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Silicon analogues of pyramidane: a quantum-chemical study

Olga A. Gapurenko, Ruslan M. Minyaev* and Vladimir I. Minkin

Institute of Physical and Organic Chemistry, Southern Federal University, 344090 Rostov-on-Don, Russian Federation. Fax: +7 863 243 4700; e-mail: minyaev@ipoc.sfedu.ru

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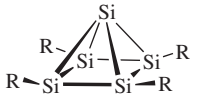
The DFT B3LYP/6-311+G(d,p) calculations predict that Si_5R_4 (R = SiH_3, $SiMe_3$) compounds may have stable effectively pyramidal structures with a bare apical silicon atom.

The electronic and spatial structures of the heavy analogues of aromatic carbocyclic compounds, in which ring carbons are replaced with silicon atoms, have been intensively studied both experimentally[1,2] and computationally.[2–4] Special attention has been given to a comparison of the aromatic character and relative stability of valence isomers and the ability to coordinate transition metal groups of analogous carbon and silicon-containing compounds. It has been found that, in spite of the general similarity of the valence electronic shells, the heavy silicon analogues possess a less pronounced aromatic character and significantly lower structural rigidity of 6π-electronic conjugate rings, as manifested by the highly folded structure of a silicon analogue of the cyclobutadiene dianion.[5] The planar rhombic Si_4 ring was recently synthesized; this structure is stabilized by the very bulky (1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-s-hydrindacen-4-yl) group.[6] The Si_4 ring was found to be distinctly planar in the pyramidal π-complex $(SiMeBu^t_2)_4Si_4{\cdot}Co(CO)_2$ formed *via* capping the ring with a $Co(CO)_2$ group.[7] Since this group is isolobal to a bare silicon atom, we were interested to study whether the pyramidal structure with a planar basal Si_4 ring can occur in silapyramidanes **1**, the heavy analogues of three-dimensional aromatic pyramidanes **2**, which have been computationally studied in much detail.[8–11]

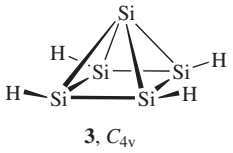


1

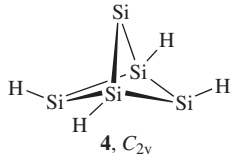
2

The only previous attempt[12] of the computational study of silapyramidane Si_5H_4 was based on simple semi-empirical calculations, which did not include the analysis of vibrational frequencies; thus, it cannot be considered sufficiently reliable. In order to properly address the question on the structure of this pyramidal structure and to assess its stability relative to other possible isomers, we report here on the density functional theory calculations of the series of cage and cyclic isomers of the Si_5R_4 (R = H, SiH_3 and $SiMe_3$) compounds containing a bare silicon atom. The calculations were performed by means of the Gaussian 03 program package[13] using the B3LYP functional and the standard 6-311+G(d,p) basis set. The stationary points on the potential energy surfaces (PESs) were located by a full geometry optimization with calculations of force constants and checked for the stabilities of Hartree–Fock solutions.

Pyramidal C_{4v} structure **3** has three imaginary frequencies ($\lambda = 3$) and corresponds to a saddle point on the Si_5H_4 PES rather than a minimum. The structure corresponding to the nearest local minimum (**4**) has C_{2v} symmetry and the most stable isomer on the Si_5H_4 established at the B3LYP/6-311+G(d,p) level is represented by structure **5** of pentasila[1.1.1]propellane, which is a conjugate



