

The chemical shift tensor of silylenes

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Abstract

The ^{29}Si -NMR chemical shift tensors of 21 simple singlet silylenes, $\text{R}_2\text{Si:}$, are studied at the GIAO/MP2/6-311+G(2df,p)//B3LYP/6-311G(d,p) level of theory. The NMR chemical shielding tensor for all silylenes is predicted to be highly anisotropic, with a very large paramagnetic eigenvalue δ_{11} in the plane of the central R_2Si unit and perpendicular to its C_2 axis. Very large substituent effects on $\delta^{29}\text{Si}$ are found, i.e., while for $\text{H}_2\text{Si:}$ $\delta^{29}\text{Si} = 772$ is predicted, the divalent silicon in F_2Si is strongly shielded ($\delta^{29}\text{Si} = -9.3$). On the other hand for $(\text{H}_3\text{Si})_2\text{Si:}$ $\delta^{29}\text{Si} = 1223$ is computed. This exceptional substituent effects are a direct consequence of large changes of the dominant eigenvalue δ_{11} . The theoretical analysis reveals, that δ_{11} in silylenes is determined by the energy difference between its lowest excited singlet state, S_1 , and the S_0 ground state. Therefore, a direct relation between the experimentally easy accessible λ_{max} of silylenes and the isotropic ^{29}Si -NMR chemical shift exists. This correlation can be used to facilitate the NMR characterization of highly substituted silylenes.

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1. Introduction

Considerable efforts have been spent to characterize and understand the electronic nature of silylenes [1]. Electronic and vibrational spectroscopy has been used to identify many small silylenes in matrices at low temperature. In combination with theoretical investigations, these studies have provided detailed descriptions of the electronic and molecular structure [1b]. After the advent of stable silylenes in 1994 [2–5], silylene chemistry opens also for one of the most powerful methods in providing structural and electronic details, solid state NMR spectroscopy [6,7]. Characterization of the anisotropy or three-dimensional nature of the chemical shielding provides a highly diagnostic probe of the electronic environment of the nucleus of interest and it allows to correlate the orientation of particular shielding or deshielding influences with the molecular structure [6]. Such an approach is particularly informative when coupled with theoretical predictions of the chemical

shielding tensor [6,7]. The present theoretical study is intended to provide the basic understanding about the chemical shielding tensor of simple silylenes and the substituent effects determining the isotropic ^{29}Si -NMR chemical shift.

2. Computational methods

All calculations were performed with the GAUSSIAN 94 and 98 programs [8]. The structures of all compounds were optimized using the hybrid density functional B3LYP [9] and the 6-311G(d,p) basis set. Stationary points were characterized by subsequent frequency calculations as minima, transition states or higher order saddle points. Chemical shielding tensors of silylenes were calculated using the GIAO/MP2 method [10,11] and an extended 6-311+G(2df,p) basis set. Theoretical shieldings σ were transformed to relative chemical shifts δ by subtracting from the calculated chemical shielding of TMS ($\sigma = 365.7$ GIAO/MP2/6-311+G(2df,p)//B3LYP/6-311G(d,p)). Isotropic chemical shifts δ and the span $\Delta\delta$ of the chemical shift tensor were calculated using standard conventions ($\delta = (\delta_{11} + \delta_{22} + \delta_{33})/3$ and $\Delta\delta = \delta_{11} - \delta_{33}$). SCF/IGLO calculations were done

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using basis II [12]. Absorption wavelengths were computed using the TD/B3LYP method using the 6-311++G(d,p) basis set [13,14].

