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S-(Trimethoxysilylmethyl)- and *S*-(Silatranylmethyl)isothiuronium Halides and Their N-Substituted Derivatives

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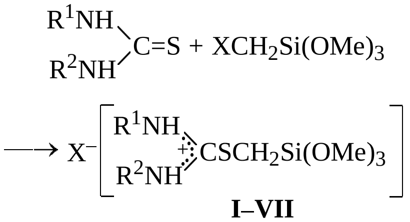
Abstract—Previously unknown *S*-(trimethoxysilylmethyl)- and *S*-(silatranylmethyl)isothiuronium halides and their N-substituted derivatives were prepared. According to the IR and UV spectra, these compounds exist in the solid state and in methanol and acetonitrile solutions in the form of two equilibrium salt structures: those with the positively charged nitrogen and carbon atoms, or predominantly in one of these. In solutions of the iodides in highly polar acetonitrile, the first salt structure can occur in an equilibrium with its dissociation products, *S*-organylisothiourea (or its N-substituted derivative) and hydrogen iodide.

Organosilicon derivatives of thiourea exhibit a wide spectrum of biological activity and have a number of valuable properties. For example, N^1,N^2-bis(triethylsilylpropyl)- and N^1,N^2-bis(triethoxysilylpropyl)thioureas exhibit antispasmodic activity, showing at the same time no toxicity and no cancerogenic and mutagenic effects [1, 2]. Some derivatives of these compounds containing *N*-organosilicon and *S*-inden-3-one substituents inhibit aggregation of thrombocytes [3]. The product of hydrolytic polycondensation of N^1,N^2-bis(triethoxysilylpropyl)thiourea is an effective cation-exchange sorbent binding ions of many metals from aqueous solutions and absorbing toxic and mutagenic components of tobacco smoke [4, 5]. *S*-(Triorganylsilylmethyl)isothiuronium chlorides and their N-substituted derivatives have been patented as antiphlogistics and analgetics [6].

Proceeding with the studies in the field of sulfur-containing alkyl(trialkoxy)silanes [7, 8] and 1-alkylsilatranes [8–11] in which the sulfur and silicon atoms form the SCH_2Si fragment, we prepared previously unknown *S*-(trimethoxysilylmethyl)- and *S*-(silatranylmethyl)isothiuronium halides and their N-substituted derivatives. *S*-(Trimethoxysilylmethyl)isothiuronium halides and their N-substituted derivatives were prepared by the reactions of thiourea and its N-substituted derivatives with (halomethyl)trimethoxysilanes (Scheme 1).

Scheme 1.



I–**VII**

$R^1 = R^2 = H$, X = Cl (**I**), I (**II**); $R^1 = R^2 = Me$, X = I (**III**); $R^1 = H$, $R^2 = Ph$, X = Br (**IV**), I (**V**); $R^1 + R^2 = (CH_2)_2$, X = Cl (**VI**), I (**VII**).

The reactions of thiourea, N^1,N^2-dimethylthiourea, and *N*-phenylthiourea with (halomethyl)trimethoxysilanes were performed in refluxing methanol, and the reactions of N^1,N^2-ethylenethiourea (imidazoline-2-thione) with (chloromethyl)- and (iodomethyl)trimethoxysilanes, in refluxing acetonitrile. At the reaction time from 4 to 14 h (depending on the starting reactants), compounds **I**–**VII** are formed in almost quantitative yield. The yields, melting points, and chemical shifts in the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **I**–**VII** are listed in Table 1.

The reactions of *S*-(trimethoxysilylmethyl)isothiuronium halides and their N-substituted derivatives with tris(2-hydroxyethyl)amine mainly yield the corresponding *S*-(silatranylmethyl)isothiuronium halides and their N-substituted derivatives (Scheme 2).

The reactions were performed in a methanol or chloroform solution. They occurred fairly vigorously without a catalyst and were complete in 1–2 min. The yield of **VIII**, **IX**, **XI**, and **XIII**–**XVI** exceeded 80%.

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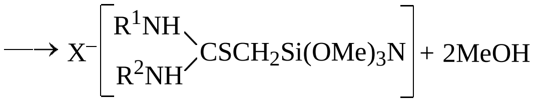
Table 1. Yields, melting points, and ^1H, ^{13}C, and ^{29}Si NMR spectra of *S*-(trimethoxysilylmethyl)isothiuronium halides **I–VII**

