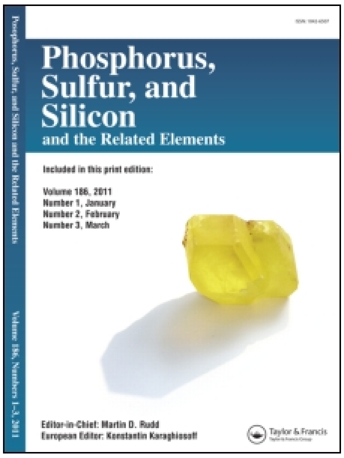

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AN AB INITIO MOLECULAR ORBITAL STUDY OF NEUTRAL ISOMERS OF SILANAPHTHALENES, SILAANTHRACENES, AND SILAPHENANTHRENES

Issa Yavari,[a] *Mahshid Nikpoor-Nezhati,*[b]
and Shoaleh Dehghan[b]
University of Tarbiat Modarres, Tehran, Iran[a] *and Islamic Azad University, Tehran, Iran*[b]

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Ab initio molecular orbital calculations at HF/6-31G* and RMP2-FC/6-31G* levels of theory for geometry optimization and MP4(SDQ)/6-31G* for a single point total energy calculation are reported for three isomers of silanaphthalene, four isomers of silaanthracene, and seven isomers of silaphenanthrene. According to these calculations, 2-silanaphthalene is only 0.4 kcal mol^{-1} more stable than 1-silanaphthalene. The isomer having Si atom at ring junction is calculated to be 5.8 kcal mol^{-1} less stable. 1-Silaanthracene is the most stable isomer of silaanthracenes. 2-Silaanthracene and 9-silaanthracene are 0.5 and 1.6 kcal mol^{-1} less stable than 1-silaanthracene respectively. The isomer with an Si atom at ring junction is 6.7 kcal mol^{-1} less stable. 1-Silaphenanthrene is the most stable isomer of silaphenanthrenes. 2-Sila-, 4-sila-, and 3-silaphenanthrene are 1.1–2.2 kcal mol^{-1} less stable than the 1-sila-isomer. Other silaphenanthrenes are less stable by 4.1–6.1 kcal mol^{-1}.

Keywords: Ab initio calculations; silaanthracene; silaaromatic compounds; silanaphthalene; silaphenanthrene

Aromaticity in the chemistry of group 14 elements heavier than carbon, sometimes called "metalloaromaticity" is a new field of research and much attention has been focused on the chemistry of these systems.[1] The aromatic nature of these compounds has been established by physico-chemical methods and supported by theoretical calculations.[1–4] An important branch of this field is silaaromatic compounds, which are usually unstable at room temperature because of their high reactivity compared with corresponding carbon analogues.[2–4] These compounds have been proposed as highly reactive intermediates. However,

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Address correspondence to I. Yavari, Department of Chemistry, University of Tarbiat Modarres, PO Box 14115-175, Tehran, Iran. E-mail: isayavar@yahoo.com

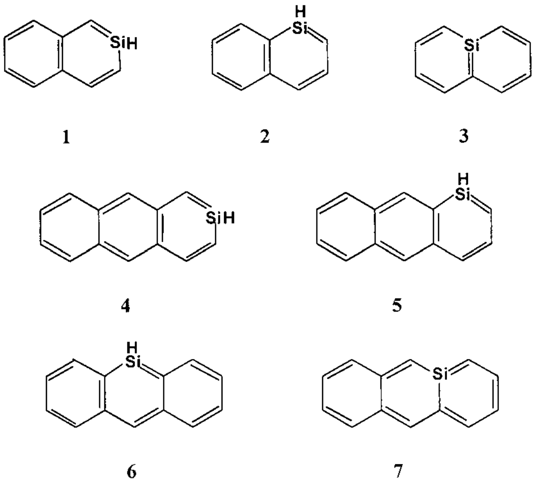


FIGURE 1 Possible positional isomers of silanaphthalenes (**1–3**) and silaanthracenes (**4–7**).

silaaromatic compounds have been observed in low temperature matrices or in the gas phase.[5] These compounds can be expected to behave both as heteroaromatic systems and conjugated double bond organosilicon compounds.[1–2]

This study was undertaken to investigate the structural optimization of various isomers of silanaphthalenes, silaanthracenes, and silaphenanthrenes by comparing the geometries (HF/6-31G*) and energies. The number of different positions that a silicon atom can occupy in naphthalene, anthracene, or phenanthrene is three, four, or seven (see Figures 1 and 2). The results from MP4(SDQ)6-31G*//RMP2-FC/6-31G* calculations are used in the energies discussions below.