3. Results and discussion

The chemical shielding tensor of the parent singlet silylene H_2Si , **1**, is exceptional in several respects. The silicon nucleus is predicted to be very strongly deshielded with an large isotropic ^{29}Si -NMR chemical shift ($\delta^{29}\text{Si}_{\text{iso}} = 772$) and the ^{29}Si chemical shift tensor is highly anisotropic with a very large span $\Delta\delta = 2291$. The strong deshielding and the large anisotropy of the silicon in singlet silylene is a result of a dominant paramagnetic tensor component lying in the plane and normal to the molecular C_2 axis ($\delta_{11} = 2095$) (Fig. 1). The intermediate eigenvector ($\delta_{22} = 417$) is aligned along the molecular axis, while the most shielded component of the ^{29}Si shielding tensor ($\delta_{33} = -196$) of H_2Si is oriented perpendicular to the molecular plane. The orbital contributions as predicted by an IGLO calculation for **1** are given, in terms of absolute shieldings σ [$\sigma(\text{Me}_4\text{Si}) - \sigma = \delta$], in Table 1. The IGLO calculation data suggest, that particularly strong paramagnetic contributions from the lone pair at silicon (lp(Si)) dominate the strongly deshielded σ_{11} and therefore δ_{11} .

A basic Walsh-type analysis for the H_2Si molecule, suggests that its electronic structure markedly depends on the bond angle $\alpha(\text{HSiH})$ [15]. This is also shown by the calculations of the chemical shift tensor for silylene **1** with varying bond angle α , which are summarized in Fig. 2a. The widening of α is accompanied by an tremendous deshielding along the δ_{11} axis, which is increased by 3000 ppm when α is changed from 80 to 120°. Consequently, the deshielding along the δ_{11} axis leads to a pronounced low field shift also for the isotropic ^{29}Si -NMR chemical shift. A similar angular dependence is found for dimethylsilylene, Me_2Si : (see Fig. 2a). This suggests that the steric bulk of an alkylsubstituent strongly influences the isotropic ^{29}Si -NMR chemical shift simply by increasing the central bond angle α . For example, for bis-1-adamantylsilylene, for which a central CSiC bond angle of 112.7° is predicted [15c], an additional deshielding of the silicon

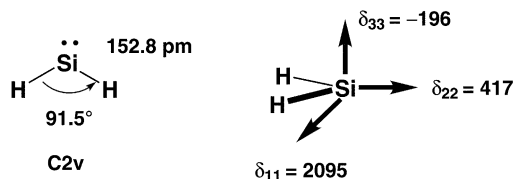


Fig. 1. Calculated structure of silylene **1** (B3LYP/6-311G(d,p)) and size and orientation of the chemical shift tensor's eigenvalues relative to the molecule (MP2/6-311++G(2df,p)/B3LYP/6-311G(d,p)).

Table 1

Calculated principal components of the chemical shielding tensor and orbital contributions for silylene **1** (IGLO/BasisII//MP2/6-311G(d,p))

	lp(Si)	L(Si) ^a	$\Sigma(\text{SiH})$ ^b	$\Sigma + \text{K}(\text{Si})$ ^c	δ ^d
σ_{11}	-1447	-42	-782	-1775	2150
σ_{22}	17	200	-684	29	346
σ_{33}	-65	234	-115	550	-175
$\Sigma/3$	-499	131	-527	-399	774

^a Si L-shell contribution without the lp(Si).

^b Sum of contributions from the SiH bonds.

^c Sum of the preceding three terms plus the K-shell contribution ($\sigma(\text{K}(\text{Si})) = 496$).

^d Relative to TMS: $\sigma^{29}\text{Si}(\text{TMS}) = 375$.

of 160 ppm compared to dimethylsilylene, Me_2Si , is to be expected [16].

The dependence of $\delta^{29}\text{Si}$ on the bond angle α is significantly less pronounced for silylenes with more electronegative and with π -electron donating substituents. The deshielding of the silicon atom in

