

A Solid-State ^{29}Si NMR and Theoretical Study of the Chemical Bonding in Disilenes

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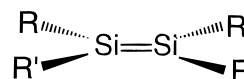
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Abstract: Nine disilenes have been studied by solid-state NMR spectroscopy, under static or slow magic-angle spinning conditions, to determine the ^{29}Si chemical shift tensors. All of the compounds show strong deshielding along one axis and correspondingly large spreads of the tensor components, $\Delta\delta$ ($=\delta_{11} - \delta_{33}$). MO calculations on model disilenes indicate that the deshielding results from a paramagnetic contribution along the in-plane axis perpendicular to the Si–Si vector. Implications of the NMR data and the theoretical computations for Si=Si bonding are discussed.

1. Introduction

The chemistry of multiply-bonded heavier main group elements has been actively investigated in recent years.^{2,3} The nature of the bonding in such low-coordinate compounds is of much interest⁴ and is still controversial.^{2,5} For organic molecules, determination of the ^{13}C chemical shielding tensors has been useful in elucidating the three-dimensional electron distribution around the carbon atoms.⁶

Shortly after the first synthesis of a stable disilene,⁷ tetramesityldisilene (**1**), the ^{29}Si chemical shift tensor was determined.⁸ Compound **1** exhibited a large chemical shift anisotropy, providing evidence for a considerable asymmetry in the charge distribution around silicon, consistent with a true Si=Si π -bond resembling that in alkenes. Studies of solid-state NMR to determine shielding tensors have also been performed recently on molecules containing P=P,⁹ P=C,¹⁰ P=C,¹⁰ and Sn=Sn¹¹



- 1, R = R' = mesityl
- 2, R = R' = 2,4,6-triisopropylphenyl
- 3, R = mesityl, R' = *t*-butyl
- 4, R = R' = (Me₃Si)₂CH
- 5, R = Me₃Si, R' = 2,4,6-triisopropylphenyl
- 6, R = R' = *i*-Pr₂MeSi
- 7, R = R' = *i*-Pr₃Si

Figure 1. Structures of disilenes studied by ^{29}Si NMR.

multiple bonds, revealing important information about the electron distribution and bonding.

We report here the solid-state NMR study of the ^{29}Si chemical shift tensors for a series of disilenes with different substitution at the Si=Si double bond (Figure 1).¹² Compounds investigated included three forms of tetramesityldisilene: The solvent-free form **1**,¹³ the toluene adduct **1**·C₇H₈,¹⁴ and the tetrahydrofuran solvate **1**·THF.¹⁵ Also studied were a second tetraaryldisilene (**2**),¹⁶ a mixed alkyl–aryl-substituted disilene, **3**,¹⁷ and the only tetraalkyldisilene known to be stable as a solid, **4**.¹⁸ Three silyl-substituted disilenes, **5**, **6**, and **7**, were also investigated.^{19,20} To assist in the interpretation of the experimental results, *ab initio*

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molecular orbital calculations of the ^{29}Si chemical shift tensors were carried out for model disilene molecules.

2. Experimental Section

Synthesis of the disilenes has been described elsewhere.^{13–20} The compounds, which are all air-sensitive, were stored and handled in a drybox.

Early experiments were carried out at Yale University, using a home-built spectrometer operating at 2.34 and 7.05 T.²¹ For these studies the samples were packed into 5-mm glass tubes to a depth of 1 cm and sealed under vacuum. Room temperature cross polarization magic angle spinning (CPMAS), low-temperature (77 K) CPMAS, and low-temperature static ^{29}Si spectra were taken at 2.34 T. The MAS turbine is designed to spin sealed 5-mm glass tubes at rates of up to 3 kHz. In addition, several static ^{29}Si spectra were taken at 7.05 T to obtain increased sensitivity. Typical radio frequency field amplitudes employed were 15 and 75 G for ^1H and ^{29}Si , respectively. Cross polarization (CP) mixing times were 2 to 3 ms, and the time τ between the CP and the π pulse in the Hahn echo was 100 to 300 ms. Typical powder spectra required approximately 4000 scans, and MAS spectra required approximately 1500 scans. All spectra were referenced externally to TMS. Chemical shift values obtained in this manner are typically accurate to within ± 2 ppm. Isotropic shifts in MAS spectra were determined by comparison of spectra taken at several spin rates.

