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Tautomerism of Aza Cycles: II.[1] Synthesis and Structure of 5-Substituted 3-(2-Hydroxyethylsulfanyl)-1*H*-1,2,4-triazoles and Their Salts. Preference of the 1*H*,4*H*-1,2,4-Triazolium Tautomers

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Abstract—New complexing agents, potentially tautomeric 3-(2-hydroxyethylsulfanyl)-1*H*-1,2,4-triazole, its 5-methyl- and 5-phenyl-substituted analogs, and some their salts, were synthesized, and their structure was discussed on the basis of the ^{1}H and ^{13}C NMR, IR, and mass spectra, X-ray diffraction data, and published data. In keeping with the rule formulated previously for N-unsubstituted 1,2,4-triazoles having dissimilar substituents, the synthesized compounds were found to exist as 3-(2-hydroxyethylsulfanyl)-5-R-1*H*-1,2,4-triazole tautomers (3-R_A-5-R_D-1*H*-1,2,4-triazoly). They are protonated at the nitrogen atom in position *4* of the triazole ring. The ^{1}H and ^{13}C NMR spectra of these compounds in trifluoroacetic acid suggest the presence of two forms due to equilibrium between the neutral and protonated species. Analysis of the crystallographic data for the triazolium salts and published data showed preference of the 1*H*,4*H*-1,2,4-triazolium tautomer.

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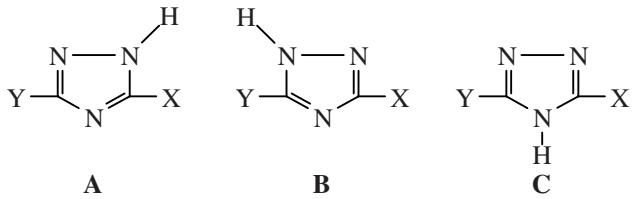
Sulfanyl derivatives of 1,2,4-triazoles, including those having a substituent on the sulfur atom, exhibit versatile biological activity, such diuretic, neuroleptic [2], antituberculous [3, 4], antimicrobial [5], antiphlogistic [6], antiarthritic [7], antimycotic [8], anti-HIV [9], etc.; they act as inhibitors of matrix metalloprotease [11] and CXXR2 receptor antagonists [12] and have been proposed for the treatment of various diseases, in particular of mental disorders [13]. Substituted sulfanyl-1,2,4-triazoles have found application in agriculture and industries [14, 15], as complexing agents capable of coordinating metal ions at different donor centers [16, 17], as precursors in organic synthesis [18], etc. [19, 20].

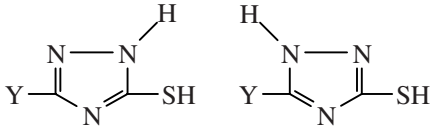
In the preceding communication [1] we reported that, unlike hydrogen atom or methyl or phenyl group), alkylsulfanyl groups exhibit electron-withdrawing effect and that N-unsubstituted 1,2,4-triazoles having an alkylsulfnayl group do not give rise to annular tautomerism. Among three possible preferential tautomers **A**–**C**, only alkylsulfanyl-5-R-1*H*-tautomer (**B**, X = AlkS, Y = H, Me, Ph) was detected in crystal and in solution. These data are consistent with the conclusion drawn in [1], according to which 3-R_A-5-R_D-1*H*-1,2,4-triazole tautomer is more favorable for 1,2,4-triazoles having no substituent on the nitrogen atom (R_A and R_D are substituents exhibiting, respectively, electron-withdrawing and electron-donor effect).



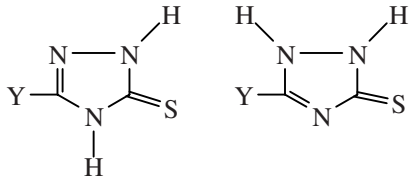
In going to C-sulfanyl-1,2,4-triazoles (X or Y = SH), the situation is complicated as a result of appearance of additional tautomers due to SH group

* For communication I, see [1].

(thione forms **D** and **E**) [19–21]. For example, 3(5)-sulfanyl-1,2,4-triazole in crystal exists as 3,4-dihydro-1*H*-1,2,4-triazole-5-thione (tautomer **D**), while the structure of 5(3)-sulfanyl-3(5)-phenyl-1*H*-1,2,4-triazole in crystal depends on the crystallization conditions [21] (the details will be reported elsewhere).

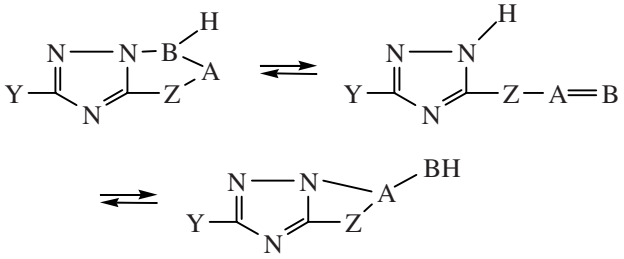


A' **B'**

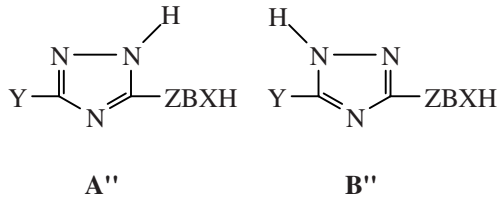


D **E**

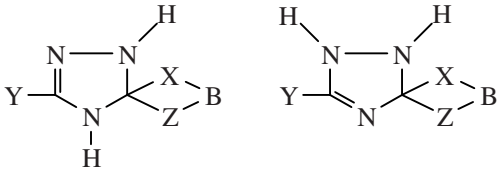
In the recent years, examples of various ring–chain tautomerism of 1,2,4-triazoles have been reported [22, 23]. For instance, the NH fragment of 1,2,4-triazole having no substituent on the nitrogen reversibly adds at an A=B double bond (C=C, C=O, C=N, C=S) in the substituent on the carbon atom, as was shown in [22]. The possibility for such tautomeric transformation is responsible for many processes leading to fused 1,2,4-triazoles (see, e.g., [18–20]).



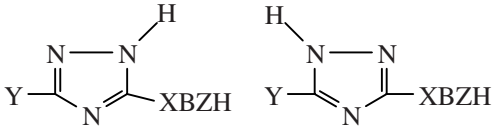
One more group of potentially tautomeric 1*H*-1,2,4-triazoles, as well of other azoles and azines, includes derivatives in which the ZB–XH moiety possessing a labile hydrogen atom is separated from the heteroring by ZB spacer. For example, ZB is an aliphatic chain, and XH = OH [3], COOH [24], SH, NHR (including NH-heterorings) [19–21, 23], etc. Such 1*H*-1,2,4-triazole derivatives give rise to another kind of ring–chain tautomerism [**A″**(**B″**) → **F**(**G**)] involving formation of a spiro-fused system. If the bridging chain in these compounds is linked to the triazole ring through a heteroatom (either the same or other), rearrangements like **A″** → **H** or **B″** → **I** may occur, which must be taken into account while determining the structure of such derivatives. When the XH group is sufficiently acidic (XH = COOH, SH, SO_2OH, etc.), internal salts like **J** may be formed.



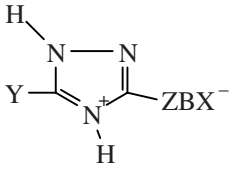
A'' **B''**



F **G**

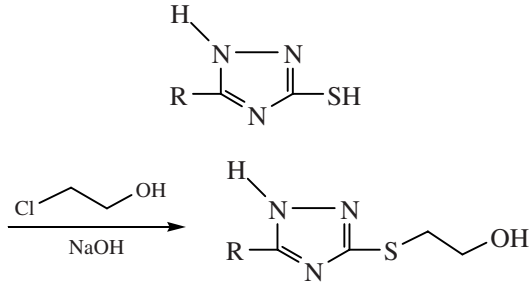


H **I**



J

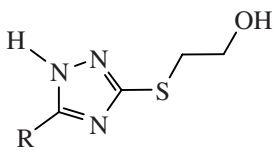
The present article reports on the results of studying the structure of 1,2,4-triazole derivatives where ABXH = SCH_2CH_2OH and their salts. 5-Substituted 3-(2-hydroxyethylsulfanyl)-1,2,4-triazoles **I–III** were synthesized by alkylation of the corresponding 5-R-3-sulfanyl-1*H*-1,2,4-triazoles (R = H, Me, Ph) with 2-chloroethanol in alkaline medium; compounds **I–III** are capable of forming salts with many acids and complexes with most transition metal ions. Triazoles **I–III** were isolated from the reaction mixtures as transparent syrupy materials which crystallized only after a long time. For example, triazole **I** turned crystalline in almost 1.5 year; the crystallization was not complete, and it was fairly difficult to separate crystals from the semiliquid material. The methyl- and phenyl-substituted analogs crystallized more readily, especially after treatment of their solutions with silica gel. The spectral parameters of their syrup-like and crystalline samples were almost identical.



