

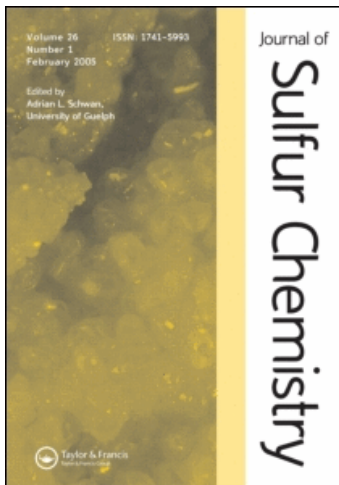
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RESEARCH ARTICLE

Effects of methyl substitution in 4-silathiane S-oxides on the stereochemistry and $^1J_{\text{CH}}$ coupling constants: Buttressing effect of axial sulfinyl group as the origin of the reverse Perlin effect

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An NMR study of the products of lithiation/methylation of 4,4-dimethyl-4-silathiane S-oxide **1**, diastereomers of 2,4,4-trimethyl-4-silathiane S-oxide **2** and 2,4,4,6-tetramethyl-4-silathiane S-oxide **3**, as well as 4,4-dimethyl-4-silathiane S,S-dioxide **4** and 2,4,4-trimethyl-4-silathiane S,S-dioxide **5** is reported. The 2-Me group in 2,4,4-trimethyl-4-silathiane S-oxides is always equatorial while the SO group may occupy either the equatorial (major isomer, **2ee**) or axial (minor isomer, **2ae**) position. 2,4,4,6-Tetramethyl-4-silathiane S-oxide exists in the form of the two isomers, the one with 2-Me, 6-Me and sulfinyl groups all equatorial (**3eee**), and the other one as an equilibrium mixture of the axial and equatorial sulfoxides with 2-Me axial and 6-Me equatorial (**3aae** \rightleftharpoons **3eae**). The normal Perlin effect ($J_{\text{CHax}} < J_{\text{CHeq}}$) is found for the CH_2 groups in all studied compounds except for the 3- and 5- CH_2 groups in **2ae** and **5**, which show a small reverse Perlin effect ($J_{\text{CHax}} > J_{\text{CHeq}}$). The experimental findings are interpreted in terms of the σ (C–Hax) \rightarrow σ^* (S=O) stereoelectronic effect for the C–H bonds in the 2- and 6-positions, and the buttressing effect of the axial SO group on the C–Hax bonds in the 3- and 5-positions and confirmed by GIAO-B3LYP/6-311G(d,p) theoretical calculations.

Keywords: Stereoelectronic effects; Perlin effect; Silathiane S-oxides

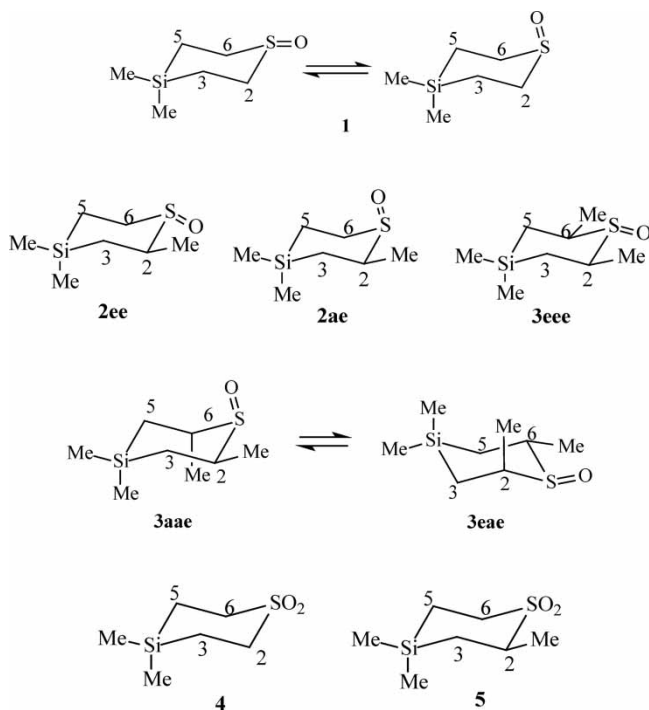
1. Introduction

Silathianes represent an interesting class of heteroatomic derivatives of cyclohexane. They are different from the previously studied diheterocyclohexanes (dioxanes, dithianes, oxathianes) in that they contain two heteroatoms of different nature: sulfur atom with the lone pair and silicon atom showing strong inductive electron donating effect and simultaneously possessing vacant *d*-orbitals. The number of works concerning silathianes is very limited [1–6] and their S-functional derivatives were unknown before our studies. In the course of our investigations of thiasilacycloalkanes we have prepared 3,3-dimethyl-3-silathiane S-oxide [7], 2,3,3-trimethyl-3-silathiane S-oxide and 2,3,3-trimethyl-3-silathiane

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S,S-dioxide [8], 3-(benzenesulfonylimino)-1,1-dimethyl-1,3-silathiane and 1,3,3-trimethyl-1,3-thiasilinan-1-ium iodide [9] and examined their transformations [9,10]. These studies mainly concerned 3-silathianes; as to experimental studies on 4-silathianes, only the synthesis of 4-silathiane and its sulfonium salt, 1,4,4-trimethyl-1,4-thiasilinan-1-ium iodide was reported [4].

