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Synthesis and Structural Aspects of Silicon-bridged [2.2]Metacyclophanes

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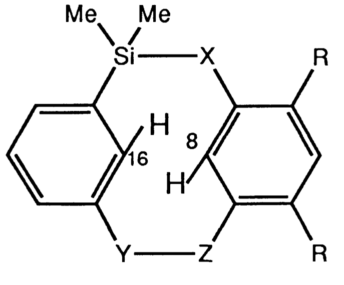
The title compounds were synthesized and the structural aspects were examined by NMR spectroscopy.

While the chemistry of [2.2]metacyclophane (MCP) is well established,1) *i.e.* electronic interaction of two benzene rings, the proximity of 8,16-positions, and the considerable strain energy, so far, that of silicon-bridged cyclophanes can not be found so much in the literatures. Only a synthetic approach to tetrasila[2.2]metacyclophane (**1**) was reported by Sakurai *et al.*2) Recently, we are interested in the properties of new organosilicon compounds with respect to the homology and the heterology with carbon analogues. In this communication, we would like to report synthesis and some structural aspects of silicon-bridged [2.2]metacyclophanes (**1-6**).

Compounds **1-3** were prepared by condensation of 1,2-dichloro-1,1,2,2-tetramethyldisilane with 1,2-bis(3-bromophenyl)-1,1,2,2-tetramethyldisilane, (3-bromobenzyl)(3-bromophenyl)dimethylsilane, or 1,2-bis(3-bromophenyl)-ethane in the presence of *t*-BuLi in THF at -50 °C in 38, 13, and 14% of yields, respectively. Similarly, **4** was obtained in a 9% of yield from a dimerization of (3-bromobenzyl)chlorodimethylsilane in the presence of *t*-BuLi in THF at -50 °C. **5** and **6** were synthesized by a reaction of 1,3-bis-(chlorodimethylsilyl)benzene with 1,3-bis(chloromethyl)-4,6-dimethylbenzene and α,α'-dibromo-*m*-xylene in the presence of magnesium in THF at room



1, X=Y=Z=$SiMe_2$, R=H
2, X=Y=$SiMe_2$, Z=CH_2, R=H
3, X=$SiMe_2$, Y=Z=CH_2, R=H
4, X=Y=CH_2, Z=$SiMe_2$, R=H
5, X=Z=CH_2, Y=$SiMe_2$, R=Me
6, X=Z=CH_2, Y=$SiMe_2$, R=H

temperature in 29 and 13% of yields. All new compounds gave satisfactory data of elemental analyses or high-resolution mass spectrometory.

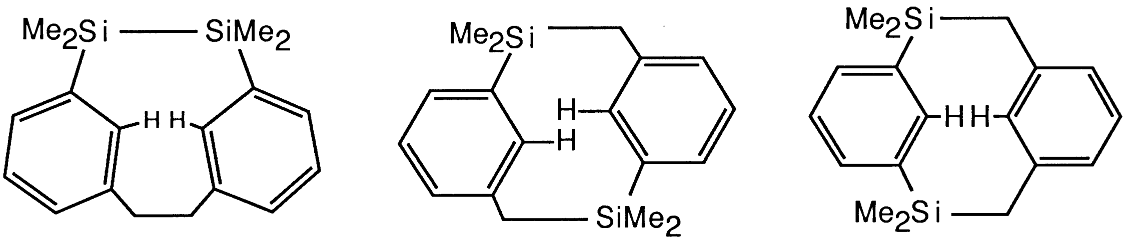
Compounds **1**, **3**, **4**, and MCP showed NMR signals of the inner aryl protons (8 and 16 positions) as an equivalent triplet at 6.43, 5.34, 5.38, and 4.27 ppm, respctively.[3)] The spectra of these aryl protons of **5** were shown as a singlet at 4.72 ppm and a triplet at 6.27 ppm, and therefore the former was assigned to C_8-H and the latter was assigned to C_{16}-H. Analogously, for **6**, a triplet signal at 4.87 ppm was assigned to C_8-H and another triplet signal at 5.97 ppm was assigned to C_{16}-H. **2** showed these protons as a set of triplets at 5.71 (C_8-H) and 6.14 (C_{16}-H) ppm. Thus, the chemical shifts of the inner aryl protons depend largely upon the number of silicon atoms included. Decreasing the number of silicon atoms led to the upfield shift of 8- and 16-aryl protons. These would be caused by the diamagnetic ring current effect of the opposite benzene ring[1)] through the increasing proximity of two benzene rings. The inner aryl carbon resonances of **1**-**6** were characteristically assigned by 2D-NMR (carbon-proton heterocosy technique). Thus the signals for C_8 were 142.44, 133.73, 138.99, 138.03, 133.23, and 131.87 ppm, and those for C_{16} were 142.44, 143.39, 138.99, 138.03, 144.59, and 144.49 ppm, respectively. The ^1H NMR signals of methyl groups attached to silicon atoms and bridging methylene groups in $CDCl_3$ at room temperature were also examined. Four methyl groups of **1** appeared as a singlet at 0.26 ppm, and **2** showed three singlets for three methyl groups at 0.22, 0.26, and 0.28 ppm and a singlet at 2.01 ppm for a methylene group. However, the spectra of **3**-**6** showed bridging methylene protons as two sets of doublets at 1.44-2.22 and 2.14-3.08 ppm (J=8.6-13.0 Hz) and methyl protons as a pair of singlet at 0.02-0.11 and 0.45-0.48 ppm. These suggest that the 10-membered rings of **1** and **2** would be flexible (ring flapping) and those of **3**-**6** and MCP would be fixed at the temperature. This assumption was unequivocally approved by the following experiments.