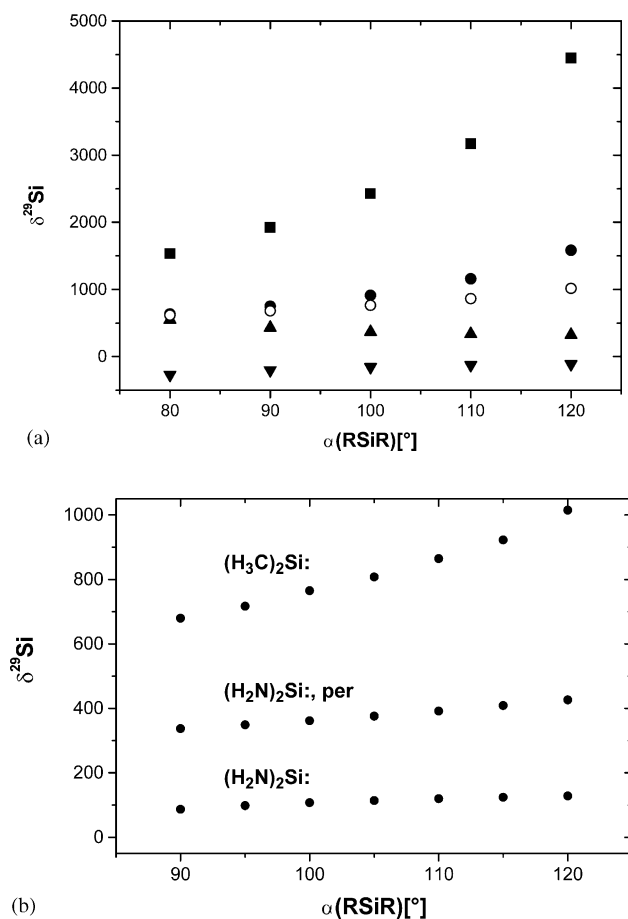


Fig. 2. (a) Angular dependence of the isotropic chemical shift δ_{iso} and the eigenvalues $\delta_{11} - \delta_{33}$ for silylene **1** (δ_{iso} (●), δ_{11} (■), δ_{22} (▲), δ_{33} (▼)) and for dimethylsilylene, Me_2Si : (δ_{iso} (○)). (b) Angular dependence of the isotropic chemical shift δ_{iso} for aminosilylene $(\text{H}_2\text{N})_2\text{Si}$: in its planar ground state conformation and in its perpendicular conformation ($(\text{H}_2\text{N})_2\text{Si}$, per) and for dimethylsilylene, Me_2Si .

diaminosilylenes upon widening of α from 90 to 120° is comparatively small ($\Delta\delta^{29}\text{Si} = \delta^{29}\text{Si}(120^\circ) - \delta^{29}\text{Si}(90^\circ) = 41$) (Fig. 2b). When the π -electron interaction between the empty 3p(Si) and the lone pairs at the nitrogen atoms in diaminosilylene is artificially switched off by fixing the amino substituent in a plane perpendicular to the central N₂Si plane, the dependence of $\delta^{29}\text{Si}$ on the bond angle α is 90 ppm, still significantly smaller than predicted for dimethylsilylene ($\Delta\delta^{29}\text{Si} = 336$).

A similar orientation of the ²⁹Si shift tensor as in H₂Si:, in particular the same strongly deshielded component perpendicular to the molecular C₂ axis in the plane of the molecule, was found experimentally for the stable cyclic diaminosilylenes **2–4** [7]. The markedly decreased $\delta^{29}\text{Si}^{\text{iso}}$ ($\delta^{29}\text{Si}^{\text{iso}} = 75$ (**2**), 93 (**4**) and 117 (**3**)) and $\Delta\delta$ of **2–4** (only 15–16% of $\Delta\delta$ of **1**), however, point to a significant substituent effect on the ²⁹Si-NMR chemical shift tensor and on the isotropic ²⁹Si-NMR chemical shift. This exceptional substituent influence is confirmed by the series of chemical shift tensor calculations for model silylenes summarized in Table 2.