Recently, we have described the synthesis of 4,4-dimethyl-4-silathiane and its S-functional derivatives including S-oxide [11]. Lithiation/methylation of the latter compound, 4,4-dimethyl-4-silathiane S-oxide **1**, was shown to lead to the mono- and dimethylated derivatives. Monomethylation goes selectively to the α -position to the sulfoxide group and affords two stereoisomers of 2,4,4-trimethyl-4-silathiane S-oxide. Its further methylation goes to the α' -position and results in the two stereoisomers of 2,4,4,6-tetramethyl-4-silathiane S-oxide [12]. In continuation of these studies in the present paper, we report on the structure, conformations and stereoelectronic interactions in the stereoisomers of 2,4,4-trimethyl-4-silathiane S-oxide **2ee** and **2ae** and 2,4,4,6-tetramethyl-4-silathiane S-oxide **3eee** and **3aae** based on a detailed ^1H and ^{13}C NMR analysis. For comparison, 4,4-dimethyl-4-silathiane S,S-dioxide **4** [11] and 2,4,4-trimethyl-4-silathiane S,S-dioxide **5** (synthesized in the present work) are also included. As will be shown below, these molecules are beneficial objects for analysis of stereoelectronic effects in six-membered rings.



SCHEME 1

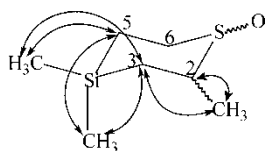
2. Results and discussion

Synthesis and isolation of all compounds (except for **5**) is described elsewhere [11, 12]. The ^1H and ^{13}C chemical shifts are given in tables 1 and 2 and the J_{HH} and $^1J_{\text{CH}}$ coupling constants are

Table 1. ^{13}C NMR chemical shifts (calculated values are given in parentheses).

Compound	2-Me	C-2	C-3	C-5	C-6	Si-Me	Si-Me	S=O
1	–	46.60	5.60	5.60	46.60	–3.52	–4.42	Equilibrium
2aa	(18.1)	(62.6)	(13.6)	(4.8)	(45.5)	(0.5)	(–0.8)	ax
2ea	(10.3)	(63.0)	(19.7)	(12.5)	(49.3)	(0.3)	(–0.9)	eq
2ee	20.69 (22.0)	56.12 (68.5)	18.38 (21.4)	9.36 (13.3)	48.81 (59.8)	–2.74 (–1.7)	–4.11 (–3.9)	eq
2ae	21.67 (23.5)	50.91 (62.6)	13.54 (15.1)	2.15 (4.6)	44.04 (53.8)	–2.44 (–1.7)	–4.62 (–4.8)	ax
3eee	20.80 (22.0)	55.08 (67.5)	19.35 (22.1)	19.35 (22.1)	55.08 (67.5)	–3.00 (–1.6)	–4.17 (–3.5)	eq
3aae	16.70 (ax) (17.7) 18.20 (eq) (23.2)	48.81 (63.3)	14.07 (12.6)	14.35 (14.6)	46.99 (54.0)	–1.12 (0.8)	–1.12 (–0.8.)	Equilibrium
3eae	(11.2 ax) (21.7 eq)	(63.9)	(20.2)	(21.5)	(56.3)	(0.8)	(–0.6)	eq
4	–	49.63	10.51	10.51	49.63	–4.26	–4.26	SO ₂
5	15.90	54.76	19.88	10.85	49.11	–2.98	–4.67	SO ₂

summarized in tables 3 and 4. The most challenging problem was to distinguish between the protons and carbons of the 3-CH₂ and 5-CH₂ groups in **2ee** and **2ae**. The signals of C-3 were assigned based on the presence of cross peaks with protons of the 2-Me groups corresponding to long-range coupling constant $^3J(\text{C,H})$ in the 2D HMBC spectra. Other correlations observed in the 2D HMBC $\{^1\text{H}-^{13}\text{C}\}$ spectra of the monomethylated species are shown below:



SCHEME 2

Note that compound **2ee** shows two different signals of SiMe protons in the ^1H NMR spectrum whereas in its isomer **2ae** they coincide to give slightly broadened singlet (table 2). For **2ee** the analysis of the 2D NOESY spectrum allowed to assign the signals of the

Table 2. ^1H NMR chemical shifts.

Compound	2-Me	2-CH	3-CH ₂	5-CH ₂	6-CH ₂	Si-Me	Si-Me	S=O
1	–	2.85 ax 3.06 eq	0.8 ax	0.8 ax	2.85 ax 3.06 eq	0.09	0.07	Equilibrium
2ee	1.41 eq	2.85 ax	0.74 ax 1.03 eq	0.95 ax 1.03 eq	2.87 ax 3.30 eq	0.03	0.12	eq
2ae	1.38 eq	2.58 ax	0.60 eq 1.28 ax	0.61 eq 1.35 ax	2.48 ax 3.30 eq	0.06	0.06	ax
3eee	1.49 eq	2.94 ax	0.89 ax 1.10 eq	0.89 ax 1.10 eq	2.94 ax	0.18	0.07	eq
3aae	1.35 (2-Me) 1.42 (6-Me)	3.26 ax	0.73 ax 1.29 eq	0.9 ax 1.29 eq	3.08 eq	0.17	0.13	Equilibrium
4	–	3.10	1.16	1.16	3.10	0.13	0.13	SO ₂
5	1.40	3.10 ax	1.02 eq 1.12 ax	1.03 eq 1.33 ax	3.00 ax 3.20 eq	0.11	0.16	SO ₂

Table 3. J_{HH} coupling constants.