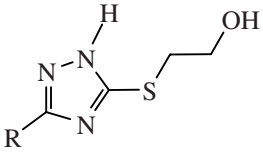
I–III

R = H (**I**), Me (**II**), Ph (**III**).

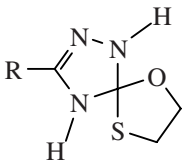
With a view to obtain additional information, we recorded the IR spectra of triazoles **I–III** (from films, dispersions in mineral oil, KBr pellets, and solutions in carbon tetrachloride), as well as their ^{1}H and ^{13}C NMR and mass spectra (Tables 1, 2; see Experimental). The spectral parameters of compounds **I–III** allowed us to conclude that, like other alkylsulfanyl-1,2,4-triazoles [1], only one tautomer is present in the crystalline and gaseous phases and in solution, except for solutions in trifluoroacetic acid where signals from two forms were observed. However, it was difficult to choose between six most favorable structures (**I–III**)**a**–(**I–III**)**f** was difficult. Furthermore, unlike tautomers **Ia–IIIa** and **Ib–IIIb** with a weakly acidic hydroxy group, structures **Ie–IIIe** and **If–IIIf** could give rise to autoprotonation of the triazole ring by the sulfanyl group (structure like **J**).



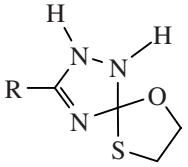
Ia–IIIa



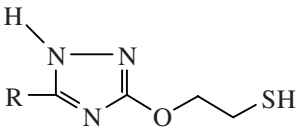
Ib–IIIb



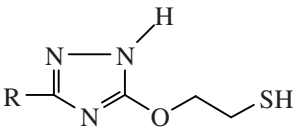
Ic–IIIc



Id–IIId



Ie–IIIe



If–IIIf

A high probability for formation of strong intra- and intermolecular hydrogen bonds (including those with participation of solvent molecules), as well as for tautomeric and various exchange processes, requires additional arguments for the choice of preferential tautomer. For example, the IR spectra of triazoles **I–III** (films and crystalline samples) contain strong absorption bands in the frequency region below 2700 cm^{-1}. These bands may be attributed to strong hydrogen bonds of different kinds in tautomers **a**, **b**, **d**, and **f** or NH···N hydrogen bonds in cyclic structures **c** and **d**, taking into account that an analogous pattern is intrinsic to the IR spectra of 5-substituted 3-butylsulfanyl-1*H*-1,2,4-triazoles [1]. On the other hand, the contribution of sulfanyl groups in tautomers **Ie–IIIe** and **If–IIIf** cannot be ruled out, provided that such tautomers exist. In the IR spectra of triazoles **I–III**, recorded from solutions in carbon tetrachloride ($c \approx 10^{-4}$ M), we observed absorption bands above 2500 cm^{-1} only at 3457(1) and 3300(1) cm^{-1}, which are typical of stretching vibrations of OH and NH groups in the triazole ring (cf. [1]). Therefore, structures **Ie–IIIe** and **If–IIIf** having free sulfanyl fragments can be excluded. This conclusion is consistent with the mass spectrometric data.

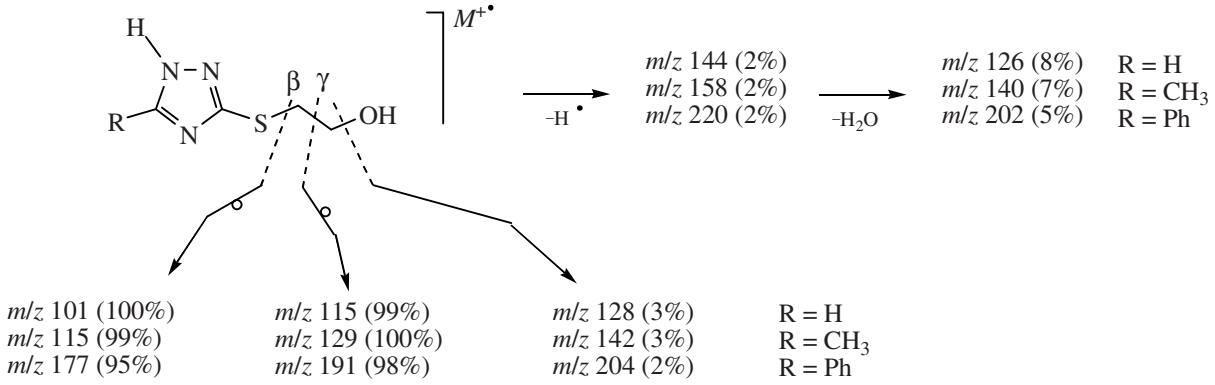
In the mass spectra of compounds **I** and **II**, the relative intensity of the molecular ion peaks $[M]^{+\cdot}$ is 9 and 7%, respectively. The intensity of the molecular ion peak of triazole **III** increases to 15% due to stabilizing effect of the phenyl group. In the region corresponding to large *m*/*z* values, which provides the most valuable information on the molecular structure, all compounds displayed peaks from fragment ions formed by elimination of hydroxy group from $[M]^{+\cdot}$. Despite low intensity (~3%), the presence of the above

Table 1. Proton chemical shifts (δ, ppm) and ^1H–^1H spin–spin coupling constants (J_{HH}, Hz) in the ^1H NMR spectra of 5-R-3-(2-hydroxyethylsulfanyl)-1*H*-1,2,4-triazoles **I**–**III** and their salts

Comp. no.	Solvent	Structure	SCH_2, t	CH_2O, t	$^3J_{HH}$	5-R	Ratio **A** : **B**
I	CD_3OD, 25°C	**A**	3.24	3.75	6.64	8.30 s	1:0
	CD_3OD, 50°C	**A**	3.24	3.73	6.64	8.25 s	1:0
I	DMSO-d_6	**A**	3.27	3.72	6.16	8.36	1:0
I	CF_3COOH, 25°C	**A**	2.81	3.85	5.92	8.45 s	1.0:0.8
		B	2.65	3.33	4.64	8.16 s	
I	CF_3COOH, 55°C	**A**	2.82	3.86	5.95	8.37 s	11:1
		B	2.64	3.33	5.31	8.08 s	
I[a]	CF_3COOH	**A**	2.80	3.84	5.78	8.43 s	4.4:1.0
		B	2.63	3.29	5.32	8.15 s	
I	93% H_2SO_4	**B**	2.49	3.45	5.41	7.94 d[b]	–[c]
II	CD_3OD	**A**	3.14	3.75	6.39	2.36 s	
II	Acetone-d_6	**A**	3.22	3.82	6.13	2.38 s	1:0
II	CD_3CN	**A**	3.32	3.79	6.58	2.40	1:0
II	DMSO-d_6	**A**	3.08	3.61	6.44	2.31 s	1:0
II	CF_3COOH	**A**	3.04	4.15	5.68	2.18 s	1:0
III	$HCCl_3$	**A**	3.23[d]	4.06[d]	–[d]	9.91 m, 7.38 m	1:0
III	DMSO-d_6	**A**	3.24	3.71	6.44	7.97 m, 7.47 m[e]	1:0
III	CF_3COOH	**A**	2.90	3.97	5.89	–[f]	1.4:1.0
		B	2.76	3.38	5.35	7.16 m[g]	
III	H_2SO_4	**A**	2.55	3.50	5.40	6.70 d[h]	10:1
		B	2.76	3.64	-	–[g]	
IV	D_2O	**A**	3.23	3.73	5.92	8.72 s	1:0
IV	DMSO-d_6	**A**	3.13	3.61	6.27	8.31 s	1:0
IV	CF_3COOH	**A**	2.94	3.91	5.92	8.67 s	1.4:1.0
		B	2.67	3.37	5.33	8.23 s	