The isotropic ²⁹Si-NMR chemical shift varies from $\delta^{29}\text{Si} = -9.3$ for difluorosilylene F₂Si: to $\delta^{29}\text{Si} = 1223$ for the bisilylsilylene (H₃Si)₂Si:. Difluorosilylene shows also the smallest span of the chemical shift tensor of all investigated silylenes ($\Delta\delta = 349$), while the silylated silylene exhibits a huge span ($\Delta\delta = 3004$). Despite these striking substituent effects on $\delta^{29}\text{Si}$, there are also similarities: common for all investigated silylenes is the orientation of the major component of the chemical shift tensor. The most deshielded component δ_{11} is always oriented perpendicular to the molecular axis and lies in the plane of the divalent silicon and its two substituents. This paramagnetic component is for each silylene by far the largest and therefore it determines greatly the isotropic ²⁹Si-NMR chemical shift.

The ²⁹Si-NMR chemical shift of silylenes depends crucially on the orientation of the substituent relative to the plane spanned by the divalent silicon and its two neighboring atoms. For example, the isotropic ²⁹Si-NMR chemical shift for diaminosilylene (H₂N)₂Si:, fixed in the perpendicular conformation of the amino groups relative to the molecular plane, is predicted to be 388, while for the planar minimum structure of (H₂N)₂Si: $\delta^{29}\text{Si}^{\text{iso}} = 107$ is calculated. A similar large conformational effect on $\delta^{29}\text{Si}$ is predicted also for

phenylsilylene, PhHSi:. A low field shift of $\delta^{29}\text{Si}^{\text{iso}}$ of 166 ppm is computed upon rotation of the phenyl group from the planar ground state structure to the perpendicular conformation. In both cases this orientational dependence can be traced back to large changes in the most deshielded component, δ_{11} , of the ²⁹Si-NMR chemical shift tensor, which varies upon rotation by 703 and 495 ppm in (H₂N)₂Si: and PhHSi:, respectively.

How can these large substituent effects be understood? In a qualitative view a magnetic field oriented along the δ_{11} eigenvector of the silylene induces a ring current perpendicular to the δ_{11} axis. This ring current results in an excitation of electrons of the silylene lone pair (lp(Si) to the empty 3p(Si). The efficiency of this process and therefore the size of the paramagnetic shielding constant, $\sigma_{11}^{\text{para}}$ is determined by the sum of the energy differences between the ground state and the excited states of the silylene (see Eq. (1)) [17,18].

$$\sigma_{\text{para}} = - \left(\frac{e^2 \mu_0}{12\pi m_e} \right) \sum_n \frac{I_{0n}(r^{-3}I)_{n0}}{\Delta E_{n0}} \quad (1)$$

where μ_0 , vacuum permeability; e , elementary charge; m_e , mass of electron; ΔE_{n0} , excitation energy; I , angular momentum operator.

Naturally, the most important contribution for σ^{para} results from an excitation from the ground state to the first excited state ($n = 1$) due to its small energy gap ΔE_{10} . For silylenes this transition from the S₀ ground state to the S₁ state, is best described by an excitation of an electron from the lp(Si) to the empty 3p(Si). This qualitative discussion is supported by the results of IGLO calculations (Table 1) which predict for H₂Si: large paramagnetic contributions to δ_{11} . The S₁ → S₀ transition is also responsible for the characteristic UV–vis band of silylenes [1]. Therefore the unusual substituent effect on $\delta^{29}\text{Si}$ in silylenes can be explained following similar arguments as has been given for the influence of the substituents on the position of the UV–vis band in silylenes [19]. The electronegativity of the substituent at silicon determines the energy of the lp(Si), that is electronegative substituents stabilize lp(Si) and ΔE_{10} increases. This results in a smaller paramagnetic shielding constant $\sigma_{11}^{\text{para}}$ (Eq. (1)) and therefore in an overall shielding of the silicon nucleus. On the other hand, an electropositive substituent rises the energy of

