Organometallics **2000,** *19,* 1477−1487

The Silabenzenes: Structure, Properties, and Aromaticity

Kim K. Baldridge*,†

San Diego Supercomputer Center, 9500 Gilman Drive, Building 109,
La Jolla, California 92093-0505

Olivier Uzan and Jan M. L. Martin*,‡

Department of Organic Chemistry, Weizmann Institute of Science, 76100 Reḫovot, Israel

Received May 18, 1999

The electronic structure and properties of the silabenzenes series have been investigated using basis sets of spdf quality and many-body perturbation theory, hybrid density functional theory, and coupled cluster methods. Basic measures of aromatic character derived from structure, molecular orbitals, isodesmic and homodesmotic bond separation reactions, and a variety of magnetic criteria (magnetic isotropic and anisotropic susceptibilities, magnetic susceptibility exaltations, NICS) are considered. Energetic criteria suggest that 1,3,5-trisilabenzene and, to a lesser extent, 1,3-disilabenzene and its complement 1,2,3,5-tetrasilabenzene enjoy conspicuous stabilization. However, by magnetic criteria, these systems are among the least aromatic of the family: population and bond order analyses reveal that they derive part of their stability from ionic contributions to the bonding. Within their isomer series, 1,2-disilabenzene, 1,2,3-trisilabenzene, and 1,2,3,4-tetrasilabenzene are the most aromatic using magnetic criteria: overall, "magnetic aromaticity" decreases with increasing number of Si atoms. The different magnetic aromaticity criteria are fairly consistent within an isomer series: over the complete set of silabenzenes, the magnetic susceptibility exaltations correlate fairly well with the magnetic susceptibility anisotropies. Second-order Jahn−Teller effects cause deviations from planarity to occur in all systems with at least four silicon ring atoms, except for 1,2,4,5-tetrasilabenzene. The relative energetics (isomers, deviation from planarity) at our highest level of theory, CCSD(T)/cc-pVTZ, are better reproduced by the B3LYP/cc-pVTZ density functional method than by any of the less accurate wave function methods (HF, MP2, CCSD) considered. In general, the use of high levels of theory with large basis sets removes some ambiguities in previously reported studies.

Introduction

The relatively weak π-bonding ability of silicon versus carbon results in interesting structural and electronic features within the benzenoid framework of silabenzenes. This substantial difference in π bonding for silicon versus carbon may well be the feature that limits the successful synthesis and isolation of these potentially aromatic silaorganic compounds and establishes them as challenges for computational organosilicon chemistry. [1] The theoretical and experimental literature comparing benzene and silabenzenes is fairly substantial,[1−12] and the theoretical aspects of silaaromatic compounds in general have recently been critically reviewed.[2] From these examinations one sees that the actual experimental knowledge concerning silaaromatic compounds is still relatively scant due to the elusive nature of such compounds. The notable exceptions are provided by studies such as those of Okazaki et al.,[6−12] in which exploitation of bulky substituents on the silaaromatic framework has provided the stability necessary to allow isolation of such compounds. Specific examples of this include stable silanethione and analogues,[8,9] distibene,[10] and dibismuthene[11] and, more recently, a series of 2-silanaphthalene structures.[6−12]

---

† E-mail: kimb@sdsc.edu.
‡ E-mail: comartin@wicc.weizmann.ac.il.

[1] Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1015.

[2] Apeloig, Y.; Karni, M. In *The Chemistry of Organic Siilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2.

[3] Brook, A. G.; Brook, M. A. *Adv. Organiomet. Chem.* **1996**, *39*, 71.

[4] Raabe, G.; Michl, J. *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 1989.

[5] Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

[6] Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1999**, *121*, 11336.

[7] Okazaki, R.; Tokitoh, N.; Matsumoto, T. *Synthetic Methods of Organometallic and Inorganic Chemistry*; Thieme: New York, 1996; Vol. 2.

[8] Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Goto, M. *J. Am. Chem. Soc.* **1998**, *120*, 11096.

[9] Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 11578.

[10] Tokitoh, N.; Arai, Y.; Sasamori, T.; Okazaki, R.; Nagase, S.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 433.

[11] Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; Schleyer, P. v. R.; Jiao, H. *J. Am. Chem. Soc.* **1997**, *119*, 6951.

[12] Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* **1997**, *227*, 78.

10.1021/om9903745 CCC: $19.00

Successful experimental ventures have been facilitated not only by many important theoretical studies but also by a general enhancement in the understanding of aromaticity[13−24] from a theoretical perspective. It is widely held that the concept of aromaticity, although very useful, is highly complicated in nature[13,23,25−29] and becomes even more difficult to "categorize" for second-row compounds. Each of the proposed definitions of aromaticity either tends to have exceptions or is not expansive enough to preclude ambiguities. Benzene tends to be the generally accepted, archetype aromatic compound,[30−32] such that "benzene-like" implies aromatic. Although the traditional structural view of aromatic compounds tended to focus on planar geometries with bonds of equalized lengths, many examples of nonplanar aromatic structures now exist (e.g., the work of Fokin et al. on [*n*]-trannulenes;[33] see also some studies concerning polynuclear aromatic hydrocarbons and structures with significant ring bond length alternation that are nevertheless aromatic[34−41]). In these cases, computed magnetic properties have shown to be a useful measure of cyclic electron delocalization manifested as ring currents.

Several criteria have been established to actually quantify the degree of "structural aromaticity", such as the Julg[13,25] or HOMA (harmonic oscillator measure of aromaticity[42,43]) parameters; however, as with many measures of aromaticity, these structural indexes by themselves cannot be regarded as a general quantitative scale of aromaticity. For example, they all provide fairly inconsistent and unsatisfying results when applied to a wide selection of compounds that would be considered aromatic by virtue of their known relative stability (e.g., ref 44). Energetically, criteria have been established that assess the stability (due to cyclic electron delocalization) of the potentially aromatic compound relative to some set of reference compounds. These criteria are widely accepted thanks to their intuitive interpretation in terms of (in)stability with respect to various reactions (e.g., decomposition, isomerization, cyclization). Because a variety of methods are used to choose the set of reference compounds with which to compare the potentially aromatic structure, these criteria are also not a conclusive measure of aromatic character. In addition, such an analysis inherently includes effects of strain and other such contributing factors that preclude an unambiguous comparison. Nonetheless, we will consider them in this work for the sake of completeness.

Because the π electron network in structures such as benzene and silabenzenes can serve as a source of electrons for electrophilic reagents, the behavior of the ring π density and the degree to which it is polarized by various substitutions (whether within or on the ring framework) are very important to the understanding of the reactivity of the ring. Recently, there has been a marked increase[23−25,45−49] in the application of computational techniques that provide information involving the characteristic magnetic nature of aromatic compounds that arises from the π electron ring currents. This increase in activity can be attributed particularly to the improvements in the accuracy at which various NMR-related computations can be performed. The very close agreement between experiment and theory for reference compounds[45,50] permits fairly accurate predictions for most measures of magnetic criteria. Several magnetic properties can currently be investigated to enhance chemical insight, including ^{1}H chemical shifts, magnetic susceptibility anisotropies, diamagnetic susceptibility exaltations Λ, and nucleus-independent chemical shifts (NICS). "Anomalous" ^{1}H chemical shift patterns are probably the most familiar magnetic aromaticity indicator, first computationally studied for benzene by Pople.[51] This measure of aromaticity is not a general criterion, however, as there are several known exceptions.[23] Magnetic susceptibility anisotropy is a characteristic of planar aromatic systems. The component of the magnetic susceptibility tensor corresponding to the normal axis with respect to the ring is also affected by ring currents. A large negative anisotropy is observed for aromatic compounds; the converse is observed for antiaromatic systems. More recently, Schleyer[24] has proposed the use of NICS and Λ as measures of ring

---

(13) Garratt, P. J. *Aromaticity*; Wiley: New York, 1986.

(14) Lloyd, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 442.

(15) Hückel, E. *Z. Physik* **1931**, *70*, 204.

(16) Hückel, E. *Z. Physik* **1932**, *76*, 628.

(17) Hückel, E. *Z. Electrochem.* **1937**, *43*, 752.

(18) Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811.

(19) Dietz, F.; Vogel, H.; Robinovitz, M. *Z. Naturfor.* **1997**, *52*, 1072.

(20) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685.

(21) Maier, G.; Schneider, M. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 809.

(22) Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 614.

(23) Schleyer, P. V.; Jiao, H. J. *Pure Appl. Chem.* **1996**, *68*, 209.

(24) Schleyer, P. V.; Maerker, C.; Dransfeld, A.; Jiao, H. J.; Hommes, N. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(25) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. I. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; J. Wiley & Sons: New York, 1994.

(26) Glukhovtsev, M. N. *J. Chem. Educ.* **1997**, *74*, 132.

(27) Shaik, S. S.; Shurki, A.; Danovitch, D.; Hiberty, P. C. *J. Mol. Struct. (THEOCHEM)* **1997**, *155*, 398.

(28) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M. *J. Phys. Chem.* **1988**, *92*, 5086.

(29) Ohanessian, G.; Hiberty, P. C.; Lefour, J.-M.; Flament, J.-P.; Shaik, S. S. *Inorg. Chem.* **1988**, *27*, 2219.

