

9,9-DIMETHYL-9H-TRIBENZO[b,d,f]SILEPIN: A STEREOCHEMICALLY RIGID  
SILICON HETEROCYCLE

Joyce Y. Corey and Eugene R. Corey

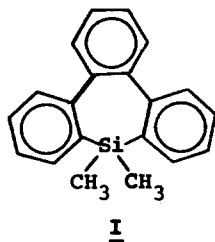
Department of Chemistry, University of Missouri-St. Louis

St. Louis, Missouri 63121, U.S.A.

(Received in USA 19 September 1972; received in UK for publication 10 October 1972)

Recent reports<sup>1,2</sup> on the calculations of structures and energies of silicon compounds suggest that silicon heterocycles are far more flexible than the corresponding carbocycles. Few quantitative studies of barriers to rotation for silicon heterocycles have been reported and the only well studied systems are 1,1-dimethylsilacyclohexane<sup>3,4</sup> and 1,1,4,4-tetramethyl-1,4-disilacyclohexane.<sup>5</sup> From line shape analysis of the low temperature NMR spectrum of 1,1-dimethylsilacyclohexane the chair-chair interconversion barrier,  $\Delta G^\ddagger$ , was determined to be  $5.5 \pm 0.1$  kcal/mole ( $-160^\circ\text{C}$ ) compared to  $\Delta G^\ddagger = 10.4$  kcal/mole ( $-60^\circ\text{C}$ ) for 1,1-dimethylcyclohexane. It has been suggested that long bonds and low barriers to rotation about the  $sp^3$ -hybridized C-Si bonds are responsible for the low barrier to interconversion in 1,1,4,4-tetramethyl-1,4-disilacyclohexane ( $\Delta G^\ddagger < 6$  kcal/mole at  $-160^\circ\text{C}$ ).<sup>5</sup>

In connection with our investigations of synthesis, stereochemistry, and conformation of seven-membered rings that contain a Group IV heteroatom, we have reexamined the compound, 9,9-dimethyl-9H-tribenzo[b,d,f]silepin, I, which was



first reported as a minor byproduct in a study of the reaction of *o*-dichlorobenzene and dimethylmethoxychlorosilane in sodium and boiling toluene.<sup>6</sup> In our study, I, m.p.  $225-226.5^\circ$  (reported,  $226-227^\circ$ <sup>6</sup>), was prepared in 3.5% yield by reaction of *o,o'*-dilithioterphenyl (generated from *o*-terphenylenemercury dimer<sup>7</sup> and lithium metal in ether) with dimethyldichloro-

silane. The molecular weight determined by mass spectroscopy is 286 at both 15 and 70 eV and an ion source temperature of  $80^\circ\text{C}$ .

The room temperature nuclear magnetic resonance spectrum of I in carbon tetrachloride, chlorobenzene or 1-bromonaphthalene shows two Si-CH<sub>3</sub> resonances of equal intensities at 9.17 and 10.13  $\tau$  (in CCl<sub>4</sub>) and with correct integrations for the ratio of aromatic to methyl protons (also in CCl<sub>4</sub>). A variable temperature study shows no evidence of line broadening even at 200°C. However, exchange of sites at 200° was indicated by double resonance.<sup>8</sup> Thus saturation of the high field Si-CH<sub>3</sub> resonance caused a sharp decrease in the intensity of the low field Si-CH<sub>3</sub> resonance. These results indicate a stereochemically rigid silicon heterocyclic species in solution at room temperature, the first such report. Stereochemical rigidity has been demonstrated for the tribenzo carbon analogs, 9,9-dimethoxy-9H-tribenzo[a,c,e]cycloheptene ( $\Delta G^\ddagger > 23$  kcal/mole at 180°C),<sup>9</sup> and 9H-tribenzo[a,c,e]cycloheptene ( $\Delta G^\ddagger = 24.0$  kcal/mole at 202°C).<sup>10</sup> Although the coalescence temperature for the Si-CH<sub>3</sub> groups in I could not be determined, the experimental data suggest that the barrier to ring inversion for the silicon heterocycle is comparable with the the analogous carbocycles, in contrast to what has been observed previously.<sup>3-5</sup>

Crystallographic data have furnished information about the minimum symmetry of I and show that a previous space group assignment is in error. Crystal data for I are given in Table 1; Table 2 lists the space group assignments and the minimum crystallographically required symmetry of I in each space group. The molecular symmetry requirement of I in the originally reported space group, Pbcn, is impossible (C<sub>1</sub>) or chemically unreasonable (C<sub>2</sub>). The space group Cmc2<sub>1</sub> is the only reasonable choice and requires that I have crystallographic mirror symmetry (C<sub>s</sub>). This mirror plane contains the silicon atom and methyl carbon atoms and bisects benzo group d (see Figure).

Our present study suggests that barriers to rotation for the silepin, I,

Table 1. Crystal Data for I\*

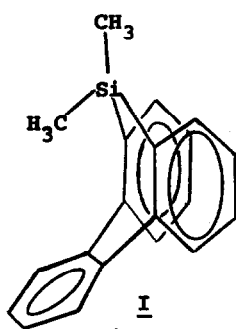
	This work	Previous Report <sup>†</sup>
<u>a</u> =	14.50(3)	14.61(5)
<u>b</u> =	15.21(3)	15.21(9)
<u>c</u> =	6.87(2)	6.89(5)
Crystal system	orthorhombic	orthorhombic
Density	obs.=calc.=	-
<u>Z</u> <sup>‡</sup>	1.26 g cm <sup>-3</sup>	-
	4	4

\*Standard deviations in the last figure in the parentheses. †reference 6. ‡number of molecules per unit cell.

