

Silaaromaticity in Polycyclic Systems: A Computational Study

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Received September 4, 2002

Abstract: Density functional theory (B3LYP) calculations were performed to examine the effect of Si substitution on the aromaticity of some polycyclic hydrocarbons using geometric criterion (HOMA), isodesmic isomerization reactions, homodesmotic equations, NICS values, chemical hardness, and out-of-plane distortive tendencies. The HOMA values are lower and the NICS values are higher in the Si-substituted rings compared to those in the hydrocarbon counterpart, whereas the homodesmotic equations predict little loss of aromaticity upon Si replacement in polycyclic systems. The chemical hardness values decrease and the out-of-plane distortive tendency increases upon silicon substitution. The relative energies of the positional isomers and the causative factors are analyzed. The high reactivity of some silaaromatics toward dimerization is explained based on local softness indices.

While significant theoretical evidence accumulated on the aromatic character of silole anions and dianions, and of diamino silylenes, simple silaaromatic compounds, namely Si-containing $(4n + 2)\pi$ ring systems, were found to be elusive for experimental maneuverings until recently.^{1–4} Utilizing the bulky group protection strategy, the synthesis and unambiguous characterization of silabenzene (**B1**), disilabenzene, silanaphthalenes (**N2**, **N3**), and silanthracene (**A1**) were accomplished in the past few years.^{5–8} Considering the intense experimental and theoretical interest in understanding the concept of silaaromaticity,^{5–10} we ventured to explore how a Si atom

affects the structure, thermodynamics, and magnetic properties of polycyclic aromatic hydrocarbons. Several criteria such as structural, magnetic, and energetic were used to gauge the aromaticity in silaaromatic compounds. The geometric criterion, harmonic oscillator model of aromaticity (HOMA),¹¹ and the magnetic criterion, nucleus independent chemical shifts (NICS),^{1,12,13} which have been widely used to evaluate aromaticity are employed in the present study. Importantly, we focused on comparing the aromatic nature of the silaaromatics by taking the corresponding hydrocarbons as reference compounds.

Five representative hydrocarbons (**B**, **N**, **A**, **P**, and **C**) were considered to study the effect of Si substitution (Figure 1). This resulted in a total of 24 Si-containing $(4n + 2)$ aromatic compounds, which includes one benzene, three naphthalene, four anthracene, seven phenanthrene, and nine chrysene isomers. The hybrid density functional theory method, B3LYP using the 6-31G* basis set, was employed for geometry optimization and frequency calculations, using the Jaguar 4.1 program package.¹⁴ The calculation of nucleus-independent chemical shifts (NICS) was done by using the gauge invariant atomic orbital (GIAO) approach at the HF/6-31G* level implemented in the Gaussian 98 program.¹⁵

All the planar forms were computed to be minima except **C2** and **C3**, which were found to be transition states. The corresponding minimum energy structures, **C2m** and **C3m**, were obtained by following the direction of the imaginary frequency normal modes. These minimum energy structures are slightly twisted and lie only 0.1 and 0.2 kcal/mol lower than the planar structures indicating that loss of planarity has no significant effect on the energy. The C–C bond lengths in all the silicon-substituted compounds are virtually identical with the corresponding bond lengths in the parent hydrocarbons in most of the cases. The HOMA values obtained with