For these measurements, spectral simulations and other calculations were performed on an IBM PS/2 Model 80 microcomputer using SPCSIM, a powder and MAS spectra simulation program, and FINDMR, a program that extracts CSA and dipolar tensor information from MAS sideband intensities by using a numerical adaptation of the graphical method of Herzfeld and Berger.²² Overlapping MAS line shapes were fit with SpectraCal, a data processing package.²³

Later, slow-spinning studies were carried out at the University of Wisconsin with a Vairan Unity 300-MHz (proton) NMR spectrometer operating at a sample frequency of 59.587 MHz, with a Doty Scientific Inc. probe. Samples (~ 100 mg) were placed in airtight 7-mm ZrO_2 rotors. Spinning speeds were 1–3 kHz, the CP mixing time was 5.0 ms followed by a 5-s delay, and the pulse width was 6.5 μs . These spectra were referenced to external $(\text{Me}_3\text{Si})_4\text{Si}$; the chemical shift values are again expected to be accurate to ± 2 ppm. Analysis of the sidebands to obtain the chemical shift tensor was done on a Sun SPARC 5 workstation with Varian VNMR software, Version 4.3 revision B.

Disilenes **1**, **1**· C_7H_8 , **1**·THF, and **3** gave powder patterns from which the shift tensors could easily be determined. The other disilenes all presented difficulties of one sort or another in the measurement of their shift tensors. In the disilenes containing silicon substituents, **4**–**8**, the signals of the trimethylsilyl substituents overlapped those of the disilene silicons. These were therefore studied by slow-spinning CPMAS experiments, yielding sidebands which could be separated and analyzed by the Herzfeld–Berger method.²²

The MAS spectrum for **2** showed evidence for two nonequivalent silicon atoms in the lattice, with isotropic shifts of 53.1 and 50.8 ppm. The relative intensity of the peaks making up the sideband pattern was nearly identical for both silicons, leading to very similar values for the tensors; these were treated as a single average tensor. Two isotropic shifts were also observed for **4**, but here the sideband patterns for the sites were somewhat different, leading to different tensors, both of which are listed in Table 1.

Theoretical Methods. The calculations utilized standard *ab initio* SCF MO theory²⁴ as implemented in the Gaussian 94²⁵ series of programs. Geometry optimizations of the molecules of interest were carried out with the 6-31G* basis set.²⁵ These basis sets have been shown previously to reproduce well the geometries of organosilicon compounds.⁴ Thus they provide an acceptable compromise between the computational resources required for calculating relatively large

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Table 1. Chemical Shift Tensors and Structural Parameters for Disilenes

disilene	δ_{11}	δ_{22}	δ_{33}	δ_{iso}		$\Delta\delta$	CSA ^a	Si=Si, ^b pm	Θ , deg ^c	ϵ , deg ^d
				solid	soln					
1	181	31	−22	63.2	63.3	203	176	214	3	13
1 · C_7H_8	185	34	−22	65.0	63.3	207	179	216	6.5	18
1 ·THF ^e	165	40	−25	59.6	63.0	190	157	215	15	0
2	155	30	−31	50.8	53.4	186	155	214	3	0
				53.2						
3	178	77	3	86.1	90.3	175	138	214	0	0
4	182	55	21	86.1	90.4	161	144			
	199	54	9	87.4	190					
5	296	46	−59	94.5	94.4	355	168	215	0	0
6	414	114	−100	143	144.5	514	408	228	0	5.4
7	412	149	−69	164	154.5	481	372	225	0	10.2

^a CSA = $\delta_{11} - (\delta_{22} + \delta_{33})/2$. ^b Data from ref 2e. ^c The dihedral angle between the RSi^1R and RSi^2R planes (Figure 5). ^d The angle between RSiR and the Si–Si vector (Figure 5). ^e Reference 15.