(30) Kikuchi, S. *J. Chem. Educ.* **1997**, *74*, 480.

(31) Heilbronner, E.; Hafner, K. *Chem. Unserer Zeit* **1998**, *32*, 34.

(32) Heilbronner, E.; Shaik, S. *Helv. Chim. Acta* **1992**, *75*, 539.

(33) Fokin, A. A.; Jiao, H.; Schleyer, P. V. *J. Am. Chem. Soc.* **1998**, *120*, 9364.

(34) Fox, M. A.; MacBride, J. H. H.; Peace, R. J.; Wade, K. *J. Chem. Soc., Dalton Trans.* **1998**, 401.

(35) Thomas, R. L.; Welch, A. J. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1996**, *52*, 1689.

(36) Gimarc, B. M.; Zhao, M. *Inorg. Chem.* **1996**, *35*, 825.

(37) Jemmis, E. D.; Subramanian, G.; Radom, L. *J. Am. Chem. Soc.* **1992**, *114*, 1481.

(38) Jemmis, E. D.; Subramanian, G.; Srivastava, I. H.; Gadre, S. R. *J. Phys. Chem.* **1994**, *98*, 6445.

(39) Takano, K.; Izuho, M.; Hosoya, H. *J. Phys. Chem.* **1992**, *96*, 6962.

(40) Schleyer, P. V.; Najafian, K.; Mebel, A. M. *Inorg. Chem.* **1998**, *37*, 6765.

(41) Mauksch, M.; Gogonea, V.; Jiao, H.; Schleyer, P. V. *Angew. Chem., Int. Ed.* **1998**, *37*, 2395.

(42) Kruszewski, J.; Krygowski, T. M. *Tetrahedron Lett.* **1972**, 3839.

(43) Krygowski, T. M. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70.

(44) Subramanian, G.; Schleyer, P. v.; Jiao, H. *Organomet.* **1997**, *16*, 2362.

(45) Chesnut, D. B. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH Publishers: New York, 1997; Vol. 8.

(46) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669.

(47) Schleyer, P. V.; Freeman, P. K.; Jiao, H. J.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337.

(48) Bühl, M.; Thiel, W.; Jiao, H.; Schleyer, P. v. R.; Saunders: M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1994**, *116*, 7429.

(49) Bühl, M.; van Wüllen, C. *Chem. Phys. Lett.* **1995**, *247*, 63.

(50) Chesnut, D. B. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: San Diego, 1989; Vol. 21.

(51) Pople, J. A. *J. Chem. Phys.* **1956**, *24*, 1111.

current effects and criteria of aromaticity. NICS(*z*) reports the absolute magnetic shielding of a hypothetical noninteracting atom at some position *z* above the center of the ring; large negative values of NICS parameters have been shown to correspond to significant aromatic character.[24,46] Λ is defined[52,53] as the difference between the magnetic susceptibility of a compound on one hand and the sum of the susceptibilities of its localized prototype fragments on the other hand. The Λ values for potentially aromatic compounds are typically quite negative (diamagnetic).

As previously noted,[24,54] in molecular systems relatively free of strain and electronic distortion, one encounters many of the above criteria of aromaticity (geometric, energetic, and magnetic), all quantitatively and qualitatively similar. However, one can find exceptions in molecules encumbered by peculiar structural and energetic distortions.[25,55,56] The present study (re)investigates the family of silabenzene compounds in light of several of these established criteria of aromaticity, using high levels of computational methodology.

Computational Methods

All calculations have been carried out using the Gaussian 94(98)[57] and MOLPRO 97.3[58] software packages, running on the hardware facilities at the Weizmann Institute of Science. For comparative purposes, a variety of levels of theory were employed. Wave function-based methods considered include second-order Møller−Plesset perturbation theory (MP2),[59] coupled cluster with all single and double substitutions (CCSD),[60−62] and the same method augmented by a quasiperturbative accounting of triple excitations (CCSD(T)).[63] In addition, we considered hybrid density functional theory (HDFT) methods.[64] The HDFT methods employed two different exchange−correlation functionals, namely, Becke's three-parameter hybrid exchange functional[64] in combination with nonlocal correlation provided by the Lee−Yang−Parr expression,[65] B3LYP, on one hand, and with the nonlocal correlation provided by the Perdew−Wang (1991) expression, B3PW91,[66] on the other hand. Dunning's correlation consistent basis sets[67] were employed for all calculations. These are denoted cc-pV*n*Z (correlation consistent polarized valence *n*-tuple ζ), where *n* = D for double, T for triple, Q for quadruple, and 5 for quintuple ζ. More specifically, in this study we considered *n* = D and T, with cc-pVDZ being a [4s3p1d/3s2p1d/2s1p] contraction of a (12s8p1d/9s4p1d/4s1p) primitive set and cc-pVTZ representing a [5s4p2d1f/4s3p2d1f/3s2p1d] contraction of a (15s9p2d1f/10s5p2d1f/5s2p1d) primitive set. For the calculation of the NMR properties, the aug-cc-pVDZ and aug-cc-pVTZ basis sets were used,[68] which differ from their cc-pV*n*Z counterparts by the addition of one diffuse (low-exponent) function of each angular momentum. Finally, some calculations were carried out using the cc-pVTZ+1 basis set, which denotes the addition of a single high-exponent d function (α_d = 1.185) on Si only. Such "inner polarization functions" were very recently shown to be crucial for accurate bond lengths and vibrational frequencies of second-row compounds by two of us.[69] Molecular orbital contour plots, used as an aid in the discussion of the results, were generated using the program 3D-PLTORB[70] and depicted using QMView.[71] In the present work, structural comparisons are made relative to the computed structures of specific prototype molecules. The computed parameters for the latter are given in Table 1.

Table 1. B3LYP/cc-pVTZ Structural Parameters (Å) for Prototype Molecules

prototype	bond	length (Å)
Si_2H_4	Si=Si	2.160
Si_2H_6	Si−Si	2.354
SiH_2CH_2	C=Si	1.706
SiH_3CH_3	C−Si	1.884
C_2H_4	C=C	1.324
C_2H_6	C−C	1.527
C_6H_6	CC	1.391

Interpretation of calculated nucleus-dependent chemical shifts, such as ^{1}H chemical shifts, requires some care as to appropriate reference for the comparison. One of us has done a regression analysis for ^{1}H chemical shifts calculated for a series of prototype molecules that span the range of the NMR field from 0 to 7 ppm (relative to tetramethylsilane, TMS), to provide a systematic comparison with experimental measurements at several levels of theory.[72] For the present work, these comparisons are made using the B3LYP/aug-cc-pVTZ//B3LYP/cc-pVTZ set of data for which the regression line is expt = 29.40 − 0.925(calc), R^2 = 0.9984. (This type of nonunit slope has been noted repeatedly before, e.g., refs 45, 73.)

Calculations of nucleus-dependent and -independent chemical shifts were carried out using the gauge-invariant atomic orbital (GIAO) approach[74,75] with the aug-cc-pVTZ and aug-cc-pVDZ basis sets, respectively. This combination has been shown to give self-consistent predictions of chemical shifts for molecules of the type considered here. The magnetic susceptibilities were computed using the individual gauge for atoms in molecules, IGAIM,[76] and continuous set of gauge transformations, CSGT,[77] methods also using the aug-cc-pVTZ basis set. The IGAIM approach takes the gauge origin as the basin of charge density within bonds, while the CSGT approach

---

(52) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L.; Snyder, J. P., Ed.; Academic Press: New York, 1971; Vol. 2, pp 167.

(53) Fleischer, U.; Kutzelnigg, W.; Lazzeretti, P.; Mühlenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298.

(54) Baldridge, K. K.; Gordon, M. S. *Organometallics* **1988**, *7*, 144.

(55) Katritzky, A. R.; Barczynski, P.; Masummarra, G.; Pisano, D.; Szafran, M. *J. Am. Chem. Soc.* **1989**, *111*, 7.

(56) Jug, K.; Kosster, A. M. *J. Phys. Org. Chem.* **1991**, *4*, 163.

(57) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN94*-DFT, Revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1994.

(58) Werner, H.-J.; Knowles, P. J.; Amos, R. D.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Leininger, T.; Lindh, R.; Lloyd, A. W.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Peterson, K.; Pitzer, R.; Pulay, P.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Taylor, P. R.; Thorsteinsson, T. MOLPRO.

(59) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(60) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(61) Scuseria, G. E.; Scheiner, A. C.; Lee, T. J.; Rice, J. E.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *86*, 2881.

(62) Scuseria, G. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1989**, *90*, 3700.

(63) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(64) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(65) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(66) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.

(67) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(68) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(69) Martin, J. M. L.; Uzan, O. *Chem. Phys. Lett.* **1998**, *282*, 19.

(70) *3D-PLTORB*, 3D version; San Diego, 1997.

(71) Baldridge, K. K.; Greenberg, J. P. *J. Mol. Graphics* **1995**, *13*, 63.

(72) Baldridge, K. K.; Siegel, J. S. *J. Phys. Chem.* **1999**, *103*, 4038.

(73) Chesnut, D. B. *Chem. Phys.* **1997**, *314*, 73.

(74) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8521.