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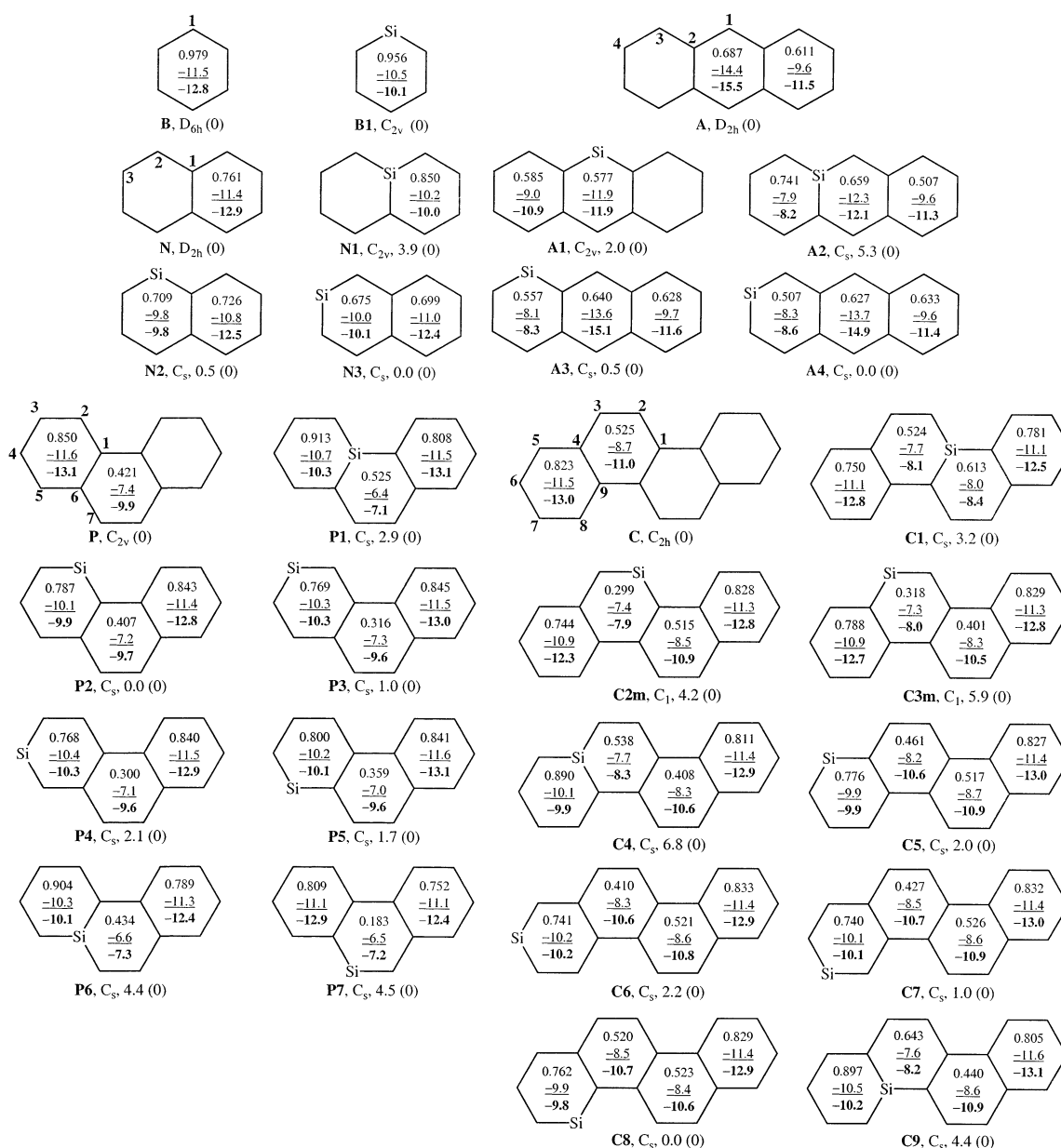


FIGURE 1. The HOMA values of the aromatic hydrocarbons and their corresponding sila-aromatic compounds obtained using the B3LYP/6-31G* equilibrium geometries and the NICS(0) (underlined) and NICS(1) (bold) values (ppm), computed using the GIAO approach at the HF/6-31G* level. The point group, relative energies (kcal/mol), and the number of imaginary frequencies (in parentheses) are also given.

use of the B3LYP/6-31G* optimized geometries are given in Figure 1.¹⁶ The HOMA values in the Si-substituted rings are slightly reduced compared to that in the parent hydrocarbons. However, in cases where three C–Si bonds are involved, the HOMA value is enhanced in the Si-containing rings except in one of the rings of **C1**. Thus, insignificant deviation of the HOMA values upon Si substitution indicates that the aromaticity of all the

sila-aromatic compounds is comparable to that of the hydrocarbons. The principal geometric parameters of all the compounds are given as a figure in the Supporting Information.