Compound	$^3J(\text{H2ax}-\text{H3ax})$	$^3J(\text{H2ax}-\text{H3eq})$	$^3J(\text{H6ax}-\text{H5ax})$	$^3J(\text{H6ax}-\text{H5eq})$	$^3J(\text{H6eq}-\text{H5ax})$	$^3J(\text{H6eq}-\text{H5eq})$	$^2J(\text{H3eq}-\text{H3ax})$	$^2J(\text{H5eq}-\text{H5ax})$	$^2J(\text{H6eq}-\text{H6ax})$
2ee	13.4	3.1	13.4	3.7	4.9	6.1	15.2	15.2	13.0
2ae	13.4	3.1	14.0	3.0	4.8	4.5	15.3	15.2	14.6
3eee	15.6	3.9	15.6	3.9	–	–	15.7	15.7	–
3aae	9.8	3.9	–	–	4.0	9.8	15.7	15.6	–
5	12.0	3.5	13.0	4.9	4.8	4.5	15.1	14.8	14.8

SiMe groups. The observed cross peak of the H-2ax proton with the less shielded SiMe signal at 0.09 ppm is indicative of the axial arrangement of this methyl group. Other Overhauser effects observed in the 2D spectra are trivial and prove the assignment made by the use of other methods.

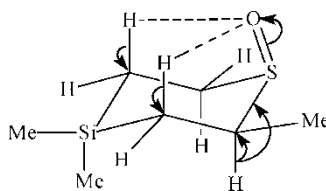
Presence of two chiral centers in the molecule of 2,4,4-trimethyl-4-silathiane S-oxide makes it possible the existence of four diastereomers with the axial and equatorial arrangement of the SO and Me groups. Since lithiation/alkylation of sulfoxides proceeds predominantly as *trans*-substitution [13–15] and the free conformational energy Δ for the methyl group ($\Delta = 7.3$ kJ/mol) [16] is much higher than that for the sulfoxide group ($\Delta = -0.75$ kJ/mol) [17], it is reasonable to assume that the major stereoisomer of 2,4,4-trimethyl-4-silathiane S-oxide **2ee** has both Me and S=O groups equatorial. Its formation from sulfoxide **1** existing probably as a mixture of the rapidly interconverting conformers with the axial and equatorial S=O group [17, 18] is the result of *trans*-methylation leading to **2ee** either directly

Table 4. $^1J_{\text{CH}}$ coupling constants (calculated values are given in parentheses).

Compound	2-CH	3-CH ₂	5-CH ₂	6-CH ₂
1	140.2 eq 137.7 ax $\Delta = 2.5$	122.5 eq 121.6 ax $\Delta = 0.9$	122.5 eq 121.6 ax $\Delta = 0.9$	140.2 eq 137.7 ax $\Delta = 2.5$
2aa	(137.4)	(119.6) eq (120.7) ax $\Delta = (-1.1)$	(121.4) eq (123.6) ax $\Delta = (-2.2)$	(138.8) eq (133.1) ax $\Delta = (5.7)$
2ea	(138.0)	(119.7) eq (115.7) ax $\Delta = (4.0)$	(120.9) eq (118.6) ax $\Delta = (2.3)$	(140.5) eq (137.4) ax $\Delta = (3.1)$
2ee	139.5 (137.5)	121.1 (119.3) eq 119.1 (117.8) ax $\Delta = 2.0$ (1.5)	121.4 (120.8) eq 120.8 (118.6) ax $\Delta = 0.6$ (2.2)	141.4 (140.2) eq 138.8 (137.7) ax $\Delta = 2.6$ (2.5)
2ae	135.3 (135.1)	120.4 (120.0) eq 121.2 (122.3) ax $\Delta = -0.8$ (-2.3)	122.2 (121.5) eq 122.4 (123.2) ax $\Delta = -0.2$ (-1.7)	141.0 (138.7) eq 133.8 (133.2) ax $\Delta = 7.2$ (5.5)
3eee	138.9 (137.5)	121.3 (119.4) eq 119.3 (118.2) ax $\Delta = 2.0$ (1.2)	121.3 (119.4) eq 119.3 (118.2) ax $\Delta = 2.0$ (1.2)	138.9 (137.5)
3aae	(137.2)	(119.7) eq (120.8) ax $\Delta = (-1.1)$	(119.8) eq (122.7) ax $\Delta = (-3.1)$	(134.9)
3ae	138.8 eq (138.1)	121.3 (119.8) eq 119.3 (115.9) ax $\Delta = 2.0$ (3.9)	121.3 (119.4) eq 119.3 (118.2) ax $\Delta = 2.0$ (1.2)	141.8 ax (137.2)
4	138.0	123.6	123.6	138.0
5	136.4 ax	121.0 eq 122.1 ax $\Delta = -1.1$	122.9 eq 124.4 ax $\Delta = -1.5$	138.8 eq 136.1 ax $\Delta = 2.7$

or after the ring inversion in the unstable axial-axial monomethylated product. The minor stereoisomer of 2,4,4-trimethyl-4-silathiane S-oxide, **2ae**, apparently, originates from the side reaction of *cis*-methylation which was actually found to account for a small percentage of the lithiation/alkylation process in the case of the carbon analogues of sulfoxide **1** [13, 14].

