, *89*, 645; *Angew. Chem., Intl. Ed. Engl.* **1977**, *16*, 627. Batich, C.; Heilbronner, E.; Hornung, H.; Ashe, A. J.; Clark, D. T.; Kilcast, D.; Scanlan, I. *J. Am. Chem. Soc.* **1973**, *95*, 928.

(35) Gaspar, P. P. In "Reactive Intermediates"; Jones, M., Jr.; Moss, R. A., Eds.; Wiley-Interscience, New York, 1981; Vol. 2, Chapter 9, p 335, Tang, Y. -N. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press, New York, 1982; Vol. 2, Chapter 4, p 297.

(36) The MNDO heats of formation of singlet and triplet 3 are 2.2 and 62.2 kcal/mol, respectively.

(37) At the UHF/6-31G* level, the singlet–triplet difference in CH_2 is calculated to be 31 kcal/mol. The best estimate is 11 kcal/mol. See for example: Bauschlicher, C. W.; Shavitt, I. *J. Am. Chem. Soc.* **1978**, *100*, 739.

(38) Meadows, J. H.; Schaefer, H. F. *J. Am. Chem. Soc.* **1976**, *98*,, 4833.