Hexasilabenzene (Si_6H_6). An *ab initio* Theoretical Study of its Aromaticity and Relative Stability

Shigeru Nagase,* Takako Kudo, and Mizuho Aoki

Department of Chemistry, Faculty of Education, Yokohama National University, Yokohama 240, Japan

Ab initio calculations show that hexasilabenzene has approximately half the aromatic stabilization energy of benzene, and lies very close in stability to its valence Si_6H_6 isomers, this being in sharp contrast with the fact that benzene is by far the most stable C_6H_6 isomer.

The silicon analogues of unsaturated carbon compounds are long-sought species,[1] and there has been much recent progress in the generation and isolation of silicon analogues of alkenes.[2] Considerable interest is now directed toward the preparation of aromatic silicon compounds. Experimental[3] and theoretical[4] investigations are at present limited to mono- or di-silabenzene, and we now report the first *ab initio* study of the properties of hexasilabenzene (**1**), the silicon analogue of benzene, in order to investigate the characteristics of aromatic silicon compounds.

All calculations were carried out at the Hartree–Fock (HF) SCF level with the split-valence 3-21G[5] or polarized 6-31G*[6] basis sets. Geometries were fully optimized at the HF/3-21G level with the analytical energy gradient method.

The equilibrium structure of (**1**) characterized by all the positive eigenvalues of the force constant matrix is found to be planar with D_{6h} symmetry, as in the case of benzene. At the HF/3-21G level, the Si–Si bond length of 2.220 Å in (**1**) is 0.077 Å longer than the Si–Si double bond in $H_2Si{=}SiH_2$ but is 0.162 Å shorter than the Si–Si single bond in $H_3Si{-}SiH_3$. This reflects the significant double bond character of the skeletal bonding in (**1**).

$$C_6H_6 + 3CH_2{=}CH_2 \rightarrow 3CH_2{=}CH{-}CH{=}CH_2 \qquad (a)$$

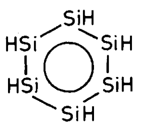
$$C_6H_6 + 3CH_2{=}CH{-}CH{=}CH_2 \rightarrow 3CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2 \qquad (b)$$

$$Si_6H_6 + 3SiH_2{=}SiH_2 \rightarrow 3SiH_2{=}SiH{-}SiH{=}SiH_2 \qquad (c)$$

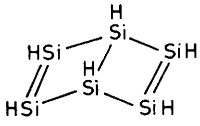
$$Si_6H_6 + 3SiH_2{=}SiH{-}SiH{=}SiH_2 \rightarrow 3SiH_2{=}SiH{-}SiH{=}SiH{-}SiH{=}SiH_2 \qquad (d)$$

It has been demonstrated that a Dewar-type resonance energy[7] can be evaluated in all-electron calculations from the homodesmotic[8] or hyperhomodesmotic[9] reaction energies (a) and (b). Equations (a) and (b) give the HF/3-21G resonance energies for benzene of 27.6 and 26.0 kcal/mol (24.7 and 23.4 kcal/mol at the HF/6-31G* level),[9] respectively, which are not significantly different from the experimental value (21.2 kcal/mol).[8] This has prompted us to evaluate the aromatic stabilization of (**1**) by using the corresponding homodesmotic or hyperhomodesmotic reactions (c) and (d). The HF/3-21G resonance energies for (**1**) calculated from equations (c) and (d) are 14.2 and 12.4 kcal/mol, respectively, and are *ca.* 13 kcal/mol smaller than those for benzene, suggesting that hexasilabenzene has aromaticity, as might be expected from the Hückel (4n + 2) rule, but has approximately half the aromatic stabilization energy of benzene.

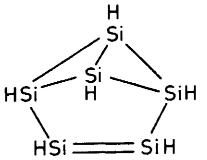
To investigate the relative stability of (**1**), we have performed calculations on the valence isomers (**2**), (**3**), and (**4**) which are the silicon analogues of Dewar benzene (bicyclo-[2.2.0]hexa-2,5-diene), benzvalene (tricyclo[3.1.0.0^{2,6}]hex-3-ene), and prismane (tetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane) respectively, which are of current interest.



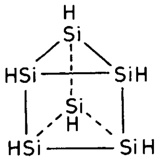
(**1**) (D_{6h})



(**2**) (C_{2v})



(**3**) (C_{2v})



(**4**) (D_{3h})

Table 1. Relative energies (kcal/mol; 1 cal = 4.184 J) of the Si_6H_6 and C_6H_6 isomers.[a]

Si_6H_6 species	HF/3-21G	HF/6-31G*[b]
(**1**)	0.0 (0.0)	0.0 (0.0)
(**2**)	11.2 (94.8)	3.7 (88.1)
(**3**)	6.2 (95.6)	0.5 (84.5)
(**4**)	−6.7 (137.9)	−9.5 (127.6)

[a] Values in parentheses are for the corresponding C_6H_6 species. [b] Calculations at the HF/3-21G optimized geometries.

Table 1 summarizes the relative energies calculated for the Si_6H_6 and C_6H_6 isomers. Particularly noteworthy is the fact that the energy differences between (**1**) and its isomers (**2**), (**3**), and (**4**) are unusually small,† and that the isomers (**2**)—(**4**) are progressively favoured as the number of double bonds decreases, reflecting the fact that silicon is reluctant to form double bonds. As a result, the saturated hexasilaprismane (**4**) is calculated to be slightly more stable than hexasilabenzene (**1**). This is in sharp contrast to the fact that the corresponding benzene valence isomers are much more unstable, as expected from their highly strained structures, than benzene itself.

Thus, a D_{6h} Kekulé-type structure with 6 delocalized π-electrons is a minimum on the Si_6H_6 potential energy surface but is close in energy to its isomeric structures with 4, 2, or 0 π-electrons. This differs drastically from the relative stability of the C_6H_6 analogues.

All calculations were carried out at the Computer Center of the Institute for Molecular Science and at the Computer Center of Tokyo University, using the GAUSSIAN 80 (WF10-24) and IMSPAK (WF10-8) programs in the IMS Computer Center library program package.

Received, 15th May 1985; Com. 668

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† However, the concerted thermal interconversions of (**1**), (**2**), and (**4**) are symmetry-forbidden, as the calculated orbital correlation diagrams suggest.

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