Comp. no	Yield, %	mp, °C	Chemical shift, δ, ppm			
			solvent	^1H	^{13}C	^{29}Si
I	90	68–70	DMSO-d_6	2.62 s (2H, CH_2Si), 3.55 s [9H, $Si(OMe)_3$], 9.24 s (4H, NH_2)	9.59 (CSi), 51.14 (SiOC), 172.40 (NCS)	–51.30
II	96	110–112	DMSO-d_6	2.61 s (2H, CH_2Si), 3.55 s [9H, $Si(OMe)_3$], 8.94 s (4H, NH_2)	9.07 (CSi), 50.80 (SiOC), 171.34 (NCS)	–51.52
III	95	58–60	$CDCl_3$	2.62 s (2H, CH_2Si), 3.06, 3.18 d (6H, MeN), 3.62 s [9H, $Si(OMe)_3$], 8.08, 8.18 d (2H, NH)	11.51 (CSi), 30.53, 32.00 d (MeN), 51.41 (SiOC), 169.49 (NCS)	–53.69
IV	89	82–84	$CDCl_3$	2.68 s (2H, CH_2Si), 3.55 s [9H, $Si(OMe)_3$], 7.30–7.36 m (5H, Ph), 9.45 (NH_2)[a]	10.56 (CSi), 51.12 (SiOC), 126.04 (C_o), 128.49 (C_p), 129.56 (C_m), 134.70 (C_i), 173.72 (NCS)	–53.14
V[b]	94	–	$CDCl_3$	2.65 s (2H, CH_2Si), 3.60 s [9H, $Si(OMe)_3$], 7.35–7.43 m (5H, Ph), 9.10 (NH_2)\$ua	11.93 (CSi), 51.43 (SiOC), 126.13 (C_o), 129.00 (C_p), 129.84 (C_m), 134.05 (C_i), 173.82 (NCS)	–53.60
VI	92	135–137	$CDCl_3$	2.61 s (2H, CH_2Si), 3.47 s [9H, $Si(OMe)_3$], 3.81 s (4H, $CH_2–CH_2$), 10.45 s (2H, 2NH)	10.46 (CSi), 45.22 ($CH_2–CH_2$), 50.82 (SiOC), 172.35 (NCS)	–53.38
VII	96	108–110	DMSO-d_6	2.62 s (2H, CH_2Si), 3.56 s [9H, $Si(OMe)_3$], 3.87 s (4H, $CH_2–CH_2$), 10.03 s (2H, 2NH)	9.92 (CSi), 45.35 ($CH_2–CH_2$), 50.85 (SiOC), 170.77 (NCS)	–52.10

[a] Center of a broadened singlet. [b] Oily substance.

Scheme 2.

I–VII + $(HOCH_2CH_2)_3N$



$$\longrightarrow X^-\left[\begin{matrix}R^1NH\\ R^2NH\end{matrix}\!\!>\!CSCH_2Si(OMe)_3N\right] + 2MeOH$$

VIII, IX, XI, XIII–XVI

$R^1 = R^2 = H$, X = Cl (**VIII**), I (**IX**); $R^1 = R^2 = Me$, X = I (**XI**); $R^1 = H$, $R^2 = Ph$, X = Br (**XIII**), I (**XIV**); $R^1 + R^2 = (CH_2)_2$, X = Cl (**XV**), I (**XVI**).

We found, however, that *S*-(silatranylmethyl)isothiuronium halides and their N-substituted derivatives are not the only products of the reactions of the corresponding trimethoxysilyl derivatives with tris(2-hydroxyethyl)amine. In almost all the cases, the corresponding tris(2-hydroxyethyl)ammonium halides were formed as by-products, but their yield did not exceed 10%. In most cases, we failed to isolate any other products of the side dehydrohalogenation reaction. Only from the reaction of *S*-(trimethoxysilylmethyl)-*N*-phenylisothiuronium bromide with tris(2-hydroxyethyl)amine we isolated, along with *S*-(silatranylmethyl)-*N*-phenylisothiuronium bromide **XIII** and tris(2-hydroxyethyl)ammonium bromide, also *S*-(silatranylmethyl)-*N*-phenylisothiurea **XVII** in ~7% yield.

$$\begin{matrix}PhN\\ H_2N\end{matrix}\!\!\begin{matrix}\diagdown\!\!\diagdown\\ \diagup\end{matrix}CSCH_2Si(OCH_2CH_2)_3N$$

XVII

S-(Silatranylmethyl)isothiuronium halides and their N-substituted derivatives **VIII**, **IX**, **XI**, **XIV**, and **XVI** were also prepared starting from the corresponding thioureas and 1-(halomethyl)silatranes (Scheme 3).