3, C_{4v}



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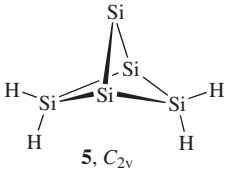
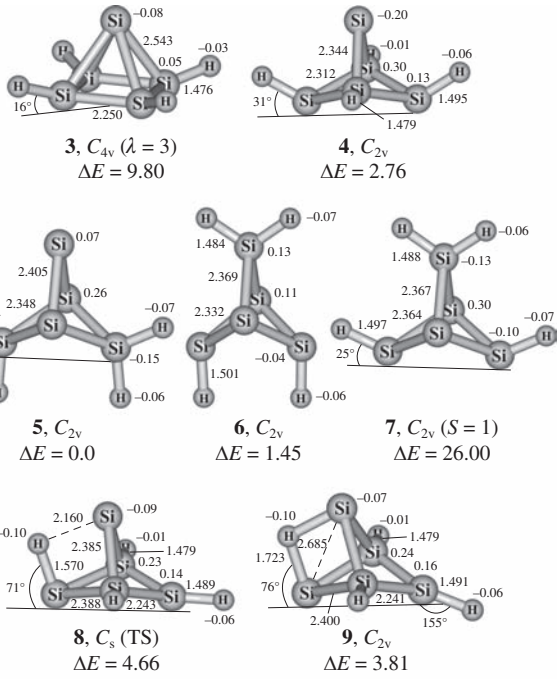


5, C_{2v}

base to the pentasila[1.1.1]propellanyl cation found to be the most stable isomer of the $Si_5H_5^+$ system.[14] Isomers **4** and **6** are less energy favorable than **5** by 2.76 (1.85 with ZPE) and 1.45 (0.92 with ZPE) kcal mol^{-1}, respectively. Structure **7** is stable on the triplet PES and 26.0 (25.14 with ZPE) kcal mol^{-1} less stable than **5**. Table 1 and Figures 1 and 2 summarize the principal results of the calculations.

Isomer **4** is susceptible to a degenerate rearrangement occurring as a sequence of the low-energy barrier ($\Delta E^{\neq}$ = 1.9 kcal mol^{-1}, $\Delta G^{\neq}$ = 1.5 kcal mol^{-1}) 1,3-migrations of hydrogen between the

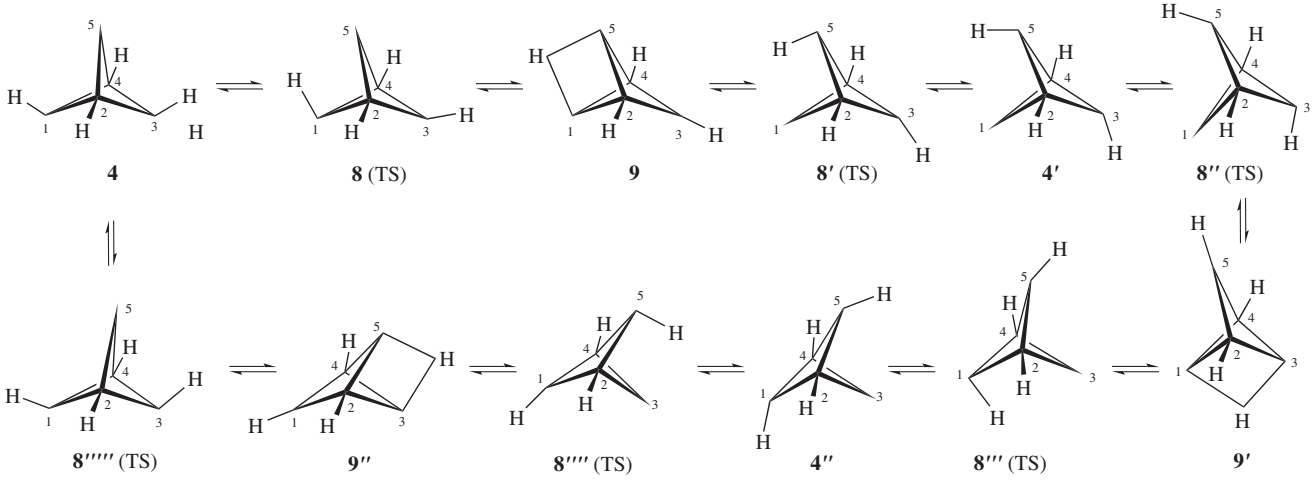


3, C_{4v} ($\lambda = 3$) $\Delta E = 9.80$ | **4**, C_{2v} $\Delta E = 2.76$

5, C_{2v} $\Delta E = 0.0$ | **6**, C_{2v} $\Delta E = 1.45$ | **7**, C_{2v} ($S = 1$) $\Delta E = 26.00$

