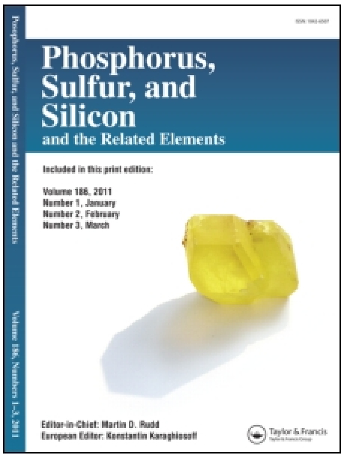

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Robert West[a]; Jefferson D. Cavalieri[a]; James Duchamp[b]; Kurt W. Zilm[b]
[a] University of Wisconsin-Madison, Wisconsin, USA [b] Yale University, Connecticut, USA

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CHEMICAL SHIFT TENSORS AND CHEMICAL BONDING IN CYCLIC SILANES

ROBERT WEST AND JEFFERSON D. CAVALIERI
University of Wisconsin-Madison, Wisconsin, USA

JAMES DUCHAMP AND KURT W. ZILM
Yale University, Connecticut, USA

Abstract Solid-state ^{29}Si NMR has been used to determine the principal values of the shielding tensors for organosilicon compounds, including cyclic silanes. Silicon atoms in three-membered rings show exceptionally large chemical shift anisotropies, similar to those of multiply-bonded Si atoms. Possible reasons for these large CSA's are discussed.

SOLID-STATE NMR AND THE SHIELDING TENSOR

NMR chemical shift values are usually determined in solution, giving a single value for each distinct nucleus, the isotropic chemical shift. Such chemical shifts have been exhaustively interpreted and are useful in both structural and chemical bonding studies. However, they represent only averages of the three independent values of the chemical shift tensor. Therefore, important information may be obscured in solution NMR studies. [1]

Although the experiment is somewhat more difficult to carry out, the NMR spectra of solid samples can provide the three principal values of the chemical shift tensor. [2] Two methods have been used: static powder spectra, illustrated for a typical example in Figure **1a**, and slow magic angle spinning, shown in Figure **1b**. Static spectra produce a broad pattern in which the three principal values of the tensor, σ_{11}, σ_{22}, and σ_{33}, are represented by the rise, peak, and fall. Slow spinning at the "magic angle" produces a pattern of several lines, actually spinning sidebands around the isotropic chemical shift peak. The principal values of the tensor may be extracted from this pattern using a known formula. [3]

The actual values of σ_{11}, σ_{22}, and σ_{33} are of interest, as is the difference between them, the chemical shift anisotropy (CSA). We will use $\Delta\sigma = \sigma_{11}-\sigma_{33}$, the spread of principal values of the tensor, as the measure of anisotropy.

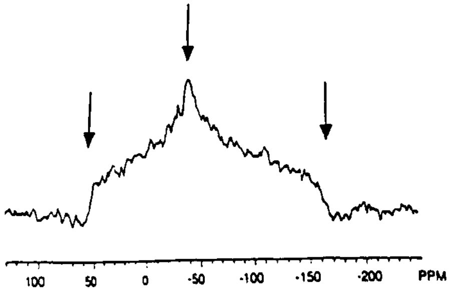

FIGURE 1a

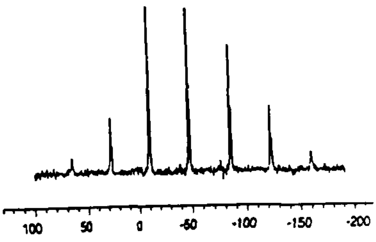

FIGURE 1b

Shielding Tensors for Organosilicon Compounds

Recently we have determined the ^{29}Si shielding tensors for a number of organosilicon compounds.[4-6] Tetracoordinate, sigma-bonded silicon compounds usually show rather small CSA's. This reflects the fact that the electron distribution is rather similar in the xy, xz, and yz planes which are sampled by the three tensor components (x, y, and z are the magnetic axes for the molecule). Typical values of $\Delta\sigma$ are 31 ppm for Me_3SiPh, 47 ppm for $Me_2Si(OMe)_2$, and 30 ppm for $Me_3SiOSiMe_3$.[7] Disilenes, however, show large $\Delta\sigma$ values, typically near 200 ppm.[4,5] Representative data for some disilenes are given in Table 1. The large CSA's of disilenes reflect the fact that the electron distribution is highly asymmetric in molecules containing a π band.