Scheme 3.

$$\begin{matrix}R^1NH\\ R^2NH\end{matrix}\!\!>\!C{=}S + XCH_2Si(OCH_2CH_2)_3N$$

⟶ **VIII, IX, XI, XIV, XVI**

The reactions of thiourea, N^1,N^2-dimethylthiourea, and *N*-phenylthiourea with the most active 1-(iodomethyl)silatrane were performed in refluxing butanol. The yield of iodides **IX**, **XI**, **XIV**, and **XVI** at the reaction time of 10–12 h reached ~90%. In the reactions

Table 2. Yields, melting points, and elemental analyses of *S*-(silatranylmethyl)isothiuronium halides and their N-substituted derivatives **VIII**–**XVI**, and also of compound **XVII**

Comp. no	Yield, %[a]	mp, °C	Found, %						Formula	Calculated, %					
			C	H	N	S	Si	X		C	H	N	S	Si	X
VIII	82 (2) 87 (3)	270–272 266–268	31.87	6.17	14.23	10.56	9.17	11.91	$C_8H_{18}ClN_3O_3SSi$	32.04	6.03	14.01	10.69	9.36	11.81
IX	86 (2) 90 (3)	246–248 240–242	24.41	4.58	10.14	8.26	6.87	32.05	$C_8H_{18}IN_3O_3SSi$	24.55	4.64	10.74	8.19	7.18	32.44
X	78 (3) 84 (2)	292–294 240–242	36.48	6.57	12.68	9.67	8.34	10.68	$C_{10}H_{22}ClN_3O_3SSi$	36.63	6.76	12.81	9.78	8.57	10.81
XI	91 (3) 83 (3)	235–237	28.35	5.14	9.87	7.38	6.54	29.91	$C_{10}H_{22}IN_3O_3SSi$	28.64	5.29	10.02	7.64	6.70	30.27
XII	83 (3)	245–247	44.23	5.99	10.87	8.67	7.40	9.43	$C_{14}H_{22}ClN_3O_3SSi$	44.73	5.89	11.17	8.53	7.47	9.43
XIII	70 (3) 83 (2)	244–246 245–247	29.14	5.56	10.40	7.51		30.73	$C_{14}H_{22}BrN_3O_3SSi$	28.78	4.83	10.06	7.68		30.43
XIV	87 (3)	240–242	40.38	4.97	9.54	7.28	6.32	19.70	$C_{14}H_{22}IN_3O_3SSi$	40.00	5.28	10.00	7.62	6.68	27.15
XV	86 (2) 88 (2)	270–272 308–310	36.34	5.02	9.06	6.72		26.85	$C_{10}H_{22}ClN_3O_3SSi$	35.96	4.74	8.98	6.85		27.15
XVI	79 (3)	312–315	36.54	5.81	12.67	9.73	8.23	10.51	$C_{10}H_{22}IN_3O_3SSi$	36.85	6.18	12.89	9.84	8.62	10.88
XVII	7	192–194	50.05	6.37	11.96	9.55	7.83		$C_{14}H_{21}N_3O_3SSi$	49.53	6.23	12.38	9.44	8.27	

[a] The synthesis scheme is given parentheses.

of less active 1-(chloromethyl)silatrane with thiourea and *N*-phenylthiourea in refluxing butanol, the yield of the corresponding chlorides **VIII** and **XII** in 24 h did not exceed 50%. However, when performed in DMF at 120–125°C, these reactions gave chlorides **VIII** and **XII** in the yield exceeding 80% at the reaction time of 4 and 6 h, respectively.

S-(Silatranylmethyl)isothiuronium halides and their N-substituted derivatives **VIII**–**XVI** are colorless high-melting finely crystalline compounds. Similarly to **I**–**VII**, they are readily soluble in lower alcohols, water, and DMSO. However, in contrast to trimethoxysilyl derivatives **I**–**VII**, silatranyl derivatives **VIII**–**XVI** are poorly soluble in $CHCl_3$ and CH_3CN and are hydrolyzed with water considerably more slowly.

The yields, melting points, and elemental analyses of *S*-(silatranylmethyl)isothiuronium halides and their N-substituted derivatives **VIII**–**XVI**, and also of compound **XVII** are listed in Table 2.

The ^1H, ^{13}C, and ^{29}Si NMR chemical shifts of **VIII**–**XVI** are listed in Table 3. The signals of the $SiCH_2$ protons in the ^1H NMR spectra of **VIII**–**XVI** are shifted upfield by 0.7–0.8 ppm relative to the signals of the same protons in the spectra of **I**–**VII** (Table 1). Contrastingly, the ^{13}C NMR signals of the $SiCH_2$ group in the spectra of **VIII**–**XVI** are shifted downfield by ~70 ppm relative to the same group in the spectra of **I**–**VII**. At the same time, the ^{13}C NMR signal of the NCS unit in the spectra of **VIII**–**XVI** is only slightly ($\Delta\delta_C$ 1–1.5 ppm) shifted downfield relative to **I**–**VII**. The signals of the MeN and NH protons in the ^1H NMR spectra of **III** (Table 1) are doublets. At the same time, in the ^1H NMR spectra of **X** and **XI** (Table 3), the signals of the similar protons are singlets. In the ^1H NMR spectrum of **XVII**, the δ values for the CH_2Si, NCH_2, and OCH_2 proton signals are close to those in the spectra of **XII**–**XIV**. However, the ^{13}C NMR signals of the C=N group and benzene ring are strongly shifted (upfield and downfield, respectively) relative to the same carbon atoms in the spectra of **XII**–**XIV**. The δ_C values for the C=N and C_H(benzene) carbon atoms in the spectrum of **XVII** are typical of the related Schiff bases [12].