[a] Isolated from oxalate **IV**. [b] Doublet, $^3J_{HH}$ = 6.48 Hz. [c] Apart from the major tautomer, no less than four minor forms were present. [d] Broadened singlet. [e] Unresolved multiplet. [f] Ph (**A**): 7.10 d (2H, ^3J = 8.58 Hz), 6.93 t (1H), 6.82 t (2H, ^3J = 7.84 Hz). [g] Overlapped signals. [h] Ph (**A**): 6.70 d (2H, ^3J = 7.27 Hz), 6.64 t (1H, ^3J = 7.58 Hz), 6.51 t (2H, ^3J = 7.84 Hz).

ion peaks is quite characteristic, for molecules **I**–**III** contain a hydroxyethylsulfanyl group. Elimination of hydrogen atom from the molecular ion gives $[M - H]^+$ ion which then lose water molecule. Unlike 1,5-dihydro-1,2,4-triazole-5-thiones [25], the main fragmentation pathway of the molecular ions derived from compounds **I**–**III** involves cleavage of bonds in the hydroxyethylsulfanyl group in the β- and γ-positions with respect to the triazole ring. It should be noted that most ions are formed as a result of rearrangement processes with elimination of neutral formaldehyde and acetaldehyde molecules and migration of hydrogen to the charged fragment. Simple bond dissociation in the substituent chain is considerably less probable (see Experimental). In contrast to 1,5-dihydro-1,2,4-triazole-5-thiones [25], no nitriles were detected among the decomposition products of compounds **III**. The general fragmentation pathways of the molecular ions of triazoles **I**–**III** are shown in the following scheme.



As a rule, the ^{1}H NMR spectra of triazoles **I–III** contain signals only from protons in the ethylene fragment and substituent in position *5* of the triazole ring (Table 1), whereas signals from OH and NH protons are rarely observed because of exchange processes. For example, signals at δ 4.33 and 12.56 ppm were present in the spectrum of triazole **II** in acetone-d_6. However, the structure of preferential tautomer cannot be determined on the basis of the chemical shifts of protons in the CH_2S and CH_2O groups and 5-substituent, even if we take into account relevant data for model compounds (cf. [1, 26, 27]).

Signals from the C^3 and C^5 atoms in the triazole ring of compounds **I–III** are often lacking in the ^{13}C NMR spectra recorded from solutions in neutral solvents. For example, prolonged acquisition (several days) is necessary to detect C^3 and C^5 signals in the spectra of solutions in CD_3OD. The chemical shifts of C^3 and C^5 range from 154 to 159 and from 143 to 156 ppm, respectively (Table 2), i.e., they are typical of other 1,2,4-triazole derivatives [26, 28]. The upfield region of the ^{13}C NMR spectra contains only two signals from sp^3-hybridized methylene carbon atoms. No signal from the sp^3-hybridized C^3 atom in spiro tautomers **Ic–IIIc** and **Id–IIId** was detected. According to the calculations, this signal should appear at δ_C 100–125 ppm. In the spectra of dihydro-1*H*-1,2,4-triazole derivatives having no electron-withdrawing groups on C_{sp^3}, the corresponding signal should be located even in a stronger field. For example, the chemical shift of C^5 in the ^{13}C NMR spectra of 1,4-diacetyl-3-acetylamino-5-aryl-4,5-dihydro-1*H*-1,2,4-triazoles is 70 to 76 ppm, while sp^2-hybridized carbon atoms resonate at δ_C 140.2–142.8 ppm [29]. The fact that the spectra of triazoles **I–III** sometimes lack signals from one or both carbon atoms in the triazole ring may be attributed to some fast dynamic processes, including those with participation of cyclic tautomers.

These findings, though ambiguously, allowed us to rule out cyclic structures **Ic–IIIc** and **Id–IIId** in neutral solutions. In most cases, the ^{13}C NMR spectra displayed $^2J_{HNC}$ spin–spin coupling for neither C^3 nor C^5 atom; such coupling would be useful to distinguish

Table 2. ^{13}C chemical shifts (δ_C, ppm) and ^{13}C–^{1}H spin–spin coupling constants (J_{CH}, Hz) in the ^{13}C NMR spectra of 5-R-3-(2-hydroxyethylsulfanyl)-1*H*-1,2,4-triazoles **I–III**

Comp. no.	Solvent	Structure	CH_2S (t)		B[d]		C^3	C^5		5-R
			δ_C	$^1J_{CH}$	δ_C	$^1J_{CH}$	δ_C	δ_C	$^1J_{CH}$	δ_C
I	CD_3OD	–	35.57	141.40	61.73	144.45	157.71[a]	147.78 d	210.06	–
I	DMSO-d_6	–	35.61	141.12	61.74	144.72	157.09	147.78	209.33	–
I	CF_3COOH	A	30.77	145.75	61.98	146.84	155.16	142.37	227.27	–
A<B		B	35.07	142.57	65.95	155.47	154.49	142.60	225.81	–

Table 2. (Contd.)

Comp. no.	Solvent	Structure	CH_2S (t)		CH_2O (t)		C^3	C^5		5-R
			δ_C	$^1J_{CH}$	δ_C	$^1J_{CH}$	δ_C	δ_C	$^1J_{CH}$	δ_C
I[b] **A≈B**	CF_3COOH	**A**	33.14	145.24	68.46	146.78	156.88[c]	–	–	–
		B	37.43	143.14	64.39	155.58	157.55[c]	145.24	225.95	–
I[b] **A>B**	95% H_2SO_4	**A**	31.86	146.05	70.62	155.49	154.65 m	143.10	228.89	–
		B[d]	32.63	142.42	–	–	–	144.87	228.88	–
IV[e]	DMSO-d_6	–	34.49	140.97	60.54	143.14	156.71	146.74	209.27	–
IV[f] **A>B**	CF_3COOH	**A**	32.36	145.46	67.64	154.36	156.17 m	144.36 d	227.33	
		B	36.63	144.50	63.38	147.95	156.65 m	144.55[g]	226.79	–
IV[h] **A>>B**	CF_3COOH	**A**	31.39	145.68	66.53	154.25	155.63 m	143.26	227.23	–
		B	–	–	–	–	155.00	143.72	225.01	–
II	CD_3OD	–	35.49	145.03	62.34	143.91	156.3[i]	156.3[i]	–	11.82 q (^1J 116.03)
II	Acetone-d_6	–	35.69[q]	140.95	63.01[q]	143.32	159.61 t[k]	156.56 q	^3J 7.24	12.81 q (^1J 128.60)
II	DMSO-d_6	–	34.22	–	60.03	–	–	–	–	12.10 q (^1J 130.45)
II	CF_3COOH	–	31.21	144.96	66.67	154.04	155.15 t[l]	155.48 q	^3J 7.27 ^1J 134.42	9.82 q (^1J 134.42)
III	$CDCl_3$	–	35.88	154.68	63.37	143.80	–	–	–	126.43 (C^m, ^1J 160.33), 129.11 (C^o, ^1J 166.96), 130.48 (C^p, ^1J 164.47), C^i not found
III	CD_3CN	–	35.81	141.67	62.46	144.21	–	–	–	126.07 (C^i), 127.07 (C^m, ^1J 161.31, ^2J 6.54), 129.82 (C^o, ^1J 161.30., ^2J 27.65), 131.15 (C^p, ^1J 161.30, ^2J 6.54)
III	CF_3COOH	**A**	31.16	144.84	66.55	153.70	156.72	155.16 t	6.63	119.38 t (C^i, J 8.85), 128.20 (C^m, ^1J 161.98, ^2J 6.64), 131.06 (C^o, ^1J 166.13, ^2J 7.74), 136.02 (C^p, ^1J 168.67, ^2J 7.18)
		B	40.54	152.04	68.66	152.58	157.15	154.03 t	6.08	119.20 (C^i), 129.59 (C^m, ^1J 160.88, ^2J 7.74), 130.93 (C^o, ^1J 165.86, ^2J 7.18), C^p not found
III	95% H_2SO_4	–	32.07	144.27	70.86	155.14	155.31 t[i]	155.22 t	4.27	117.60 m (C^i), 128.94 (C^m, ^1J 163.4, ^2J 7.51), 130.85 (C^o, ^1J 166.72, ^2J 7.27), 136.02 (C^p, ^1J 164.94, ^2J 7.51)

[a] Multiplet including at least five lines, Δν = 5.17, 5.09, 6.01 Hz. [b] Triazole **I** isolated from oxalate **IV** contained traces of oxalic acid; δ (HOCOCOOH) 161.36 ppm, q. [c] Quartet, J = 7.25 Hz. [d] The amount of the minor structure was small, and many signals from it were not observed. [e] δ_C($HOOCCOO^-$)161.14 (J = 61.40 Hz), 165.80 ppm. [f] Not crystallized, δ(HOCOCOOH) 161.36 ppm, q. [g] The spectrum was recorded in 4 days after dissolution, δ(HOCOCOOH) = 161.36 ppm, q. [h] Doublet of doublets, ^3J = 23.18 Hz. [i] Weak signal. [j] Triplet of triplets; CH_2S, ^3J = 2.24 Hz; CH_2O, ^3J = 3.86 Hz. [k] ^3J = 4.66 Hz. [l] ^3J = 6.95 Hz. [m] J = 5.98 Hz.