Table 2. Space Group Assignments and Required Molecular Symmetry of I.<sup>11</sup>

Space Group	Required Molecular Symmetry
Pbcn*	C <sub>2</sub> (unreasonable)
	C <sub>i</sub> (impossible)
Cmcm†	C <sub>2h</sub> (impossible)
	C <sub>2v</sub> (unreasonable)
Cmc2 <sub>1</sub>	C <sub>s</sub> (reasonable)

\* Incorrect space group assignment by previous workers (ref. 6) who overlooked the C-centering in the data. † This work: systematic absences of  $h + k = 2n + 1$  for general  $hkl$  data and of  $l = 2n + 1$  for  $h0l$  data indicate space groups Cmcm or Cmc2<sub>1</sub>.



Figure

of a singlet Si(CH<sub>3</sub>)<sub>2</sub> in variable temperature NMR studies may not necessarily mean ring flexibility.<sup>16</sup> Clearly, the problem of stereochemical rigidity for silicon heterocycles requires more careful scrutiny before the factors influencing ring flexibility can be ascertained.<sup>17</sup>

**Acknowledgements.** We thank Dr. T. J. Curphey for assistance with the high temperature NMR measurements and Dr. R. E. K. Winter for helpful discussions.

#### REFERENCES

- 1) M. T. Tribble and N. L. Allinger, *Tetrahedron*, **28**, 2147 (1972).
- 2) R. J. Oullette, D. Baron, J. Stolfo, A. Rosenblum and P. Weber, *ibid.*, **28**, 2163 (1972).
- 3) F. R. Jensen and C. H. Bushweller, *Tetrahedron Lett.*, 2825 (1968).
- 4) C. H. Bushweller, J. W. O'Neil and H. S. Bilofsky, *Tetrahedron*, **27**, 3065 (1971).
- 5) R. W. Murray and M. L. Kaplan, *ibid.*, **25**, 1651 (1969).

and the corresponding carbocycles are comparable. However, in a related system, 5,5-dimethyl-5H-dibenzo[b,f]silepin, II, the NMR spectrum shows a singlet at room temperature<sup>12,13</sup> with only a slight broadening attributed to effects of increased viscosity at -80°C.<sup>13</sup> A study of the variable temperature NMR spectrum of 9,9-dimethylsilaanthracene, III, also shows a sing-

let Si-CH<sub>3</sub> at -40°C<sup>14</sup> whereas 9-alkylanthracenes are stereochemically rigid at room temperature.<sup>15</sup> These results suggest that silicon compounds such as II and III are more flexible than the carbocycles or that one conformer is present but with very small  $\Delta\tau$  for the Si(CH<sub>3</sub>)<sub>2</sub> group. The latter observation has been reported for the low temperature (-163°C) spectrum of 1,1-dimethylsilacyclohexane.<sup>3,4</sup> Therefore, the persistence

- 6) K. A. Andrianov, L. M. Volkova, N. V. Delazari and N. A. Chumaeskii, Khim. geterotskil. Soedinenii, 435 (1967); Chem. Abstr., 67, 108695c, (1967).
- 7) G. Wittig, E. Hahn and W. Tochtermann, Chem. Ber., 95, 431 (1962).
- 8) Reviewed in R. A. Hoffman and S. Forsen, Adv. Nucl. Magn. Resonance, 1, 15 (1966).
- 9) W. Tochtermann, G. Schnabel and A. Mannschreik, Annalen, 705, 169 (1967).
- 10) M. N6grádi, W. D. Ollis and I. O. Sutherland, Chem. Comm., 159 (1970).
- 11) "International Tables for X-ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England.
- 12) J. Y. Corey, M. Dueber and B. Bichlmeir, J. Organometal. Chem., 26, 167 (1971).
- 13) T. J. Barton, W. E. Volz and J. L. Johnson, J. Org. Chem., 36, 3365 (1971).
- 14) P. Jutzi, Chem. Ber., 104, 1455 (1971).
- 15) A. W. Brinkman, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Strothers and A. L. Ternay, Jr., J. Amer. Chem. Soc., 92, 5912 (1970).
- 16) Accidental coincidence of the chemical shifts for nonequivalent methylene protons has been reported for the stereochemically rigid system, dibenz[c,e]-thiepin; cf., K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon and G. H. Wahl, Jr., J. Amer. Chem. Soc., 86, 1710 (1964).
- 17) Structural data for two stereochemically rigid heterocycles with long carbon-metalloid bonds, comparable to a C-Si bond distance, have been reported recently; cf., D. A. Pulman and D. A. Wittig, Chem. Comm., 831 (1971), (cis-1,4-dimethylisothiochroman-2,2-dioxide) and A. T. McPhail, J. J. Breen, J. H. Somers, J. C. H. Steele, Jr. and L. D. Quin, Chem. Comm., 1020 (1970), (1-phenyl-4,4-dimethoxyphosphorinan).