8, C_s (TS) $\Delta E = 4.66$ | **9**, C_{2v} $\Delta E = 3.81$

Figure 1 Optimized geometries, Mulliken atomic charges and relative total energies (ΔE/kcal mol^{-1}) of the most stable isomers of Si_5H_4 calculated by the DFT [B3LYP/6-311+G(d,p)] method. Bond lengths are given in Å.

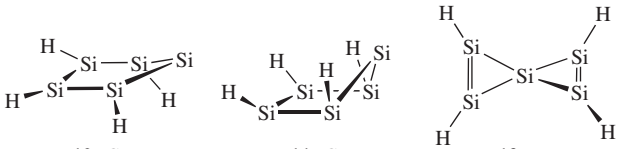


Scheme 1 Degenerate rearrangement of Si_5H_4 isomers **4**. Structures **8** and **9** represent the transition states and the intermediates, respectively, at the each step of the rearrangement.

silicon centers (see Scheme 1). Note that hydrogen atoms in the 2- and 4-positions are not involved into the rearrangement.

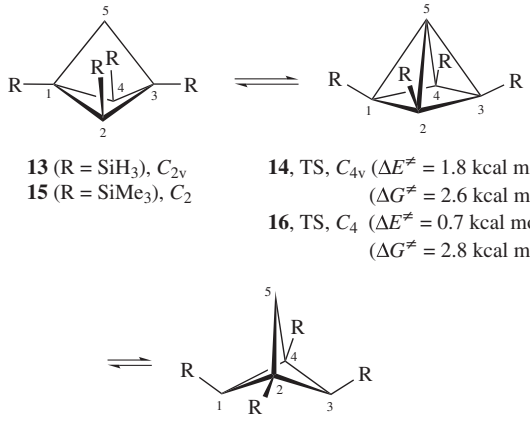
To compare the stability of tricyclic Si_5H_4 structures **3–7** with a few other isomeric forms, we also performed calculations for structures **10–12** (Table 1), which turned out to be 25–54 kcal mol^{-1} less energy favorable than **5**. Minima **10** and **11** have C_1 structures and transform to degenerate analogous minima **10′** and **11′** (their mirror image) through symmetric (C_s) transition states **10a** and **11a**, respectively.

To exclude the dynamic processes related to the permutational rearrangement shown in Scheme 1 and in the expectation that



the larger than hydrogen substituents might stabilize pyramidal structures **1**, we carried out calculations for compounds Si_5R_4 with R = SiH_3 and $SiMe_3$. Although the energy gap between the pyramidal form and the most stable isomer of these compounds was found to be appreciably narrower than that for Si_5H_4, the C_{4v} structures (**14** and **16**) remain unstable and correspond to the transition states for the conformational rearrangement of C_{2v} isomers **13** and **15** (Scheme 2). Because of the very low energy barriers against this rearrangement, compounds **14** and **16** can be regarded as possessing effectively pyramidal structures. The calculated geometries of the structures involved into this rearrangement are pictured in Figure 2. For $Si_5(SiH_3)_4$ and $Si_5(SiMe_3)_4$, the most stable isomers are represented by C_{2v} and C_2 structures **13** and **15**, respectively, while other isomers formed by the replacement of hydrogen atoms in **5**, **6** and **10–12** with SiH_3, $SiMe_3$ groups are 6–48 kcal mol^{-1} less energy stable (Table 1).

In **4**, **13** and **15**, the basal Si_4 rings are folded along the Si(2)–Si(4) line and the calculated dihedral angles of this distor-



Scheme 2 Conformational rearrangement of Si_5R_4 isomers **13** and **15** that includes passage through the effectively pyramidal transition state structures **14** and **16**, respectively.