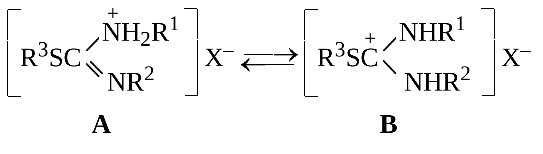
Data on the sites of predominant localization of the positive charge in *S*-(trimethoxysilylmethyl)- and *S*-(silatranylmethyl)isothiuronium halides and their N-substituted derivatives in the solid state and in methanol and acetonitrile solutions can be derived from the IR spectra of **I** and **VIII**–**XIV**, UV spectra of **I**, **VI**, **VIII**, **IX**, **XI**, and **XIV**, and spectra of the model compounds: *S*-methylisothiuronium iodide **XX** and *S*-methyl-N^1,N^2-dimethylisothiuronium iodide **XXI** (Table 4).

Table 3. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of *S*-(silatranylmethyl)isothiuronium halides and their N-substituted derivatives **VIII–XVI**, and also of compound **XVII** in DMSO-d_6

Comp. no	Chemical shift, δ, ppm		
	^{1}H	^{13}C	^{29}Si
VIII	1.83 s (2H, CH_2Si), 2.94 t (6H, CH_2N), 3.69 t (6H, OCH_2), 8.79, 9.07 d (4H, NH_2)	16.71 (CSi), 50.58 (CN), 57.24 (OC), 175.65 (NCS)	–81.87
IX	1.82 s (2H, CH_2Si), 2.94 t (6H, CH_2N), 3.67 t (6H, OCH_2), 8.54 s (4H, NH_2)	16.50 (CSi), 50.14 (CN), 56.78 (OC), 174.50 (NCS)	–82.12
X	1.81 s (2H, CH_2Si), 2.87 s (6H, MeN), 2.95 t (6H, CH_2N), 3.70 t (6H, OCH_2), 8.44, 9.34 d (4H, NH)	15.86 (CSi), 29.83, 30.83 d (MeN), 50.03 (CN), 56.68 (OC), 170.20 (NCS)	–82.07
XI	1.78 s (2H, CH_2Si), 2.89 s (6H, MeN), 2.97 t (6H, CH_2N), 3.71 t (6H, OCH_2), 8.31, 8.69 d (4H, NH)	15.74 (CSi), 30.08, 30.56 d (MeN), 50.07 (CN), 56.74 (OC), 171.20 (NCS)	–82.36
XII	1.92 s (2H, CH_2Si), 2.92 t (6H, CH_2N), 3.67 t (6H, OCH_2), 5.50, 9.40 (3H, NH + NH_2), 7.27–7.50 m (5H, Ph)	16.51 (CSi), 50.02 (CN), 56.75 (OC), 125.63 (C_o), 127.81 (C_p), 129.70 (C_m), 135.50 (C_i), 173.71 (NCS)	–82.18
XIII	1.92 s (2H, CH_2Si), 2.93 t (6H, CH_2N), 3.68 t (6H, OCH_2), 5.25, 9.40 (NH + NH_2), 7.28–7.50 m (5H, Ph)	16.78 (CSi), 50.10 (CN), 56.78 (OC), 125.73 (C_o), 127.98 (C_p), 129.83 (C_m), 135.46 (C_i), 173.37 (NCS)	–82.06
XIV	1.97 s (2H, CH_2Si), 2.94 t (6H, CH_2N), 3.69 t (6H, OCH_2), 8.95 (NH), 7.28–7.51 m (5H, Ph)	16.79 (CSi), 50.06 (CN), 56.73 (OC), 125.68 (C_o), 127.99 (C_p), 129.81 (C_m), 135.25 (C_i), 173.11 (NCS)	–82.23
XV	1.93 s (2H, CH_2Si), 2.93 t (6H, CH_2N), 3.69 t (6H, OCH_2), 3.78 s (4H, CH_2CH_2), 10.07 s (2H, NH)	16.61 (CSi), 45.00 (C–C), 50.18 (CN), 56.71 (OC), 174.16 (NCS)	–82.25
XVI	1.90 s (2H, CH_2Si), 2.94 t (6H, CH_2N), 3.68 t (6H, OCH_2), 3.80 s (4H, CH_2CH_2), 9.55 s (2H, NH)	16.66 (CSi), 44.98 (C–C), 50.09 (CN), 56.66 (OC), 174.16 (NCS)	–82.51
XVII	1.97 s (2H, CH_2Si), 2.81 t (6H, $3NCH_2$), 3.78 t (6H, $3OCH_2$), 7.18–7.33 m (5H, Ph)	15.94 (CSi), 50.08 (NC), 120.44 (C_p), 120.65 (C_o), 127.66 (C_m), 147.77 (C_i), 158.42 (NCS)	–75.8