The equatorial orientation of the methyl group both in **2ae** and **2ee** follows from the values of the vicinal $^3J(\text{H}_2, \text{H}_3)$ coupling constants in these molecules, which are equal to 13.4 and 3.1 Hz. This is clearly suggestive of the axial orientation of the H-2 proton and, hence, the equatorial 2-Me group. The experimental criterion allowing to distinguish between the axial and equatorial cyclic sulfoxides is the shielding of the ring carbon atoms in the ^{13}C NMR spectra for axial sulfoxides. Carbon analogs of **2ee** and **2ae**, equatorial and axial 4,4-dimethylthiane S-oxides, show substantial shielding of all ring carbon atoms in the axial versus equatorial conformer: 41.9 vs. 47.5 ppm for C-2 and C-6, $\Delta\delta = 5.6$ ppm, and 27.5 vs. 35.3 ppm for C-3 and C-5, $\Delta\delta = 7.8$ ppm [19]. We observed nearly the same values of the β -effect, $\Delta\delta = 5.36$ and 4.77 ppm for the C-2 and C-6 carbon atoms, as well as of the γ -effect, $\Delta\delta = 4.84$ and 7.21 ppm for the C-3 and C-5 carbon atoms in **2ee** and **2ae** (table 1).[†] The nature of the β - and γ -effects was disputable. In [20] it was ascribed to the electrostatic effect of dipolar S=O bond, but it was called into question in [21] since the same effect is observed for nonpolar C–C bonds, like in methylcyclohexanes. However, regardless of its nature, the effect itself is a reliable criterion of arrangement of the S=O group. The β -effect is connected with the stereoelectronic interaction $\sigma(\text{C–H}_{\text{ax}}) \rightarrow \sigma^*(\text{S=O})$ between the axially oriented C–H and S=O bonds, that increases the electron density on the C-2 and C-6 carbon atoms as depicted below in scheme 3.



SCHEME 3

The γ -effect most likely is the result of the buttressing effect of the S=O group on the C-3–H-3_{ax} and C-5–H-5_{ax} bonds that should increase the electron density on these carbon atoms. Proximity of the sulfinyl oxygen in **2ae** to the H-3_{ax} and H-5_{ax} atoms results in their deshielding. Indeed, unlike all other pairs of signals of the CH₂ groups, only 3-CH₂ and 5-CH₂ groups in **2ae** show the axial protons resonance in a lower field as compared to the equatorial ones (table 2). Similar effect of the P=O group on the H(4,6-ax) atoms in 2-(dimethylphosphinoyl)-1,3-dithiane [22] as well as 2-(dimethylphosphinoyl)-1,3,5-trithiane and 2-(dimethylphosphinoyl)-1,3-dithiane 1,1,3,3-tetraoxide [23] was analyzed within the frame of the AIM approach and substantial hydrogen bonding of the P=O ···H(4,6-ax) type was observed.

The ^1H and ^{13}C NMR spectra for compound **3eee** are substantially simplified as compared to **3aae** due to the C_s symmetry of the former molecule. The presence of five signals in the ^{13}C NMR spectrum of **3eee** and eight signals in the spectrum of **3aae** means that in the former molecule the atoms C-2 and C-6, C-3 and C-5, as well as 2-Me and 6-Me groups are identical in pairs. The ^1H NMR spectrum of **3eee** also shows the corresponding protons to be identical in

[†]Here we follow the terminology used in [19] where it was referred to as β - and γ -effect as reflecting the effect on atoms β and γ to oxygen. This is distinct from α - and β -effect used by the same authors [20] to describe the effect of the whole substituent on the carbons α and β to a sulfur-containing moiety.

pairs. The equatorial orientation of both methyl groups in **3eee** is corroborated by the values of the vicinal coupling constants $^3J(\text{H-2,H-3})$ and $^3J(\text{H-5,H-6})$ (table 3). In the ^1H NMR spectrum the signal of H-2 and H-6 represents a complex multiplet at 2.94 ppm. The double resonance experiment with decoupling the signal of the 2-Me and 6-Me groups at 1.49 ppm transforms it into a doublet of doublets with vicinal constants $^3J(\text{H-3eq,H-2ax}) = 3.9$ Hz and $^3J(\text{H-3ax,H-2ax}) = 15.6$ Hz. Large value of the latter constant unequivocally points to the axial orientation of the H-2 and H-6 protons, *i.e.* the equatorial orientation of the 2-Me and 6-Me groups. The same constants are observed for the signals of H-3eq and H-3ax protons. In a similar way it was shown that in compound **3aae** the 2-Me group occupies the equatorial and the 6-Me group the axial position. The adjacent 3-CH₂ and 5-CH₂ groups were unambiguously assigned by the use of the 2D HMBC spectra.