Activation energies[4)] for ring flapping derived from the coalescence

Table 1. Coalescense Temperature and Activation Energy for Ring Flapping

Compd	$T_C/^\circ C$	$\Delta G^{\neq}/kJ \cdot mol^{-1}$
1	<-50	
2	-17	51
3	69	66
4	103	75
5	131	78
6	>131	>80
MCP	>190	>113

temperature and the chemical shift were estimated and listed in Table 1. For **2**, **3**, **4**, **5**, and **6**, the energies were 51, 66, 75, 78, and >80 kJ/mol, respectively. However, $\Delta G^{\neq}$ value for **1** was not determined due to the too low coalescence temperature. Considering the atomic radius of carbon and silicon, and bond lengths of C-C, C-Si, and Si-Si, these results must be acceptable. The difference of the energy barriers between **3** or **4** and **6** is remarkable although same numbers of carbon (8 atoms) and silicon (2 atoms) are included in the ring system. These are interpreted in terms of the relative positions of C-8 and C-16 protons in a ground state and/or transition state, as shown in Fig. 1. On **5** and **6**, the difference in the energy barrier would be attributed to the difference in energy of ground state, due to a repulsive effect between bridging methylene and methyl group on benzene ring for **5**, because energy levels of both transition states are considered to be nearly equal. This was supported by the fact that ^{13}C resonance of bridging methylene carbon of **5** showed upfield shift (γ-effect)$^{5)}$ of 4.18 ppm, comparing with **6** while chemical shifts for methyl groups on silicon atoms of both compounds were almost similar (around -5 ppm).



3 **4** **6**

Fig. 1. Emphasized structures of **3**, **4**, and **6**.

References

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3) NMR spectra of compounds **1-6** in $CDCl_3$: **1**; ^1H NMR: δ 0.26 (s), 6.43 (t), 7.36, and 7.45. ^{13}C NMR: δ -5.64, 127.06, 133.07, 138.53, and 142.44. ^{29}Si NMR: δ -21.73. **2**; ^1H NMR: δ 0.22 (s), 0.26 (s), 0.28 (s), 2.01 (s), 5.71 (t), 6.14 (t), 7.04, 7.21, 7.23, 7.36, 7.46, and 7.50. ^{13}C NMR: δ -5.99, -4.70, 27.77, 127.06, 127.34, 127.99, 128.92, 132.75, 133.73, 134.02, 134.71, 135.58, 136.92, 137.12, and 143.39. ^{29}Si NMR: δ -20.57, -19.94, and -3.38. **3**; ^1H NMR: δ 0.02 (s), 0.45 (s), 2.22 (d, *J*=8.6 Hz), 3.08 (d, *J*=8.6 Hz), 5.34 (t),

7.18, 7.31, and 7.33. ^{13}C NMR: δ -6.50, -6.20, 39.19, 128.03, 128.15, 130.71, 134.72, 138.48, and 138.99. ^{29}Si NMR: δ -17.89. **4**; ^{1}H NMR: δ 0.02 (s), 0.47 (s), 1.77 (d, J=12.8 Hz), 2.14 (d, J=12.8 Hz), 5.38 (t), 7.05, 7.25, and 7.26. ^{13}C NMR: δ -5.50, -4.73, 127.41, 128.49, 128.50, 134.23, 136.79, and 138.03. ^{29}Si NMR: δ -1.06. **5**; ^{1}H NMR: δ 0.11 (s), 0.48 (s), 1.44 (d, J=13.0 Hz), 2.20 (s), 2.31 (d, J=13.0 Hz), 4.72 (s), 6.27 (t), 6.89, 7.40, and 7.53. ^{13}C NMR: δ -4.82, -4.71, 19.61, 24.40, 127.30, 129.97, 131.28, 132.79, 133.23, 133.64, and 144.59. ^{29}Si NMR: δ -1.35. **6**; ^{1}H NMR: δ 0.10 (s), 0.46 (s), 1.67 (d, J=12.8 Hz), 2.14 (d, J=12.8 Hz), 4.87 (t), 5.97 (t), 6.79, 7.11, 7.36, and 7.52. ^{13}C NMR: δ -5.10, -4.86, 28.58, 123.45, 127.07, 127.38, 131.87, 133.18, 133.41, 137.36, and 144.49. ^{29}Si NMR: δ -1.95.

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