In the IR spectrum of **VIII**, there is a broad strong band in the range 2900–3100 cm^{-1}, characteristic of ν(N^+H_3) stretching vibrations [13]. The spectra also contain the ν(NH_2) stretching bands at 3260 and 3300 cm^{-1}. These bands are shifted toward higher frequencies relative to the ν(NH_2) bands in the IR spectrum of thiourea **XVIII** [ν(NH_2) 3170–3270 cm^{-1}]. The ν(N^+H_3) and ν(NH_2) stretching bands with close frequencies are also present in the IR spectra of **I**, **IX**, and model *S*-methylisothiuronium iodide **XX**. These spectroscopic data show that compounds **I**, **VIII**, **IX**, and **XX** exist in the solid state in the form of two equilibrium salt structures with the positively charged N (**A**) or C (**B**) atoms (Scheme 4).

Scheme 4.



For R^1, R^2, R^3, and X, see above.

The IR spectrum of *S*-(silatranylmethyl)-*N*^{1},*N*^{2}-dimethylisothiuronium chloride **X** contains the absorption bands ν(N^+H_2) in the range 2700–3000 cm^{-1} and ν(NH) in the range 3100–3200 cm^{-1}, which can also belong to equilibrium structures **A** and **B**. On the contrary, in the IR spectra of iodides **XI** amd **XXI**, only the ν(NH) stretching vibration bands are observed; these bands (3150–3250 cm^{-1}) are somewhat shifted toward lower frequencies relative to ν(NH) in the IR spectrum of *N*^{1},*N*^{2}-dimethylthiourea **XIX** [ν(NH) 3200–3300 cm^{-1}]. This fact suggests that iodides **XI** and **XXI** mainly occur in the salt form with the positively charged carbon atom (**B**).

The IR spectra of *S*-(silatranylmethyl)-*N*-phenylisothiuronium bromide (**XIII**) and iodide (**XIV**) contain the bands ν(N^+H_2) at 2700–3000 cm^{-1} and ν(NH), ν(NH_2) at 3250–3390 cm^{-1}; the IR spectra of *S*-(silatranylmethyl)-*N*^{1},*N*^{2}-ethyleneisothiuronium chloride (**XV**) and iodide (**XVI**) contain the bands ν(N^+H_2) at 2700–3100 cm^{-1} and ν(NH) at 3100–3300 cm^{-1}.

These data show that, in compounds **XIII**–**XVI**, forms **A** and **B** coexist.

Along with the stretching vibration bands ν(NH), ν(NH_2), and ν(N^+H_3), the IR spectra of almost all the compounds studied contain bands in the range 1610–1640 cm^{-1} belonging, apparently, to the δ(NH) bending and ν(C=N) stretching vibrations [14]. Compounds **XV** and **XVI** are exceptions; in their spectra, the related strong bands are located at ~1540 cm^{-1}. The low-frequency shift allows assignment of these bands to the ν(C=N) stretching vibrations in the ring [14].

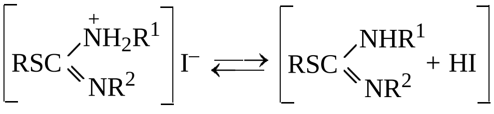
The UV spectra of thiourea **XVII** and *N*^{1},*N*^{2}-dimethylthiourea **XIX** contain bands of π–π* and *n*–π* electronic transitions [15]. In the UV spectra of solutions of *S*-methylisothiuronium (**XX**) and *S*-(silatranylmethyl)isothiuronium (**IX**) iodides in MeCN, the absorption band of the π–π* electronic transition is observed at 40 400 and 40 700 cm^{-1}, respectively (Table 4). It is shifted hypsochromically relative to the similar band in the spectrum of thiourea (λ_{max} 39 500 cm^{-1}). The spectra of iodides **IX** and **XX** contain no band of the *n*–π* electronic transition, whereas in the spectrum of thiourea in MeCN it is manifested as a shoulder at 34 700 cm^{-1}. The UV spectra of iodides **IX** and **XX** in MeOH contain only the π–π* band at 45 400 cm^{-1}, which is shifted hypsochromically relative to the corresponding band in the spectrum of a solution of thiourea **XVIII** in MeOH (λ_{max} 41 300 cm^{-1}).

The UV spectra of solutions of iodides **XI** and **XIV** and of *S*-methyl-*N*^{1},*N*^{2}-dimethylisothiuronium iodide **XXI** are similar to the spectra of iodides **IX** and **XX**, recorded in the same solvents.