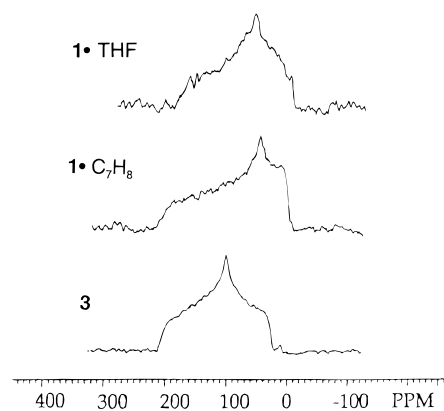


Figure 2. Static ^{29}Si NMR spectra for disilenes.

model molecules and the reliability of the results. Different geometrical distortions of the parent molecule $\text{H}_2\text{Si}=\text{SiH}_2$ were studied also at the correlated MP2/6-31G** level of theory.²⁵ The ^{29}Si chemical shifts and chemical shielding tensors were calculated by using the hybrid DFT-SCF version (using Becke's three-parameter hybrid method employing the LYP correlation functionals, B3LYP)^{26,27} of the GIAO (Gauge Included Atomic Orbitals)²⁸ method as implemented in the Gaussian 94 package. The 6-311+G(2df,p) basis set was employed for the GIAO calculations.²⁹

3. Results and Discussion

Chemical shift tensors for the doubly-bonded silicon atoms in the nine disilene samples are given in Table 1. Typical powder patterns are shown in Figure 2, and the slow-spinning spectrum for **7** is illustrated in Figure 3.

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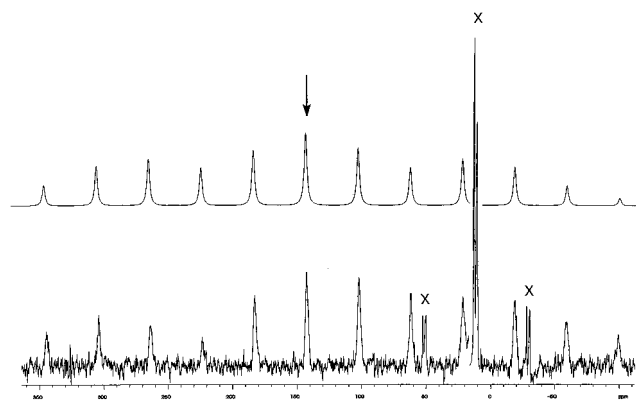


Figure 3. Slow-spinning MAS ^{29}Si NMR spectrum for $(\text{iPrMe}_2)_2\text{Si}=\text{Si}$ ($(\text{iPrMe}_2\text{Si})_2$ (**6**)): below, recorded spectrum; above, computer simulation for the doubly-bonded silicons. The isotropic peak for the disilene silicons is marked with an arrow. Peaks marked \times are due to the *i*-Pr $_3$ -Si silicons; these isotropic peaks are shown at reduced gain.

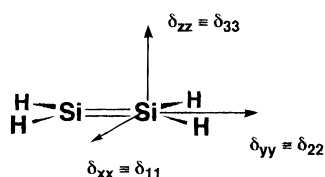


Figure 4. Orientation of the principal shielding tensor components in planar $\text{H}_2\text{Si}=\text{SiH}_2$.

All of the disilenes show significant deshielding along one axis (δ_{11}). For tetrasilyldisilenes this deshielding is extreme, +414 ppm for **7**. Together with greater shielding in the δ_{33} direction, these lead to $\Delta\delta$ values ($\Delta\delta = \delta_{11} - \delta_{33}$) more than a factor of 2 greater than any previously reported for ^{29}Si .³⁰ The $\Delta\delta$ values for the doubly-bonded silicon atoms in all of the disilenes are significantly larger than those for singly-bonded silicon compounds, which typically have $\Delta\delta$ values of 0–60 ppm.³⁰ For disilenes **6** and **7**, tensors for the four-coordinate silicon atoms were also determined: for **6**, $\delta_{11} = 36.4$, $\delta_{22} = -0.9$, and $\delta_{33} = -4.2$ ppm; and for **7**, the corresponding values are 46.0, 21.1, and 17.8 ppm, giving $\Delta\delta$ values of about 30 ppm, as expected for sp^3 -type silicons.