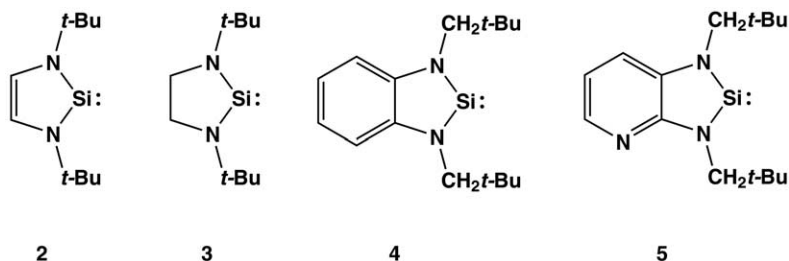


Table 2

Calculated bond angles α ($^\circ$), calculated eigenvalues of the ^{29}Si shielding tensor, of the ^{29}Si -NMR chemical shift tensor and calculated absorption wave length λ_{max} (nm) of the $S_1 \rightarrow S_0$ transition in silylenes

Entry	Silylene	α	σ_{iso}^a	σ_{11}^a	σ_{22}^a	σ_{33}^a	δ_{iso}^b	δ_{11}^b	δ_{22}^b	δ_{33}^b	$\Delta\delta$	λ_{max}^c
1	H ₂ Si:	91.5	-406.1	-1729.0	-51.0	562.0	771.8	2094.7	416.7	-196.3	2291.0	526.9
2	F ₂ Si:	100.4	375.0	213.0	350.0	562.1	-9.3	152.7	15.7	-196.4	349.1	227.4
3	FHSi:	96.9	-60.2	-835.7	184.0	471.0	425.9	1201.4	181.7	-105.3	1306.7	421.8
4	Me ₂ Si:	97.8	-373.9	-1462.5	-47.1	388.0	739.6	1828.2	412.8	-22.3	1850.5	489.3
5	MeHSi:	94.4	-405.3	-1623.8	-27.4	435.2	771.0	1989.5	393.1	-69.5	2059.0	509.2
6	(H ₂ N) ₂ Si:	100.2	258.7	33.8	356.6	385.8	107.0	331.9	9.1	-20.1	352.0	239.8
7	(H ₂ N) ₂ Si:, per ^d	108.9	-22.7	-669.3	271.9	329.4	388.4	1035.0	93.8	36.3	998.7	418.5
8	H ₂ N(H)Si:	94.1	79.2	-440.3	310.0	367.8	286.5	806.0	55.73	-2.1	808.1	345.4
9	H ₂ N(H)Si:, per ^d	102.1	-349.6	-1527.1	184.5	293.7	715.3	1892.8	181.2	72.0	1820.8	633.7
10	PhHSi:	95.0	-273.2	-1269.3	77.9	371.9	638.9	1635.0	287.8	-6.2	1641.2	525.0
11	PhHSi:, per ^d	95.7	-439.1	-1764.5	-3.1	450.3	804.8	2130.2	368.83	-84.6	2214.8	599.5
12	(H ₃ Si) ₂ Si:	92.7	-857.7	-2346.3	-884.7	657.9	1223.4	2712.0	1250.4	-292.2	3004.2	815.2
13	(H ₃ Si)HSi	89.0	-617.9	-2137.2	-332.5	616.0	983.6	2502.9	698.2	-250.3	2753.2	668.2
14	(H ₂ C=CH) ₂ Si:	101.1	-166.7	-979.6	95.9	383.7	532.4	1345.3	269.8	-18.0	1363.3	522.5
15	H ₂ N(Me)Si:	99.0	73.4	-415.9	284.3	351.8	292.3	781.6	81.4	13.9	767.7	326.2
16	H ₂ N(Me)Si:, per ^d	102.8	-266.0	-1268.9	193.5	277.3	631.7	1634.6	172.2	88.4	1546.2	545.9
17	(MeO) ₂ Si:	97.0	270.5	88.0	281.5	442.2	95.2	277.7	84.2	-76.5	354.2	285.1
18	(MeO)MeSi:	96.6	-11.2	-603.4	208.9	361.0	376.9	969.1	156.8	4.7	964.4	380.3
19	PhMeSi:	101.3	-279.5	-1247.8	40.6	368.6	645.2	1613.5	325.1	-2.9	1616.4	523.2
20	PhMeSi, per ^d	97.9	-379.9	-1527.0	-9.7	387.3	745.6	1892.7	375.4	-21.6	1914.3	527.5
21	(F ₃ C) ₂ Si:	94.7	-176.1	-1122.9	205.9	388.8	541.8	1488.6	159.8	-23.1	1511.7	493.6

^a Calculated GIAO/MP2/6-311+G(2df,p)//B3LYP/6-311G(d,p).