Table 1 Data of DFT [B3LYP/6-311+G(d,p)] calculations for compounds **3–16**.[a]

Structure, symmetry	E_{tot}	ΔE	ΔE_{ZPE}	ΔG	λ	ω_1
3, C_{4v}	–1449.910753	9.80	8.22	9.84	3	*i*198
4, C_{2v}	–1449.921977	2.76	1.85	2.04	0	130
5, C_{2v}	–1449.926370	0	0	0	0	85
6, C_{2v}	–1449.924056	1.45	0.92	1.28	0	143
7,[b] C_{2v}	–1449.884940	26.00	25.14	24.72	0	142
8, C_s	–1449.918946	4.66	3.24	3.54	1	*i*206
9, C_{2v}	–1449.920302	3.81	2.78	3.08	0	76
10, C_1	–1449.876911	31.03	22.54	28.33	0	58
10a, C_s	–1449.876374	31.37	29.89	29.57	1	*i*101
11, C_1	–1449.885547	25.62	24.17	23.33	0	93
11a, C_s	–1449.882403	27.59	25.60	25.10	1	*i*150
12, D_{2d}	–1449.839483	54.52	51.78	50.91	0	77
13, C_{2v}	–2612.852605	0	0	0	0	41
14, C_{4v}	–2612.849668	1.84	1.87	2.56	1	*i*127
15, C_2	–3084.921150	0	0	0	0	7
16, C_4	–3084.920055	0.69	0.88	2.77	1	*i*63
5, C_1 (R = SiH_3)	–2612.840026	7.89	7.72	8.45	0	35
5, C_1 (R = $SiMe_3$)	–3084.892319	18.09	18.23	20.49	0	13
6, C_2 (R = SiH_3)	–2612.842348	6.44	6.63	8.51	0	44
6, C_1 (R = $SiMe_3$)	–3084.899303	13.71	13.61	13.02	0	5
10, C_1 (R = SiH_3)	–2612.806412	28.99	28.56	27.65	0	22
10, C_1 (R = $SiMe_3$)	–3084.872574	30.48	30.19	29.79	0	9
11, C_1 (R = SiH_3)	–2612.810412	26.48	25.85	24.53	0	27
11, C_1 (R = $SiMe_3$)	–3084.872413	30.58	30.21	30.62	0	13
12, D_{2d} (R = SiH_3)	–2612.775455	48.41	47.51	44.55	0	22
12, D_{2d} (R = $SiMe_3$)	–3084.845009	47.78	46.84	40.20	0	2

[a] E_{tot} (a.u.) is the total energy (1 a.u. = 627.5095 kcal mol^{-1}); ΔE (kcal mol^{-1}) is the relative total energy; ΔE_{ZPE} (kcal mol^{-1}) is the relative total energy including a harmonic zero-point correction; ΔG (kcal mol^{-1}) is the relative Gibbs free energy; λ is a number of the imaginary frequencies; ω_1 (cm^{-1}) is the smallest harmonic vibration frequency. [b] The structure is stable on the triplet PES.

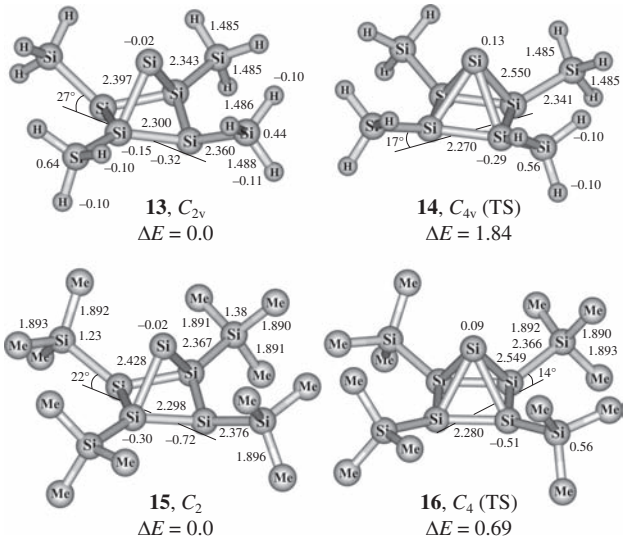


Figure 2 Optimized geometries, Mulliken atomic charges and relative total energies (ΔE/kcal mol^{-1}) of the isomers of $Si_5(SiH_3)_4$ and $Si_5(SiMe_3)_4$ calculated by the DFT [B3LYP/6-311+G(d,p)] method. Bond lengths are given in Å.