(75) Ditchfield, R. *J. Chem. Phys.* **1972**, *56*, 5688.

(76) Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1992**, *194*, 1.

(77) Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1993**, *210*, 223.

Table 2. Comparison of Computed Structural Parameters (Å) for Various Silaaromatic Compounds at RHF/cc-pVDZ, B3LYP/cc-pVDZ, and B3LYP/cc-pVTZ Levels of Theory

	r(CC)			*r*(CSi)			*r*(SiSi)		
structure	**I**^{a}	**II**^{b}	**III**^{c}	**I**	**II**	**III**	**I**	**II**	**III**
C_6H_6	1.389	1.399	1.391						
SiC_5H_6	1.393	1.402	1.394(5)^d	1.767	1.780	1.770(65)^d			
	1.396	1.405	1.398(7)^d						
Si_5CH_6				1.770	1.782	1.770	2.221	2.222	2.216
							2.217	2.220	2.213
Si_6H_6							2.219	2.250	2.238(3)^4
o-$Si_2C_4H_6$	1.372	1.393	1.384	1.811	1.804	1.794	2.159	2.182	2.175
	1.425	1.418	1.411						
m-$Si_2C_4H_6$	1.399	1.406	1.398	1.761	1.774	1.762			
				1.772	1.785	1.775			
p-$Si_2C_4H_6$	1.392	1.401	1.393	1.786	1.794	1.785			
1,2,3-$Si_3C_3H_6$	1.397	1.404	1.396	1.780	1.793	1.783	2.204	2.208	2.201
1,2,4-$Si_3C_3H_6$	1.371	1.392	1.383	1.832	1.815	1.807	2.177	2.200	2.194
				1.811	1.804	1.795			
				1.745	1.769	1.757			
				1.793	1.792	1.780			
1,3,5-$Si_3C_3H_6$				1.764	1.775	1.763			
1,2,3,4-$Si_4C_2H_6$	1.368	1.389	1.380	1.825	1.812	1.803	2.180	2.205	2.199
							2.243	2.226	2.219
1,2,3,5-$Si_4C_2H_6$				1.766	1.776	1.764	2.218	2.218	2.212
				1.767	1.780	1.768			
1,2,4,5-$Si_4C_2H_6$				1.777	1.786	1.775	2.218	2.221	2.217

[a] RHF/cc-pVDZ. [b] B3LYP/cc-pVDZ. [c] B3LYP/cc-pVTZ. [d] B3LYP/cc-pVTZ+1; digits that are different for B3LYP/cc-pVTZ+1 are given in parentheses.

continuously transforms the gauge back to the reference. Both of these methods, while superior to single gauge origin (SGO) methods, require adequate basis set flexibility to give reliable results.

Results and Discussion

Structure. A summary of structural parameters for the whole set of silaaromatic compounds is presented in Table 2. A full set of data across all basis sets investigated is available upon request from the authors. Theoretical computations on monosilabenzene predicted[78] a stable structure nearly 10 years before its matrix isolation and spectral analysis.[79−82] More recently, Markl et al.[83] synthesized 2,6-bis(trimethylsilyl)-1,4,-di(terbutyl)monosilabenzene, a molecule that is stable only in solution. The first available computations[54,84−87] using semiempirical techniques[78] predicted a structure with a CSi bond length of 1.75 Å and CC bond lengths of approximately 1.41 Å. While these results agree well with our best calculations, due to error compensation, the methods are not uniformly reliable. In the present study, one sees a convergence of structural parameters toward a SiC bond length of 1.765 Å and an average CC bond length of 1.396 Å, both about 0.02 Å below the corresponding average of the double- and single-bond prototype systems (Table 1). This is indicative of structural aromaticity analogous to that seen in benzene. Addition of a tight d function on Si only shortens *r*(CSi) by 0.005 Å, reflecting the fairly nonpolar character of the C−Si bond.

Pentasilabenzene exhibits significant structural delocalization, with SiC and SiSi bond lengths just below the average of the respective double- and single-bond lengths. There is perhaps more delocalization in the SiC bonds than in the SiSi bonds, the former being about 0.02 Å below average and the latter being some 0.03 Å below average. Additionally, the SiC bond lengths are almost identical to those in monosilabenzene. Basis set and correlation effects are not particularly dramatic for pentasilabenzene, being essentially nonexistent in the prediction of the SiSi linkage, but amounting to about 0.01 Å in the CSi bond length. It is also worth noting that the MP2 method tends to exaggerate correlation effects, accounting for a nearly 0.02 Å expansion in the CSi bond over the RHF value (r(SiC) = 1.791 Å, r(SiSi) = 2.222, 2.221 Å, at the MP2/cc-pVDZ level).[88]

Monosilabenzene and hexasilabenzene are probably the two systems considered here that have been most studied computationally. Unlike SiC_5H_6, however, Si_6H_6 has not been observed experimentally. Since one would intuitively expect hexasilabenzene to be as symmetric as benzene, the behavior of this molecule is of considerable interest. Previous conclusions about the symmetry of the minimum energy structure for hexasilabenzene (D_{6h} vs D_{3d}) vary considerably with the level of theory.[76,79,80,89,90] Structural predictions at the RHF level of theory are inconsistent with increasing levels of basis sets, changing back and forth between D_{6h} and D_{3d} as

---

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

(79) Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1978**, *100*, 5246.

(80) Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem., Int. Engl. Ed.* **1980**, *19*, 52.

(81) Maier, G.; Mihm, G.; Reisenauer, H. P. *Chem. Ber.* **1982**, *115*, 801.

(82) Solouki, B.; Rosmus, P.; Bock, H.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 51.

(83) Markl, G.; Hofmeister, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 789.

(84) George, P.; Bock, C. W.; Trachtman, M. *Theor. Chim. Acta* **1987**, *71*, 289.

(85) Baldridge, K. K.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 4204.

(86) Gordon, M. S.; Boudjouk, P.; Anwari, F. *J. Am. Chem. Soc.* **1983**, *105*, 4972.

(87) Schlegel, H. B.; Coleman, B.; Jones, M., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 6499.

(88) Martin, J. M. L.; El-Yazal, J.; François, J. P. *Chem. Phys. Lett.* **1995**, *242*, 570.

(89) Dewar, M. J. S. *J. Am. Chem. Soc.* **1975**, *97*, 6591.

(90) Nagase, S.; Teramae, H.; Kudo, T. *J. Chem. Phys.* **1987**, *86*, 4513.

one varies both the basis set split or the number and type of basis functions. Consistent results are not observed until correlation is included. MP2 or HDFT methods predict a D_{3d} structure with equal bond lengths ranging from 2.22 to 2.25 Å. The deviation from planarity is highly dependent on the level of theory, with an angle ranging from 6° to 33°, and a puckered-planar energy difference under 5 kcal/mol. At the highest level of theory considered in the present work for geometries (B3LYP/cc-pVTZ+1), the predicted D_{3d} structure has a SiSi bond length of 2.233 Å, an out-of-plane torsion angle of 29.4°, and a preference over the D_{6h} conformation of 1.43 kcal/mol. CCSD(T)/cc-pVTZ calculations at the B3LYP/cc-pVTZ reference geometry, which represent the highest level of theory considered for energetics in this work, are in close agreement (1.29 kcal/mol); interestingly, connected triple excitations make up most of the small difference, the CCSD energy difference being only 0.40 kcal/mol. MP2 fortuitously yields 1.03 kcal/mol due to an error cancellation.

Why is Si_6H_6 nonplanar? The ring puckering mode leading from the D_{6h} to the D_{3d} structure has b_{2g} symmetry. To satisfy the Pearson criterion[91] for second-order Jahn−Teller (SOJT) distortion, there should then be a low-lying excited singlet state of B_{2g} symmetry (since the ground state is a closed-shell singlet). The lowest-lying $^1B_{2g}$ state would be generated from a HOMO(e_{1g}) → LUMO+2(e_{2g}) excitation: from a time-dependent DFT[92,93] (specifically, TD-B3LYP/aug-cc-pVDZ) calculation of the electronic spectrum, we find that this excitation results in a $^1B_{1g}$ state at 4.02 eV, a $^1E_{1g}$ state at 4.10 eV, and a $^1B_{2g}$ state at 4.22 eV, the latter of which is low enough to cause a second-order Jahn−Teller effect. It should be pointed out that since the 4s, 4p, and 3d orbitals of Si are *much* more accessible than the 3s and 3p orbitals in C, the structure of the virtual orbitals of Si_6H_6 is radically different from that of benzene: for instance, neither LUMO+1 nor LUMO+2 are π^* orbitals, and LUMO+2 has appreciable d participation. It was previously noted by Sax et al.[94] that no significant ring-puckering energy was seen in a π-electron only CI calculation, but that a significant puckering energy resulted when correlation outside the π space was allowed: this finding is consistent with the present results.

Does a similar effect occur in Si_2H_4? This molecule indeed undergoes distortion[95] from the D_{2h} to the C_{2h} geometry, corresponding to an imaginary frequency with B_{1g} symmetry at the D_{2h} geometry. At the TD-B3LYP/aug-cc-pVDZ level, we find a $^1B_{1g}$ excited state (resulting from a HOMO(b_{3u}) → LUMO+1(b_{2u}) excitation) at 4.38 eV, which incidentally is not much higher than the $\pi-\pi^*$ excitation at 3.97 eV. (For comparison, the $^1B_{1g}$ state in ethylene lies at 7.25 eV.) This again provides an explanation in terms of second-order Jahn−Teller effects and more accessible Si virtual orbitals.