^b Calculated using $\delta = \sigma(\text{TMS}) - \sigma$; $\sigma(\text{TMS}) = 365.7$; (GIAO/MP2/6-311+G(2df,p)//B3LYP/6-311G(d,p)).

^c TD/B3LYP/6-311++G(d,p)//B3LYP/6-311G(d,p).

^d Amino (phenyl) group(s) in perpendicular orientation relative the SiR₂ plane.

the lp(Si), resulting in the opposite effect: ΔE_{10} is reduced and $\sigma_{11}^{\text{para}}$ is amplified. The effect of π -donor substituents on the energy of the $S_1 \rightarrow S_0$ transition, ΔE_{10} , can be analyzed with the help of the orbital interaction diagram in Fig. 3. The interaction of the empty $3p(\text{Si})$ orbital with the filled orbitals of a π -donor substituent results in a destabilization of the $(3p)\text{Si}$ with an concomitant increase of ΔE_{10} and, as a consequence, to a smaller paramagnetic deshielding of the silicon nuclei. The MO diagram provides also a rationalization for the marked conformational dependence of $\delta^{29}\text{Si}$. The interaction between the donor orbitals and the $3p(\text{Si})$ are strongly orientation dependent and vanish when the vectors of the interacting orbitals are perpen-

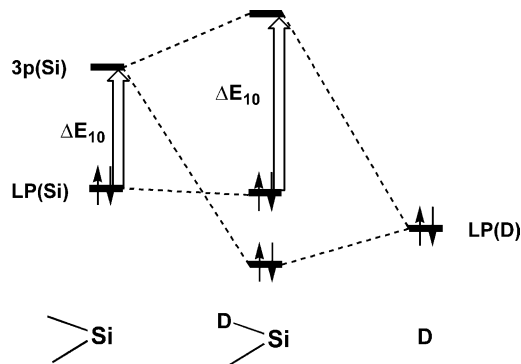


Fig. 3. Qualitative orbital diagram for the interaction between a π -donor and the divalent silicon in silylenes.

dicular as for example in the aminosilylenes with the amino groups oriented perpendicular to the plane spanned by the silicon and its two direct neighbor atoms (Table 2, entries 7, 9, 16) [20] or in the perpendicular conformations of phenylsubstituted silylenes PhHSi: and PhMeSi: (entries 11, 20).

Following the presumption that (1) σ_{para} mainly depends on the energy difference ΔE_{10} and higher excitations are not important ($\sigma_{\text{para}} \sim 1/\Delta E_{10}$; since $\Delta E_{10} \ll \Delta E_{20}, \Delta E_{30}, \dots$) and that (2) the diamagnetic contribution, σ_{dia} , to the ^{29}Si -NMR chemical shielding for silylenes is constant, this qualitative analysis suggest, that there is a linear correlation between σ_{11} (and between δ_{11}) and the wave length of the $S_1 \rightarrow S_0$ UV transition in silylenes. The plot of the calculated λ_{max} for the low energy $S_1 \rightarrow S_0$ transition (at TD/B3LYP/6-311++G(d,p)//B3LYP/6-311G(d,p)) versus δ_{11} for 21 investigated silylenes indeed shows an approximate linear correlation (see Fig. 4). Under consideration that (3) $\delta_{\text{iso}}^{29}\text{Si}$ in silylenes is determined by the strongly deshielded δ_{11} component ($\delta_{11} \gg \delta_{22}; \delta_{33}$), a correlation also between $\delta_{\text{iso}}^{29}\text{Si}$ and λ_{max} results (Fig. 5). The correlation shown in Fig. 5 is far from being ideal, but this should not be expected in regard of the simplifications (1–3). Deviations from linearity can be found for relatively small ^{29}Si -NMR chemical shifts since in these cases δ_{11} is not dominating (condition (3)) and for very large ^{29}Si -NMR chemical shifts since higher excitations

