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Stereoelectronic Structure and Self-Association of *N*-Trimethylsilylsulfonamides $RSO_2NHSiMe_3$ (R = Me, CF_3, Ph)

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Abstract—The effect of trimethylsilyl group Me_3Si on the intramolecular electronic interactions and acid-base properties of *N*-trimethylsilylmethanesulfonamide, *N*-trimethylsilyltriflamide, and *N*-trimethylsilylbenzenesulfonamide was studied by the methods of quantum chemistry (DFT/ B3LYP/6-311+G**, NBO-analysis). Structural effects of the O- and N-protonation of these *N*-trimethylsilylsulfonamides and their isostructural carbon analogs were investigated.

Keywords: *N*-trimethylsilylsulfonamides, IR spectroscopy, quantum-chemical calculations, self-association, intermolecular hydrogen bonding

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Sulfonamides possess a wide spectrum of biological activity and find application in medicine as antimicrobial agents, saluretics, inhibitors of carboanhydrase, peroral antidiabetic sulfanilamide drugs, non-nucleoside inhibitors of reverse transcriptase, inhibitors of HIV-1, etc. [1–7]. Similar to amides of carboxylic acids, sulfonamides are capable of formation of hydrogen bonds [8–13], both the oxygen and the nitrogen atoms being able to act as the center of basicity in these compounds. Thus, according to the data of NMR spectroscopy and quantum chemistry, the protonation at the nitrogen atom of the sulfonamide group is somewhat preferable than at the oxygen atom [9–11, 14–17]. However, the oxygen atom can also be involved in the formation of a hydrogen bond, and its spectroscopic basicity has been measured by IR spectroscopy by evaluating the constants of complex formation with MeOH and *p*-FC_6H_4OH [18, 19]. Similar to carboxamides, sulfonamides form hetero- and self-associates [8, 12, 13, 20–23]. Self-association is most pronounced in the derivatives of trifluoromethanesulfonic acid, since the presence of trifluoromethyl substituent at the sulfur atom decreases the basicity of the sulfonyl oxygen and simultaneously substantially increases the acidity of the NH group [10, 11, 24, 25]. The introduction of a silicon atom in the molecule results in substantial changes in its stereoelectronic structure and, consequently, in the physicochemical properties of the compounds. First representatives of triorganylsilyl sulfonamides were synthesized in the middle of the last century [26, 27]. *N*-Trimethylsilylcarboxamides are known to exist in solution as amido-imidate tautomers due to the migration of the trimethylsilyl group between the nitrogen and oxygen atoms, the amide form being 10–20 kcal/mol more stable than the imidate form [28–34] (Scheme 1).

Scheme 1.

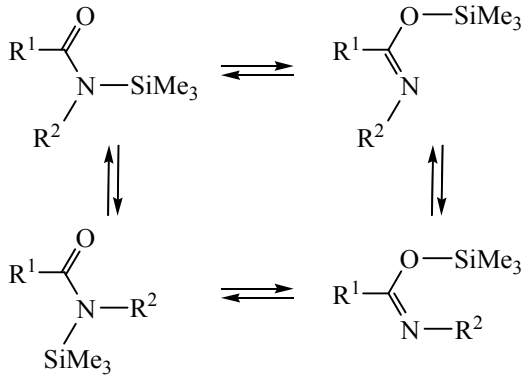


Table 1. Energies of the amide and imidate forms of compounds **I–III** (B3LYP/6-311+G**)

Amide	$-E_{amide}$, a.u.	$-E_{imidate}$, a.u.	ΔE(amide–imidate), kcal/mol
I	1053.315778	1053.295236	12.89
II	1351.115696	1351.094946	13.02
III	1245.092212	1245.070841	13.41

A similar process may occur in solutions of silylated sulfonamides. However, unlike trimethylsilylcarboxamides, these compounds, according to the data of ^{29}Si NMR spectroscopy, exist in solution mainly as O-silylated tautomers, whereas the *N*-silylated tautomer is observed only for compounds containing a strong electron-withdrawing group at the nitrogen atom [34]. Although, as mentioned above, sulfonamides form hydrogen bonds and are capable of formation of associates, the ability of the silylated sulfonamides to form hydrogen bonds is practically not studied. We have found only one investigation on the molecular structure of *N*-trimethylsilylmethanesulfonamide [35]. According to these data, the molecules of $MeSO_2NHSiMe_3$ in the crystal are bound into chain self-associates by intermolecular hydrogen bonds.