The results for silicon parallel closely those for carbon. Singly-bonded, sp^3 carbons generally show small $\Delta\delta$ values in the ^{13}C NMR spectrum, reflecting the near-tetrahedral electron distribution about the carbon atom. Multiply-bonded carbons display marked deshielding along δ_{11} and resulting large $\Delta\delta$ values, often 200 ppm or greater.^{6,31}

Molecular Orbital Calculations. Before attempting to interpret the ^{29}Si shielding tensors for the disilenes, it will be useful to consider the results from theoretical computations. Therefore we calculated the tensor components for the model molecules listed in Table 2; their 6-31G* optimized geometries are given in the Supporting Information. The MO calculations for the archetypal planar disilene $\text{H}_2\text{Si}=\text{SiH}_2$ predict a strong deshielding along the in-plane axis perpendicular to both the π -bond and the Si–Si axis, δ_{xx} (Figure 4). A magnetic field along this axis will mix the $\sigma(\text{Si}-\text{Si})$ orbital with the Si–Si π^* orbital. The intermediate principal value is calculated to lie along the axis of the Si–Si bond, δ_{yy} , and the most shielded value along δ_{zz} , the axis perpendicular to the molecular plane. A magnetic

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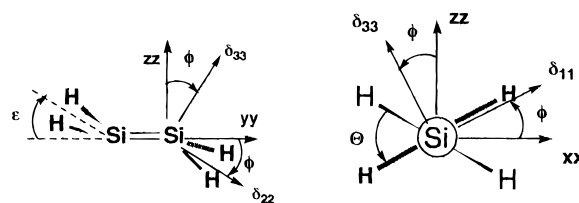


Figure 5. Definition of the pyramidalization angle ϵ (left) and the twisting angle Θ (right) in distorted $\text{H}_2\text{Si}=\text{SiH}_2$.

field applied along the latter axis involves only the σ -electrons in the Si–Si and Si–H bonds, with no π -contribution.

These results are quite parallel to IGLO calculations for ethylene, which likewise predict strong deshielding along the corresponding in-plane axis, δ_{xx} .³¹ Unlike alkenes, however, disilenes are often somewhat distorted from planarity, either by pyramidalization or by twisting about the Si=Si bond, or both.^{12–21} Furthermore the length of the Si=Si bond varies considerably in differently substituted disilenes.^{2e,32} We have therefore explored computationally for $\text{H}_2\text{Si}=\text{SiH}_2$ the effect of these three distortion modes of the Si=Si double bond on the chemical shielding tensor.³³

Pyramidalization around the silicon atoms in $\text{H}_2\text{Si}=\text{SiH}_2$ by up to $\epsilon = 25^\circ$ has little effect on the energy, lowering it by 0.5 kcal/mol at $\epsilon = 25^\circ$ (at MP2(fc)/31G**//MP2(fc)/31G**); for the definition of ϵ , see Figure 5). The results of the GIAO tensor calculations for pyramidalization in $\text{H}_2\text{Si}=\text{SiH}_2$ in the range of $\epsilon = 0$ to 25° are shown in Figure 6a. The major result of pyramidalization is a further downfield shift of δ_{xx} . At a pyramidalization angle of 18° , the maximum observed in a disilene, δ_{xx} is increased by about 30 ppm relative to $\epsilon = 0^\circ$. It should be noted that the collinearity of δ_{22} and δ_{33} with δ_{yy} and δ_{zz} will hold only for D_{2h} , planar disilenes. In nonplanar unsymmetrically substituted disilenes the collinearity is broken (see Figure 5).³³ For example, for a pyramidalization angle ϵ of 25° , the angle ϕ is 10.4° . However, the relative order of the components, i.e. $\delta_{xx} > \delta_{yy} > \delta_{zz}$, does not change upon pyramidalization (see Figure 6a).