RESULTS AND DISCUSSION

Silanaphthalenes 1–3

In recent decades, much attention has been focused on silaaromatic compounds since they represent the heavier congeners of the carbocyclic aromatic compounds which play such important role in organic chemistry. First successful synthesis of stable 2-silanaphthalenes which are stabilized kinetically by an extremely bulky [{2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl}] group on silicon atom was reported in 1991.[6] The large negative NICS (nucleus independent chemical shifts) values obtained for the three possible silanaphthalenes, suggest that the

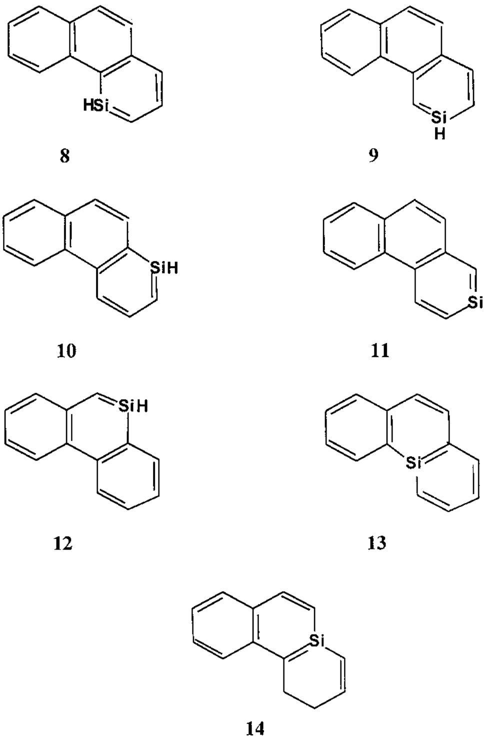
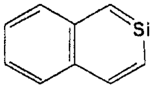
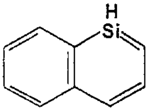
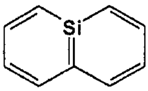


FIGURE 2 Possible positional isomers of silaphenanthrenes **8–14**.

aromatic character will not be much reduced by the replacement of a ring carbon by a silicon atom.[4] However, results show that 1-sila- and 9-silanaphthalenes can be synthetic targets if an effective steric protection group is introduced and an adequate synthetic route is developed.[3] Stable 2-silanaphthalene also has been produced as colorless crystals by using bromosilane precursors. These silaaromatics are moisture sensitive but very thermally stable in the solid state or even in solution up to 100°C.[7] 2-Silanaphthalene is reported to be highly reactive due to its polarized Si=C moiety, but relatively stable toward air in the solid state.[3]

The results of ab initio calculations for three isomers of silanaphthalene **1–3** (Figure 1) are given in Table I. Both of the basis sets employed in these calculations give the same order of stabilities for these planar compounds (Table I). 2-Silanaphthalene (**1**) is the most stable isomer of silanaphthalenes. The 1-sila- and 9-sila-isomers are less stable than **1** by 0.42 and 5.79 kcal mol^{-1} respectively. As mentioned before, the position of Si atom in the junction between the rings, lead to destabilization of the molecule and raises its energy. This destabilization can

TABLE I Total Energies (Hartree) of Neutral Isomers of Silanaphthalene (**1–3**). Values in Parenthesis are Relative Energies (kcal mol^{-1})

Structure	 1, C_S	 2, C_S	 3, C_S
HF/6-31G*//HF/6-31G*	−634.350051 (0.0)	−634.349281 (0.57)	−634.341140 (6.87)
ZPE	0.148498	0.148652	0.150744
RMP2-FC/6-31G*//RMP2-FC/6-31G*	−635.56.9911 (0.0)	−635.569663 (0.24)	−635.561136 (6.79)
MP4(SDQ)/6-31G*//RMP2-FC/6-31G*	−635.618991 (0.0)	−635.618454 (0.42)	−635.611815 (5.79)

be attributed to the polarizability of Si=C bond and the quality of local charge development in these systems.

Silaanthracenes (4–7)

Attempts for preparation of silaanthracenes by elimination of hydrogen halide from suitable dihydro precursors, lead to generation of dimeric or polymeric materials.[6,7] Although there has been no report on the preparation of stable silaanthracenes, 9-silaanthracene was generated by using flash vacuum thermolysis technique at 15 K.[6] Generation of 9-silaanthracene by photolysis of 9,10-dihydro-9-silaanthracene, has been unsuccessful.

The results of ab initio study of silaanthracenes **4–7** (Figure 1) are shown in Table II. All isomers are planar. According to these calculations, 2-silaanthracene (**4**) is the most stable isomer of silaanthracenes. 1-Sila-, 9-sila- and 11-sila isomers are less stable than **4** by 0.48, 1.63, and 6.69 kcal mol^{-1} respectively. The calculated energy difference between 1-silaanthracene (**5**) and 9-silaanthracene (**6**) is 1.15 kcal mol^{-1}, which is less than the energy difference (5.06 kcal mol^{-1}) between 9-silaanthracene (**6**) and 11-silaanthracene (**7**). 1-Silaanthracene (**5**) is 6.21 kcal mol^{-1} more stable than the 11-sila isomer **7**. As shown in Table II, structures containing Si atom in the junction between the rings are less stable than the other isomers.

