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Solid-State ^{29}Si NMR Study of RSiSiR: A Tool for Analyzing the Nature of the Si−Si Bond

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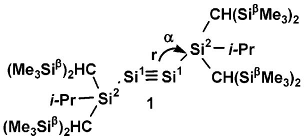
The first stable disilynes, RSiSiR, R = $Si(CH(SiMe_3)_2)_2(i\text{-}Pr)$[1] (**1**) and R = $SiMe(Si\text{-}t\text{-}Bu_3)_2$[2] were recently synthesized after years of frustrating attempts. **1** was characterized by X-ray crystallography.[1] **1** is trans-bent ($\alpha = 137.4°$) with $r(Si^1{-}Si^1) = 2.062$ Å, significantly shorter than in R′RSi═SiRR′ (e.g., 2.15 Å for R = $SiMe_3$, R′ = 2,4,6-triisopropylphenyl[3]). This is in line with earlier theoretical (E = Si−Pb)[4] and experimental (E = Ge−Pb)[5] studies showing that REER are trans-bent, in contrast to the linear geometry of acetylenes. **1** was assigned a Si−Si triple bond on the basis of its structure, its UV−vis spectrum, and the calculated $Si^1{-}Si^1$ bond order of 2.6.[1]



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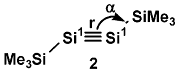


2

$Me_3Si-Si^1\equiv Si^1-SiMe_3$

3

Are the trans-bent E−E bonds in REER triple bonds? The answer to this fundamental question is highly controversial and under vigorous discussion.[5a,b,6−8] The recent synthesis of **1** has only intensified the debate rather than settling it.[6h,7,8]

Experimental information on the nature of a chemical bond can be obtained from solid-state NMR by measuring the directional NMR chemical shift tensors (CST) and the chemical shift anisotropy (CSA[9]).[10] Large CSA values indicate the presence of π-bonds.[10] Thus, ^{13}C CSA values for HC≡CH, $H_2C{=}CH_2$, and H_3CCH_3 are −240,[10a,b] −153,[10a] and 15 (calculated) ppm, respectively. The large CSA of HC≡CH results from two strongly deshielded CST components directed perpendicularly to its molecular axis (Scheme 1a).[10] Measured CST and CSA of compounds with C═Si,[11a] Si═Si,[11b] and Sn═Sn[11c] bonds revealed large CSA values, consistent with the existence of π-bonds. Note that the absolute size of the CSA value does not reflect the π-bond strength.[11d]

Here we report the first solid-state ^{29}Si NMR spectrum of a disilyne, that is, **1**, as well as quantum mechanical calculations which provide the size and orientation of the CST of **1** and of the smaller models, **2** and **3**. On the basis of the size and direction of the CST components and the large ^{29}Si CSA values, we conclude that **1** (and other bent disilynes) possesses a triple bond, although with weakened π-bonds[6d] and a smaller bond order (2.6)[1,6d] than that of the classic triple bond in acetylene (3.0).

The solid-state ^{29}Si NMR measurements were carried out[12] using the CPMAS technique.[13] Experimental and calculated[14] data are given in Figure 1 and Table 1. The tensor directions are shown in Scheme 1.

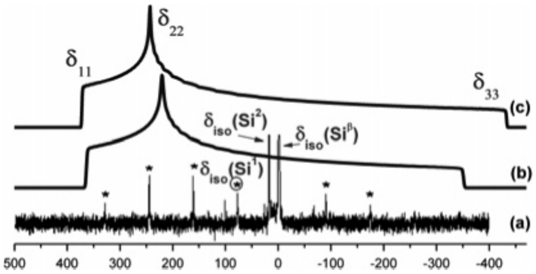


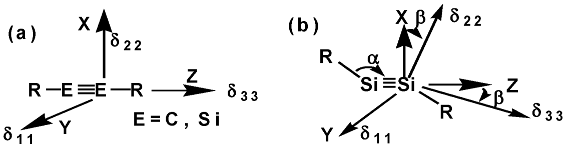
Figure 1. (a) CPMAS ^{29}Si MNR spectrum of **1**; (b) and (c) show simulations of the static ^{29}Si NMR spectrum of **1** using (b) the experimental data[12c] and (c) the calculated (C_2-symmetry) CST components.

