

Unusual Silicon-29 Chemical Shift Anisotropies in Three-Membered Rings

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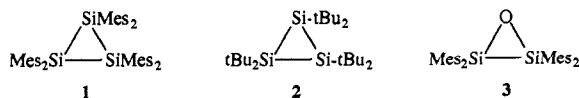
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Despite much work on the subject, there is still disagreement over the nature of bonding in three- and four-membered rings containing carbon and silicon.¹⁻⁹ Studies of chemical shift anisotropy (CSA) have been useful in comparing the bonding and electronic structures of compounds of the heavier main-group elements with those of analogous carbon compounds.^{10,11} The ¹³C CSAs of several three-membered rings (3MRs) containing carbon were previously measured and found to be similar to those of larger cycloalkanes.¹² In this communication we report the ²⁹Si CSAs for hexamesitylcyclotrisilane (**1**), hexa-*tert*-butylcyclotrisilane (**2**), and tetramesityldisiloxirane (**3**), which are significantly larger than those of other cyclopolysilanes^{13,14} and similar in magnitude to that reported for a disilene.¹¹



The compounds under study were synthesized as previously described.¹⁵⁻¹⁷ Samples were prepared in a drybox by packing 5-mm glass tubes to a depth of 1 cm and sealing under vacuum.

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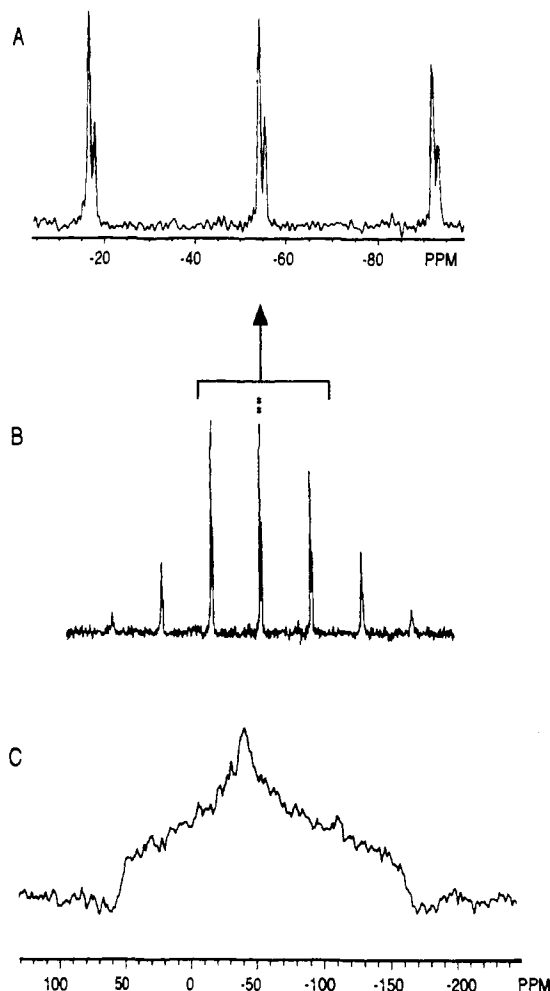


Figure 1. (a) Center portion of the ²⁹Si MAS spectrum of **1**. (b) ²⁹Si MAS spectrum of **1** at 2.34 T. ** marks the isotropic shifts. (c) ²⁹Si static spectrum of **1** taken at 7.04 T. All spectra are referenced externally to TMS.

Cross polarization magic angle spinning (CPMAS) and static NMR experiments were carried out at fields strengths of 2.34 and 7.05 T using homebuilt spectrometers and probes.¹⁸ CPMAS and static spectra for **1** are shown in Figure 1 (all spectra were externally referenced to tetramethylsilane). Two CSA spinning sideband manifolds are observed for **1**, with a 2:1 intensity ratio and isotropic chemical shifts of -55.6 and -54.4 ppm. MAS line shapes were fit with SpectraCalc, a data processing package,¹⁹ and CSAs of 35, -47, -155 ppm and 50, -42, -167 ppm were determined using FINDMR, a numerical adaptation of the graphical method of Herzfeld and Berger.²⁰ In a closely related molecule, hexakis(2,6-dimethylphenyl)silirane, the three silicon atoms in the ring form an isosceles triangle.¹⁵ Although a crystal structure is not available for **1**, a similar structure would account for the 2:1 intensity ratio. The CPMAS spectrum for **2** gives a single isotropic peak at -4.4 ppm in the solid. The MAS spectrum was used to determine the CSA of 90, -7, -97 ppm. Static and slow spinning CPMAS were used to examine **3**; its isotropic shift is -27.7 ppm, and the CSA is 61, -20, -122 ppm, giving a spread²¹ similar in magnitude to those for **1** and **2**.