1*H*- and 2*H*-tautomers **Ia**–**IIIa** and **Ib**–**IIIb**. Only in the ^{13}C NMR spectrum of triazole **I** in CD_3COD, recorded without decoupling from protons, we observed a signal from the C^3 atom at δ 157.71 ppm as a multiplet including no less than 5 lines. The multiplicity of that signal indicates interaction not only with the SCH_2 protons but also with 5-H or NH. Taking into account the above data and our previous conclusions [1] we believe that structure **a** is preferred to **b** and assigned triazoles **I**–**III** in crystal and neutral solutions the structure of 1*H*-tautomers, i.e., 5-substituted 3-(2-hydroxyethylsulfanyl)-1*H*-1,2,4-triazoles.

The choice of the structure of predominant tautomer was hindered by the fact that the ^1H and ^{13}C NMR spectra of triazoles **I**–**III** in trifluoroacetic acid always contained signals from two forms. Initially, we supposed the presence of two tautomeric triazolium ions [30], as was reported for protonation of 1-methyl-1,2,4-triazole [28] and other azoles (1,2,3-triazoles, 1,3,4-oxadiazoles, and tetrazoles) [31]. Signals from the C^3 and C^5 atoms of triazoles **I**–**III** in trifluoroacetic acid were located in the region typical of 1,2,4-triazolium cations (Table 2) [28, 32, 33]. As might be expected, protonation of the triazole ring in **I**–**III** leads to upfield displacement of the C^3 and C^5 signals (δ_C 157–158 and 142–144 ppm for 5-fluoroalkyl-1,2,4-trimethyl-1,2,4-triazolium salts [32] and 154–149 and 140–138 ppm for 4-alkyl-5-amino-1-(pyridiniomethyl)-1,2,4-triazolium chlorides [33]).

The species observed in trifluoroacetic acid were arbitrarily denoted as **A** and **B**, and their ratio depended on the method of purification and conditions of NMR experiments, including the time elapsed after dissolution. The upfield CH_2S carbon signal was assumed to belong to structure **A**. The **A**-to-**B** ratios (Tables 1, 2) were estimated from the intensities of proton and carbon signals of the CH_2S and CH_2O groups.

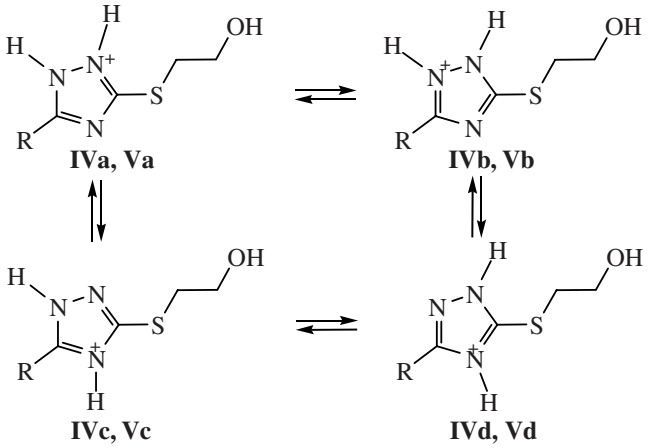
We prepared a series of salts from triazoles **I**–**III**. Hydrochlorides and hydrobromides derived from triazoles **I** and **II** turned out to be very hygroscopic, and we failed to isolate these salts as crystalline substances. Crystals suitable for X-ray analysis were obtained only from triazole **I** oxalate (salt **IV**) and triazole **III** hydrochloride (**V**). The isolation of triazoles **I**–**III** from the corresponding salts also involved strong difficulties. For example, we did not succeed in completely removing oxalic acid from oxalate **IV**, and its traces were detected in the spectra of triazole **I** isolated from **IV**.

The ^1H and ^{13}C NMR spectra of salts **IV** and **V** in trifluoroacetic acid differed from the spectra of the free bases only by the **A/B** ratio (Tables 1, 2), though the spectral pattern of the salts in the region corresponding to carbon atoms in the triazole ring was sometimes more distinct. The ^1H and ^{13}C NMR spectra of oxalate **IV** in D_2O and DMSO-d_6 almost coincided with the spectra of triazole **I** in CD_3OD and DMSO-d_6, respectively. Analogous patterns were observed for the triazole **III**–hydrochloride **V** couple in DMSO-d_6. The spectra of triazoles **I**–**III** and salts **IV** and **V** in concentrated sulfuric acid indicated mainly the presence of one form (Tables 1, 2); in some cases, small amounts of two and more species were detected; presumably, these impurities are products of some transformations. We presumed that solutions of triazoles **I**–**III** in trifluoroacetic acid contain mixture of the free bases and protonated forms. Compounds **I**–**III** are likely to possess a weak basicity, and they undergo complete protonation only in concentrated sulfuric acid. The larger concentration of unprotonated phenyltriazole **III** in H_2SO_4 as compared to triazole **I** is very consistent with the above assumption. Introduction of a phenyl group into the triazole molecule reduces its basicity, and the fraction of unprotonated molecules increases. Dissolution of salts **IV** and **V** (as well as of other salts derived from a weak base and a strong acid) in water, alcohols, and DMSO is accompanied by almost complete hydrolysis, which is responsible for the observed spectral patterns (Tables 1, 2).

1,2,4-Triazolium salts continuously attract researchers' attention [19, 20, 28, 32, 34, 35]. In the recent years, some 1,2,4-triazolium salts were shown to inhibit corrosion of copper [36] and iron [37] and act as ionic liquids [32, 38]. 3-Amino-1,2,4-triazolium salts are used in agriculture (e.g., Amitrole) and organic synthesis, as well as individual explosives and components of rocket fuels and emulsion explosives [19, 20, 23, 39]. However, the structure of 1,2,4-triazolium salts (as well as of salts derived from other heterocyclic systems) was studied to a considerably lesser extent than the structure of initial heterocycles, although most practically important 1,2,4-triazole derivatives are used just as salts. A few studies were performed on triazolium salts having no substituent on the nitrogen, their protonation, and charge localization, though these problems have long attracted attention, specifically of chemists working in the field of 3-amino-1,2,4-triazoles [34, 35]. The main reasons for such situation in the azole chemistry are related to

difficulties arising from limited solubility of triazolium salts and inevitability of exchange processes; in addition, potential tautomerism of NH-triazolium salts strongly restricts the choice of subjects for study [28].

The IR and ^{1}H and ^{13}C NMR spectral data obtained in this work were insufficient to unambiguously determine the structure of protonated forms of triazoles **I–III**; the most probable structures are shown below.



Taking into account the above conclusions excluding spirocyclic and thiol structures (**I–III**)**c**–(**I–III**)**f**, the formation of the corresponding protonated species may also be ruled out, though such structures may sometimes be more stable than open-chain tautomers. Furthermore, protonation of triazoles **I–III** may be accompanied by change of the position of hydrogen atoms. For instance, the ^{13}C NMR spectra of salts **IV** and **V** sometimes revealed additional couplings for the C^3 and C^5 atoms in those species which were assumed to bear a positive charge (Table 2). Insofar as no spin–spin coupling with the NH hydrogen atom was observed for C^3 and C^5 in neutral triazole molecules, the observed spectral patterns are fairly difficult to interpret.

