Effects of Substituents on Silicon upon the Ring Inversion of Silepins Annelated with Bicyclo[2.2.2]octene Frameworks

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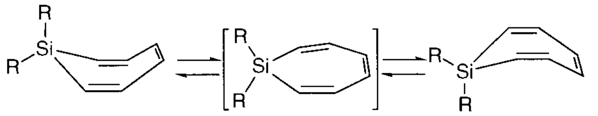
The energy barrier for ring inversion of the silepin annelated with bicyclo[2.2.2]octene was found to decrease as the electronegativity of substituents on silicon increases.

Silacycloheptatriene (silepin) (**1a**) is considered to take the boat conformation, which undergoes rapid ring inversion (eq. 1) in solution.[1] In our previous study we prepared metallacycloheptatrienes containing group 14 elements (Si, Ge, Sn), which were annelated with rigid σ-frameworks, *i.e.* bicyclo[2.2.2]octene (abbreviated as BCO).[2] This structural modification was found to be advantageous for structural elucidation by X-ray crystallography and also for determination of the energy barrier for ring inversion. In the present study, we have synthesized a series of BCO-annelated silepins **4a–g** bearing various substituents on the silicon atom, and examined the correlation between electronic effects of the substituents and the energy barrier for ring inversion.



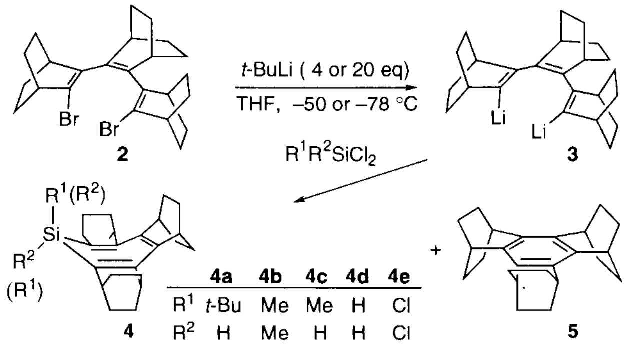
(1)

1a R = H **1b** R = Me **1c** R = F **1d** R = Cl

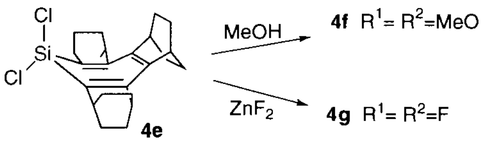
Silepins **4b–e**[2,3] were prepared by dilithiation of the dibromide of BCO trimer **2** followed by the reaction with chlorosilanes, as shown in Scheme 1. Silepin **4a**[3] was formed together with **4d**, presumably by the action of excess *t*-BuLi upon the primary product **4d**. In all of these reactions, benzene **5** was formed in 15–35% yield. Control experiments indicated that **5** was produced in competition with dilithiation of **2** but not by the reaction of dilithiated compound **3** with chlorosilanes. No transformation of silepins **4** to benzene **5** was observed under the employed reaction conditions. Silepins **4f**[3] and **4g**[3] were prepared by the reaction of **4e** with excess methanol and with ZnF_2 as shown in Scheme 2.

The X-ray crystallography was performed for compound **4e**,[4] and indicated that its structure (Figure 1) is quite similar to that of **4b**.[2] In particular, the bending angles of boat structure α (45.6°) and β (33.5°) of **4e** are quite similar to those (45.7 and 32.7°) of **4b**. The obvious difference can only be seen in the C-Si-C angle of the seven-membered ring, which is 108.4(2)° for **4e** and 103.2(1)° for **4b**. This difference was also reproduced by the PM3 calculations (**4e**, 109.7°; **4b**; 103.7°).[5] The wider C-Si-C angle of **4e** would be due to the effect of the higher electronegativity of the chlorine substituent: the electronegative substituents demand more *p* character in the Cl–Si bonds and donate the relatively larger *s* character to the Si–C bonds, which results in the widening of the C–Si–C angle.[6]

The ^{1}H and ^{13}C NMR spectra of these silepins in THF-d_8 exhibited characteristic dynamic behavior depending upon the nature of the substituents on the silicon atom. For example, two signals were observed for the Si-H protons of **4a** (in a ratio of 2:1) in the ^{1}H NMR (300 MHz) spectrum at room temperature indicating that the ring inversion is slow relative to the NMR time scale. In contrast, the proton signals for two substituents on the silicon atom of **4b**,[2] **4d**, and **4f** could not be differentiated due to much faster ring inversion process.



