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Chemical Shift Tensors and NICS Calculations for Stable Silylenes

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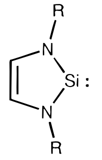
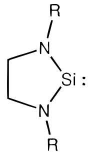
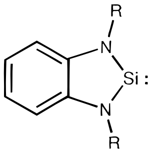
Significant efforts have been expended to characterize and understand the electronic nature of silylenes. The diaminosubstituted silylenes **1**,[1] **2**,[2] and **3**[3] enjoy a special interest, both theoretically[1,4,5] and experimentally,[2,6] because of their unusual high thermodynamic and kinetic stability. Silylene **1** can be regarded as a 6π-electron aromatic molecule, and the nature and degree of electron delocalization in this silyene has been controversial.[4−6] We report here the chemical shift tensors for



1, R = t-Bu
4, R = H



2, R = t-Bu
5, R = H



3, R = Neopentyl
6, R = H

1−**3** (**1** $\delta_{11} = 284.9$, $\delta_{22} = -16.1$, $\delta_{33} = -43.3$; **2** $\delta_{11} = 350.7$, $\delta_{22} = -2.1$, $\delta_{33} = -4.5$; **3** $\delta_{11} = 316.4$, $\delta_{22} = 21.1$, $\delta_{33} = -60.0$ ppm), along with theoretical calculations for model molecules, including nucleus-independent chemical shift (NICS) calculations.[7] The latter support the model that **1** and **3** are cyclically delocalized and have some "aromatic" character.

The slow-spinning ^{29}Si CPMAS NMR spectra of **1**−**3** were determined at 59.6 MHz, and the results were analyzed using the Herzfeld−Berger method[8] to determine the chemical shielding tensors. The isotropic shifts δ ^{29}Si of the silylenes in the solid (see Table 1) are very similar to those observed in solution for these compounds (78, 117, and 92 ppm for **1**, **2**, and **3,** respectively). In all three silylenes, the silicon atoms have chemical shielding tensors of nearly axial symmetry. One tensor component (δ_{11}) is significantly deshielded, while δ_{22} and δ_{33} have nearly the same magnitude and are in the expected shift range for sp^3-type silicons, +30 to −60 ppm (see Table 1). Therefore, the measured values for the spread of the tensor, $\Delta\delta$ ($=\delta_{11} - \delta_{33}$) for the silylene silicons are very large. The results for the silylenes parallel those for stable disilenes[9] and analogous diaminocarbenes,[10] reflecting a highly anisotropic electron distribution around the central silicon.

Table 1. Calculated and Observed Chemical Shift Tensors for Silylenes

	B3LYP/GIAO^a						
	δ_{iso}	δ_{xx}	δ_{yy}	δ_{zz}	$\Delta\delta$	CSA^c	Θ (deg)
1^d	93.7	334.1	−14.8	−38.3	372.4	360.7	
2^d	140.4	432.8	10.0	−20.8	452.6	417.4	4.7
4^e	84.8	326.9	−42.2	−30.2	369.1	363.1	
5^e	131.9	430.3	−16.6	−18.1	448.4	447.7	13.5
6^e	90.8	327.4	−15.1	−39.4	366.8	354.6	

	MP2/GIAO^b						
	δ_{iso}	δ_{xx}	δ_{yy}	δ_{zz}	$\Delta\delta$	CSA	Θ (deg)
4	64.0	277.9	−46.2	−39.6	324.1	320.8	
5	115.1	390.1	−18.7	−26.0	416.1	412.5	0.5

	experimental values					
	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	$\Delta\delta$	CSA
1	75.2	284.9	−16.1	−43.3	328.2	314.6
2	114.7	350.7	−2.1	−4.5	355.2	354.0
3	92.5	316.4	21.1	−60.0	376.4	335.8

^{a} The 6-311+G(2df,p) basis set was used; for **1**, **2**, and **6** a 6-311+G(2df,p)(Si), 6-31G*(C,N,H) basis set was used. ^{b} A tz2p(Si), tzp(C,N), dz(H) basis set was used. ^{c} Chemical shift anisotropy. ^{d} Relative to TMS. σ(^{29}Si(TMS): B3LYP/GIAO/(6-311+G(2df,p)(Si). 6-31G*(C,N,H))//HF/6-31G*: 332.5. ^{e} Relative to TMS. σ(^{29}Si(TMS): B3LYP/GIAO/6-311+G(2df,p//MP2/6-31G*: 327.9. σ(^{29}Si(TMS): MP2/GIAO/(tz2p(Si)tzp(C,N),dz(H))//MP2/6-31G* 371.1

The chemical shielding tensors of silylenes **1** and **2** and of model compounds **4**−**6** were calculated using the DFT-hybrid GIAO method[11] and are summarized in Table 1.[12] Since this theoretical approach is known to overestimate the deshielding contributions to the chemical shielding tensor in cases when electron correlation is important,[12c] we also performed MP2/GIAO calculations[13] for the smaller molecules **4** and **5**. The chemical shielding tensors of **4** and **5** were also calculated using the IGLO

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(11) The calculated geometries of **1**−**6** are very similar and match closely the experimental structures of **1**,[1a] **2**,[2] and **3**.[3a] All geometry optimizations and DFT/GIAO calculations, except for the MP2/GIAO calculations, were performed with Gaussian 94: Gaussian, Inc. Pittsburgh, PA, 1995. Because the HF/6-31G* theory proved superior to the DFT-hybrid B3LYP/6-31G* method in predicting the structures of **1** and **2**, we used the HF/6-31G* optimized geometries for calculation of the chemical shielding tensors. MP2/6-31G* geometries were used for **4** and **5**, and the B3LYP/6-31G* geometry was used for **6**.