With a view to determine the structure of protonated forms of triazoles **I–III**, oxalate **IV** and hydrochloride **V** were studied by the X-ray diffraction method. Suitable single crystals were grown from aqueous methanol. Figure 1 shows the structure of the cationic and anionic fragments of oxalate **IV**. The asymmetric part of a unit cell includes two cation–anion couples where cations **IVA** and **IVB** differ in the

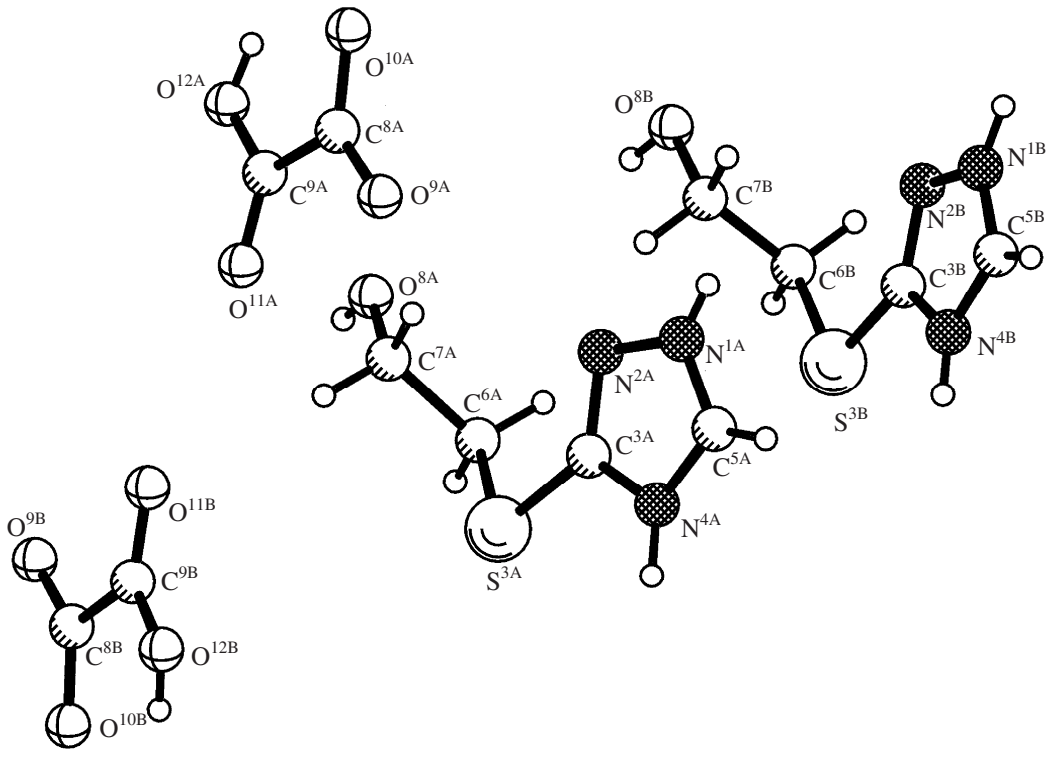
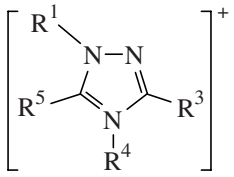


Fig. 1. Structure of cations **IVA** and **IVB** and oxalic acid monoanions in 3-(2-hydroxyethylsulfanyl)-1*H*,4*H*-1,2,4-triazolium hydrogen oxalate (**IV**) in crystal according to the X-ray diffraction data. Cation **IVA** with larger population of the disordered hydroxyethyl fragment is shown.

Table 3. Bond lengths (*d*, Å) in the triazole ring of N-unsubstituted and substituted 1,2,4-triazolium salts **IV**–**XXIII**

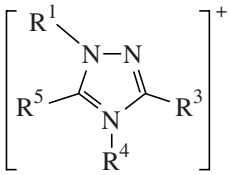


Comp. no.	R^1	R^3	R^4	R^5	K^+C[a]	K^+A[a]	N^1–N^2	N^1–C^5	N^2–C^3	N^4–C^3	N^4–C^5	Reference
IVA	H	SCH_2CH_2OH	H	H	–	1,4$^+$-C	1.36(1)	1.29(1)	1.31(2)	1.34(1)	1.32(1)	–[b]
IVB	H	SCH_2CH_2OH	H	H	–	1,4$^+$-C	1.375(8)	1.28(1)	1.287(9)	1.35(1)	1.33(1)	–[b]
V	H	SCH_2CH_2OH	H	Ph	–	1,4$^+$-C	1.387(9)	1.34(1)	1.29(1)	1.39(1)	1.34(1)	–[b]
VI[c]	H	H	H	H	1$^+$,4-C	1$^+$,2-C	1.363(2)	1.307(2)	1.295(2)	1.349(2)	1.321(3)	[43]
VII[d]	H	H	H	H	1,4$^+$-C	1,4$^+$-C	1.343[e]	1.313	1.289	1.368	1.327	[44]
VIII[f]	H	H	H	H	1$^+$,4-C	[Tr]$^+$	1.365(2)	1.309(2)	1.302(2)	1.356(2)	1.332(2)	[45]
IX[g]	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	1.377(3)	1.321(3)	1.288(3)	1.361(3)	1.343(3)	[46]
X[h]	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	1.382[e]	1.328	1.293	1.368	1.340	[47]
XI[i]	H	H	H	NH_2	1$^+$,4-C	1,4$^+$-C	1.386(5)	1.326(5)	1.295(6)	1.366(7)	1.349(5)	[48]
XII[j]	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	1.374[e]	1.322	1.286	1.356	1.338	[49]
XIII[k]	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	1.387[e]	1.330	1.291	1.363	1.343	[50]
XIV[l]	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	1.388(3)	1.329(3)	1.291(4)	1.367(4)	1.347(3)	[51]
XV[m]	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	1.368(3)	1.330(3)	1.290(3)	1.349(3)	1.342(3)	[52]
XVI[n]	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	1.375(5)	1.316(6)	1.282(6)	1.346(7)	1.361(6)	[52]
XVII[o]	H	$HN–NH_3^+$	H	NH_2	1,4$^+$-C	[Tr]$^+$	1.397(6)	1.322(6)	1.291(6)	1.363(6)	1.352(6)	[53]
XVIII[p]	Me	C_8F_{17}	Me	Me	1,4$^+$-C	[Tr]$^+$	1.353[e]	1.327	1.303	1.368	1.340	[32]
XIX[q]	H	Et	NH_2	Et	1,4$^+$-C	1,4$^+$-C	1.365[e]	1.296	1.310	1.379	1.316	[54]
XX[r]	H	NH_2	NH_2	NH_2	1$^+$,4-C	1$^+$,4-C	1.408(5)	1.311(5)	1.298(5)	1.382(5)	1.343(5)	[55]
XXI[f]	H	Me	NH_2	NHR[t]	1$^+$,4-C	–	1.378[e]	1.326	1.300	1.378	1.343	[56]
XXII[f]	Me	NMe_2	Ar[t]	NMe_2	1,4$^+$-C	–	1.385[e]	1.315	1.323	1.400	1.353	[57]
XXIII[r]	CH_2R[u]	H	NH_2	H	–	1$^+$,4-C	1.39[e]	1.31	1.33	1.36	1.32	[23]
Average value							1.376	1.317	1.297	1.365	1.338	–
Average value for neutral analogs[v]							1.371	1.334	1.317	1.355	1.327	[1]

[a] 1$^+$,4-C stands for positive charge localization on the N^1 atom of the triazole ring, 1,4$^+$-C denotes charge localization on the N^4 atom, and [Tr]$^+$ stands for delocalization of the positive charge over the triazole ring according to the CSD [C^+(C)] and authors' data [C^+(A)]. [b] This work. [c] Bis(methanesulfonyl)amidate. [d] Perchlorate; the dihydro-1,2,4-triazolium cation forms a host–guest complex with dibenzocrown-6. [e] No standard deviations for bond lengths and bond angles were given. [f] Chloride. [g] 3-Nitrobenzoate. [h] Thiophene-2-carboxylate. [i] 4-Nitrobenzoate. [j] 5-Nitrofuran-2-carboxylate. [k] Pyrazinedicarboxylic acid monoanion. [l] 3-Nitro-1,2,4-triazol-5-olate. [m] 2-Hydroxy-5-nitrobenzoate. [n] 2-Hydroxy-3,5-dinitrobenzoate. [o] Two chloride ions. [p] BF_4^-. [q] $[(NC)_2Au]^-$. [r] Bromide. [s] R = 2,6-$Cl_2C_6H_3CH$=N. [t] Ar = 2-HOC_6H_4. [u] R = 2-(4-amino-1,2,4-triazol-1-io)methyl bromide. [v] Average values for neutral 1*H*-mono-, 1*H*-3,5-di-, and 1,3,5-trisubstituted 1,2,4-triazoles according to [1].