The position of the π–π* absorption bands in the UV spectra of iodides **IX**, **XI**, **XIV**, **XX**, and **XXI** is consistent with salt structures **A** and **B** found by IR spectroscopy for the solid state. Structure **A** is predominant in MeOH solution.

Salt structure **A** of iodides **IX**, **XI**, and **XIV** in highly polar acetonitrile, in turn, can dissociate into S-derivative of isothiourea (or its N-substituted derivative) and hydrogen iodide (Scheme 5).

Scheme 5.



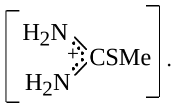
A **C**

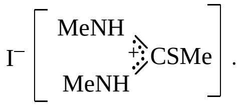
IX, XI, XIV

Table 4. Bands of π–π* electronic transition in the spectra of **I, VI, VIII, IX, XI, XIV**, and model compounds **XVIII**–**XXI**

Comp. no.	λ_{max}, cm^{-1}	
	in MeOH	in MeCN
I	45 300	44 800
VI	45 000	45 000
VIII	44 100	44 200
IX	45 400	40 700
XI	45 500	40 500
XIV	45 200	40 600
XVIII[a]	41 300	39 950
XIX[b]	41 900	40 600
XX[c]	45 400	40 400
XXI[d]	45 600	40 600

[a] $(H_2N)_2C=S$. [b] $(MeNH)_2C=S$.

[c] 

[d] 

Chlorides **I**, **VI**, and **VIII** are less prone to dissociation in both solvents and mainly occur in salt form **A** exhibiting π–π* absorption maxima at λ_{max} 45 300, 45 000, and 44 100 cm^{-1}, respectively.

Thus, according to IR and UV data, *S*-(trimethoxysilylmethyl)- and *S*-(silatranylmethyl)isothiuronium halides and their N-substituted derivatives both in the solid state and in MeCN and MeOH solutions exist in the form of two equilibrium salt structures with positively charged nitrogen (**A**) and carbon (**B**) atoms, or predominantly in one of these. In turn, in solutions of the iodides in MeCN, salt structure **A** can exist in equilibrium with its dissociation products, S-derivatives of isothiourea (or its N-substituted derivatives) and hydrogen iodide.

EXPERIMENTAL

The IR (KBr pellets) and UV spectra (solutions in MeOH and MeCN) were recorded on Specord IR-75 and Specord UV-Vis spectrophotometers, respectively. The ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DPX-400 spectrometer, working frequencies 400.13, 100.61, and 79.49 MHz for ^1H, ^{13}C, and ^{29}Si, respectively. Samples were prepared as 10–15% solutions in $CDCl_3$ and DMSO-d_6. The chemical shifts were measured relative to internal HMDS. The solvents were dehydrated and purified by common procedures [16].

Thiourea, N^1,N^2-dimethylthiourea, *N*-phenylthiourea, and N^1,N^2-ethylenethiourea (imidazoline-2-thione), and also model *S*-methylisothiuronium and *S*-methyl-N^1,N^2-dimethylisothiuronium iodides were recrystallized from methanol and vacuum-dried. All the syntheses were performed under argon.

(Bromomethyl)trimethoxysilane was prepared as described in [17]. (Iodomethyl)trimethoxysilane and 1-(iodomethyl)silatrane, described in [18, 19], were prepared by new procedures.

(Iodomethyl)trimethoxysilane. To a refluxing solution of 11.1 g of freshly calcined sodium iodide in 50 ml of acetonitrile, we added dropwise with stirring over a period of 0.5 h 12.1 g of (chloromethyl)trimethoxysilane. The mixture was stirred with weak refluxing for an additional 2 h and the cooled to 20°C. The NaCl precipitate was filtered off. The solvent was removed from the filtrate, and the residue was fractionated in a vacuum. Yield of (iodomethyl)trimethoxysilane 15.8 g (85%), bp 67–69°C (5 mm Hg), n_D^{20} 1.4690 {published data: bp 76–77°C (11 mm Hg), n_D^{20} 1.4692 [18]; bp 74–75°C (10 mm Hg), n_D^{20} 1.4690 [19]}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.95 s (2H, CH_2Si), 3.63 s (9H, 3MeO).

1-(Iodomethyl)silatrane. A mixture of 11.2 g of 1-(chloromethyl)silatrane and 8.5 g of freshly calcined sodium iodide was dissolved with stirring in 50 ml of DMF while heating the mixture from 20 to 130–140°C over a period of 0.5 h. The solution was stirred at 130–140°C for an additional 2.5 h. The mixture was cooled to 100°C, and the fine precipitate of NaCl was filtered off on a glass frit. The crystalline product that precipitated from the filtrate was filtered off on a glass frit, washed with hot methanol and then with ether, and vacuum-dried. Yield of 1-(iodomethyl)silatrane 11.7 g (74%). Colorless heavy fine crystals, mp 190–191°C {published data: mp 187–188°C, 191–192°C [18], 187–188°C [19]}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.80 s (2H, CH_2Si), 2.85 t (6H, $3CH_2N$), 3.80 t (6H, $3CH_2O$).