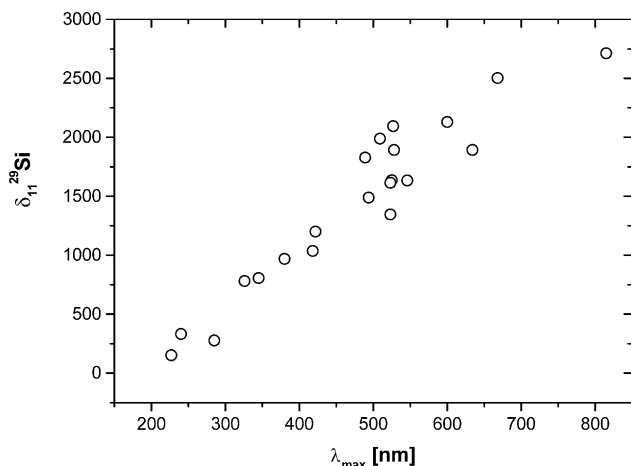


Fig. 4. Plot of calculated λ_{\max} (TD/B3LYP/6-311++G(d,p)//B3LYP/6-311G(d,p)) versus the calculated eigenvalue δ_{11} of the ^{29}Si -NMR chemical shielding tensor (GIAO/MP2/6-311+G(2df,p)//B3LYP/6-311G(d,p)) ($r^2 = 0.953$).

become important (condition (1)). Nevertheless, the correlation shown in Fig. 5 is in reasonable agreement with available experimental data for the cyclic aminosilylenes 3–5 and for the only persistent dialkylsilylene 6 (see Table 3 and Fig. 5) [4–6,21].

This $\delta_{\text{iso}}^{29}\text{Si}/\lambda_{\max}$ relation, shown in Fig. 5, certainly can not replace an accurate calculation of the isotropic ^{29}Si -NMR chemical shift for silylenes using advanced quantum mechanical methods, it can be used, however, to estimate $\delta_{\text{iso}}^{29}\text{Si}$ from the experimentally easy accessible long-wave absorption of silylenes. We think, that this relation is valuable for the NMR characterization of highly substituted silylenes, when accurate calculations of the ^{29}Si -NMR chemical shift become demanding and when calculations for smaller model compounds are not reliable because of a non-adequate description of the influence of the substituent's conformation relative to the important frontier orbitals of the silylene.

The acyclic diaminosilylene 7 was identified by a long-wave absorption $\lambda_{\max} = 335$ nm [22]. The $\delta_{\text{iso}}^{29}\text{Si}/\lambda_{\max}$ correlation suggests for this silylene $\delta_{\text{iso}}^{29}\text{Si} = 200$ –250 (Fig. 5), in reasonable agreement with a DFT/B3LYP/GIAO calculation which predict $\delta_{\text{iso}}^{29}\text{Si} = 203$ [23]. This is surprisingly far down-field shifted compared to the topological very similar cyclic aminosilylenes 2–5. It