The orientation of the S=O group in **3eee** and **3aae** was determined by analysis of the ^{13}C chemical shifts for atoms C-3 and C-5 (table 1) and vicinal coupling constants $^3J(\text{H-2,H-3})$ and $^3J(\text{H-5,H-6})$. In the symmetrical isomer **3eee**, the chemical shift of the C-3 and C-5 atoms (19.35 ppm) is very close to that of C-3 in **2ee** (18.38 ppm) suggesting the equatorial orientation of the S=O group. In the unsymmetrical isomer **3aae** both C-3 (14.07 ppm) and C-5 (14.35 ppm) chemical shifts are very close to that of C-3 in **2ae** (13.54 ppm). At first glance it would seem to be indicative of the axial orientation of the S=O group. However, if so, one would expect the H-3ax and H-5ax protons to be less shielded than the H-3eq and H-5eq protons, as in **2ae**, but this is not the case (table 2). Moreover, the vicinal coupling constants $^3J(\text{H-2ax,H-3ax})$ and $^3J(\text{H-5eq,H-6eq})$ are identical and equal to 9.8 Hz (table 3). This value is exactly the mean of the coupling constants $^3J(\text{H-2ax,H-3ax})$ and $^3J(\text{H-2ax,H-3eq})$ in **3eee** (table 3) and most reasonably can be rationalized suggesting the equilibrium **3aae** \rightleftharpoons **3ae**. That such an equilibrium is plausible was confirmed by calculation of the energies of the conformers.

We examined the energies and geometries of the stereoisomers of 4,4-dimethyl-4-silathiane S-oxide **1**, 2,4,4-trimethyl-4-silathiane S-oxide **2** and of 2,4,4,6-tetramethyl-4-silathiane S-oxide **3** by the B3LYP/6-311G(d,p) method as implemented in the Gaussian03 package [24]. The energies and the bond lengths in the calculated molecules are given in scheme 4. As one could expect, the 2,6-dimethylated species with two axial methyl groups **3aaa** and **3eaa** are energetically strongly unfavorable as compared to the most stable form **3aee** (by 26.7 kJ/mol for S=O axial and by 25.0 kJ/mol for S=O equatorial) and should suffer ring inversion converting them into **3eee** and **3aee**, respectively.

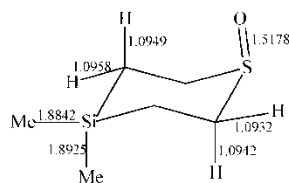
The theoretically predicted in the gas phase the axial preferability for the S=O group decreases with α -substitution and amounts to 9.3, 7.3, 4.5, 4.7, and 2.0 kJ/mol for the pairs of isomers **1a–1e**, **2ae–2ee**, **2aa–2ea**, **3aee–3eee**, and **3aae–3ae**, respectively. The lowest value of ΔE for the latter pair is in compliance with the above made suggestion on the equilibrium **3aae** \rightleftharpoons **3ae**. In solution, due to perceptibly higher dipole moments for the S=O equatorial species **1–3**, this difference should be attenuated and may even be reversed [18]. The exception is the pair of energetically unfavorable conformers **3aaa** and **3eaa**, where the energy difference ΔE already in the gas phase inverts to -1.7 kJ/mol (in favor of the equatorial isomer).

A priori, stereoelectronic interactions in **1–3** should most strongly reflect on the lengths of the most long and polarizable bonds S=O and Si–Me. The elongation of the axial versus equatorial S=O bonds in **1–3**, $\Delta l(\text{SO}_{\text{ax-eq}})$, depends on the number and position of the α and α' -methyl groups and is excellently described by the equation (in pm):

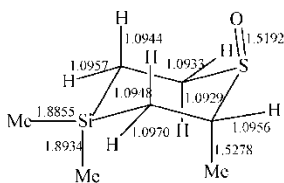
$$\Delta l(\text{SO}_{\text{ax-eq}}) = (0.406 \pm 0.008) - (0.184 \pm 0.006)n_{\text{ax}} - (0.050 \pm 0.006)n_{\text{eq}}$$

$$N = 6, R = 0.997, s_d = 0.01$$

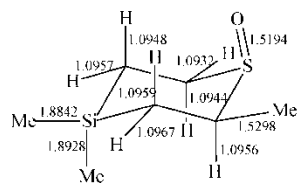
where n_{ax} and n_{eq} is the number of methyl groups α to SO in the axial and equatorial positions, respectively. The decrease of $\Delta l(\text{SO}_{\text{ax-eq}})$ with methyl substitution and its considerably higher



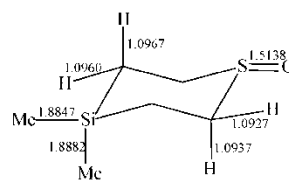
1a, $E = -1000.112324$ au, $\mu = 3.92$ D