***S*-(Trimethoxysilylmethyl)isothiuronium chloride I.** A mixture of 3.5 g of thiourea, 7.8 g of (chloromethyl)trimethoxysilane, and 10 ml of MeOH was placed in a 25-ml two-necked flask equipped with a reflux condenser and filled with dry argon. The outlet of the reflux condenser was equipped with a calcium chloride tube. The mixture was carefully refluxed for 10 h under agitation with a weak argon flow. The resulting solution was concentrated in a vacuum. The residue (thick colorless syrupy mass) was crystallized in a refrigerator. The crystalline mass was thoroughly ground, washed with ether, and vacuum-dried. Yield of **I** 10.2 g (90%). Finely crystalline powder, mp 68–70°C.

Compounds **II**–**V** were prepared similarly.

***S*-(Trimethoxysilylmethyl)isothiuronium iodide II** was prepared by refluxing 1.0 g of thiourea and 3.4 g of (iodomethyl)trimethoxysilane in 10 ml of MeOH for 4 h. Yield 4.2 g (96%), mp 110–112°C.

***S*-(Trimethoxysilylmethyl)-N^1,N^2-dimethylisothiuronium iodide III** was prepared by refluxing 1.6 g of N^1,N^2-dimethylthiourea and 4.0 g of (iodomethyl)trimethoxysilane in 10 ml of MeOH for 6 h. Yield 5.2 g (95%), mp 58–60°C.

***S*-(Trimethoxysilylmethyl)-*N*-phenylisothiuronium bromide IV** was prepared by refluxing 2.0 g of *N*-phenylthiourea and 2.8 g of (bromomethyl)trimethoxysilane in 10 ml of MeOH for 10 h. Yield 4.2 g (89%), mp 82–84°C.

***S*-(Trimethoxysilylmethyl)-*N*-phenylisothiuronium iodide V** was prepared by refluxing 1.0 g of *N*-phenylthiourea and 3.4 g of (iodomethyl)trimethoxysilane in 10 ml of MeOH for 8 h. Yield 4.1 g (94%); light yellow viscous oil.

***S*-(Trimethoxysilylmethyl)-N^1,N^2-ethyleneisothiuronium chloride VI**. A mixture of 2.6 g of N^1,N^2-ethylenethiourea, 4.3 g of (chloromethyl)trimethoxysilane, and 10 ml of acetonitrile was refluxed for 14 h in the device described above. The resulting solution was cooled to 20°C and diluted with 20 ml of ether. The precipitate was filtered off on a glass frit, washed with ether, and vacuum-dried. Yield of **VI** 6.3 g (92%), mp 135–137°C.

***S*-(Trimethoxysilylmethyl)-N^1,N^2-ethyleneisothiuronium iodide VII** was prepared similarly by refluxing 1.6 g of N^1,N^2-ethylenethiourea and 4.1 g of (iodomethyl)trimethoxysilane in 10 ml of MeCN for 10 h. Yield 5.5 g (96%), mp 108–110°C.

***S*-(Silatranylmethyl)isothiuronium chloride VIII.** *a*. By Scheme 2. A solution of 2.7 g of tris(2-hydroxyethyl)amine in 5 ml of $CHCl_3$ was added with stirring to a solution of 4.5 g of **I** in 10 ml of $CHCl_3$. After completion of the exothermic reaction (1.5–2 min), the solid product was filtered off on a glass frit, washed with ether, and vacuum-dried. Compound **VIII** was obtained as a finely crystalline powder; yield 4.5 g (82%), mp 270–272°C (from MeOH).

b. By Scheme 3. A mixture of 3.8 g of thiourea and 11.2 g of 1-(chloromethyl)silatrane was dissolved in 20 ml of DMF at 120–125°C within 0.5 h. The resulting solution was stirred at this temperature for an additional 3.5 h and then cooled to 20°C. A half of the solvent was distilled off in a vacuum (1.0–1.5 mm Hg). The residue was diluted with 50 ml of ether and thoroughly stirred. The resulting solid reaction product was recrystallized from C_2H_5OH. Yield of **VIII** 13 g (87%), mp 266–268°C.

***S*-(Silatranylmethyl)isothiuronium iodide IX.** *a*. By Scheme 2. Compound **IX** was prepared similarly to **VIII** from 1.3 g of *S*-(trimethoxysilylmethyl)isothiuronium iodide and 0.6 g of tris(2-hydroxyethyl)amine in 1 ml of MeOH. Yield of **IX** 1.3 g (86%), mp 246–248°C (from MeOH).

b. By Scheme 3. To 2.0 g of thiourea and 8.3 g of 1-(iodomethyl)silatrane, 10 ml of butanol was added, and the mixture was refluxed for 10 h in the device described above (see synthesis of **I**). The solution was cooled to 20°C, and the precipitate of **IX** was filtered off on a glass frit, washed with ether, and vacuum-dried. Yield 9.3 g (90%), mp 240–242°C.