Scheme 1.



Scheme 2.

The variable temperature NMR study was carried out for silepins **4a–g**. For compounds **4e** and **4g**, the temperature dependence of ^{13}C NMR signals for the methylene carbons of the bicyclic framework was used to follow the dynamic behaviors. The results are shown in Table 1, together with the net positive charge on the silicon atom (δ+(Si)) calculated by PM3 and the $\Delta\Delta H_f$ value, *i.e.* the difference in heat of formation calculated by PM3 between the optimized boat-shaped structure and the planar transition-state structure.[2,7]

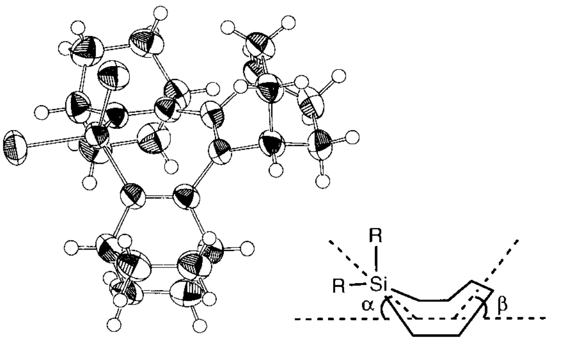


Figure 1. ORTEP view (50% probability) of X-ray crystal structure of **4e**.

Table 1. Results of variable-temperature NMR measurements and PM3 calculations

compd	$T_{coales.}$ ℃	$\Delta G^{\ddagger}$ [a] kcal mol^{-1}	δ+(Si)	$\Delta\Delta H_f$ kcal mol^{-1}
4a	>20	>14.1	+0.47	11.1 (10.6)[b]
4b[c]	-17	12.4	+0.50	9.9
4c[c]	-20	11.9	+0.51	9.9 (9.4)[b]
4d[c]	-40	11.1	+0.52	9.1
4f[c]	-55	10.3	+0.90	9.3
4e[d]	-80	9.6[e]	+0.88	8.6
4g[d]	-105	8.2[e]	+0.96	9.4

[a] Value at the coalescence temperature. [b] The values in parentheses are those for conformers with the *t*-butyl group at the axial position and the methyl group at the equatorial position. [c] In THF-d_8. [d] In CD_2Cl_2. [e] Exchange rate for methylene-carbons was estimated according to the previous work on the BCO-annelated cycloheptatriene: Reference 7

As shown in Table 1, there is a qualitative correlation that the $\Delta G^{\ddagger}$ value for ring inversion of silepins decreases as the substituents on silicon become more electronegative and generate more positive charge on the silicon atom. This decrease in energy barrier for ring inversion could be ascribed mainly to the relative stabilization of the tropylium-ion-like electronic structure[8] at the planar transition state caused by the electronegative substituents on silicon. This is in contrast to the calculated antiaromaticity of dichlorosilole due to the "partial silylenium ion character." [9] The calculated value of $\Delta\Delta H_f$ appears to give the general tendency similar to that of $\Delta G^{\ddagger}$ although the change is quite small. The relative energy difference caused by the steric effect of substituents between each derivative either in the boat or planar structure seems to be smaller than anticipated except for **4a**, which apparently has a larger $\Delta G^{\ddagger}$ value due to the steric hindrance.[10]

As a different approach for interpretation of the present results, the inversion barrier was estimated for the boat and planar structures of C-unsubstituted silepins **1a–d** by ab initio calculation using B3LYP/6-31G* level. Also the values of nuclear independent chemical shift (NICS),[11] proposed by Schleyer as a new index for aromaticity, were calculated. The results are shown in Table 2. The inversion barriers of **1c** and **1d** calculated from the difference of the total energy for the boat and planar structures (ΔE) were found to be smaller than that of **1a** and **1b** by 0.7–0.9 kcal mol^{-1}, showing the same tendency, albeit to a smaller extent, as observed in the BCO-annelated systems.