Table 1. Measured Solid-State ^{29}Si NMR Parameters of **1** and Calculated Values for **1**−**3**

	^{29}Si^1 values (in ppm)				
	δ_{11} (σ_{11})	δ_{22} (σ_{22})	δ_{33} (σ_{33})	δ_{iso}[a] (σ_{iso})	CSA[b]
			1		
δ exptl	364 ± 20[c]	221 ± 16[c]	−350 ± 13[c]	78.4[d] 89.9[e]	−643 ± 20[c]
calcd[f−h]					
δ total (C_2)[i]	373.1	244.4	−431.9	61.9	−740.6
δ total (C_i)[i]	381.6	249.5	−435.2	65.3	−750.7
σ^{p} [j]	(−964.9)	(−837.4)	(−141.7)	(−648.0)	(759.5)
			2, bent (C_i)[k]		
δ total[i]	442.4	285.2	−471.2	85.5	−835.1
σ^{p}	(−999.1)	(−843.6)	(−87.9)	(−643.6)	(833.5)
			3, linear (D_{3d})[k]		
δ total[i]	162.5	162.5	−518.5	−64.5	−681.0
σ^{p}	(−719.4)	(−719.4)	(−42.7)	(−493.9)	(676.7)

[a] $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. [b] Reference 9. [c] Reference 12b. [d] $\delta_{iso}(^{29}Si^2) = 18$ ppm, $\delta_{iso}(^{29}Si^{\beta}) = 0.4$, 0.3, −0.4, and −1.0 ppm. [e] In d_6-benzene solution.[1] [f] $\delta(^{29}Si) = \sigma(^{29}Si_{TMS}) - \sigma(^{29}Si)$; TMS = Me_4Si, calculated $\sigma(^{29}Si_{TMS}) = 331$ ppm. [g] Reference 14e. [h] Geometries are given in ref 15. [i] $\delta_{ii}(\text{total}) = \delta(^{29}Si_{TMS}) - [\sigma_{ii}(\text{paramagnetic}) + \sigma_{ii}(\text{diamagnetic})]$. [j] C_i. [k] Geometries are given in the Supporting Information.

Scheme 1. Calculated Orientation of the Principal CST Components: (a) in Linear REER; (b) in Bent RSiSiR[16]



The observed isotropic $\delta(^{29}Si^1)$ of **1** in the solid state is 78.4 ppm, shifted by 11 ppm to a higher field relative to that in benzene solution (89.9 ppm[1]). This difference may result from small conformational changes in solution relative to that in the solid state, for example, twisting of the RSiSiR skeleton or rotation about the R−Si bond.[15]

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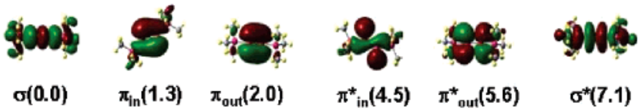

Figure 2. Frontier molecular orbitals of trans-bent $Me_3SiSi{\equiv}SiSiMe_3$ (in parentheses, their relative energies in eV, at B3LYP/6-31G(d,p)).

The measured CSA of Si^1 in **1** of −643 ppm (calculated: −740 to −764 ppm, Table 1) is considerably larger than in disilenes (e.g., −364 ppm for $(i\text{-}Pr_3Si)_2Si{=}Si(Si\text{-}i\text{-}Pr_3)_2$[11b]).[11d] The measured δ_{11} and δ_{22} (Scheme 1b)[16] are 364 and 221 ppm, respectively, considerably deshielded relative to δ_{33} of −350 ppm.

The measured CSTs of **1** (which are generally in reasonable agreement with the calculated values) provide strong evidence for its Si−Si triple bond character. To understand this statement, let us first analyze the CSTs of model systems **3** (linear) and **2** (trans-bent) realizing that the measured and calculated CST of **1** exhibits a very similar behavior to that calculated for **2** (Table 1).