Of the three possible isomers of disilabenzene, i.e., *ortho*, *meta*, and *para* arrangements of silicon atoms within the ring, only the *para* isomer is known experimentally, having been observed in a noble gas matrix.[96] The series was first investigated[97] at the Hartree−Fock level with small basis sets and without consideration of magnetic properties. Density functional calculations using several basis sets all predict planar geometries for the three isomers, as was found previously. All three structures display some degree of delocalization, all ring bond lengths being between the corresponding isolated single and double bond lengths. However, the *ortho* isomer exhibits a distinct alternating long−short character (Table 2), suggesting a geometry leaning toward a Kékulé structure in which the Si−Si and two C−C bonds are localized. More careful analysis, however, reveals that the C−Si and remaining C−C bonds are only slightly longer than the average of the corresponding single and double bond lengths (1.794 and 1.411 Å, respectively, at the B3LYP/cc-pVTZ level of theory), and this implies that there is significant delocalization of π electron density in this isomer. The *ortho* structure is rigorously planar (C_{2v} symmetry), despite the fact that disilene prefers to be nonplanar,[95] which is further evidence for conjugation within the six-electron π system. The other two isomers of disilabenzene have predicted bond lengths within the ring that are indicative of significant structural delocalization. Basis set effects are relatively significant in the bonds involving silicon, lengthening by nearly 0.02 Å from the minimal basis sets to the more extensive polarized basis sets. Addition of dynamic correlation results in an additional 0.01−0.02 Å lengthening.

Of the three isomers of trisilabenzene, 1,3,5-trisilabenzene has been studied theoretically in the past[98−101] at both RHF and correlated (CISD and CCSD(T) with DZP basis sets[100] and MP2 [102]) levels of theory. (Very tentative evidence from collision-induced dissociation experiments exists for its successful synthesis.[103]) As in the present HDFT results, a planar D_{3h} geometry is consistently found. As pointed out,[100] there is a significant bond shortening at the RHF level upon progressing to larger, more polarized basis sets. The ring bond length is shortened by about 0.015 Å from RHF/DZ to RHF/cc-pVDZ and further decreases by 0.005 Å with the full double-ζ plus polarization. Addition of another set of valence functions shortens r(CSi) again by 0.005 Å (also from HDFT/cc-pVDZ to HDFT/cc-pVTZ). Correlation effects are very small, amounting to ~0.001 Å at the CISD[87] level, as does the B3LYP−HF difference. All three trisilabenzene isomers are predicted to be planar. (Note that the 1,2,3-isomer has a tiny out-of-plane imaginary frequency of 32i cm^{-1} at the B3LYP/cc-pVDZ level, which disappears upon enlarging the basis set.) The 1,3,5-isomer exhibits the most uniform bond delocalization of all three isomers, with equal r(SiC) values

---

(91) Pearson, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 4947.
(92) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439.
(93) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 8218.
(94) Sax, A. F.; Kalcher, J.; Janoschek, R. *J. Comput. Chem.* **1988**, *9*, 564.
(95) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201.
(96) Maier, G.; Schottler, K.; Reisenauer, H. P. *Tetrahedron Lett.* **1985**, *26*, 4079.
(97) Baldridge, K. K.; Gordon, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 369.
(98) Matsunaga, N.; Gordon, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 11407.
(99) Matsunaga, T. R.; Cundari, T. R.; Schmidt, M. W.; Gordon, M. S. *Theor. Chim. Acta* **1992**, *83*, 57.
(100) King, R. A.; Vacek, G.; Schaefer, H. F., III. *J. Mol. Struct. (THEOCHEM)* **1995**, *358*, 1.
(101) Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916.
(102) Apeloig, Y.; Hrusak, J. Unpublished results.
(103) Bjarnason, A.; Arnason, I. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1633.

Table 3. Comparison of Computed Relative Energetics (kcal/mol) for Various Silaaromatic Compounds at RHF/cc-pVDZ, B3LYP/cc-pVDZ, B3LYP/cc-pVTZ, and CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ Levels of Theory

	1,2-$Si_2C_4H_6$	1,3-$Si_2C_4H_6$	1,4-$Si_2C_4H_6$	1,2,3-$Si_3C_3H_6$	1,2,4-$Si_3C_3H_6$	1,3,5-$Si_3C_3H_6$	1,2,3,4-$Si_4C_2H_6$	1,2,3,5-$Si_4C_2H_6$	1,2,4,5-$Si_4C_2H_6$
RHF/cc-pVDZ	1.9	0	16.1	8.7	16.5	0	7.4	0	15.5
B3LYP/cc-pVDZ	0	1.2	9.8	1.2	8.4	0	2.3	0	8.1
B3LYP/cc-pVTZ	3.0	0	11.3	9.2	13.6	0	6.4	0	9.0
MP2/cc-pVTZ	3.2	0	11.9	11.5	16.5	0	7.0	0	6.8
CCSD(T)// cc-pVTZ//B3LYP/ cc-pVTZ	3.3	0	12.2	10.4	14.9	0	7.0	0	9.1

about 0.033 Å below the average of the corresponding double and single bond lengths. In contrast, the 1,2,3-isomer displays more double bond character in the SiSi linkages; the other bonds in the ring are near the average of the respective double and single bond lengths (with *r*(CC) taking on the benzene value at this level of theory). The SiSi linkages are nearly 0.05 Å shorter than the average of the Si═Si and Si−Si prototypes. In the 1,2,4-isomer, one sees even more localization, closest to a Kékulé structure having Si═Si, and alternating Si═C and C═C, with the SiSi and CC linkages being 0.05 and 0.04 Å shorter than the average of the respective double and single bond lengths.

Very little attention has been paid to the tetrasubstituted silicon ring systems in the literature. Of the three isomers, only the 1,2,4,5-isomer has a planar ground state at our highest levels of theory. However, the deviation from planarity in the 1,2,3,4-isomer is negligible (0.16 kcal/mol at the CCSD(T)/cc-pVTZ level, 0.14 kcal/mol at the B3LYP/cc-pVTZ level), while an only slightly more meaningful deviation (0.43 kcal/mol at the CCSD(T)/cc-pVTZ level, 0.66 kcal/mol at the B3LYP/cc-pVTZ level) is seen for the 1,2,3,5-isomer.

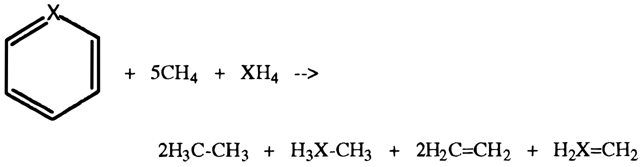
The 1,2,3,4-isomer undergoes SOJT distortion along an a_2 mode into a "twisted" structure with C_2 symmetry because of a low-lying HOMO(a_2) → LUMO+2(a_1) excitation at 3.59 eV (computed at the TD-B3LYP/aug-cc-pVDZ level). At the same level of theory, we find a HOMO(b_1) → LUMO+2(a_1) excitation in the 1,2,3,5-isomer at 3.89 eV (consistent with SOJT distortion along a b_1 mode into C_s symmetry). For the 1,2,4,5-structure, however, the lowest vibrational frequency (a_u symmetry) has a small but real value: the lowest excitation that has the correct symmetry properties to cause SOJT distortion is a HOMO(b_{1g}) → LUMO+4(b_{1u}) excitation that lies at 4.62 eV, rather higher than in the two other cases. Pentasilabenzene, finally, undergoes SOJT distortion along a b_1 mode into C_s symmetry because of two low-lying $^1B_1$ states at 4.04 and 4.22 eV, which are HOMO-1(b_1) → LUMO+2(a_1) and HOMO(a_2) → LUMO+4(b_1) excitations, respectively. (We note in passing that both pentasilabenzene and hexasilabenzene are predicted to have absorptions at the blue end of the visible range.)

Interestingly, in the Si_5CH_6 case, both HF and MP2 erroneously predict the planar geometries to be more stable, while neglecting the (T) contribution (i.e., CCSD), which is somewhat biased toward the planar structure, as it is in hexasilabenzene. In short, of the less accurate methods considered, only B3LYP consistently predicts the same structural tendencies as CCSD(T). A careful look at the three structures suggests relatively delocalized structures for the 1,2,3,5- and 1,2,4,5-isomers, while the 1,2,3,4-isomer displays significant localization, emphasizing a Kékulé structure having two Si═Si linkages and one C═C linkage. In the 1,2,3,4- and 1,2,3,5-isomers, the bond lengths within the ring structure deviate from the average of the respective single and double bond lengths by a relatively consistent 0.03 Å. The 1,2,3,4-isomer has SiSi and CC linkages nearly 0.05 Å shorter than the average of the corresponding single and double bond lengths, the intervening SiSi linkage being 0.03 Å shorter and the SiC linkages 0.01 Å shorter. Additionally, the "localized" 1,2,3,4-isomer structural predictions display significant effect due to dynamical correlation (a lengthening of *r*(CC) by nearly 0.02 Å); this remark also applies to the "localized" 1,2,4-trisilabenzene isomer.