The relative energies of the positional isomers of the silanaphthalenes (**N1–N3**), silanthracenes (**A1–A4**), silaphenanthrenes (**P1–P7**), and silachrysenes (**C1–C9**) obtained at the B3LYP/6-31G* level are given in Table 1. Among the three silanaphthalenes, **N2** and **N3** are of comparable stability; **N1** is less stable than **N3** by about 4 kcal/mol. This can be explained based on the fact that **N1** has three weak C–Si bonds compared to only two in **N2** and **N3**.^{17,18} **A** and **P** are $C_{14}H_{10}$ isomers; **P** is computed to be more stable than **A** by 5.0 kcal/mol. Also, most of the silicon analogues of **P** are more stable than

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TABLE 1. The Relative Energies, ΔE (kcal/mol), of the Positional Isomers, the Chemical Hardness, η (eV), and Lower Vibrational Frequency, ν (cm^{-1}), Corresponding to the Out-of-Plane Distortion Obtained at the B3LYP/6-31G* Level

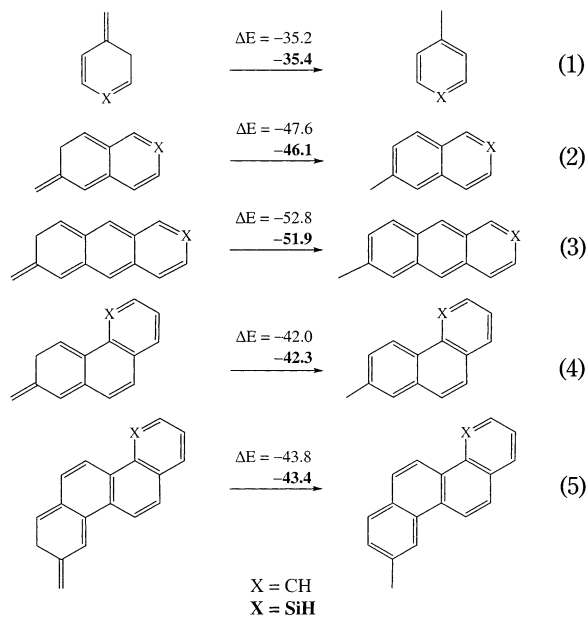
structure	ΔE (kcal/mol)	η (eV)	ν (cm^{-1})
B		3.40	416.3
B1		2.52	272.1
N		2.42	178.6
N1	3.9	2.13	124.8
N2	0.5	1.97	143.7
N3	0.0	2.11	140.7
A	– (5.0) ^a	1.80	98.6
A1	2.0 (6.4) ^b	1.48	73.5
A2	5.3 (9.7) ^b	1.68	75.1
A3	0.5 (4.9) ^b	1.57	80.0
A4	0.0 (4.4) ^b	1.66	76.8
P		2.37	103.9
P1	2.9	2.01	71.5
P2	0.0	2.03	79.2
P3	1.0	2.05	69.0
P4	2.1	2.16	56.7
P5	1.7	2.01	62.3
P6	4.4	2.00	79.5
P7	4.5	1.95	12.5
C		2.13	60.9
C1	3.2	1.82	43.3
C2	4.3	1.90	40.1i
C2m	4.2	1.89	36.1
C3	6.1	1.80	42.6i
C3m	5.9	1.79	33.7
C4	6.8	1.94	13.0
C5	2.0	1.88	27.7
C6	2.2	2.00	21.5
C7	1.0	1.95	32.4
C8	0.0	1.90	42.8
C9	4.4	1.88	34.9

^a Relative to **P**. ^b Relative to **P2**.

those of **A**. Similar to silanaphthalenes, those isomers with three unfavorable C=Si bonds are the less stable ones among the silanthracenes (**A1–A4**), silaphenanthrenes (**P1–P7**), and silachrysenes (**C1–C9**). In addition, isomers where Si is present in the central ring(s) are found to be less stable. Among the polycyclic sila-aromatic compounds, the most stable isomer has Si substituted in the outer rings. A recent study on the polycyclic aromatic hydrocarbons identifies that some regions of the compound behave more like benzene and others behave more like olefins, which is in conformity with Clar's aromatic sextet theory.¹⁹ In **P**, **A**, and **C**, the C–C bonds in the central ring(s) have enhanced olefinic character and the outer rings behave like benzene. Hence, those compounds with Si substitution in the central ring(s) are less stable due to the presence of an unfavorable C=Si bond. It is to be noted that the planar forms of **C2** and **C3** correspond to transition state structures. Thus, the placement of Si in

the hydrocarbon skeleton has only a minor effect (within 5–7 kcal/mol) on the relative energies of the positional isomers.