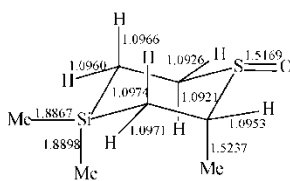
2aa, $E = -1039.435541$ au, $\mu = 4.00$ D



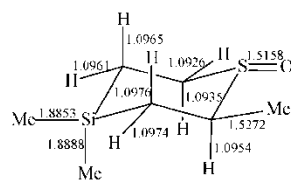
2ae, $E = -1039.438734$ au, $\mu = 3.85$ D



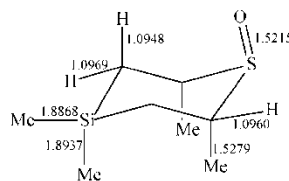
1e, $E = -1000.108797$ au, $\mu = 5.07$ D



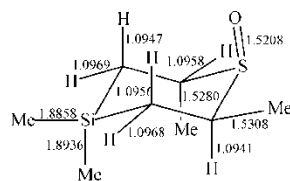
2ea, $E = -1039.433822$ au, $\mu = 4.83$ D



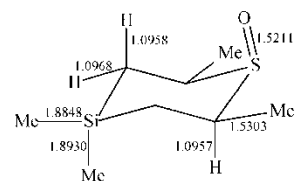
2ee, $E = -1039.435954$ au, $\mu = 4.85$ D



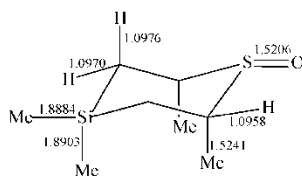
3aaa, $E = -1078.754712$ au, $\mu = 4.08$ D



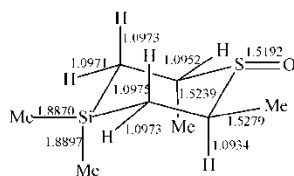
3aae, $E = -1078.761622$ au, $\mu = 3.94$ D



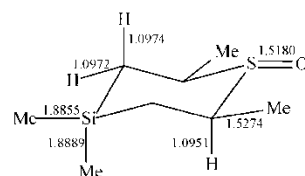
3aee, $E = -1078.764873$ au, $\mu = 3.79$ D



3eaa, $E = -1078.755359$ au, $\mu = 4.61$ D



3eae, $E = -1078.760873$ au, $\mu = 4.63$ D



3eee, $E = -1078.763086$ au, $\mu = 4.62$ D

SCHEME 4 Energies, dipole moments and selected bond distances in substituted 4-silathiane S-oxides.

sensitivity to replacement of axial than of equatorial protons by methyl groups is consistent with the $\sigma(\text{C-H}_{\text{ax}}) \rightarrow \sigma^*(\text{S=O})$ stereoelectronic interaction as the origin of the β -effect since the ability of a C–C bond to hyperconjugation is less than that of a C–H bond and since the effect is most profound for the antiperiplanar arrangement of the C–H_{ax} and S=O bonds.

Interestingly, the elongation of the Si–Me_{ax} over the Si–Me_{eq} bond in **1–3** depends on the orientation of the S=O group; for the S=O equatorial it does not go beyond 0.003 Å, whereas for the S=O axial it approaches or even exceeds 0.008 Å. The Si–C-3 and Si–C-5 bonds are by 0.002–0.003 Å shorter for the axial than for the equatorial sulfoxides **1–3**. We believe that this is a manifestation of the aforementioned buttressing effect of the S=O group on the C-3–H-3_{ax} and C-5–H-5_{ax} bonds and, circuitously, on the Si–C bonds. The buttressing effect, by analogy with that of the sulfinyl and sulfonyl groups in enamines [25] should result in shielding of the C-3 and C-5 carbons, *i.e.*, in the γ -effect, and this is what is observed in the spectra (table 1).

An experimental criterion which is useful for stereochemical assignment in six-membered heterocycles and allows one to estimate stereoelectronic interactions in them is the Perlin effect [26–34], that is, the difference between the values of direct constants $^1J_{\text{CH}}$ of the axial versus equatorial C–H bond adjacent to a heteroatom. Normal Perlin effect ($^1J_{\text{CH}_{\text{ax}}} < ^1J_{\text{CH}_{\text{eq}}}$) reflects elongation and weakening of the C–H_{ax} bond adjacent to N, O, or S atoms and was for a long time attributed to hyperconjugation of the $n_{\text{X}} \rightarrow \sigma^*(\text{C-H})$ type [32]. However, recently the concept of the $n_{\text{X}} \rightarrow \sigma^*(\text{C-H})$ hyperconjugation was rejected as primarily responsible for $^1J_{\text{CH}}$ (the Perlin effect) [35] and $^1J_{\text{CC}}$ coupling constants [36] at least, in ethers. Yet, as the authors specially emphasized [35, 36], their conclusion is not necessarily general and, therefore, depending on the energy gap between the interacting orbitals and their ability to delocalization, hyperconjugation effects might play an important and even the seminal role in determining the values of coupling constants.