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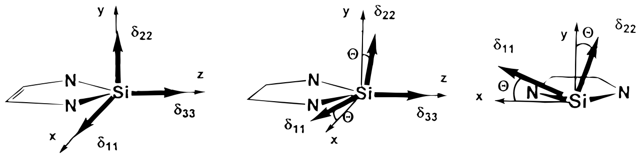

1 and 3

2

Figure 1. Molecular and magnetic axes for silylenes **1**, **2**, and **3**.

method,[14] which allows the chemical shielding tensor to be broken down into distinct orbital contributions.

The orientation of the principal components of the chemical shielding tensor relative to the molecular frame in **1**−**3** as predicted by our MO calculations is shown in Figure 1. In **1** and **3**, the strongly deshielded δ_{xx} is normal to both the silicon lone pair and its empty 3p-orbital ($\delta_{xx} = \delta_{11}$). The intermediate principal value δ_{22} is perpendicular to the molecular plane ($\delta_{22} = \delta_{yy}$). The most shielded component δ_{33} is aligned along the symmetry axis of **1** and **3** ($\delta_{33} = \delta_{zz}$). The spatial orientation of the chemical shielding tensor in the saturated diaminosilylenes **2** and **5** is very similar to that in **1** except that due to the lower symmetry the principal axes of the shielding tensor are slightly rotated by the angle Θ around the molecular z-axis (see Figure 1).[15]

The orbital contributions as predicted by IGLO calculations for **4** and **5** are given in Table 2, in terms of absolute shieldings, σ [$\sigma(\mathrm{Me_4Si}) - \sigma = \delta$]. The values are very similar for both silylenes. The strongly deshielded δ_{xx} is a result of a very strong paramagnetic contribution to σ_{xx} ($\sigma < 0$) of the silicon lone pair. A magnetic field along this axis mixes 1p(Si) with the empty 3p(Si). In addition, strong paramagnetic ring currents from the nitrogen lone pairs contribute significantly to the deshielded δ_{xx} component and to the isotropic chemical shift δ_{iso}.

The calculated orbital contributions to δ_{xx} in **4** and **5** are also quite similar with the exception of a larger deshielding contribution of 1p(Si) in the saturated **5** (1p(Si): −319.2 and −412.9 ppm for **4** and **5**, see Table 2). This results from a smaller 3p(Si)/1p(Si) gap in **5** compared to **4** (11.6 and 12.1 eV, respectively, at MP2/6-31G*//MP2/6-31G*), due mainly to stabilization of the silicon lone pair by the inductive effect of the β-vinyl group.

Table 2. Calculated Chemical Shielding Tensors and Orbital Contributions of **4** and **5** (absolute shieldings σ in ppm, IGLO//BasisII/MP2/6-31G*)

	1p(Si)	1p(N)	L(Si)[a]	ΣSiX[b]	Σ + K(Si)[c]	δ[d]
4 σ_{xx}	−319.2	−287.5	183.7	−51.9	21.3	353.8
σ_{yy}	−133.1	−164.5	227.3	−16.6	409.3	−34.2
σ_{zz}	17.0	−299.1	262.0	−26.8	449.3	−74.2
Σ/3	−145.1	−250.4	224.3	−31.8	293.5	81.6
5 σ_{xx}	−412.9	−283.3	173.3	−28.3	−55.5	430.6
σ_{yy}	−157.1	−185.1	217.9	−19.5	352.4	22.7
σ_{zz}	16.5	−326.0	259.7	−25.0	421.4	−46.2
Σ/3	−184.5	−265.0	216.7	−24.3	239.4	135.7

[a] Si L-shell contributions without the lp(Si). [b] Sum of contributions from remote atoms, except the lp(N). [c] Sum of the preceding four terms plus the K-shell contribution, 496.2. [d] Relative to TMS: σ^{29}Si (TMS) = 375.1.

The chemical shift tensors do not provide evidence about electron delocalization in **1** and **3**, but nucleus independent chemical shift (NICS) calculations may provide a test for cyclic conjugation.[7] A ghost atom placed in the center of the five-membered ring in each of the silylenes is strongly shielded (**1**, −11.9; **2**, −7.0; **6**, −10.5 ppm). This results, however, from local contributions of nearby σ-bonds.[16] Placing the ghost atoms 2 Å above the ring center (NICS(2.0)) shows that, for typical aromatic molecules, the shielding influence of the ring current is still appreciable (−5.3 for benzene, −4.7 for thiophene). Judging from their NICS(2.0) values, both **1** (−2.7) and **6** (−2.6) are significantly less aromatic than benzene but nevertheless possess a discernible ring current, in contrast to **2** for which NICS (2.0) is negligible, only −0.6. Similar NICS(2.0) calculations for model molecules (**4**, −2.9; **5**, −0.7) are consistent with the conclusion that the unsaturated silylenes have a diamagnetic ring current about half as large as that in benzene.

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