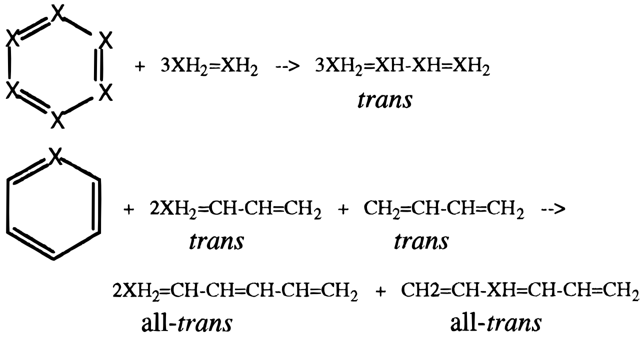
Relative Energetics. Relative energetics at several levels of theory are reported in Table 3. Over all basis sets considered in this work, we noticed a general deficiency in the cc-pVDZ basis set in prediction of relative stabilities among the isomers of the various sets. Consistent results require more flexible basis sets and inclusion of dynamical correlation, especially for establishing the ordering of those isomers that lie very close in energy (e.g., the *ortho* and *meta* disilabenzene isomers; 1,2,3,4- and 1,2,4,5-tetrasilabenzene isomers). Correlated ab initio or HDFT wave functions using the cc-pVTZ basis set tend to be the lowest level one would consider in order to establish consistent predictions. This being said, CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ predicts the following relative stabilities: for disilabenzenes *meta* (0.0 kcal/mol) > *ortho* (3.3 kcal/mol) > *para* (12.2 kcal/mol); for trisilabenzenes 1,3,5 (0.0 kcal/mol) > 1,2,3 (10.4 kcal/mol) > 1,2,4 (14.9 kcal/mol); and for tetrasilabenzenes 1,2,3,5 (0.0 kcal/mol) > 1,2,3,4 (7.0 kcal/mol) > 1,2,4,5 (9.1 kcal/mol). The importance of triple substitutions in the CCSD method actually varies across the three sets of isomers; the most dramatic effects are observed in the trisilabenzene series, amounting to a slightly more than 2 kcal/mol decrease in energy relative to 1,3,5. Incidentally, this series also exhibits the largest differences between CCSD(T) and B3LYP (the latter being biased in the same direction as CCSD, by about 1.2−1.3 kcal/mol).

Bond Separation Reactions. As has been pointed out previously,[44] estimates of aromatic stabilization energies are quite variable depending on the particular type of equations used (isodesmic, homodesmotic, superhomodesmotic) as well as the reference molecules used. In the present work, we have limited ourselves to isodesmic stabilization energies (ISE values), which are intended as an energetic measure of delocalization, and homodesmotic stabilization energies (HSE values), which attempt to separate the contribution of the closed aromatic ring system from that of simple conjugation.

Scheme 1 . Example of Isodemic Bond Separation Reaction



Scheme 2 . General Examples of Homodesmotic and Superhomodesmotic Reactions



Calculation of the isodesmic[104] and homodesmotic[105,106] delocalization stabilization energies (ISE and HSE, respectively) via the appropriate bond separation reactions establishes the trends shown in Table 4. In the cases of 1,2-disilabenzene, 1,2,4-trisilabenzene, and 1,2,3,4-tetrasilabenzene, two nonequivalent Kekule structures exist, leading to ambiguities in both the isodesmic and homodesmotic bond separation reactions. (This was previously noted for heterocyclic compounds in, for example, ref 107.) For instance, in the isodesmic 1,2-disilabenzene case, one obtains

$$C_4Si_2H_6 + 4CH_4 + 2SiH_4 \rightarrow \text{(a) } 2C_2H_4 + Si_2H_4 + 2CH_3{-}SiH_3 + C_2H_6$$

$$\text{or} \rightarrow \text{(b) } 2SiH_2{=}CH_2 + C_2H_4 + 2C_2H_6 + Si_2H_6$$

This ambiguity can be partially resolved by assuming that the “true” structure is an exact 50:50 average of the two Kekule structures, which corresponds to averaging the isodesmic/homodemotic stabilization energy over the two possible alternatives. One argument in favor of this admittedly somewhat makeshift solution is that, within the disila-, trisila-, and tetrasilabenzene isomer series, it leads to ISE or HSE orderings that parallel the trends in the relative stability of the respective isomers (see previous paragraph).

Inclusion of zero-point corrections affects the ISE values in fairly direct proportion to the number of carbon atoms present, with essentially no change seen for Si_6H_6, but an increase of 5 kcal/mol for benzene. Effects on the HSE are much weaker, amounting to only 0.8 kcal/mol for benzene at the B3LYP/cc-pVTZ level. The larger difference in the ISE case is easily explained by the fairly significant difference between paraffinic and olefinic C−H stretching frequencies; the corresponding change in the HSE case, namely, that between alkene and alkadiene C−H stretches, is much less pronounced.

Basis set effects on the ISE values are (predictably) somewhat stronger at the CCSD(T) level than at the B3LYP level; the largest difference between the cc-pVDZ and cc-pVTZ basis sets is seen for 1,3,5-trisilabenzene (B3LYP, 2.3 kcal/mol; CCSD(T), 3.6 kcal/mol). Basis set effects on the HSE values are less than 1 kcal/mol at all levels of theory.

ISEs are systematically overestimated (by 13−30%) at the MP2 level (which is known to overestimate delocalization); interestingly, the effect of adding connected triple excitations to the CCSD results is to increase ISE values by up to 17%. We also note that the CCSD(T)−B3LYP difference exhibits a fairly linear correlation with the number of silicon atoms, with the B3LYP values being 3.3 kcal/mol too high for benzene and 3.6 kcal too low for Si_6H_6. Similar convergence trends are present in the HSE values, albeit less pronounced and less systematic.

In previous work,[54,84,87] bond separation reactions predicted monosilabenzene to have roughly two-thirds of the aromaticity of benzene. (In the very recent work of Wakita et al.,[6] the isomerization energies from 1-methylene-2,4-cyclohexadiene to benzene and from 1-methylene-4-sila-2,4-cyclohexadiene—in principle a much better measure of aromatic stabilization—were calculated at the B3LYP/6-311+G* level and found to be essentially identical.) In the present work, we find the ISE and HSE of monosilabenzene to be about three-fourths of the corresponding values for benzene, at both the B3LYP/cc-pVTZ and CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ levels. Similar values are obtained using the smaller cc-pVDZ basis set, suggesting our prediction to be converged with respect to the level of theory.

Using the same criteria, hexasilabenzene is likewise found to have about three-fourths of the aromatic stabilization energy of benzene. (At the B3LYP/6-311+G* level and using *cis*- rather than *trans*-dienes, Si_6H_6 was found[46] to have about 46% of the HSE of benzene in the D_{6h} saddle point geometry and about 52% at the D_{3d} equilibrium geometry. This result in fact does agree better with magnetic measures of aromaticity; see below.) The most conspicuous feature among the other structures is the prediction that 1,3,5-trisilabenzene will be highly aromatic: not only is its ISE about 87% that of benzene, but its HSE—which should be a better measure of aromatic stabilization energy than ISE—actually slightly *exceeds* that of benzene. This molecule would appear to be an interesting synthetic target.

Interestingly, 1,3-disilabenzene and its “complement”, 1,2,3,5-tetrasilabenzene, are both predicted to have about three-fourths of the ISE and four-fifths of the HSE of benzene, while both ISE and HSE suggest that pentasilabenzene will have about two-thirds of the aromatic stabilization energy of benzene. By the ISE criterion, 1,4-disilabenzene is predicted to be the least aromatic compound (with about half the ISE of benzene), followed by 1,2,4-trisilabenzene and the 1,2,3,4- and 1,2,4,5-tetrasilabenzenes (all with about three-fifths of the ISE of benzene). By the HSE criterion, 1,2,4,5-

---

(104) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

(105) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Theor. Chim. Acta* **1975**, *38*, 121.

(106) George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**.

(107) Chesnut, D. B.; Davis, K. M. *J. Comput. Chem.* **1997**, *18*, 584.