That hyperconjugation of the type $\sigma(\text{C-H}_{\text{ax}}) \rightarrow \sigma^*(\text{S=O})$ is the case for compounds **1–5** is confirmed by analysis of the data presented in table 4. On going from **2ee–2ae**, that is, from SO_{eq} to SO_{ax}, the $^1J_{\text{CH}_{\text{ax}}}$ coupling constants in the α -position to the SO group substantially decrease: by 5.0 Hz for the 6-CH₂ group and by 4.2 Hz for the 2-CHMe group whereas the value of $^1J_{\text{CH}_{\text{eq}}}$ for H-6 is virtually insensitive ($\Delta J = 0.4$ Hz). Increase of the delocalization ability of the acceptor orbital $\sigma^*(\text{S=O})$, that is, going from sulfoxide **2ee** to sulfone **5**, also decreases $^1J_{\text{CH}_{\text{ax}}}$ by 2.7 Hz for the 6-CH₂ group and by 3.1 Hz for the 2-CHMe group. Introduction of the equatorial methyl group only slightly affects $^1J_{\text{CH}}$ values (**2ee** vs. **3eee** and **4** vs. **5**) whereas the axial methyl group brings about maximum changes of $^1J_{\text{CH}_{\text{ax}}}$ ($\Delta J = 6.5$ Hz on going from **2ae** to the equilibrium mixture of **3aae** and **3ae** – compare experimental values of $^1J_{\text{CH}(2)\text{ax}}$ for **2ae** 135.3 Hz and $^1J_{\text{CH}(6)\text{ax}}$ for **3ae** 141.8 Hz, table 4).

Yet, an alternative explanation based on the dipolar interaction [35, 36] cannot be irrevocably ruled out at least unless the behavior of $^1J_{\text{CH}}$ as a function of the HCSO dihedral angle is not monitored in the whole range from 0 to 180°. The investigated silathiane S-oxides probe it only of 60° for SO_{eq} and of 160° for SO_{ax} and do not allow going to small angles that would make it possible to distinguish between the hyperconjugation effects and dipolar interactions.

A novel and intriguing result is a small reverse Perlin effect on atoms C-3 and C-5 in sulfoxide **2ae** and sulfone **5**. This experimental observation was confirmed by the GIAO-B3LYP/6-311G(d,p) theoretical calculations of the NMR parameters (^1H and ^{13}C chemical shifts and $^1J_{\text{CH}}$ coupling constants) for compounds **2aa**, **2ae**, **2ea**, **2ee**, **3eee**, **3aae** and **3ae** performed on the optimized geometry and presented in tables 1 and 4. As can be seen from these data, the calculations qualitatively well reproduce the relative ^{13}C chemical shifts and $^1J_{\text{CH}}$ coupling constants, and especially the largest normal Perlin effect for 6-CH₂ in **2ae** and the reverse Perlin effect for 3-CH₂ and 5-CH₂ in **2ae**. Note that the reverse Perlin effect was also calculated for 3-CH₂ and 5-CH₂ in **2aa** but not in **2ea**. The same is true for **3aae**

and **3eae**: theory calculates the reverse Perlin effect for **3aae** and normal effect for **3eae**, that is consistent with the suggestion of the **3aae** \leftrightarrow **3eae** equilibrium made above from analysis of the ^{13}C chemical shifts. These results are suggestive of the seminal role of the axial arrangement of the β -SO group for the experimentally observed and theoretically proved reverse Perlin effect on the C-3 and C-5 atoms. It is in line with the buttressing effect of the S=O group that strengthens the C–H-3ax and C–H-5ax bonds and is responsible not only for the γ -effect itself but also for the reversed Perlin effect on these carbon atoms.

3. Conclusion

The stereochemistry and stereoelectronic effects in the products of lithiation/methylation of 4,4-dimethyl-4-silathiane S-oxide, that is, stereoisomers of 2,4,4-trimethyl-4-silathiane S-oxide and 2,4,4,6-tetramethyl-4-silathiane S-oxide, as well as 4,4-dimethyl-4-silathiane S,S-dioxide and 2,4,4-trimethyl-4-silathiane S,S-dioxide have been studied by ^1H and ^{13}C NMR spectroscopy and GIAO-B3LYP/6-311G(d,p) theoretical calculations, to rationalize different effects of the equatorial and axial sulfinyl group on the C–H bonds in the α - and β -position. The 2-Me group in 2,4,4-trimethyl-4-silathiane S-oxides is always equatorial whereas the SO group may occupy either the equatorial or axial position. 2,4,4,6-Tetramethyl-4-silathiane S-oxide exists in the form of the two isomers, the one with 2-Me, 6-Me and sulfinyl groups all equatorial, and the other one as an equilibrium mixture of the axial and equatorial sulfoxides with 2-Me axial and 6-Me equatorial. All compounds show the normal Perlin effect except for 2,4,4-trimethyl-4-silathiane S-oxide and S,S-dioxide possessing the axial S=O group and showing the reverse Perlin effect for the 3- and 5- CH_2 groups. The results are satisfactorily explained in terms of the $\sigma(\text{C–H}_{\text{ax}}) \rightarrow \sigma^*(\text{S=O})$ hyperconjugative interaction and the buttressing effect of the axial SO group for the α and β positions to the sulfinyl group.