The magnetic properties have played a pivotal role in gauging the aromaticity in hydrocarbons and heteroaromatics.^{1,9,12,13} Figure 1 gives the NICS(0) and NICS(1) (underlined and bold face, respectively) values obtained for each of the rings of all the isomers considered in this study. All the rings possess negative NICS values indicating aromatic character. In silabenzene, the NICS(1) value increases by 2.7 ppm upon Si substitution, whereas NICS(0) increases only by 1 ppm. Similarly in naphthalene, silicon substitution leads to an increase in the NICS up to 3.1 ppm in **N2**. In anthracene (**A**), the central ring possesses a lower NICS value compared to the outer rings and even to benzene; in contrast, in **P** and **A**, the outer rings have lower NICS values. The maximum difference in the NICS values between the unsubstituted and the Si-substituted polycyclic aromatic carbons in **A**, **P**, and **C** is 3.6, 3.2, and 3.2 ppm, respectively. The NICS values are consistently increased in the Si-containing rings compared to their hydrocarbon counterparts. NICS(1) values uniformly show higher deviation compared to NICS(0) values in all cases. When the Si atom is a part of two rings, the NICS values in both rings are increased compared to the unsubstituted ones. In the absence of an Si atom in the ring the values are very similar to the corresponding rings in hydrocarbons. The variation of the NICS values upon Si substitution in the polycyclic aromatic hydrocarbons indicates that the aromaticity in these compounds is only slightly affected.

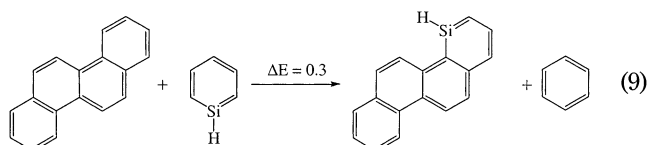
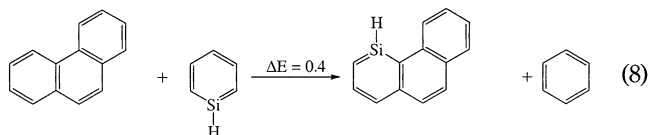
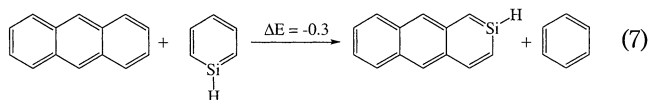
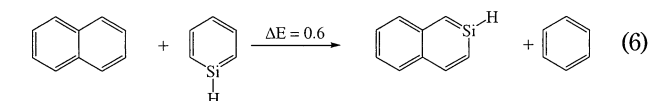


Two complementary energetic criteria were employed to assess the aromaticity: (a) the energy required for disrupting π -delocalization (eqs 1–5) both in sila-aromatics (bold) and in hydrocarbons (normal) and (b) a comparison of the stability of the sila-aromatic compounds with reference to the corresponding hydrocarbons (eqs 6–9). The most stable isomers are considered in each of the positional isomers. The reaction energies of the isodesmic isomerization reactions (eqs 1–5) of both