geometric parameters of the hydroxyethylsulfanyl fragment. The latter in cation **IVA** is disordered by two positions with populations of 0.58 and 0.42. The major fragment has the same geometric parameters of the hydroxyethylsulfanyl group as in cation **IVB**. The geometric parameters of the heterorings in both cations are similar (Tables 3, 4), and the torsion angles in cation **IVA** refer to the fragment with the larger

Table 4. Bond angles (ω, deg) in the triazole ring of N-unsubstituted and substituted 1,2,4-triazolium salts **IV**–**XXIII** (for anions and references, see Table 3)



Comp. no.	R^1	R^3	R^4	R^5	K^+C[a]	K^+A[a]	$N^2N^1C^5$	$N^1N^2C^3$	$C^3N^4C^5$	$N^2C^3N^4$	$N^4C^5N^1$
IVA	H	SCH_2CH_2OH	H	H	–	1,4$^+$-C	111.9(8)	102.1(7)	105.8(8)	112.4(7)	107.8(9)
IVC	H	SCH_2CH_2OH	H	H	–	1,4$^+$-C	111.3(3)	103.6(7)	106.0(8)	111.5(8)	107.7(9)
V	H	SCH_2CH_2OH	H	Ph	–	1,4$^+$-C	112.2(7)	102.5(7)	105.4(7)	113.5(7)	106.5(7)
VI	H	H	H	H	1$^+$,4-C	1$^+$,2-C	110.9(2)	103.8(1)	106.5(2)	111.5(2)	107.2(2)
VII	H	H	H	H	1,4$^+$-C	1,4$^+$-C	111.5[b]	104.9	106.4	110.5	106.5
VIII	H	H	H	H	1$^+$,4-C	$[Tr]^+$	111.7(1)	103.5(1)	106.5(2)	111.5(2)	106.7(2)
IX	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	111.5(2)	103.2(2)	105.8(2)	112.9(2)	106.5(2)
X	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	111.2[b]	103.8	106.6	112.0	106.4
XI	H	H	H	NH_2	1$^+$,4-C	1,4$^+$-C	112.4(3)	102.7(4)	106.6(4)	112.8(4)	105.5(3)
XII	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	111.4[b]	103.4	106.2	112.7	106.3
XIII	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	111.3[b]	103.7	107.0	112.1	105.9
XIV	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	111.8(2)	103.3(2)	106.8(2)	112.4(2)	105.7(2)
XV	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	111.6(2)	103.2(2)	106.2(2)	113.0(2)	105.9(2)
XVI	H	H	H	NH_2	1,4$^+$-C	1,4$^+$-C	112.0(4)	103.6(4)	106.5(4)	112.7(4)	105.2(4)
XVII	H	$HN–NH_3^+$	H	NH_2	1,4$^+$-C	$[Tr]^+$	111.5(4)	102.6(4)	105.7(4)	113.6(4)	106.6(4)
XVIII	Me	C_8F_{17}	Me	Me	1,4$^+$-C	$[Tr]^+$	112.0[b]	103.8	105.8	111.9	106.5
XIX	H	Et	NH_2	Et	1,4$^+$-C	1,4$^+$-C	114.0[b]	101.8	106.6	111.3	106.3
XX	H	NH_2	NH_2	NH_2	1$^+$,4-C	1$^+$,4-C	111.4(4)	103.8(4)	107.1(4)	110.0(4)	106.7(4)
XXI	H	Me	NH_2	NHR[c]	1$^+$,4-C	–	111.5[b]	105.0	107.9	110.0	105.7
XXII	Me	NMe_2	Ar[d]	NMe_2	1,4$^+$-C	–	112.6[b]	103.8	106.5	110.4	106.7
XXIII	CH_2R[e]	H	NH_2	H	–	1$^+$,4-C	110.6[b]	103.5	107.7	110.1	108.2
Average value							111.7	103.4	107.7	111.8	106.5
Average value for neutral analogs[f]							110.3	101.6	101.7	114.9	110.6

[a] 1$^+$,4-K stands for positive charge localization on the N^1 atom of the triazole ring, 1,4$^+$-C denotes charge localization on the N^4 atom, and $[Tr]^+$ stands for delocalization of the positive charge over the triazole ring according to the CSD [C^+(C)] and authors' data [C^+(A)]. [b] No standard deviations for bond lengths and bond angles were given. [c] R = 2,6-$Cl_2C_6H_3CH$=N. [d] Ar = 2-HOC_6H_4. [e] R = 2-(4-amino-1,2,4-triazol-1-io)methyl bromide. [f] Average values for neutral 1*H*-mono-, 1*H*-3,5-di-, and 1,3,5-trisubstituted 1,2,4-triazoles according to [1].

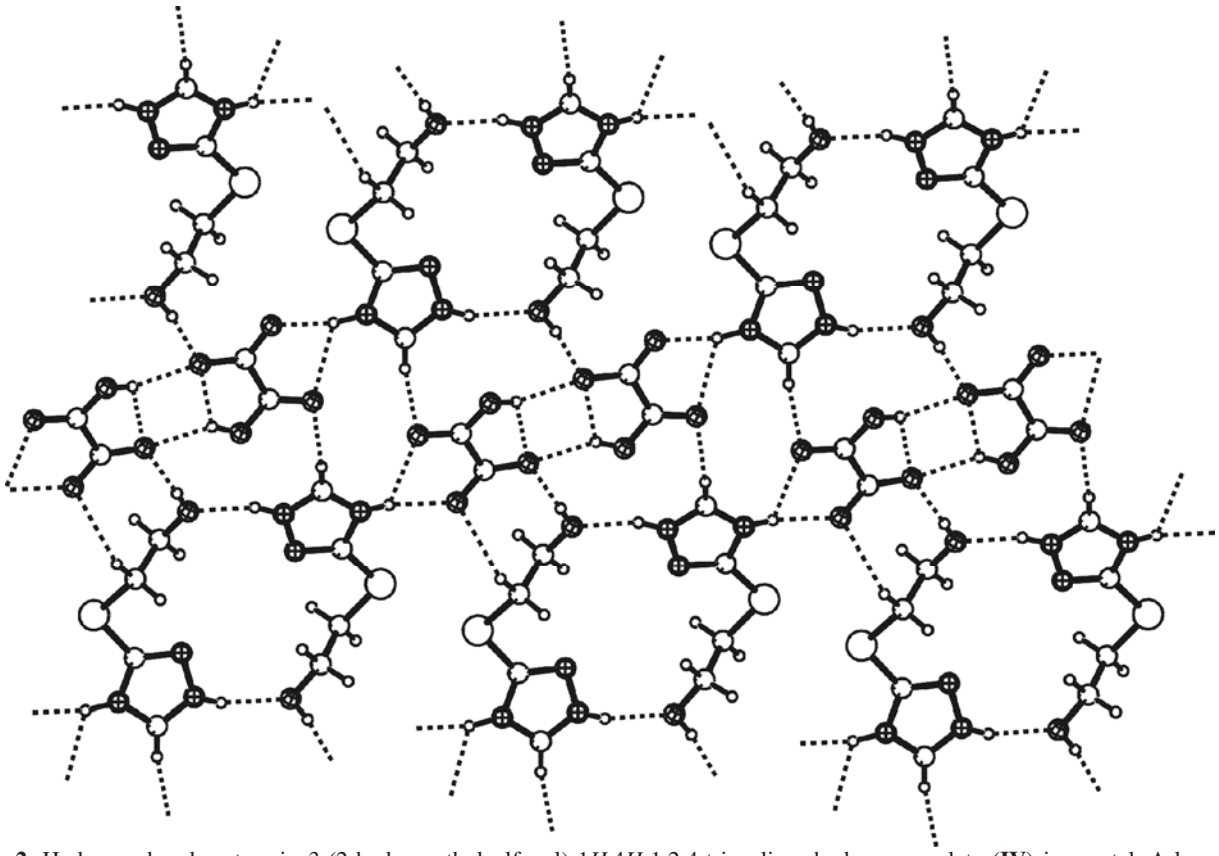


Fig. 2. Hydrogen bond system in 3-(2-hydroxyethylsulfanyl)-1*H*,4*H*-1,2,4-triazolium hydrogen oxalate (**IV**) in crystal. A layer of molecules formed via hydrogen bonding (dashed lines) is shown.

population (0.58; Table 5).