The goal of the present study is the investigation of the structure of *N*-trimethylsilylsulfonamides, their acid–base properties, and the ability to form hydrogen bonds. As the objects of investigation, *N*-trimethylsilylmethanesulfonamide (**I**), *N*-trimethylsilyltriflamide (**II**), *N*-trimethylsilylbenzenesulfonamide (**III**) and their isostructural carbon analogs *N*-*tert*-butylmethanesulfonamide (**IV**), *N*-*tert*-butyltriflamide (**V**), *N*-*tert*-butylbenzenesulfonamide (**VI**) were chosen.

N-Trimethylsilylsulfonamides **I–III** are readily hydrolyzed in water or alcohols, so it is impossible to measure their pK_a values in these media.

Quantum-chemical calculations of the energy of protonation and dissociation. Secondary sulfonamides can exist as amido-imidate tautomers [36, 37]. The data of quantum-chemical calculations suggest that the amide tautomers of compounds **I–III** are ca. 13 kcal/mol more stable than the imidate tautomers (Table 1). Therefore, all further calculations of the acid-base properties of *N*-trimethylsilylsulfonamides **I–III** and the isostructural *N*-*tert*-butylsulfonamides were carried out only for the most stable amide tautomers.

Total energies of the neutral molecules, their O- and N-protonated forms (*E*), energy difference of the O- and N-protonated forms ($\Delta E = E_O - E_N$), proton affinity (PA), and the energies of dissociation of the N–H bond of sulfonamides RSO_2NHMMe_3 (M = C, Si) are given in Tables 2, 3.

The protonation of *N*-trimethylsilylsulfonamides **I–III** and their isostructural organic analogs **IV–VI** at the nitrogen atom is 4–6 kcal/mol more preferable than at the oxygen atom. Similar results were obtained when studying the acid-base properties of a series of sulfonamides [10], whereas in carboxamides the protonation at the oxygen atom is preferable by energety due to the conjugation in the amide moiety, which increases the basicity of the carbonyl oxygen in the amide group. The basicity of the nitrogen and oxygen atoms is decreased in the derivatives of triflamide **II, IV** and increased in benzenesulfonamides **III, VI**.

The silicon atom increases the acidity of the NH group of *N*-trimethylsilylsulfonamides **I, II** by ca. 10 kcal/mol with respect to the isostructural carbon analogs **IV, V**. For *N*-trimethylsilylbenzenesulfonamide **III** this enhancement is less pronounced and equals to ~5 kcal/mol. The presence of the CF_3 group increases the acidity of the NH group both in the silylated and non-silylated sulfonamides.

Structural effects of the O- and N-protonation of amides I–VI. For amides **I–VI** the geometry of neutral molecules, O- and N-protonated forms, and the anionic form generated by dissociation of the N–H bond was calculated (Table 3). From the X-ray diffraction analysis, the N–S, S=O, and N–Si bond distances in amide **I** [35] are 1.602, 1.770, and 1.447 Å respectively. The calculated values are by 0.2–0.4 Å larger. The calculated angles SNH and SNSi (Table 3) are close to the experimental ones (111.46 and 127.84 respectively [35]).

Both protonation of molecules **I–VI** and dissociation of the N–H bond give rise to substantial changes in geometric characteristics of the amide fragment. For the O- and N-protonated forms these changes are oppositely directed with respect to the neutral amides, as is clearly seen from the correlation diagram (see figure). The O-protonation leads to the elongation of the S=O bond and the shortening of the S–N bond both in sulfonamides **I–III** and in their carbon analogs **IV–VI**. On the diagram, the O-protonated amides are located in the upper left corner