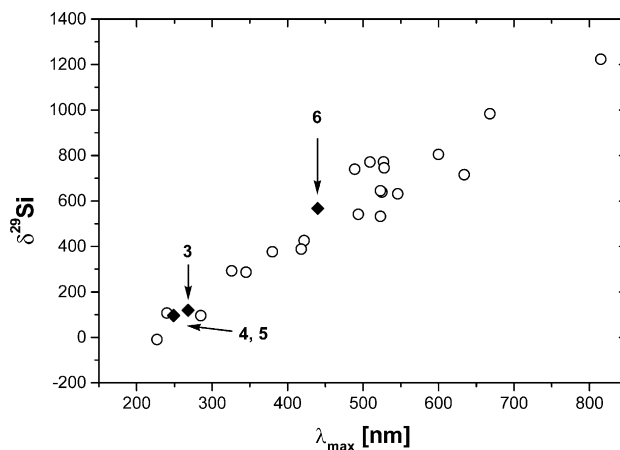


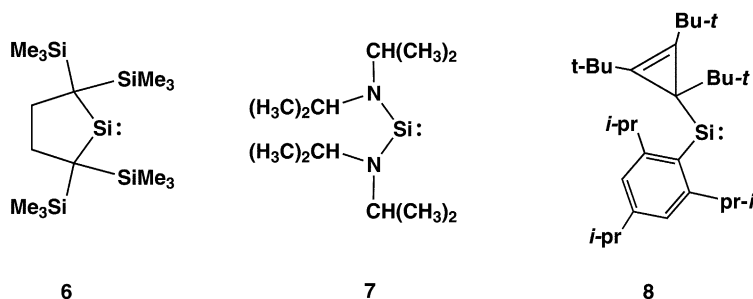
Fig. 5. Plot of calculated λ_{\max} (TD/B3LYP/6-311++G(d,p)//B3LYP/6-311G(d,p)) versus the calculated isotropic ^{29}Si -NMR chemical shift $\delta_{\text{iso}}^{29}\text{Si}$ (GIAO/MP2/6-311+G(2df,p)//B3LYP/6-311G(d,p)); (◆) experimental values for silylenes 3–6 ($r^2 = 0.964$).

is, however, easily rationalized taking into account the strong twisting of silylene 7 induced by the large isopropyl substituents (twist angle φ between the R_2N and SiN_2 plane: $\varphi = 25.5^\circ$) [24]. This twist of the molecule hampers the interaction between $\text{lp}(\text{N})$ and the empty $3\text{p}(\text{Si})$ and this results in a markedly decreased ΔE_{10} compared to the planar cyclic aminosilylenes.

The silylene 8 was synthesized by Fink and coworkers and it is persistent at -70°C [25]. Several attempts to record a ^{29}Si -NMR spectrum failed. Its long-wave absorption at $\lambda_{\max} = 448$ nm suggest, however, a very low-field shifted ^{29}Si -NMR resonance $\delta_{\text{iso}}^{29}\text{Si} \approx 600$ (calculated for the model compound $\text{Ph}(\text{C}_3\text{H}_3)\text{Si}:$: $\delta_{\text{iso}}^{29}\text{Si} = 677$) [23] a quite unusual frequency region which was not checked experimentally [25b].

Table 3
Isotropic ^{29}Si -NMR chemical shift and long-wave absorption of stable silylenes [4–6,21]

Silylene	$\delta_{\text{iso}}^{29}\text{Si}$	λ_{\max}
3	119	268
4	97	249
5	95	249
6	567	440



4. Conclusion

This theoretical study shows that singlet silylenes in general have a strongly deshielded silicon nuclei. The actual chemical shift of silylenes depends however substantially on the substituent. The chemical shielding tensor of silylenes is highly anisotropic with a dominant, strongly paramagnetic in-plane component σ_{11} perpendicular to the molecular axis. These magnetic properties of singlet silylenes parallel closely those of singlet carbenes [26,27] and point to the close relationship between the two classes of divalent group 14 compounds.

The strongly deshielded σ_{11} component is closely related to the energy difference ΔE_{10} , between the S_1 and S_0 state. Therefore, the large substituent effects on $\delta^{29}\text{Si}$ can be rationalized by a basic frontier orbital analysis: substituent transmitting $-I$ and $+M$ effects increase ΔE_{10} and this results in a shielding of the silicon nuclei. On the other hand substituents having $+I$ effects reduce ΔE_{10} and lead to a paramagnetic shift. The dominance of σ_{11} in silylenes and the relation between σ_{11} and ΔE_{10} suggests, that from the measurement of the $S_1 \rightarrow S_0$ transition in silylenes the isotropic ^{29}Si -NMR chemical shift, $\delta^{29}\text{Si}$, can be estimated. This can greatly facilitate the NMR characterization of highly substituted silylenes in the future.

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