The energy potential for twisting deformations around the Si=Si bond (while keeping each silicon atom planar) is very flat up to a twisting angle of ca. 25° . Twisting the Si=Si bond by $\Theta = 15^\circ$ requires merely 1.4 kcal/mol (at MP2(fc)/6-31G**); for the definition of the twisting angle Θ , see Figure 5).³³ The effect of twisting distortions on the shielding tensors of $\text{H}_2\text{Si}=\text{SiH}_2$ is also small. As shown in Figure 6b, at twist angles Θ of 13° or less, as found in known disilenes, the influence on the tensor components is negligible.

For most of the stable disilenes, the Si=Si distance falls in a relatively narrow range from 214 to 216 pm.^{2e} For **6** and **7**, however, the Si=Si separation is significantly longer (225–228 pm, Table 1). The calculated stretching potential for the Si=Si bond in planar $\text{H}_2\text{Si}=\text{SiH}_2$ is very flat; stretching the Si=Si bond by 20 pm (215 to 235 pm) requires only 7.7 kcal/mol (at MP2(fc)/6-31G** geometry, 8.1 kcal/mol at CISD/6-31G**).³³ The effect of lengthening the Si=Si bond on the chemical shielding tensors is shown in Figure 6c. In contrast to the twisting and pyramidal deformations, the calculated effect on the tensor for the stretching deformations is quite significant. Upon elongations of the Si=Si bond all of the principal values

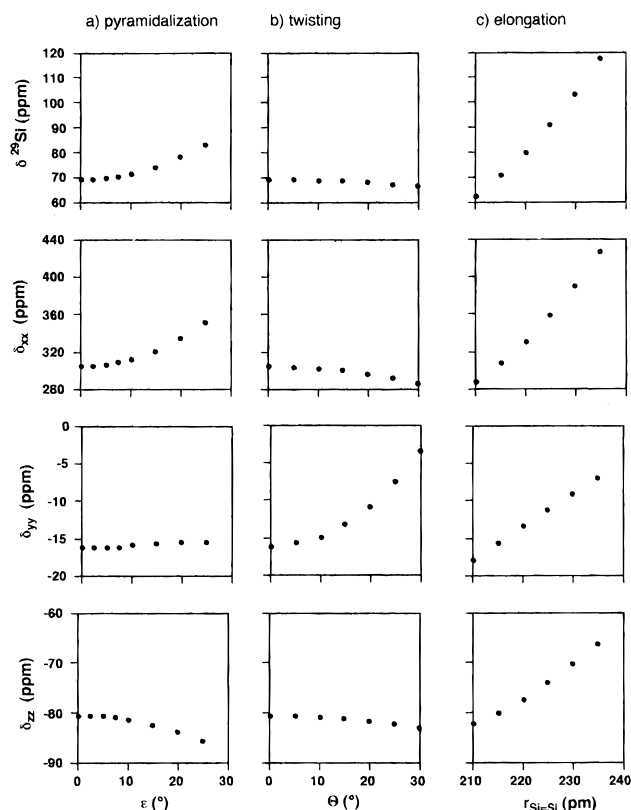
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(33) These calculations were carried out as follows: The pyramidalization angles (ϵ) and the twist angles (Θ) were fixed at certain values and all other geometrical parameters were optimized except for $r_{\text{Si}=\text{Si}}$, which was kept at 214.2 pm, the equilibrium distance for planar $\text{H}_2\text{Si}=\text{SiH}_2$ at MP2(fc)/6-31G**. The effect of changing $r_{\text{Si}=\text{Si}}$ was studied by keeping $\text{H}_2\text{Si}=\text{SiH}_2$ planar and optimizing all other geometrical parameters.