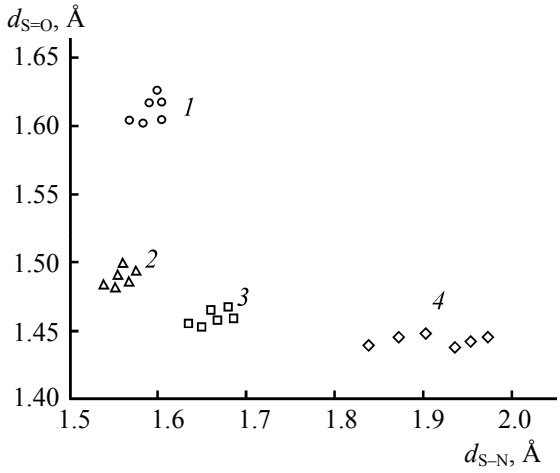
Table 2. Calculated proton affinities of the nitrogen and oxygen atoms and dissociation of N–H bond in amides **I–VI**

Amide	–*E*, a.u.	$\Delta E = \lvert E_O - E_N \rvert$	PA	$-E_{ion}$	*D*(N–H)
I	1053.3157779			1052.7626135	347.11
SOH^+	1053.6450552	–4.93	206.62		
NH^+	1053.6529166		211.55		
II	1351.1156957			1350.5855358	332.67
SOH^+	1351.4256584	–4.06	194.50		
NH^+	1351.4321298		198.56		
III	1245.0922121			1244.5429115	344.69
SOH^+	1245.4327451	–6.15	213.68		
NH^+	1245.4425395		219.83		
IV	801.8364480			801.2647443	358.74
SOH^+	802.1666747	–10.09	207.22		
NH^+	802.1827525		217.31		
V	1099.6252707			1099.078072	343.37
SOH^+	1099.9333897	–16.25	193.34		
NH^+	1099.9592934		209.59		
VI	993.6195743			993.0590581	351.72
SOH^+	993.9589412	–9.86	212.95		
NH^+	993.9746499		222.81		

having the longest S=O and the shortest S–N bonds (see figure, curve *1*). The protonation of the nitrogen atom leads to the elongation of the S–N bond and shortening of the S=O interatomic distance, and, respectively, the N-protonated amides are shifted to the right bottom corner of the diagram (see figure, curve *4*). These results are consistent with those obtained in investigation of the structure of the O- and N-protonated forms of lactames [38]. The dissociation of the N–H bond results in the elongation of the S=O bond and shortening of the S–N bond as compared to neutral molecules of amides **I–VI**.

NBO analysis. The analysis of electronic interactions leading to changes in the acid-base properties of amides **I–VI** was performed by calculation of the orbital characteristics using the NBO method at the B3LYP/6-311+G** level of theory. The calculated second-order energies of electron delocalization $E^{(2)}$ related with the charge transfer from lone electron pairs (LEP) of nitrogen and oxygen on the antibonding π*- and σ*-orbitals are presented in Table 4. According to the results of the NBO analysis, the interaction between the nitrogen and sulfur atoms in the molecules of sulfonamides has predominantly the electrostatic nature, the π-conjugation is lacking, and the S–N bond is strongly polarized due to the reverse hyperconjugation [10, 39, 40].

Both in *N*-trimethylsilylsulfonamides **I–III** and in their isostructural carbon analogs **IV–VI** the largest energy corresponds to the interaction of the LEP of oxygen with the σ*-orbitals of the S–C and N–S bonds: $n_O \rightarrow \sigma^*_{S-C}$ (18–25 kcal/mol) and $n_O \rightarrow \sigma^*_{S-C}$



Correlation of the S–N and S=O bond distances in sulfonamides **I–VI**: (*1*) O-protonated forms; (*2*) anionic forms; (*3*) neutral molecules; and (*4*) N-protonated forms.

Table 3. Calculated geometrical characteristics of sulfonamides **I–VI**, their forms protonated at oxygen (OH^+) and nitrogen (NH^+), and the deprotonated forms