4. Experimental

All solvents were dried and purified by standard procedures and stored over molecular sieves 4A. Merck Kieselgel 60 (35–70 mesh) was used for column chromatography. Melting points were determined with a Boetius apparatus (VEB Analytik) and are uncorrected. ^1H and ^{13}C NMR spectra were taken for CDCl_3 solutions on a Bruker DPX250 and Bruker AV400 spectrometers at 250.13 and 400.13 (^1H) and 62.9 and 100.60 (^{13}C) MHz. ^{29}Si NMR spectra were taken on a Bruker AV400 spectrometer at 79.46 MHz. Chemical shifts are given in ppm relative to tetramethylsilane. All experiments were performed at room temperature utilizing a 5 mm wide band probe.

The assignment of signals in the ^1H and ^{13}C NMR spectra was made by the use of the HSQC (Heteronuclear Single Quantum Correlation) [37] and HMBC (Heteronuclear Multiple Bond Correlation) [38] techniques. The proton chemical shifts were determined from analysis of cross sections of the 2D HSQC spectra. Direct coupling constants $^1J_{\text{CH}}$ for all compounds were obtained from cross sections of the 2D heteronuclear $\{^1\text{H}–^{13}\text{C}\}$ HSQC spectra recorded without wide band decoupling from ^{13}C by the use of the composite GARP pulse sequence. This technique allowed observing the non-distorted multiplets of the protons separated by direct coupling constant $^1J_{\text{CH}}$ in one-dimensional cross sections of the 2D spectra at the resonance frequency of the corresponding carbon atoms, and made it possible to unfailingly determine and assign coupling constants for the CH_2 fragments. Digital resolution for the proton channel in 2D heteronuclear $\{^1\text{H}–^{13}\text{C}\}$ HSQC experiments was 0.2 Hz.

4.1 Preparation of 4,4-dimethyl-4-silathiane S,S-dioxide 4

To a solution of 0.15 g (0.9 mmol) of 4,4-dimethyl-4-silathiane S-oxide in 4 mL of absolute CH_2Cl_2 at 0°C 0.23 g (1.3 mmol) of 75% *m*-chloroperbenzoic acid was added during 15 min. The solution was stirred for 1 h at 0°C and allowed to stay overnight in the fridge. The precipitate formed was filtered, the solution washed with 10% aqueous NaHCO_3 (3×50 mL) and dried over MgSO_4 . The crude product (0.23 g) was purified by column chromatography on silica gel with successive eluting with hexane, hexane–ether (7:1–1:1) and ether–MeOH (20:1–8:1). 0.11 g (65%) of sulfone **4** was isolated as white needles, mp 128 – 129°C . ^{29}Si NMR, CDCl_3 : -6.27 . Calcd (%) for $\text{C}_6\text{H}_{14}\text{O}_2\text{SSi}$: C, 40.41; H, 7.91; S, 17.98; Si, 15.75. Found: C, 39.83; H, 8.15; S, 18.54; Si, 15.86.

4.2 Preparation of 2,4,4-trimethyl-4-silathiane S-oxides

To 0.18 g (1.1 mmol) of 4,4-dimethyl-4-silathiane S-oxide in 1.7 mL of absolute THF at -78°C and stirring in an argon atmosphere 0.8 mL of 1.6 M. *n*-BuLi in hexane was added dropwise. The mixture was stirred at -78°C for 1 h, the solution of 0.48 g (3.4 mmol) MeI in 2 mL of THF added, stirred for 30 min at -78°C and 1.5 h at room temperature and decomposed with saturated solution of NH_4Cl , extracted with CH_2Cl_2 , dried over MgSO_4 . After removal of the solvent obtained 0.12 g of the crude product was obtained, whose NMR spectrum contained the signals of two isomeric 2-substituted sulfoxides **2ee** and **2ae** in the ratio of 3:1. Compounds **2ee** and **2ae** were separated using column chromatography with successive elution with hexane, hexane–ether (21:3), and ether–methanol (from 40:1 to 8:1). Sulfoxide **2ae** was obtained as an oil, and sulfoxide **2ee** as white crystals with m.p. 54 – 56°C . ^{29}Si NMR, CDCl_3 : -3.18 (**2ee**), -5.49 (**2ae**). Calcd (%) for $\text{C}_7\text{H}_{16}\text{SSiO}$: C, 47.68; H, 9.14; S, 18.18; Si, 15.93%. Found: C, 47.61; H, 9.08; S, 17.97; Si, 16.30.

4.3 Preparation of 2,4,4-trimethyl-4-silathiane S,S-dioxide 5

The CDCl_3 solution of ~ 50 mg (0.3 mmol) of sulfoxide **2eee** was oxidized with 90 mg (0.5 mmol) of 80% *m*-chloroperbenzoic acid in the NMR tube. After addition of MCPBA the mixture was vigorously shaken and allowed to stay at room temperature for 16–17 hours. The ^1H and ^{13}C NMR spectra showed no starting sulfoxide remaining in the mixture. ^{29}Si NMR, CDCl_3 : -4.90 .

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