Table 2. Calculated Chemical Shift Tensors and Structural Parameters for Disilenes (GIAO/B3LYP/6-311+G(2df,p)//6-31G*) and Relative Chemical Shifts Versus Calculated TMS ($\delta_{\text{iso}} = 327.9$ ppm) (Angles in deg, Bond Lengths in pm, E in eV)

compd	symm	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	$\Delta\delta^b$	CSA ^a	Si=Si	ϕ^c	ΔE^d
H ₂ Si=SiH ₂ ^e	<i>D</i> _{2h}	294.8	-15.1	-81.8	65.9	376.6	343.3	212.5	0.0	13.7
(<i>E</i>)-MeHSi=SiHMe	<i>C</i> _{2h}	258.7	27.0	-28.5	85.8	287.2	259.1	212.8	-10.2	13.7
Me ₂ Si=SiMe ₂	<i>D</i> _{2h}	189.4	91.4	7.5	96.1	181.9	140.0	212.9	0.0	13.9
(<i>E</i>)-H ₃ SiHSi=SiHSiH ₃	<i>C</i> _{2h}	399.3	12.2	-83.7	109.3	483.0	435.1	213.5	-5.6	11.5
(<i>E</i>)-(H ₃ Si)MeSi=SiMe(SiH ₃)	<i>C</i> _{2h}	337.6	70.6	-28.3	126.6	365.9	316.5	214.3	-0.5	11.6
(H ₃ Si) ₂ Si=Si(SiH ₃) ₂	<i>D</i> _{2h}	447.0	96.4	-100.8	147.5	547.8	444.8	215.4	0.0	11.2

^a CSA = $\delta_{11} - (\delta_{22} + \delta_{33})/2$. ^b $\Delta\delta = \delta_{11} - \delta_{33}$. ^c For a definition of ϕ see Figure 5. ^d $\Delta E = [E(\sigma\text{Si-Si}) - E(\pi\text{Si=Si})]$. ^e Not an energy minimum at HF/6-31G*.

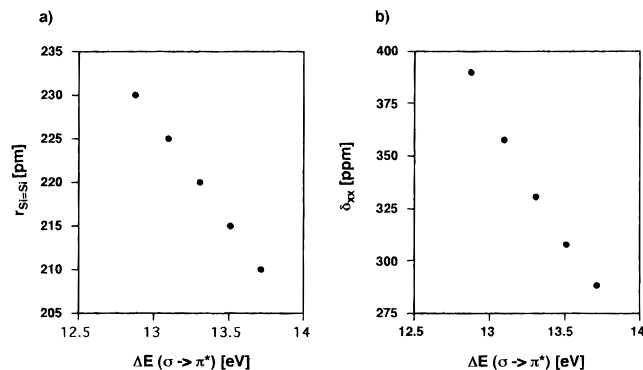
**Figure 6.** Calculated influence of (a) pyramidalization, (b) twisting, and (c) elongation on the isotropic chemical shift and the individual shielding tensor components in H₂Si=SiH₂ (at GIAO/B3LYP/6-311+G(2df,p)//MP2/6-31G**).

shift downfield, but the effect is especially large for δ_{xx} , which increases by 118 ppm for a 20-pm increase in $r_{\text{Si=Si}}$; δ_{yy} and δ_{zz} increase by 10 and 15 ppm, respectively, for the same stretching (Figure 6c). The large deshielding along δ_{xx} can be understood in terms of the Ramsey equation, which indicates that the deshielding paramagnetic term is strongly dependent on ΔE_{ave} , the average excitation energy for the molecule.³⁴ Calculations for H₂Si=SiH₂ at fixed bond distances indeed show good correlations both between $r_{\text{Si=Si}}$ and $\Delta E(\sigma-\pi^*)$ ³⁵ and between δ_{xx} and $\Delta E(\sigma-\pi^*)$ (Figure 7). Elongation of the Si=Si bond leads to a poorer overlap of both the σ - and π -type orbitals. Consequently, the Si-Si σ -orbital will be raised in energy, while the Si-Si π -orbital will be lowered in energy.³⁶ A smaller $\sigma-\pi^*$ separation gives rise to a strong paramagnetic contribution to δ_{xx} , which results in the strong deshielding of this component.

(34) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699.

(35) $\Delta E(\sigma-\pi^*)$ is employed rather than $\Delta E(\pi-\pi^*)$, following calculations by Tossell and Lazzarotti on the chemical shift tensor of H₂Si=SiH₂. See ref 29b.