Amide	N–S	S=O	N–H	N–Si/C(t)	SNH	SNSi/C(t)
I	1.662	1.464	1.014	1.797	110.81	126.71
II	1.636	1.454	1.014	1.815	111.33	127.92
III	1.662	1.463	1.014	1.796	111.01	126.78
IV	1.686	1.462	1.015	1.497	106.51	124.57
V	1.652	1.453	1.014	1.505	109.07	126.57
VI	1.684	1.464	1.016	1.497	106.46	125.08
I-OH^+	1.592	1.616	1.019	1.884	108.62	133.28
II-OH^+	1.571	1.603	1.019	1.922	113.73	128.19
III-OH^+	1.605	1.615	1.017	1.878	113.38	128.18
IV-OH^+	1.607	1.602	1.016	1.546	114.05	126.65
V-OH^+	1.582	1.601	1.017	1.561	114.68	126.93
VI-OH^+	1.598	1.625	1.015	1.533	112.88	129.26
I-NH^+	1.876	1.444	1.023	1.987	106.85	117.18
II-NH^+	1.842	1.439	1.025	2.020	107.92	117.33
III-NH^+	1.905	1.446	1.023	1.956	105.64	117.73
IV-NH^+	1.958	1.441	1.025	1.556	100.65	123.96
V-NH^+	1.937	1.438	1.026	1.567	100.97	123.43
VI-NH^+	1.973	1.444	1.023	1.554	103.02	120.80
$\mathbf{I}^-$	1.564	1.495		1.702		128.53
$\mathbf{II}^-$	1.539	1.481		1.715		130.33
$\mathbf{III}^-$	1.557	1.491		1.706		129.42
$\mathbf{IV}^-$	1.573	1.489		1.466		121.96
$\mathbf{V}^-$	1.552	1.482		1.474		123.31
$\mathbf{VI}^-$	1.568	1.486		1.471		122.59

(22–25 kcal/mol). The energy of interaction of the LEP of nitrogen with the σ*-orbitals of the Si–C bonds in amides **I–III** (C–C bonds in amides **IV–VI**), S–C and S=O bonds is substantially lower and depends on the substituents at the nitrogen.

The calculations have shown that introduction of the silicon atom in the molecule increases the electron density on the nitrogen atom. Therewith, the N–S bond in sulfonamides **I–III** is more polar than in their carbon analogs **IV–VI**.

Self-association of N-trimethylsilylsulfonamides I–III in CCl_4 solution. A specific feature of *N*-trimethylsilylsulfonamides is the presence of free NH groups not only in solution but also in the solid state and in neat liquid. The stretching vibration bands of NH groups in the IR spectra of amides **I–III** appear in the range 3386–3220 cm^{-1}. In diluted solutions in an inert solvent (CCl_4) the amides exist as monomeric molecules characterized by high-frequency absorption band ν(NH) 3365–3386 cm^{-1}, and form self-associates upon increasing the concentration [ν(NH) = 3237–3249 cm^{-1}] (Table 5).

Table 4. Data of NBO analysis

Molecule	Interaction	$E^{(2)}$, kcal/mol	Molecule	Interaction	$E^{(2)}$, kcal/mol
I	$n_N \rightarrow \sigma^*_{Si–C}$	9.34	**IV**	$n_N \rightarrow \sigma^*_{C–C}$	8.39
	$n_N \rightarrow \sigma^*_{S–C}$	6.86		$n_N \rightarrow \sigma^*_{S–C}$	4.58
	$n_N \rightarrow \sigma^*_{S=O}$	5.38		$n_N \rightarrow \sigma^*_{S=O}$	5.28
	$n_{O1,2} \rightarrow \sigma^*_{N–S}$	22.72, 24.24		$n_{O1,2} \rightarrow \sigma^*_{N–S}$	22.95, 25.96
	$n_{O1,2} \rightarrow \sigma^*_{S–C}$	17.54, 18.30		$n_{O1,2} \rightarrow \sigma^*_{S–C}$	18.41, 17.98
II	$n_N \rightarrow \sigma^*_{Si–C}$	8.24	**V**	$n_N \rightarrow \sigma^*_{C–C}$	7.74
	$n_N \rightarrow \sigma^*_{S–C}$	11.93		$n_N \rightarrow \sigma^*_{S–C}$	9.99
	$n_N \rightarrow \sigma^*_{S=O}$	5.47		$n_N \rightarrow \sigma^*_{S=O}$	4.76
	$n_{O1,2} \rightarrow \sigma^*_{N–S}$	24.21, 21.94		$n_{O1,2} \rightarrow \sigma^*_{N–S}$	22.93, 24.34
	$n_{O1,2} \rightarrow \sigma^*_{S–C}$	25.34, 25.25		$n_{O1,2} \rightarrow \sigma^*_{S–C}$	24.67, 24.75
III	$n_N \rightarrow \sigma^*_{Si–C}$	1.21	**VI**	$n_N \rightarrow \sigma^*_{C–C}$	8.97
	$n_N \rightarrow \sigma^*_{S–C}$	7.07		$n_N \rightarrow \sigma^*_{S–C}$	4.34
	$n_N \rightarrow \sigma^*_{S=O}$	10.30		$n_N \rightarrow \sigma^*_{S=O}$	6.48
	$n_{O1,2} \rightarrow \sigma^*_{N–S}$	21.85, 24.00		$n_{O1,2} \rightarrow \sigma^*_{N–S}$	22.08, 25.85
	$n_{O1,2} \rightarrow \sigma^*_{S–C}$	18.09, 17.95		$n_{O1,2} \rightarrow \sigma^*_{S–C}$	18.17, 17.76