Silaphenanthrenes (8–14)

The results of ab initio calculations for silaphenanthrenes **8–14** (Figure 2) are given in Table III. 4-Silaphenanthrene (**8**) is the most

TABLE II Total Energies (Hartree) of Neutral Isomers of Silaanthracen (**4–7**). Values in Parenthesis are Relative Energies (kcal mol^{-1})

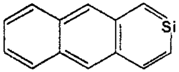
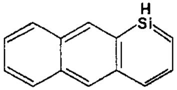
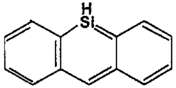
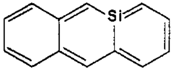
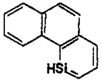
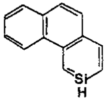
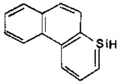
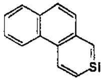
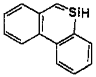
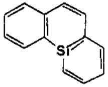
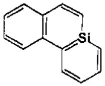
Structure	 **4**, C_S	 **5**, C_S	 **6**, C_S	 **7**, C_S
HF/6-31G*//HF/6-31G*	−786.994887	−786.993912	−786.991535	−786.984394
	(0.0)	(0.68)	(2.33)	(7.92)
ZPE	0.198586	0.198723	0.198988	0.200925
RMP2-FC/6-31G*//RMP2-FC/6-31G*	−788.719958	−788.719686	−788.718307	−788.709290
	(0.0)	(0.25)	(1.26)	(8.03)
MP4(SDQ)/6-31G*//RMP2-FC/6-31G*	−788.778912	−788.778270	−788.776676	−788.770387
	(0.0)	(0.48)	(1.62)	(6.69)

TABLE III Total Energies (Hartree) of Neutral Isomers of Silaphenanthrene (**8–14**). Values in Parenthesis are Relative Energies (kcal mol^{-1})

Structure	 **8**, C_S	 **9**, C_S	 **10**, C_S	 **11**, C_S	 **12**, C_S	 **13**, C_S	 **14**, C_S
HF/6-31G*//HF/6-31G*	−787.004334	−787.002521	−787.001292	−787.000935	−786.996908	−786.998080	−786.995466
	(0.0)	(1.04)	(1.90)	(2.05)	(4.59)	(5.22)	(6.82)
ZPE	0.199082	0.198916	0.199076	0.198944	0.198969	0.201346	0.201282
RMP2-FC/6-31G*//RMP2-FC/6-31G*	−788.730570	−788.728703	−788.727637	−788.726787	−788.724425	−788.723411	−788.720822
	(0.0)	(1.07)	(1.83)	(2.29)	(3.79)	(5.79)	(7.37)
MP4(SDQ)/6-31G*//RMP2-FC/6-31G*	−788.788230	−788.786338	−788.785189	−788.784666	−788.781602	−788.782810	−788.780556
	(0.0)	(1.09)	(1.90)	(2.15)	(4.09)	(4.69)	(6.07)

stable isomer of silaphenanthrenes. The 3-sila-, 1-sila- and 2-sila isomers are less stable than **8** by 1.09, 1.90, and 2.15 kcal mol^{-1} respectively. The energy differences between 10-sila-, 12-sila- and 11-sila isomers and **8** are in order: 4.09, 4.69 and 6.07 kcal mol^{-1}. The energy difference between 12-silaphenanthrene (**13**) and 11-silaphenanthrene (**14**) is 1.38 kcal mol^{-1}. The 3-silaphenanthrene (**9**) is more stable than the 1-silaphenanthrene (**10**) by 0.81 kcal mol^{-1}. On the other hand, the energy difference between **11** and **12** is 1.93 kcal mol^{-1}. Similar to silanaphthalenes and silaanthracenes, the high energy isomers are the molecules in which the silicon atom is in the junction between the rings. All seven isomers of silaphenanthrene are planar.

In summary, ab initio SCF-MO calculations provide a fairly clear picture of the silanaphthalenes, silaanthracenes, and silaphenanthrenes, from energetic point of view. Isomers **1** and **4**, with Si atom in 2-position and isomer **8** with Si atom in 4-position are the most stable isomers in the corresponding series. Structures in which Si atom is located in the junction between the rings have higher energies.

CALCULATIONS

The ab initio molecular orbital calculations, were carried out using the Gaussian 98 program.[8] Geometries for all structures were fully optimized by means of analytical energy gradients by Berny optimizer with no geometrical constraints.[9,10] Initial geometry optimizations were carried out at HF/6-31G* level, and zero point energies, obtained at this level, were scaled by 0.9135. In light of the fact that correction for electron correlation is often important in conformation studies, we have made use of several methods for calculating this correction. Geometry optimizations were also carried out using HF/6-31G and RMP2-FC/6-31G* followed by a MP4(SDQ)/6-31G* calculations using the RMP2-FC/6-31G* geometry.

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