Both anionic species in salt **IV** are oxalic acid monoanions linked to 10-membered cyclic dimers by two O–H···O hydrogen bonds (Fig. 2). These H-dimers are involved in a complex system of intermolecular hydrogen bonds with cations **IVA** and **IVB**, giving rise to alternation of positively and negatively charged fragments in the crystalline structure of oxalate **IV** (Fig. 2). An analogous hydrogen bond motif formed by oxalic acid monoanion (denoted in [40] as *B*) together with chain-like motif *A* and motif *C* formed by isolated hydrogen oxalate ion was described for alkylammonium oxalates, while oxalates derived from α-amino acids contained oxalate dianion [41]. Hydrogen bonds between molecules **IV** in crystal also produce a two-dimensional supramolecular structure, a layer parallel to the (101) crystallographic plane.

The asymmetric part of a unit cell of hydrochloride **V** monohydrate in crystal (Fig. 3) consists of one cation–anion couple [3-(2-hydroxyethylsulfanyl)-5-phenyl-1*H*,4*H*-1,2,4-triazolium chloride] and one water molecule. The bond lengths and bond angles therein are given in Tables 3 and 4. Unlike cations **IVA** and **IVB**, the cation in salt **V** contains a phenyl group and is characterized by a different conformation with respect to the C^6–C^7 bond. The torsion angle $S^3C^6C^7O^8$ in that cation is equal to 60.7(9)° against 178.7(1) and 175.6(7)° in **IVA** and **IVC**, respectively (Table 5). The triazole ring in **V** is planar, and the dihedral angle

Table 5. Some torsion angles (φ, deg) in the cationic parts of oxalate **IV** and hydrochloride **V**

Angle	**IVA**	**IVB**	**V**[a]
$N^2C^3S^3C^6$	–28(1)	1(1)	1.3(9)
$N^4C^3S^3C^6$	151.8(9)	179.0(8)	–179.3(7)
$C^3S^3C^6C^7$	85(1)	75.8(8)	73.7(7)
$S^3C^6C^7O^8$	177(1)	176.1(7)	60.7(9)

[a] $N^1C^5C^9C^{10}$ –6(1); $N^4C^5C^9C^{10}$ 171.4(8); $N^1C^5C^9C^{14}$ 174.3(8); $N^4C^5C^9C^{14}$ –8(1).

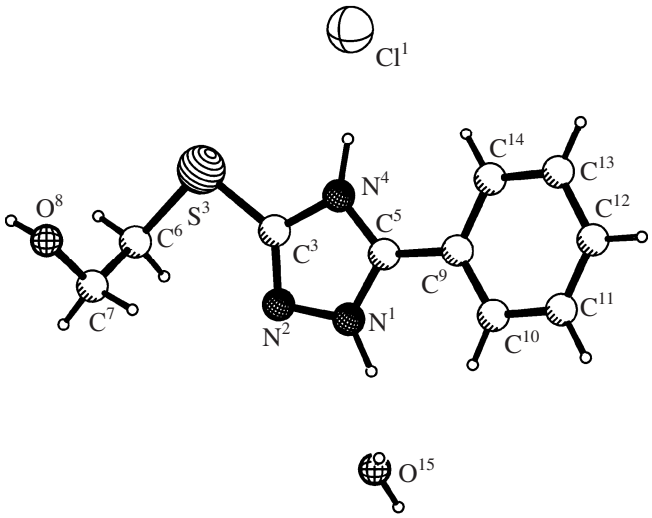


Fig. 3. Structure of 3-(2-hydroxyethylsulfanyl)-5-phenyl-1*H*,4*H*-1,2,4-triazolium chloride monohydrate (**V**) in crystal according to the X-ray diffraction data (independent part of a unit cell is shown).

between the triazole and benzene ring planes is 7.8 (4)°. The cation and anion of salt **V** and water molecule in crystal give rise to three-dimensional supramolecular structure (Fig. 4); the hydrogen bond parameters are collected in Table 6. In addition, one C–H···N intramolecular contact was revealed (Table 6).

As previously [1], we performed comparative analysis using the data from the Cambridge Crystallographic Data Center [42]. It turned out that the umber of 1,2,4-triazolium salts studied by X-ray diffraction is lesser by an order of magnitude than the number of neutral 1,2,4-triazole derivatives. We found the data for three slats of parent 1,2,4-triazole with different anions, ten salts derived from 5-amino-1,2,4-triazole, and eight N-substituted 1,2,4-triazolium salts (Tables 3, 4).

Comparison of the data for salts **IV** and **V**, neutral 1*H*-mono-, 1*H*-3,5-di-, and 1,3,5-trisubstituted 1,2,4-triazoles [1], and 1,2,4-triazolium salts **VI–XXIII** [23, 32, 43–57] shows a weak effect of protonation on the geometric parameters of the 1,2,4-triazole ring [1, 23, 32, 43–57] (Tables 3, 4). The cations in salts **IV** and **V** retain bond length alternation and clearly display conjugation effect, especially in the $N^1C^5N^4$ amidine fragment of hydrochloride **V** (Table 3). Analysis of the bond lengths in **IV** and **V** and in particular groups of neutral 1,2,4-triazoles [1] does not allow us to determine the protonation center and charge localization in the former. Insofar as the NH hydrogen atoms in the cationic species of **IV** and **V** were localized from difference series of electron density, we can conclude (Figs. 1, 3) that one hydrogen atom is attached to N^1 and that acidic proton adds at the nitrogen atom in position *4* of the triazole ring. This conclusion is consistent with the X-ray diffraction data for a series of 1,2,4-triazolium salts [23, 32, 43–57],

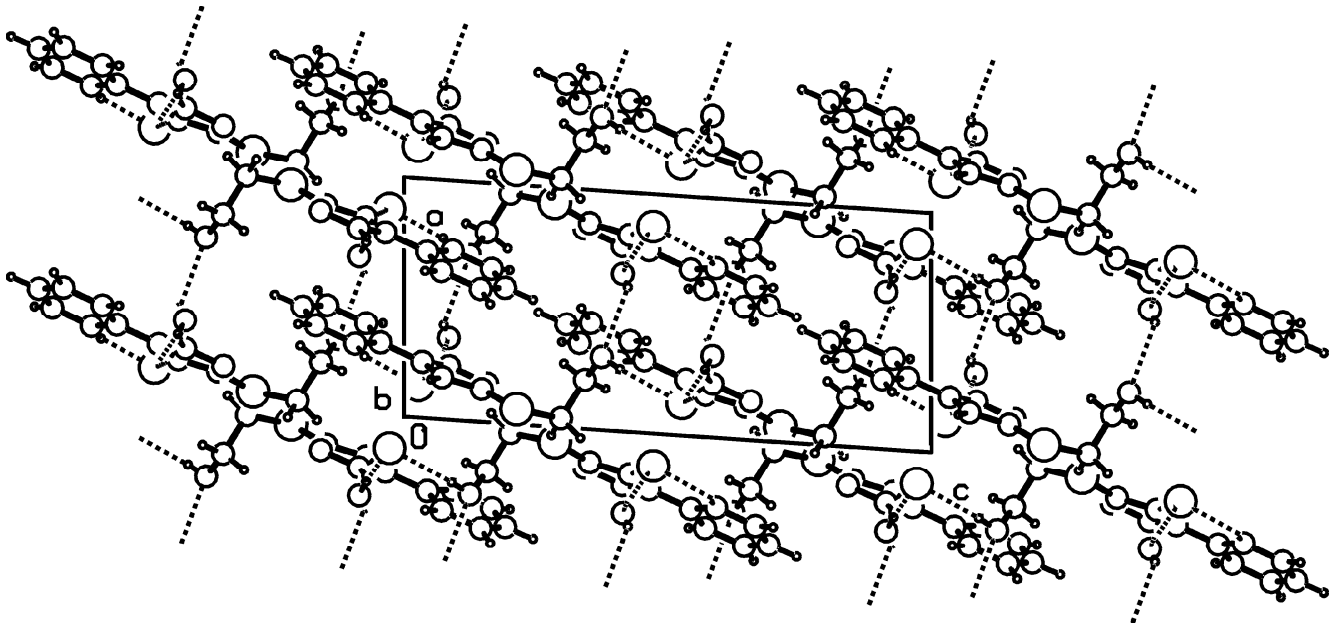


Fig. 4. Packing of 3-(2-hydroxyethylsulfanyl)-5-phenyl-1*H*,4*H*-1,2,4-triazolium chloride monohydrate (**V**) molecules in crystal and hydrogen bond (dashed lines) system therein.