Table 4. Comparison of Computed Bond Separation Reaction Energies at 0 K (kcal/mol) for Various Silaaromatic Compounds at RHF/cc-pVDZ, B3LYP/cc-pVDZ, B3LYP/cc-pVTZ, and CCSD(T)/cc-pVTZ//B3LYP/cc-pVTZ Levels of Theory

	isodesmic stabilization energy (ISE)					homodesmotic stabilization energy (HSE)				
	B3LYP/cc-		CCSD(T)/cc-		relative to C_6H_6 (%)	B3LYP/cc-		CCSD(T)/cc-		relative to C_6H_6 (%)
	pVDZ	pVTZ	pVDZ	pVTZ		pVDZ	pVTZ	pVDZ	pVTZ	
C_6H_6[a]	67.5	67.9	62.9	64.7	100.0	22.5	23.2	22.4	22.8	100.0
SiC_5H_6	51.9	51.9	48.7	49.2	76.1	17.1	17.3	17.6	17.6	77.0
1,2-$Si_2C_4H_6$[b]	43.0	42.9	40.3	41.2	63.8	13.5	13.8	13.4	14.1	61.9
c	31.2	31.2	28.8	29.4	45.4	7.8	8.1	7.4	8.0	35.1
d	54.7	54.7	51.7	53.1	82.2	19.3	19.6	19.4	20.3	88.8
1,3-$Si_2C_4H_6$	48.1	48.8	46.0	47.2	73.0	17.3	17.7	18.4	18.5	81.0
1,4-$Si_2C_4H_6$	38.2	37.4	35.7	35.0	54.1	11.7	11.4	12.7	12.1	53.0
1,2,3-$Si_3C_3H_6$	40.5	40.9	39.5	40.6	62.7	13.7	14.0	14.1	15.0	65.5
1,2,4-$Si_3C_3H_6$[b]	39.2	39.3	38.0	38.8	59.9	12.5	12.5	13.3	13.6	59.4
c	27.5	27.6	26.5	26.9	41.6	7.1	7.2	7.7	7.8	34.2
d	51.0	51.1	49.4	50.6	78.3	17.8	17.8	18.9	19.3	84.6
1,3,5-$Si_3C_3H_6$	53.6	55.8	52.8	56.4	87.2	20.8	21.5	22.5	23.3	102.2
1,2,3,4-$Si_4C_2H_6$[b]	37.3	37.6	38.0	38.4	59.4	12.2	12.2	13.5	13.6	59.8
c	25.6	25.9	26.6	26.5	41.0	7.4	7.4	8.3	8.3	36.2
d	49.1	49.4	49.4	50.3	77.8	17.1	17.0	18.7	19.0	83.3
1,2,3,5-$Si_4C_2H_6$	45.6	46.9	45.8	48.1	74.4	15.8	16.0	17.0	17.5	76.8
1,2,4,5-$Si_4C_2H_6$	37.5	38.0	37.8	39.0	60.3	9.6	9.5	10.9	10.9	47.6
Si_5CH_6	41.5	42.4	43.4	44.8	69.3	12.7	12.1	15.1	14.4	63.1
Si_6H_6	43.3	44.2	47.0	47.8	73.9	14.1	13.2	16.0	15.2	66.7

[a] For comparison, ISE and HSE values derived from experimental $\Delta H°_{f,298}(g)$ values are 64.2 ± 1.5 and 21.6 ± 1.7 kcal/mol, respectively.[26] Combination with $H_{298} - H_0[C_2H_6(g)] = 2.78$ kcal/mol from ref 114 and calculated (from B3LYP/cc-pVTZ harmonic frequencies). $H_{298} - H_0$ values for the other species, we obtain at 0 K: ISE = 65.7 ± 1.5, HSE = 21.9 ± 1.7 kcal/mol. [b] Average of values for both alternative sets of bond separation reactions (corresponding to nonequivalent limiting Kekule structures). [c] Value corresponding to limiting Kekule structure with smaller number of formal Si=Si bonds. [d] Value corresponding to limiting Kekule structure with greater number of formal Si=Si bonds.

Table 5. Comparison of Ionization Potentials (eV) and Homodesmotic Stabilization Energies (kcal/mol) for Various Silaaromatic Compounds at the B3LYP/cc-pVTZ Level of Theory

structure	IP	HSE
C_6H_6	9.25[a]	22.8
SiC_5H_6	7.99[b]	17.6
1,2-$Si_2C_4H_6$	7.57	14.1
1,3-$Si_2C_4H_6$	7.69	18.5
1,4-$Si_2C_4H_6$	7.07	12.1
1,2,3-$Si_3C_3H_6$	7.78	15.0
1,2,4-$Si_3C_3H_6$	7.02	13.6
1,3,5-$Si_3C_3H_6$	8.02	23.3
1,2,3,4-$Si_4C_2H_6$	7.13	13.6
1,2,3,5-$Si_4C_2H_6$	7.40	17.5
1,2,4,5-$Si_4C_2H_6$	6.82	10.9
Si_5CH_6	7.14	14.4
Si_6H_6	7.22	15.2

[a] Experiment: 9.24384(6) eV,[115] 9.24372(5) eV[116]. [b] Experiment: 8.11 eV[117].

tetrasilabenzene is actually predicted to be the least aromatic, closely followed by its complement 1,4-disilabenzene (both with about half the HSE of benzene); 1,2,4-trisilabenzene and 1,2,3,4-tetrasilabenzene are both predicted to have about three-fifths of the HSE of benzene.

Ionization Potentials. Computed vertical ionization potentials, IP_V, for the series of silaaromatic compounds are shown in Table 5. These have been computed as ΔE values at the B3LYP/cc-pVTZ level of theory, a method that has recently been shown to be quite successful for this purpose.[108] (For comparison, note that B3LYP/cc-pVTZ+1 yields values for IP_V and IP_a for monosilabenzene of 8.0 and 7.9 eV, respectively.) One must take care in linking properties such as IP, dipole, and orbital energy splittings directly to (de)localization. The IP could be explained by virtue of there being more Si atoms, which are less electronegative than C. Thus, Si=Si has a lower IP than C=C, but it is not more delocalized. In fact, within the series, the highest values of IP occur where isolated Si=Si linkages have essentially been avoided (i.e., 1,3,5-trisilabenzene (8.02 eV), benzene (9.26 eV), and monosilabenzene (7.99 eV)). The next grouping is only slightly lower than this set, ranging from 7.40 to 7.78 eV, consisting of 1,2,3-trisilabenzene, 1,3-disilabenzene, 1,2-disilabenzene, and 1,2,3,5-tetrasilabenzene. Each of these four still retains significant aromatic character with respect to structure and energetics when compared to benzene (>62%). The remaining silaaromatic structures have IPs below 7.22 eV, with the 1,2,4,5-tetrasilabenzene being the easiest to ionize, with an IP of 6.82 eV. This structure also is the least aromatically stable by energetic measures (48% that of benzene). We note that the qualitative ordering of IP_v values within an isomer series parallels the stability ordering of the isomers.

Magnetic Properties. Magnetic properties, including magnetic shieldings, NICS, magnetic susceptibilities, χ_M, magnetic susceptibility anisotropies, $\Delta\chi$, and diamagnetic susceptibility exaltations, Λ, have been computed for the set of silaaromatic compounds and are summarized in Tables 6−8. The magnetic susceptibility tensor describes the quadratic response of a molecule to an external magnetic field, and as such its isotropic and anisotropic components are relevant quantities to consider for the types of molecules studied here.

For the problem at hand, the magnetic susceptibility and exaltation data cannot be used in their unmodified form because of the variation in ring size. Schleyer and co-workers[46] advocate the use of ring-size-adjusted (anti)aromaticity indices, e.g., $\Lambda_{rel} = kn\Lambda/S^2$, in which k is an arbitrary proportionality constant, n is the number of electrons in the (anti)aromatic system, and S is the area of the ring. For easy reference, we have

Table 6. B3LYP/aug-cc-pVTZ Computed Magnetic Properties (ppm) Related to Aromaticity for Silaaromatic Compounds[d]

			magnetic susceptibility				exaltation	
			isotropic		anisotropy		homodesmotic	
	NICS(0)	NICS(1)	raw χ	RSA χ_{rel}	raw $\Delta\chi$	RSA $\Delta\chi_{rel}$	raw Λ	RSA Λ_{rel}
C_6H_6	−7.2	−9.9	−56.1	100.0	−64.8	100.0	−12.8	100.0
SiC_5H_6	−7.1	−8.5	−64.6	81.4	−63.2	68.9	−13.4	74.0
1,2-$Si_2C_4H_6$	−8.9	−9.1	−77.1	69.7	−67.6	52.9	−17.1[a]	67.9
1,3-$Si_2C_4H_6$	−6.5	−6.8	−73.3	67.3	−58.1	46.2	−13.2	53.4
1,4-$Si_2C_4H_6$	−6.8	−7.2	−72.7	65.3	−69.5	54.0	−14.7	57.8
1,2,3-$Si_3C_3H_6$	−9.9	−9.3	−90.5	59.9	−71.1	40.7	−19.9	58.0
1,2,4-$Si_3C_3H_6$	−8.2	−7.7	−85.4	56.6	−70.2	40.3	−17.5[b]	51.0
1,3,5-$Si_3C_3H_6$	−6.3	−5.5	−82.4	56.9	−47.7	28.5	−12.6	38.1
1,2,3,4-$Si_4C_2H_6$	−10.6	−9.5	−103.9	50.4	−82.8	34.8	−23.5[c]	50.1
1,2,3,5-$Si_4C_2H_6$	−9.3	−8.3	−99.2	49.6	−84.4	36.6	−22.3	48.4
1,2,4,5-$Si_4C_2H_6$	−9.0	−7.6	−98.8	48.7	−66.0	28.1	−19.3	42.4
Si_5CH_6	−11.1	−9.5	−118.2	43.5	−90.4	28.8	−30.8	49.9
Si_6H_6	−11.0	−9.7	−139.3	38.6	−113.5	27.2	−33.5	40.8

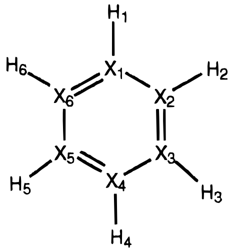
[a] Average of values corresponding to two limiting Kekule structures (−16.9 and −17.3 ppm). [b] Average of values corresponding to two limiting Kekule structures (−17.2 and −17.8 ppm). [c] Average of values corresponding to two limiting Kekule structures (−22.9 and −24.0 ppm). [d] The acronym RSA stands for "ring-size-adjusted" (see the text). NICS(0) and NICS(1) values were computed using the GIAO method; other data, using the CSGT method.