***S*-(Silatranylmethyl)-N^1,N^2-dimethylisothiuronium chloride X** was prepared by Scheme 3, by refluxing 2.5 g of N^1,N^2-dimethylthiourea and 5.4 g of 1-(chloromethyl)silatrane in 15 ml of butanol for 10 h. Yield 6.1 g (78%), mp 292–294°C (dec.).

***S*-(Silatranylmethyl)-N^1,N^2-dimethylisothiuronium iodide XI.** *a*. By Scheme 2. Compound **XI** was prepared similarly to **IX** from 3.3 g of trimethoxy derivative **III** and 1.4 g of tris(2-hydroxyethyl)amine in 5 ml of MeOH. Yield 3.2 g (84%), mp 240–242°C.

b. By Scheme 3. A mixture of 5.2 g of N^1,N^2-dimethylthiourea and 15.6 g of 1-(iodomethyl)silatrane in 40 ml of butanol was refluxed for 10 h. The resulting solution was cooled to 0°C, and the precipitate was filtered off on a glass frit, washed with ether, and vacuum-dried. Yield of **XI** 18.8 g (91%), mp 235–237°C.

***S*-(Silatranylmethyl)-*N*-phenylisothiuronium chloride XII** was prepared by Scheme 3 similarly to **VIII**. A mixture of 4.8 g of *N*-phenylthiourea and 7.0 g of 1-(chloromethyl)silatrane in 20 ml of DMF was kept at 120–125°C for 12 h. Yield of **XII** 9.8 g (83%), mp 245–247°C (from MeOH).

***S*-(Silatranylmethyl)-*N*-phenylisothiuronium bromide XIII and *S*-(silatranylmethyl)-*N*-phenylisothiourea XVII.** A solution of 3.2 g of *S*-(trimethoxysilylmethyl)-*N*-phenylisothiuronium bromide in 5 ml of MeOH was mixed with a solution of 1.6 g of tris(2-hydroxyethyl)amine in 2 ml of MeOH. After completion of the exothermic reaction, a mixture of solids was obtained, from which 1.5 g (70%) of **XIII** (mp 244–246°C), 0.6 g (7%) of **XVII** (mp 194°C), and 0.7 g of tris(2-hydroxyethyl)ammonium bromide (mp 190°C) were isolated.

***S*-(Silatranylmethyl)-*N*-phenylisothiuronium iodide XIV.** *a*. By Scheme 2. A solution of 3.5 g of *S*-(trimethoxysilylmethyl)-*N*-isothiuronium iodide in 5 ml of $CHCl_3$ was mixed with a solution of 1.3 g of tris(2-hydroxyethyl)amine in 1 ml of $CHCl_3$. The exothermic reaction was complete in 1–2 min. After cooling to 20°C, a mixture of solids was obtained, from which 3.2 g (83%) of **XIV** (mp 245–247°C, from MeOH) and 0.5 g of tris(2-hydroxyethyl)ammonium iodide (mp 181°C) were isolated.

b. By Scheme 3. A mixture of 2.4 g of *N*-phenylthiourea, 4.8 g of 1-(iodomethyl)silatrane, and 15 ml of butanol was refluxed for 12 h in the device described above. The resulting solution was cooled to 20°C. The precipitate was filtered off on a glass frit and washed with ether. Yield of **XIV** 6.3 g (87%), mp 240–242°C (from MeOH).

***S*-(Silatranylmethyl)-N^1,N^2-ethyleneisothiuronium chloride [2-(silatranylmethylthio)imidazolinium chloride] XV** was prepared similarly to **VIII** from 2.6 g of trimethoxysilyl derivative **VI** and 1.4 g of tris(2-hydroxyethyl)amine in $CHCl_3$ solution. Yield 3.4 g (86%), mp 270–272°C (from MeOH).

***S*-(Silatranylmethyl)-N^1,N^2-ethyleneisothiuronium iodide [2-(silatranylmethylthio)imidazolinium iodide] XVI.** *a*. By Scheme 2. Compound **XVI** was preepared similarly to **IX** in MeOH from 1.3 g of the corresponding trimethoxysilyl derivative and 0.5 g of tris-(2-hydroxyethyl)amine. Yield of **XVI** 1.3 g (88%), mp 308–310°C (dec.).

b. By Scheme 3. Compound **XVI** was prepared by refluxing a mixture of 2.1 g of N^1,N^2-ethylenethiourea (imidazoline-2-thione) and 6.6 g of 1-(iodomethyl)silatrane in 15 ml of butanol for 12 h. Yield of **XVI** 6.9 g (79%), mp 312–315°C (dec.).

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