According to the NICS values, the planar structures of **1a** and **1b** have a weakly antiaromatic character whereas no such character is observed in those of **1c** and **1d** nor in the boat forms of **1a–d**. Such antiaromaticity, if present even in a minute amount, might be ascribed to the two electron hyperconjugative contribution of the exocyclic σ bonds on the silicon atom, and could cause destabilization of the transition state of ring inversion.[12] Such a hyperconjugative contribution of σ bonds can not operate in the case of **1c** and **1d** with the electronegative substituents on silicon, and rather the tropylium-ion-like stabilization should be generated.[13]

Table 2. The calculated inversion barriers (ΔE) and NICS[a] values of **1a-d**

compd	(R)	ΔE kcal mol^{-1}	NICS (ppm) boat	NICS (ppm) planar
1a[b]	(H)	0.9	-0.5	3.5
1b[b]	(Me)	1.0	-0.5	3.1
1c	(F)	0.2	-0.9	0.1
1d	(Cl)	0.1	0.3	0.9

[a] GIAO/6-31+G*//B3LYP/6-31G*. [b] Reference 9.

In summary, the gradual increase in electronegativity of the substituents on the silicon atom was found to decrease the energy barrier for ring inversion of silepins. This could be interpreted most probably by the weak tropylium-ion-like stabilization of the planar transition-state structure for the ring inversion when the substituents become more electronegative.

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References and Notes

1 Y. Nakadaira, R. Sato, and H. Sakurai, *Organometallics*, **10**, 435 (1991) and references cited therein.

2 T. Nishinaga, K. Komatsu, and N. Sugita, *J. Org. Chem.*, **60**, 1309 (1995).

3 All new compounds were obtained as colorless crystals and gave satisfactory elemental analyses. **4a**: 28% yield (*t*-BuLi, 20 eq); mp 144–145 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 4.47 and 4.04 (s, 1H), 2.84 (s, 2H), 2.80 (s, 2H), 2.74 (s, 2H), 1.1–1.5 (m, 24H), 1.08 and 1.00 (s, 9H). **4c**: 46% yield (*t*-BuLi, 20 eq); mp >300 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 4.47 (brs, 1H), 2.80 (s, 4H), 2.74 (s, 2H), 1.2–1.5 (m, 24H), 0.22 (s, 3H). **4d**: 21% yield (*t*-BuLi, 20 eq); mp >300 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 4.42 (s, 2H), 2.86 (s, 2H), 2.79 (s, 2H), 2.72 (s, 2H), 1.2–1.5 (m, 24H). **4e**: 52% yield (*t*-BuLi, 4 eq); mp 194–195 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 3.30 (s, 2H), 2.78 (s, 2H), 2.70 (s, 2H), 1.1–1.5 (m, 24H). **4f**: 98% yield; mp 139–140 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 3.45 (s, 6H), 3.14 (s, 2H), 2.84 (s, 2H), 2.76 (s, 2H), 1.1–1.5 (m, 24H). **4g**: 25% yield; mp 154–155 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 3.10 (s, 2H), 2.77 (s, 2H), 2.69 (s, 2H), 1.1–1.5 (m, 24H).

4 Crystallographic data of **4e**: F.W. = 417.49, *P*nma, a = 13.964(6), b = 16.143(4), c = 9.368(4), V = 2111(1) Å^3, Z = 4, D_{calc}= 1.313 g cm^{-3}, unique reflections = 1350 (I>3σ(I)), R = 0.046 (R_w=0.050).

5 MOPAC 93.

6 For a review of this concept, see W. A. Bingel and W. Lüttke, *Angew. Chem., Int. Ed. Engl.*, **20**, 899 (1981).

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8 The tris(bicyclo[2.2.2]octeno)tropylium ion is the most stable tropylium ion ever known: K. Komatsu, H. Akamatsu, Y. Jinbu, and K. Okamoto, *J. Am. Chem. Soc.*, **110**, 633 (1988).

9 B. Goldfuss, P. v. R. Schleyer, and F, Hampel, *Organometallics*, **15**, 1755 (1996).

10 We assume that the electronic effect of substituents upon the C-Si-C angle is similar in both the boat and planar forms, and can mostly be canceled out: for example, the angle calculated for the planar form of **4e** (115.3°) is larger than that of **4b** (111.9°) similarly to the case of the boat forms (see text).

11 P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, and N. J. R. v. E. Hommes, *J. Am. Chem. Soc.*, **118**, 6317 (1996).

12 T. Nishinaga, Y. Izukawa, and K. Komatsu, *J. Phys. Org. Chem.*, in press.

13 The values of magnetic susceptibility exaltation (Λ/ppm cgs) were also calculated for the planar forms of **1a–d** (CSGT/6-311+G** //B3LYP/6-31G*) to give the following results: **1a**; 2.2, **1b**; 4.2, **1c**; -4.4, **1d**; -5.2. For the calculation method of Λ, see B. Goldfuss, and P. v. R. Schleyer, *Organometallics*, **16**, 1543 (1997).