Table 7. Previously Tabulated Aromatic Stabilization Energies (ASE)[a] and Magnetic Properties[b] for Selected Compounds[46]

structure	ASE (kcal/mol)	NICS(0) (ppm)	NICS(0.5) (ppm)	Λ	χ_{anis}
C_6H_6	−34.1[c]	−8.9	−10.7	−13.9	−67.5
Si_6H_6	−15.6	−13.1	−12.8	−32.8	−114.6
Ge_6H_6	−15.3	−14.6	−14.5	−40.8	−130.8

[a] B3LYP/6-311+G**. [b] CSGT-B3LYP/6-311+G**. [c] Homodesmotic, but relative to *cis*-butadiene rather than *trans*-butadiene.

Table 8. Computed B3LYP/aug-cc-pVTZ ^1H Chemical Shifts for Silaaromatic Compounds[a]



structure	sym	^1H-1	^1H-2	^1H-3	^1H-4	^1H-5	^1H-6
C_6H_6	D_{6h}	7.14	7.14	7.14	7.14	7.14	7.14
$X_1 = Si$	C_{2v}	5.96	7.25	7.80	6.68	7.80	7.25
$X_1,X_2 = Si$	C_{2v}	6.14	6.14	7.90	7.64	7.64	7.90
$X_1,X_3 = Si$	C_{2v}	6.15	6.48_5	6.15	6.49_5	8.40	6.49_5
$X_1X_4 = Si$	D_{2h}	5.88	8.43	8.43	5.88	8.43	8.43
$X_1,X_2,X_3 = Si$	C_{2v}	6.39	5.80	6.39	7.44	8.45	7.44
$X_1,X_2,X_4 = Si$	C_s	5.90	6.71	7.36	6.09	7.86	9.20
$X_1,X_3,X_5 = Si$	D_{3h}	6.39	5.35	6.39	5.35	6.39	5.35
$X_1,X_2,X_3,X_4 = Si$	C_{2v}	6.29	6.33	6.33	6.29	8.99	8.99
$X_1,X_2,X_3,X_5 = Si$	C_{2v}	7.20	4.69	7.20	6.44_9	6.44_6	6.44_9
$X_1,X_2,X_4,X_5 = Si$	D_{2h}	6.47	6.47	8.78	6.47	6.47	8.78
$X_1-X_5 = Si$	C_{2v}	7.11	5.66	7.54	5.66	7.11	8.11
Si_6H_6	D_{6h}	6.94	6.94	6.94	6.94	6.94	6.94

[a] For reference, chemical shifts in some relevant model systems are Si_2H_4, $\delta^1H = 5.26$ ppm; $SiCH_4$, $\delta^1H(C) = 5.40$, $\delta^1H(Si) = 5.01$ ppm; C_2H_4, $\delta^1H = 5.35$ ppm.

chosen k such that a value of 100 is obtained for benzene. (By analogy we obtain χ_{rel} and $\Delta\chi_{rel}$.) In the cases of 1,2-disilabenzene, 1,2,4-trisilabenzene, and 1,2,3,4-tetrasilabenzene, the two alternative bond separation reactions yield slightly different exaltation values (see footnote to table). We have again chosen to consider the average of the two alternatives.

An adequate correlation ($R^2 = 0.84$) is seen between the ring-adjusted magnetic susceptibilities and the ring-adjusted exaltation values, while the latter correlate quite well ($R^2 = 0.95$) with the magnetic susceptibility anisotropies. All three criteria (Λ_{rel}, χ_{rel}, and $\Delta\chi_{rel}$) systematically predict decreasing aromaticity with increasing number of silicon atoms. Our computed data for Si_6H_6 agree with the prediction of Schleyer and coworkers[46] that the molecule would have about 40% of the aromaticity of benzene. Correlation between the exaltation values and the NICS(1) values is fairly poor. This is to some extent to be expected, since the height above the ring at which the π system has its maximum extent will vary considerably between C_6H_6 and Si_6H_6, and therefore NICS(z) values at any constant nonzero z will not provide a consistent measure across our series. Nevertheless, they may still be of value in predicting stability ordering within an isomer series.

As has been previously discussed,[46] local paramagnetic contributions of the σ bonds counteract the diamagnetic π ring current effects, thereby influencing NICS values.[53,109,110] Schleyer et al.[46] have shown that benzene NICS(0.5) values are actually lower than those of second-row homologues of benzene, (e.g., Si_6H_6, Ge_6H_6) due to the large paratropic effect of the C−C σ bonds, i.e., NICS(σ). Let us now consider the disilabenzene isomers. Λ_{rel}, NICS(0), and NICS(1) all predict the aromaticity ordering 1,2 > 1,4 > 1,3, while $\Delta\chi_{rel}$ suggests 1,4 $\gtrsim$ 1,2 > 1,3 and χ_{rel} predicts 1,2 > 1,3 > 1,4. For the trisilabenzene isomers, Λ_{rel}, NICS(0), and NICS(1) are likewise in agreement, predicting 1,2,3 > 1,2,4 > 1,3,5. Again minor variations from this theme are seen in the χ_{rel} (1,2,3 > 1,3,5 $\approx$ 1,2,4) and $\Delta\chi_{rel}$ (1,2,3 $\approx$ 1,2,4 > 1,3,5) trends. For the tetrasilabenzene isomers, Λ_{rel}, NICS(0), and NICS(1) once more predict the same trend in aromaticity, namely, 1,2,3,4 > 1,2,4,5 > 1,2,3,5, albeit with variations in the size of the difference between two isomers. In this case, χ_{rel} in fact does

---

(108) De Proft, F.; Geerlings, P. *J. Chem. Phys.* **1997**, *106*, 3270.

(109) Fowler, P. W.; Steiner, E. *J. Phys. Chem. A* **1997**, *101*, 1409.

(110) Bader, R. F. W.; Keith, T. A. *J. Chem. Phys.* **1993**, *99*, 3683.

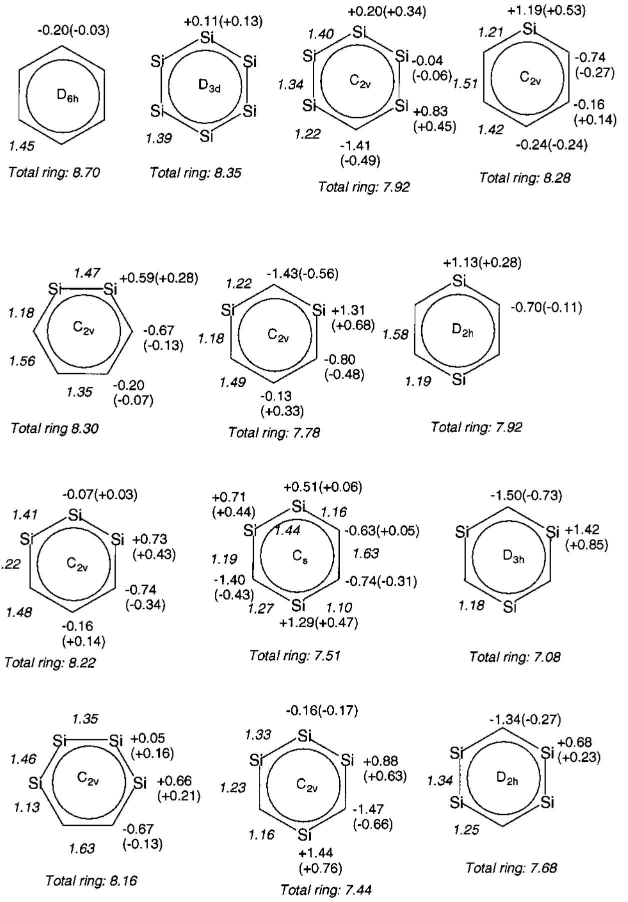


Figure 1. B3LYP/cc-pVTZ charge distributions and bond orders. NPA charges, followed by APT charges in parentheses, are given in roman type, while Wiberg bond orders are given in italic type. Only symmetry-unique values for the heavy atoms are given.

predict the same ordering, while $\Delta\chi_{\mathrm{rel}}$ instead suggests 1,2,4,5 1,2,3,4 > 1,2,3,5.