In linear **3**, σ_{11} (δ_{11}) and σ_{22} (δ_{22}) are identical, and are oriented perpendicularly to the RSiSiR molecular axis (Z), that is, along the X and Y axes (Scheme 1a). σ_{33} (δ_{33}) points along the Z axis, and it is shifted to a higher field (Table 1). ^{13}C NMR of HCCH exhibits the same tensor pattern, that is, $\delta_{11} = \delta_{22} = 150$ ppm, $\delta_{33} = -90$ ppm.[10,11d] The paramagnetic contribution (σ^p)[17a,b] to the CST of Si^1 in **3** is highly anisotropic ($CSA^p = 677$ ppm) with high degenerate deshielding contributions along X and Y ($\sigma^p_{11} = \sigma^p_{22} = -719$ ppm) and a very small contribution along Z ($\sigma^p_{33} = -43$ ppm) (Table 1). σ^p_{11} and σ^p_{22} in linear disilynes (and acetylenes[10]) are attributed primarily[15,18] to the coupling, induced by the applied magnetic field, between σ(Si−Si) and the two degenerate π^*-orbitals, which in linear structures are oriented in perpendicular planes.

Upon bending of **3** → **2**, the degeneracy of the π- and π^*-orbitals is lifted, forming two π-orbitals, π_{in} and π_{out} (and π^*_{in}, π^*_{out}) (Figure 2), leading consequently to different σ^p_{11} and σ^p_{22} CST components (Table 1), which are attributed primarily to the Si−Si $\sigma-\pi^*_{in}$ and $\sigma-\pi^*_{out}$ orbital coupling, respectively.[15,18] σ^p is inversely proportional to the energy difference between the interacting orbitals (ΔE),[17c] the smaller is ΔE the larger is the shift of σ^p to lower field. Upon bending, $\Delta E(\sigma-\pi^*_{in})$ and $\Delta E(\sigma-\pi^*_{out})$ decrease from 6.1 eV in **3** to 4.5 and 5.6 eV, respectively, in **2** (Figure 2), causing a significant downfield shift of σ^p_{11} and σ^p_{22} and consequently of δ_{11} and δ_{22} (Table 1). δ_{11}, oriented perpendicularly to the RSiSiR XZ molecular plane has the largest paramagnetic contribution (most downfield shifted). σ^p_{33} (−88 ppm) and δ_{33} (−471 ppm) remain highly shielded, as in **3** and in acetylene.[10b]

In conclusion, the measured and calculated orientations and values of the CST components of bent disilyne **1** strongly support the description of the Si−Si bond as a triple bond composed of a σ*-bond and two nondegenerate* π*-bonds*.

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Supporting Information Available: Calculated Cartesian coordinates of **2** and **3** and geometry parameters of **1**, **2**, and **3**; complete ref 14a. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) (a) Approximately 37 mg of **1** were placed in an air-tight 7.5 mm ZrO_2 rotor under vacuum conditions. ^{29}Si solid-state CPMAS NMR measurements were carried out at 59.606 MHz on a 300 MHz Chemagnetics/Varian CMX-infinity spectrometer at room temperature using a double-resonance Chemagnetics probe and spinning speeds of 5.000 and 5.333 kHz. A CPMAS echo sequence was applied with $\pi/2$ and π pulses of 5 and 10 μsec, respectively, and a 200 μsec echo interval and 3 sec repetition time. ^{29}Si chemical shifts were referenced to TMS. The rf levels of the 5 msec Hartman−Hahn CP match was set at 50 kHz and at 100 kHz for ^1H decoupling. Signal averaging employed up to 30 000 transients. Sidebands intensities were extracted from the experimental data using Bruker XwinNMR V3.5 patch level 6. (b) The CSA tensors were obtained by the Herzfeld−Berger method[12c] using 30 input files with the centerband and sideband intensities varied by the noise level, serving to estimate the standard deviation. (c) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.

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(16) The calculated δ_{22} and δ_{33} are rotated about the Y axis by $\beta = 17°$ and 20° for **1** and **2**, respectively.

(17) (a) The total chemical shielding value (and CST) is a sum of diamagnetic and paramagnetic contributions.[17b] The behavior of the CST and the CSA is primarily determined by the paramagnetic contribution σ^p. (b) *Molecular Quantum Mechanics*, 3rd ed.; Atkins, P. W., Friedman, R. S., Eds.; Oxford University Press: Oxford, 1997. (c) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699.

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