tion are 139°, 151° and 157°, respectively (for labels see **13′** and **15′** in Scheme 2), revealing the trend of increase in the dihedral angle with increasing the steric volume of the substituents R. This trend is in parallel with the notable decrease in the energy barrier to the planar inversion of the basal ring in **13**, as compared with **15**. Thus, the replacement of trimethylsilyl substituents (R = $SiMe_3$) in **15** with much bulkier groups may lead to the stabilization of the perfectly pyramidal Si_5 framework.

The aromaticity of the basal ring was estimated according to the NICS[15] value (nucleus independent chemical shifts) which calculated numbers for the basal rings of the pyramidal species are –29.8 for **3**, –26.5 for **14** and –26.2 for **16**. These values are very close to the NICS of the basal cycle of pyramidane **2** (R = H) (–30.4) and suggest the similarity of silicon and carbon pyramidal systems.

In conclusion, the results of the calculations of the silapyramidanes demonstrate that they have effective pyramidal structures in case their basal rings contain bulky substituents.

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References

1 V. Ya. Lee and A. Sekiguchi, *Angew. Chem. Int. Ed.*, 2007, **46**, 6596.
2 V. Ya. Lee and A. Sekiguchi, *Chem. Soc. Rev*., 2008, **37**, 1652.
3 Y. Apeloig and M. Karni, *The Chemistry of Organic Silicon Compounds*, eds. Z. Rappoport and Y. Apeloig, Wiley, Chichester, 1998, ch. 1, vol. 2, part 1.
4 P. v. R. Schleyer, H. Jiao, N. J. R. van Eikema Hommes, V. G. Malkin and O. L. Malkina, *J. Am. Chem. Soc.*, 1997, **119**, 12669.
5 V. Ya. Lee, K. Takanashi, R. Kato, T. Matsuno, M. Ichinohe and A. Sekiguchi, *J. Organomet. Chem.*, 2007, **692**, 2800.
6 K. Suzuki, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka and K.Tamao, *Science*, 2011, **331**, 1306.
7 K. Takanashi, V. Ya. Lee, T. Matsuno, M. Ichinohe and A. Sekiguchi, *J. Am. Chem. Soc*., 2005, **127**, 5768.
8 V. I. Minkin, R. M. Minyaev and G. V. Orlova, *J. Mol. Struct. (Theochem)*, 1984, **110**, 241.
9 J. P. Kenny, K. M. Krueger, J. C. Rienstra-Kiracofe and H. F. Schaefer III, *J. Phys. Chem. A*, 2001, **105**, 7745.
10 V. I. Minkin and R. M. Minyaev, *Dokl. Ross. Akad. Nauk*, 2002, **385**, 502 [*Dokl. Chem. (Engl. Transl.)*, 2002, **385**, 203].
11 V. I. Minkin, R. M. Minyaev and R. Hoffmann, *Usp. Khim*., 2002, **71**, 989 (*Russ. Chem. Rev.*, 2002, **71**, 869) and references therein.
12 Ş. Erkoç and L. Türker, *Turkish J. Phys.*, 1998, **22**, 1069.
13 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03. Revision C.02*, Gaussian Inc., Wallingford, CT, 2004.
14 A. A. Korkin, V. V. Murashov, J. Leszczynski and P. v. R. Schleyer, *J. Phys. Chem.*, 1995, **99**, 17742.
15 P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317.

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