(36) $\Delta E(\sigma-\pi^*)$ is 0.50 eV for $r_{\text{Si=Si}} = 215$ pm and 0.48 eV for $r_{\text{Si=Si}} = 235$ pm (at MP2(fc)/6-31G**).

**Figure 7.** Relationship between $\Delta E(\sigma-\pi^*)$ (at MP2/6-31G**) and (a) Si=Si bond distance and (b) δ_{xx} (at B3LYP/6-311+G(2df,p)//MP2/6-31G**).

Substitution of the disilene with silyl or alkyl groups does not change the orientation of the shielding tensor components relative to the molecular frame. For the three planar tetrasubstituted disilenes which were investigated computationally, the orientation of the principal components was calculated to be the same as for the parent H₂Si=SiH₂, although the magnitude of the components is strongly dependent on the substituents. In the unsymmetrically substituted disilenes, (*E*)-MeHSi=SiHMe, (*E*)-H₃SiHSi=SiHSiH₃, and (*E*)-H₃SiMeSi=SiMeSiH₃, the tensor components δ_{xx} and δ_{yy} are slightly rotated around δ_{zz} (by 10.2°, 5.6°, and 0.5°, respectively).

²⁹Si Chemical Shielding Tensors in Disilenes. With the MO results in mind, we now turn to the observed tensors for the stable disilenes. According to this modeling, the upfield principal value δ_{33} will involve only the σ -bonding electrons in the disilene. The measured values for δ_{33} are consistent with this assignment. They lie in the usual range for four-coordinate organosilicon compounds, and the substituent effects on δ_{33} parallel those in sp³ silicon compounds. Taking the tetraalkyl-substituted disilene **4** as a reference, data in Table 1 show that aromatic substituents lead to moderate upfield shifts, and silyl substituents to large upfield shifts, in δ_{33} . The same trends are found in the isotropic chemical shift values for tetrahedral silicon compounds.³⁰

The tensors for **1** and **1**·C₇H₈ are almost identical, in spite of the differences in conformation between these two forms. The twisting and pyramidal distortions are smaller in **1** than in **1**·C₇H₈, and the ring tilt angles are also different (42, 52, 67, 70° in **1**; 35, 35, 78, 78° in **1**·C₇H₈). Apparently the electronic distribution around the silicon is relatively insensitive to minor deformations of the molecular structure. This is fully consistent with the results for deformed H₂Si=SiH₂ (Figure 5, parts a and b). In **1**·THF, values for δ_{22} and δ_{33} are similar to those for **1** and **1**·C₇H₈, but the deshielding along δ_{11} is smaller, perhaps because the Si=Si bond in **1**·THF is not pyramidally distorted and is more strongly twisted. The difference is well-modeled

by the MO calculations for $\text{H}_2\text{Si}=\text{SiH}_2$, which predict decreased shielding along δ_{xx} with pyramidal distortion and increased shielding along δ_{xx} with twisting deformation of the Si=Si bond (Figure 6a,b). The sum of both effects leads to a decrease in δ_{xx} similar to that observed. Disilene **2**, with different aryl groups, also has no pyramidal distortion and therefore a smaller positive value for δ_{11} .

The tensors for the tetraalkyldisilene **4** are well modeled by calculations for planar tetramethyldisilene. The experimental values of δ_{11} and δ_{33} are quite close to those calculated for δ_{xx} and δ_{zz} , respectively. Comparing data in Tables 1 and 2, a major difference between experiment and the calculations is found only for δ_{22} , which is predicted by theory to be more deshielded for $\text{Me}_2\text{Si}=\text{SiMe}_2$ than is actually found for **4**. In the dialkyldiaryldisilene **3**, the aromatic rings are nearly orthogonal (88°) to the Si=Si double bond, so that conjugation between the aromatic rings and the Si=Si π orbital is not possible. It is therefore understandable that the tensor components for **3** resemble those of the tetraalkyl compound **4** and those calculated for $\text{Me}_2\text{Si}=\text{SiMe}_2$, rather than those for the tetraaryldisilenes.