Table 5. Frequencies of stretching vibrations (cm^{-1}) of free and associated NH groups in the IR spectra of amides **I–III**

Amide	NH_{free}		NH_{ass}		Δν(N–H)	
	CCl_4	KBr	CCl_4	KBr	CCl_4	KBr
I	3386	–	3238	3220	148	–
II	3365	3383[a]	3249	3268[a]	116	115[a]
III	3382	3348[a]	3237	3244[a]	149	104[a]

[a] Neat liquid.

Table 6. Calculated characteristics of the dimers of compounds **I–III**. Total energies (–*E*) and energies of formation of the dimers (Δ*E*), dipole moments, shift of the NH stretching vibrations with respect to the monomer, H-bond distance

Dimer	–*E*, a.u.	Δ*E*, kcal/mol	μ, D	Δν(N–H)	*l*, Å
Cyclic **I**	2106.6530078	13.46 (6.73)[a]	2.18	200	1.898
Linear **I**	Converted to cyclic dimer				
Cyclic **II**	2702.2514110	12.56 (6.28)[a]	2.04	180	1.910
Linear **II**	2702.2426041	7.04	3.83	100	1.969
Cyclic **III**	2490.2056239	13.3 (6.65)[a]	2.77	180	1.934
Linear **III**	Converted to cyclic dimer				

[a] Energy of intermolecular hydrogen bond calculated per one H-bond.

N-Trimethylsilylmethanesulfonamide **I** in the crystal is fully associated (KBr), whereas amides **II** and **III** even in the crystal or in microlayer exist in the equilibrium between the monomeric and associated forms. The simplest of associates formed by amides **I–III** are chain and cyclic dimers. In order to elucidate what dimers these compounds are prone to form in inert media we performed quantum-chemical

calculations of their structure, energy, dipole moment, as well as vibrational modes of the dimers (Table 6). The calculated differences of the stretching vibration frequencies of the free and associated NH groups [Δν(NH)] are compared with the data of the IR spectra.

The spectral shift Δν(NH) for amide **II** in KBr/neat liquid and an CCl_4 solution practically coincide (Table 6) suggesting the formation of associates of the same type. According to calculations (Table 6) this spectral shift is indicative of a linear self-associate. *N*-Trimethylsilylsulfonamides **I** and **III** have large spectral shifts of the NH stretching vibration bands of self-associates with respect to the monomeric molecules [Δν(NH) ~150 cm^{-1}, Table 6]. This is indicative of the formation of stronger hydrogen bonds typical of cyclic associates, just those which sulfonamides **I** and **III** form in CCl_4 solution, although in the crystal compound **I**, according to the XRD data, it forms chains by means of H-bonds of 2.117 Å length [35], apparently, due to the packing effects. The comparison of the experimental and theoretical spectral shifts of *N*-trimethylsilyltriflamide **II** suggests that in CCl_4 solution it forms linear associates, unlike the earlier studied *N*-methyltriflamide, which in CCl_4 solution forms two types of self-associates, both linear and cyclic [41].

EXPERIMENTAL

IR spectra of solutions were recorded on a FTIR Varian 3100 spectrophotometer. Quantum chemical calculations were performed using the GAUSSIA*N*-09 program package [42]. NBO analysis was performed using the GAUSSIA*N*-03 program on the pre-optimized geometry at the DFT level with 6-311+G** basis set [43, 44]. Compounds **I–III** were synthesized according to [45].

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