Minor variations aside, all magnetic criteria by and large agree on one thing: that the isomer that is energetically the most stable in each case (that is, 1,3, 1,3,5, and 1,2,3,5, respectively)—and that is found to be the *most* "aromatic" by energetic criteria—is in fact the *least* "aromatic", magnetically speaking! To shed some light on the reason for this, let us consider the example of 1,3,5-trisilabenzene. As seen from the computed NPA (natural population analysis)[111] and APT (atomic polarizability tensor)[112] charge distributions in Figure 1, this molecule has a pronounced $+ - + - + -$ charge alternation, to the degree that the molecule is more reminescent of borazine, $B_3N_3H_6$ (with Si taking the place of B and C that of N) than of benzene. Likewise, the computed Wiberg bond indices,[113] which for the SiC bonds are 1.18 at the B3LYP/cc-pVTZ level, suggest considerable contributions to the wave function from localized Si^+C^- structures. The borazine comparison is particularly relevant here, since the molecule has a HSE comparable to benzene (and for that reason is known as "the inorganic benzene"), while in fact the wave function is highly localized in character and magnetic criteria for aromaticity suggest that borazine is essentially nonaromatic.[46,109] Given the electronegativity difference between Si and C, this suggests that a lot of the stability of 1,3,5-trisilabenzene may stem not from aromaticity but from the fact that the 1,3,5-arrangement is the most favorable one for Si^+C^- systems. The computed APT charges for the other two isomers, 1,2,3- and 1,2,4-trisilabenzene, suggest that bonding in these two systems is considerably less ionic in character (since obviously neither adjacent $Si^{\delta+}$ atoms nor negative partial charges on Si are very desirable energetically) and in turn that the stability ordering between them could be driven by the greater aromaticity of the 1,2,3-isomer. The sum of the Wiberg bond orders in the ring, $\sum BO_R$, takes on values of 8.22, 7.51, and 7.08, respectively, for 1,2,3-, 1,2,4-, and 1,3,5-trisilabenzene: for comparison, the corresponding values for benzene and Si_6H_6 are 8.70 and 8.35, respectively. (The deviation from 9.00 for benzene is mostly due to three "Dewar-benzene" type *para* interactions with Wiberg bond orders of about 0.10. It should be pointed out that, while $\sum BO_R$ is a good indicator of ionic/covalent character, it is *not* an aromaticity criterion since a hypothetical 1,3,5-cyclohexatriene would have a $\sum BO_R$ value close to 9.00 as well.) In short, the 1,3,5 > 1,2,3 > 1,2,4 stability ordering can be explained as an interplay between ionic bonding and aromaticity considerations.

Turning now to the disilabenzene isomers, we note from the partial charges and Wiberg indices that bonding in 1,2-disilabenzene is largely covalent ($\sum BO_R = 8.30$), while both 1,3- and 1,4-disilabenzene ($\sum BO_R =$ 7.78 and 7.92, respectively) exhibit appreciable ionic character. Of these latter two, and all other things being equal, 1,3-disilabenzene would be the more stable since it does not involve juxtaposition of like partial charges. Since the 1,2-isomer is more aromatic than its 1,4-counterpart, the 1,3 > 1,2 > 1,4 stability ordering can again be rationalized as an interplay between ionic bonding and aromaticity. Similar considerations apply for the tetrasilabenzenes, where $\sum BO_R = 8.16$ suggests 1,2,3,4-tetrasilabenzene to be fairly covalent, while $\sum BO_R = 7.68$ for 1,2,4,5-tetrasilabenzene and particularly $\sum BO_R = 7.44$ for 1,2,3,5-tetrasilabenzene suggest rather more ionic bonding. Of the latter two, the 1,2,4,5-isomer is destabilized by adjacent charges of like sign, while the alternating charge pattern in 1,2,3,5-tetrasilabenzene leads to enhanced stability. At the end of the day, one obtains the 1,2,3,5 > 1,2,3,4 > 1,2,4,5 stability ordering, which is in fact observed in this work.

As a byproduct of the above analysis, we obtained the B3LYP/aug-cc-pVTZ-computed ^1H NMR chemical shifts for the set of silaaromatic compounds. After applying the linear regression expt = 29.40 − 0.925(calc), $R^2 = 0.9984$, discussed in the methods section, we obtain the values in Table 8, which may assist in the future experimental identification of these species. (To the

---

[111] Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

[112] Cioslowski, J. *J. Am. Chem. Soc.* **1989**, *111*, 8333.

[113] Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

[114] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

[115] Nemeth, G. I.; Selzle, H. L.; Schlag, E. W. *Chem. Phys. Lett.* **1993**, *215*, 151.

[116] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, G. *Gas-Phase Ion and Neutral Thermochemistry*; American Chemical Society and The American Institute of Physics for the National Bureau of Standards: 1988; Vol. 17.

[117] Bock, H.; Rosmus, P.; Solouki, B.; Maier, G. *J. Organomet. Chem.* **1984**, *271*, 145.

same end, the computed B3LYP/cc-pVTZ-computed frequencies and infrared intensities of all species have been made available as Supporting Information at http://theochem.weizmann.ac.il/web/papers/silabenzenes.html.) Consideration of the ^{1}H shifts for H(−C) atoms in monosilabenzene suggests a strong *meta* upfield effect, a moderate *para* downfield effect, and a weak *ortho* upfield effect. From considering the shift on H_2, in 1,3-disilabenzene, it appears that a "double-*ortho*" Si substitution results in a moderate downfield effect.

The trends in the ^{1}H shifts on H(−C) atoms in Table 8 can largely be rationalized in terms of these effects, e.g., the conjunction of two *meta* interactions leading to conspicuously high shifts (in the 9 ppm range). A similar analysis for the influence of C atoms on H(−Si) shifts, relative to hexasilabenzene, suggests a strong downfield *meta* effect, a moderate upfield *para* effect, and a weak upfield *ortho* effect, as well as a moderate downfield double-*ortho* effect, for instance, the very low δH(Si$_2$) = 4.7 ppm in 1,2,3,5-tetrasilabenzene as the result of a double-*meta* effect.

Conclusions

In the present article, we have described the electronic structure and properties of the silabenzenes as given by MP2, coupled cluster, and hybrid density functional methods. Basic measures of aromatic character, such as those gauged from assessment of structure, molecular orbitals, and bond separation reactions, are reported in addition to new magnetic properties. Basic trends in the disilabenzene isomer series confirm those seen in earlier, lower level studies. Comparing structural, energetic, and magnetic effects in benzene with those in silaaromatic compounds, several points are noted. First, energetics, structural parameters, and orbital structures (including partial charges and computed bond orders) effectively provide insight in π electron delocalization tendencies. The homodesmotic stabilization energy of 1,3,5-trisilabenzene is predicted to be comparable to that of benzene, and three-quarters of the latter are found for 1,3-disilabenzene and 1,2,3,5-tetrasilabenzene. These three molecules are also the most stable within their respective isomer series. However, magnetic criteria consistently predict them to have the *lowest* aromaticity within their series, and consideration of charge distributions and Wiberg bond orders suggests bonding in these species to have pronounced ionic components. (In the limiting case of Si^+C^- species, 1,3-, 1,3,5,-, and 1,2,3,5-silabenzenes are intrinsically the most advantageous arrangements within their series.) The second most stable isomers within their series, namely, 1,2-disilabenzene, 1,2,3-trisilabenzene, and 1,2,3,4-tetrasilabenzene, exhibit both the largest magnetic aromaticity criteria and (again based on partial charges and Wiberg bond orders) the most covalent bonding within their series. In short, the relative stability of the isomers is the product of an interplay between aromaticity and polar binding. Ring-size-adjusted susceptibility exaltations, Λ_{rel}, suggest a decrease in aromaticity as more Si atoms are introduced into the ring. Aromaticity tendencies within isomer series run parallel between Λ_{rel}, NICS(0), and NICS(1), and largely so with other magnetic criteria.

As a result of the greater accessibility of the 4s, 4p, and 3d orbitals in Si (compared to C), deviations from planarity caused by second-order Jahn−Teller effects occur in all systems with at least four silicon ring atoms, except for 1,2,4,5-tetrasilabenzene, where the lowest excited state with the correct symmetry lies too high.

The relative energetics (isomers, deviation from planarity) at our highest level of theory, CCSD(T)/cc-pVTZ, are better reproduced by the B3LYP/cc-pVTZ density functional method than by any of the less accurate wave function methods (HF, MP2, CCSD) considered. In general, the use of high levels of theory with large basis sets removes some ambiguities in previously reported results, especially for those molecular systems with localized electron density. The computed vibrational spectra and ^{1}H NMR chemical shifts may facilitate experimental identification.

Computed B3LYP/cc-pVTZ Cartesian geometries, NPA and APT charges, harmonic frequencies, and infrared intensities of all species, as well as total energies at various levels of theory and Gaussian 98 archive entries, are available in machine-readable form on the Internet World Wide Web at the Uniform Resource Locator (URL) http://theochem.weizmann.ac.il/web/papers/silabenzenes.html.

Acknowledgment. K.K.B. was a Fulbright Visiting Scholar at the Weizmann Institute of Science (on leave of absence from SDSC: ASC-9212619) during the course of this work. J.M. is a Yigal Allon Fellow and the Incumbent of the Helen and Milton A. Kimmelman Career Development Chair. O.U. acknowledges a Doctoral Fellowship from the Feinberg Graduate School (Weizmann Institute). This research was supported by the Minerva Foundation, Munich, Germany. The authors would like to thank Prof. Paul von Ragué Schleyer, Prof. Peter R. Taylor, and Dr. Andreas Sundermann for their helpful comments on the manuscript.

OM9903745