The ²⁹Si shielding anisotropies for **1**, **2**, and **3** are unusual as they are larger than those found for other cyclopolysilane rings.^{13,14}

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 (21) The spread in the CSA is taken as $|\sigma_{11} - \sigma_{33}|$.

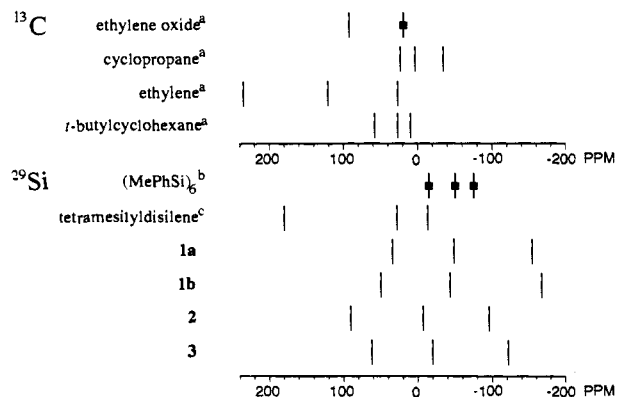


Figure 2. Comparison of experimental CSA tensor elements for carbon and silicon. All ^{13}C and ^{29}Si shifts are referenced to TMS. Upfield position for ethylene oxide represents two coincident tensor elements. (a) ^{13}C data from Duncan, T. M. *A Compilation of Chemical Shift Anisotropies*; Farragut Press: Chicago, 1990. (b) ^{29}Si data from ref 14. Edges and high point of overlapped pattern are given. (c) ^{29}Si data from ref 11.

Furthermore, this increase is not paralleled by the ^{13}C shielding anisotropies for the analogous series of organic compounds. For example, the width in the powder pattern in the six-membered ring *t,t,t,t,t*-(MePhSi)₆ is only 59 ppm,²² about one-third of the spread in the CSA found for **1**, **2**, and **3** as illustrated in Figure 2. A comparison of the spreads in the ^{13}C shielding anisotropies for *tert*-butylcyclohexane and cyclopropane show them to be similar.¹² Although the spread in the ^{13}C CSA for cyclopropane is only 30% of that for ethylene,²³ the spreads in the ^{29}Si CSAs

(22) This value is only a rough measure of the spread in the ^{29}Si CSA for this compound, as the spectrum is a composite of several similar overlapping powder patterns as a result of the distorted solid-state structure.

of **1**, **2**, and **3** are quite similar to that for tetramesityldisilene (180, 27, -15).¹¹

The spread in a ^{13}C shielding anisotropy is usually taken as indicative of the anisotropy in the 3D electronic structure reflecting the hybridization at the particular carbon center. The observation made here, that the ^{29}Si CSAs for **1**, **2**, and **3** are more similar to those for sp^2 Si rather than those for sp^3 Si, is striking. This would seem to imply that significant differences exist between the bonding in silanes and that in either cyclopropanes or larger cyclosilanes. For molecules like **3**, models have been developed that invoke partial π -bonding between the silicon atoms.⁷⁻⁹ This effect can be used to rationalize the large CSA observed for **3** but cannot account for the results for **1** and **2**. The unusual ^{29}Si CSA results for these three-membered Si rings may be related to the same electronic effect which results in large strain energies for siliranes but not for cyclopropanes.^{9a,24} Ab initio calculations of the ^{29}Si CSAs in these compounds should prove useful in determining whether the unusual findings reported herein arise from a fundamentally different bonding arrangement for the Si-containing systems or are a result of shielding anisotropies in three-membered rings being much more sensitive to structural variations than previously recognized.

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