Silyl substituents greatly affect the disilene experimental shielding tensors in **5**, **6**, and **7**, causing shielding along δ_{33} and profound deshielding along δ_{11} . The deshielding in the δ_{11} direction can be related to $\Delta E(\sigma \rightarrow \pi^*)$ for these compounds (Table 2). Consider first compound **5**, which has a normal Si=Si bond distance of 215 ppm. In this compound the deshielding may be partly electrostatic, since the silyl groups should be relatively electron-releasing toward disilene silicons. Electropositive substitution is expected to raise the energy of the Si-Si σ orbital and decrease the $\sigma \rightarrow \pi^*$ gap. In addition, σ -conjugation, as found in polysilanes,³⁷ may also raise the energy of the Si-Si σ orbital. Silyl substitution shifts the high-field component δ_{33} to still higher field, as is also known for tetrahedral silicon.³⁰ Both effects are modeled by the calculations for silyl-substituted disilenes in Table 2.

In compounds **6** and **7**, deshielding along δ_{xx} is further dramatically increased by lengthening of the Si=Si bond, presumably the result of steric strain in these molecules. (The calculated Si=Si distance in $(\text{H}_3\text{Si})_2\text{Si}=\text{Si}(\text{SiH}_3)_2$ is only 215 ppm.) As explained earlier, this large deshielding effect with bond stretching is also consistent with our MO calculations (Figure 7). The extreme deshielding along δ_{11} , combined with the strong shielding of δ_{33} , produces $\Delta\delta$ values of unprecedented magnitude in **6** and **7**.³⁸

(37) For a discussion see: West, R. In *Comprehensive Organometallic Chemistry II*; Pergamon: Oxford, 1995; Vol. 2, Chapter 4.

(38) For planar tetrasilyldisilene with a fixed Si=Si bond length of 228 ppm, which is the experimentally measured value for **6**, an even higher $\Delta\delta$ of 624.8 ppm is calculated (at GIAO/B3LYP/6-311+G(2df,p)//6-31G*).

4. Conclusion

All of the disilenes studied showed a high anisotropy $\Delta\delta$ of the chemical shielding tensor, indicating a highly asymmetric electron distribution around the silicon which is typical for a genuine Si=Si π bond.^{6b,8} The disilenes showed significant deshielding along one magnetic axis, which we can identify from theoretical calculations to be in the molecular plane and perpendicular to the Si-Si bond (δ_{xx} direction). The deshielding is attributed to a paramagnetic circular shielding current arising from angular momentum along this axis, which mixes the Si-Si σ orbital with the Si=Si π^* orbital. Consistent with this model the δ_{yy} tensor components (along the Si-Si bond) are only weakly deshielded. This deshielding arises from paramagnetic currents that mix the π electrons with the σ electrons involved in the two Si-R bonds. The δ_{zz} principal components (perpendicular to the molecular plane) are even less deshielded; here the shielding arises from circular shielding currents that lie in the molecular plane and involve only the tightly held σ -bonded electrons. Thus, the δ_{zz} values fall in the chemical shift region typical for sp^3 -hybridized silicon. Our chemical shift tensor determinations for disilenes strongly corroborate the classical π -bond model for the Si=Si bond, involving two sp^2 -hybridized Si atoms. Significant deformations of the molecular structure, such as twisting or pyramidalization at Si by 15 – 20° , or the presence of aryl-Si=Si conjugation, have little effect on the shielding tensors in aryl- or arylalkyl disilenes. Evidently such deformations have only a small influence on the electronic characteristics of the Si=Si bond. In contrast even moderate elongation of the Si=Si bond leads to marked deshielding of δ_{xx} . Introduction of silyl substituents leads to further deshielding of δ_{xx} and increases shielding of δ_{zz} , thus leading to very large values of $\Delta\delta$. In general, the effect of substituents on the shielding tensors correlates with the energy difference between the $\sigma(\text{Si-Si})$ and the $\pi^*(\text{Si=Si})$ orbitals.

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Supporting Information Available: Calculated geometries and orientation of tensor axes in model disilenes (6 pages). See any current masthead page for ordering and Internet access instructions.

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