Similar effects are found in the ^{13}C shielding tensors for carbon compounds; that is, saturated compounds have small CSA's, <50 ppm,[8] while for olefins the CSA is large, ~ 200 ppm.[8,9]

TABLE I Chemical Shielding Tensors for Some Disilenes

	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$
$Mes_2Si{=}SiMes_2$	181	31	-22	203
t-Mes(tBu)Si=Si(tBu)Mes	178	77	3	175
$Tip_2Si{=}SiTip_2$ [a]	155	30	-31	186
$[(Me_3Si)_2CH]_2Si{=}Si[CH(SiMe_3)_2]_2$	182	55	21	161
	199	54	9	190

[a] Tip = 2,4,6-triisopropylphenyl

Chemical Shift Anisotropy in Cyclosilanes

Cyclic polysilanes show a number of properties consistent with σ- delocalization of the Si-Si bonding electrons.[10] In fact, their properties somewhat resemble those of π-delocalized aromatic hydrocarbons.[11] We have studied the chemical shielding tensors for various cyclosilanes. Surprisingly, the Δσ values for cyclosilanes depend strongly on ring size. Chemical shielding tensors for some cyclosilanes are shown in Table 2.[4] The five-and six-membered ring compounds have small CSA's, as expected for tetrahedral, σ-bonded silicon. For the one four-membered ring the CSA is somewhat larger, but the most striking data are for the three-membered rings. The latter have Δσ values near 200 ppm, about the same as those for disilenes. This small-ring effect persists even for compounds with a heteroatom in the ring; the Si-Si-O ring compound tetramesityldisilaoxirane has Δσ=183 ppm.

Table II Chemical Shielding Tensors for Some Cyclosilanes[5,6]

	σ_{11}	σ_{22}	σ_{33}	Δσ
$(Me_2Si)_6$	-33	-36	-56	23
$[(CH_2)_5Si]_6$	-23	-44	-58	35
$(nPr_2Si)_5$	-13	-30	-67	54
$[(CH_2)_5Si]_5$	-12	-43	-64	52
$(MeSitBu)_4$ [a]	37	-14	-62	99
$(tBu_2Si)_3$	90	-7	-97	190
$(Mes_2Si)_3$	35	-47	-155	190
	50	-42	-167	217
Mes_2Si_2O	61	-20	-122	183

[a] trans-trans-cis

The trends in ^{29}Si CSA with ring size found in cyclosilanes are not mirrored by the corresponding carbon compounds. Thus cyclopropane $(CH_2)_3$, has ^{13}C Δσ of 58 ppm, only slightly higher than those for $(CH_2)_4$ (25 ppm), $(CH_2)_5$ (37 ppm) and $tBuCH(CH_2)_5$ (48 ppm).[9]

Theoretical Considerations

What is the reason for the unexpectedly large ^{29}Si CSA for cyclotrisilanes, not found for ^{13}C in cyclopropanes? The nature of bonding in small rings, both of silicon and carbon, has been controversial, and a number of different bonding models have been suggested.[10] The difference between silicon and carbon might therefore be due to significant differences in chemical bonding and orbital occupancy in the Si_3 and C_3 rings. However, recent experimental as well as theoretical studies tend to discount this explanation. For both carbon and silicon 3-membered rings, the intra-ring one-bond coupling constants, $^1J_{CC}$ and $^1J_{SiSi}$, are reduced by about 60% from those in linear compounds.[12] This suggests that both cyclopropane and cyclotrisilanes have very high and nearly equal P character (~85%) in the intra-ring bonds. In addition a natural bond order analysis suggests that the bonding in $(CH_2)_3$ and $(SiH_2)_2$ is quite similar.[13]

In a discussion of ^{29}Si CSA's for disilenes, Tossell and Lazaretti have pointed out that the paramagnetic deshielding of σ_{11} is due mainly to a low excitation energy for the Si-Si σ-π^* electronic transition. [14] For cyclotrisilanes, the σ-π^* excitation energy is also low, resulting in electronic absorption bands at energies similar to those for disilenes. This decrease is due mainly to destabilization of the HOMO. For $(tBu_2Si)_2$, the oxidation potential is about 1 V less than for typical five- and six-membered ring cyclosilanes. [15] The behavior of silicon four-membered rings is intermediate, that is, the σ-π^* excitation energy is lower than for Si_5 and Si_6 rings but greater than for cyclotrisilanes. Correspondingly the CSA of the Si_4 ring is greater than for Si_5 and Si_6 but less than for Si_3 rings.

Tentatively, therefore, we suggest that the large CSA's for small-ring cyclosilanes reflect paramagnetic deshielding due to the low σ-π^* excitation energy in these rings. For cyclopropanes and cyclobutanes no such low-energy transition occurs, so they show normal low values of $\Delta\sigma$. The question is not settled, however, and further experimental and theoretical studies are needed.

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