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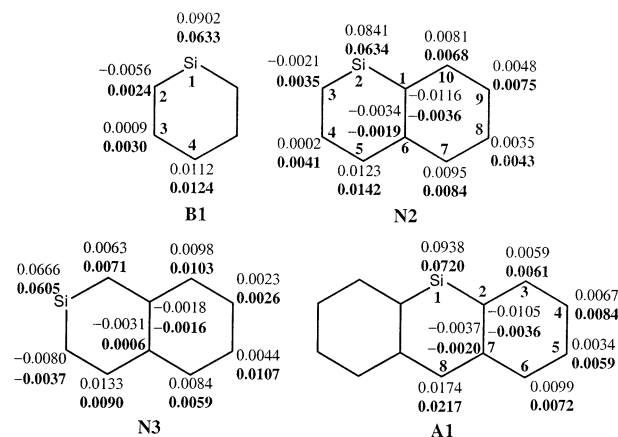
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hydrocarbons and sila-aromatic compounds are very similar with a maximum difference of 1.5 kcal/mol. The reaction energies of the homodesmotic eqs 6–9 are less than 1 kcal/mol in all cases, indicating that the polycyclic sila-aromatics are of comparable stability to the hydrocarbons. These results substantiate that aromaticity of polycyclic aromatic hydrocarbons remains unaffected upon Si substitution according to the energetic criteria.

Chemical hardness (η), defined as half of the energy difference between the HOMO and LUMO ($\eta = (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})/2$), was proved to be a useful measure for aromaticity.²⁰ The η values for all the structures considered are given in Table 1. **B** is found to be the most aromatic and **A** is found to be the least aromatic among the hydrocarbons. On Si substitution, the hardness values decrease in all cases. However, hardness values of the positional isomers of a given skeleton do not vary much with a maximum difference of 0.21 eV. The difference between the hardness values of the benzene (**B**) and silabenzene (**B1**) is 0.88 eV. In contrast, the differences in the polycyclic compounds are low (0.45, 0.32, 0.42, and 0.34 eV for **N**, **A**, **P**, and **C**, respectively). We have used the out-of-plane distortive tendency as a measure to evaluate the kinetic stability of 6π -heteroaromatic compounds in our previous studies.¹⁷ The lower vibrational frequency corresponding to the out-of-plane distortion mode of the molecules considered in the study is given in Table 1. In all cases, Si substitution leads to lowering of the frequency corresponding to the out-of-plane distortion. For **C2** and **C3**, the first out-of-plane mode corresponds to an imaginary frequency. This lowering of hardness values and the high propensity toward out-of-plane distortion explains the high reactivity of the sila-aromatic compounds. Recently, Tokitoh and co-workers have synthesized bulky group substituted **B1**, **N2**, **N3**, and **A1**.^{5,7,8} The main difference between the hydrocarbon and silicon counterparts is the latter's high reactivity. **N2** is found to undergo dimerization and **B1** is found to equilibrate between two monomers and the corresponding dimer via

1,4-addition. **A1** is also found to be reactive and undergoes 1,4-addition; in contrast, **N3** is stable as a monomer. This can be explained based on the local softness values obtained at the B3LYP/6-31G* level (s_k^+ and s_k^- values are given in ordinary and bold face, respectively).^{21,22} In all cases, the Si atom is the softest; also, C₄, C₅, and C₈ in **B1**, **N2**, and **A1**, respectively, are the softest among the carbon atoms, indicating the preference of 1,4-addition. In contrast, C₆ (the 1,4-addition site) in **N3** is not softer and hence does not undergo 1,4-addition. Similarly, the reactivity toward 1,4-additions of this class of compounds may be derived from the local softness values.²¹



This note presents a detailed analysis of geometric, magnetic, and energetic criteria, hardness, and the tendency for out-of-plane distortion for a series of sila-aromatic compounds. The geometric and energetic criteria indicate that the sila-aromatics are nearly as aromatic as hydrocarbons. The negative and comparable NICS values to the aromatic compounds are obtained for all the isomers studied here. The reactivity measures, the hardness, and out-of-plane tendencies of the sila-aromatic compounds point to the high reactivity compared to the hydrocarbons. The local softness values successfully explain the preference for 1,4-addition in some sila-aromatics. Therefore, polycyclic sila-aromatics are viable targets for experimental studies and synthetic efforts in this direction should be rewarding.

Acknowledgment. Recognition and support by DST, New Delhi through FIST scheme to the Department of Chemistry, Pondicherry University is gratefully acknowledged. U.D.P. thanks UGC, New Delhi for a senior research fellowship.

Supporting Information Available: The Cartesian coordinates of the B3LYP/6-31G* optimized structures and the total energies and figures depicting the principal geometric parameters and the local softness values of all the compounds considered in the present study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO0263972

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