Table 6. Parameters of shortened contacts (Å, deg) in the crystalline structures of oxalate **IV** and hydrochloride **V**

D–H···A	D–H	H···A	D···A	∠DHA	Symmetry operation
3-(2-Hydroxyethylsulfanyl)-1*H*,4*H*-1,2,4-triazolium hydrogen oxalate (**IV**)					
N^{1A}–H^{1A}···O^{8B}	0.76(8)	1.94(8)	2.67(1)	162(8)	1–*x*, 2–*y*, 1–*z*
N^{1B}–H^{1B}···O^{8A}	0.86(8)	1.83(8)	2.65(1)	159(8)	1–*x*, 2–*y*, 1–*z*
N^{4A}–H^{4A}···O^{9A}	0.94(8)	1.79(8)	2.65(1)	151(7)	–1+*x*, *y*, *z*
N^{4A}–H^{4A}···O^{11A}	0.94(8)	2.36(7)	2.95(1)	120(6)	–1+*x*, *y*, *z*
N^{4B}–H^{4B}···O^{9B}	0.82(6)	1.90(6)	2.67(1)	158(6)	1–*x*, 1–*y*, –*z*
N^{4B}–H^{4B}···O^{11B}	0.82(6)	2.42(6)	2.95(1)	124(5)	1–*x*, 1–*y*, –*z*
O^{8A}–H^{8A}···O^{10B}	0.82	1.89	2.70(1)	170.9	*x*, *y*, 1+*z*
O^{8B}–H^{8B}···O^{10A}	0.82	1.88	2.686(9)	169.3	2–*x*, 1–*y*, 1–*z*
O^{12A}–H^{12A}···O^{10B}	0.82	1.94	2.663(9)	145.9	*x*, –1+*y*, *z*
O^{12B}–H^{12B}···O^{10A}	0.82	1.95	2.660(9)	145.0	*x*, 1+*y*, *z*
O^{12A}–H^{12A}···O^{10A}	0.82	2.24	2.696(9)	115.8	–
O^{12B}–H^{12B}···O^{10B}	0.82	2.25	2.70(1)	114.0	–
C^{5A}–H^{5A}···O^{11B}	0.89(9)	2.40(9)	3.25(1)	162(9)	–1+*x*, *y*, *z*
C^{5B}–H^{5B}···O^{11A}	0.84(7)	2.40(7)	3.24(1)	174(7)	1–*x*, 1–*y*, –*z*
C^{6A}–H^{62A}···O^{9B}	0.97	2.56	3.41(2)	145.5	*x*, *y*, 1+*z*
3-(2-Hydroxyethylsulfanyl)-5-phenyl-1*H*,4*H*-1,2,4-triazolium chloride monohydrate (**V**)					
N^1–H^1···O^{15}	1.0(1)	1.7(1)	2.714(9)	159(8)	–
N^4–H^4···Cl^1	1.00(8)	1.96(8)	2.945(8)	172(6)	–
O^8–H^8···Cl^1	0.81(7)	2.29(7)	3.060(7)	160(7)	*x*, 3/2–*y*, 1/2+*z*
O^{15}–H^{151}···Cl^1	0.93(8)	2.21(8)	3.134(7)	173(6)	*x*, –1+*y*, *z*
O^{15}–H^{152}···O^8	0.51(5)	2.40(4)	2.731(9)	125(5)	1–*x*, –1/2+*y*, 1/2–*z*
C^7–H^{71}···N^2	1.0(1)	2.6(1)	3.25(1)	128(9)	–

given in Table 3. Unfortunately, most data refer to salts derived from amino-substituted 1,2,4-triazoles possessing even larger number of possible protonation centers. These salts were previously assigned the structure of iminium cations on the basis of only IR data [34, 35].

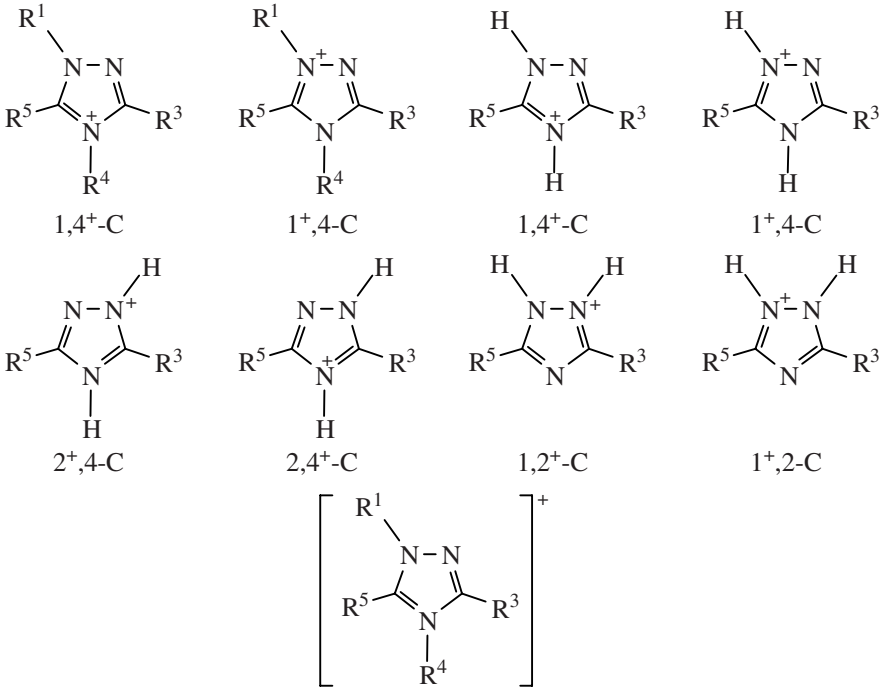
The C^3–S^3 bond length in cations **IVA**, **IVB**, and **V** is 1.741(9), 1.730(8), and 1.746(9) Å, respectively; i.e., it differs only slightly from the corresponding bond length in neutral analogs of 3-alkylsulfanyl-1,2,4-triazoles [1]. The C^3–S^3 bond is appreciably shorter than the S^3–C^6 bond with the hydroxyethyl fragment (1.77–1.79 Å) and is closer to standard single C_{sp^2}–S bond (1.751 Å; cf. 1.671 Å for double C_{sp^2}=S bond [58]). The C–C and C–O bond lengths in **IVA**, **IVB**, and **V** approach those typical of hydroxyethyl groups [58].

Changes of the bond angles upon protonation of the examined 1,2,4-triazoles are more appreciable. The $C^3N^4C^5$ angle changes most strongly, while variations of the $N^1N^2C^3$ angle are minimal (Table 4). These data indicate that protonation affects the $N^1C^5N^4$ fragment to the greatest extent. Naturally, the character of protonation-induced variations also depends on the nature of substituents present in the molecule (Tables 3, 4). For example, bond length leveling in the heteroring of hydrochloride **V** is on the whole less pronounced than in oxalate **IV** but is stronger in the amidine $N^1C^5N^4$ fragment.

The average $N^2N^1C^5$ angle in neutral triazoles is 110.3° [1]; the corresponding values for salts **IVA**, **IVB**, and **V** are 111.9(8), 111.3(8), and 112.2(7)°, respectively. The endocyclic bond angles at the N^2, C^3, and C^5 atoms also coincide within experimental error with those found for their neutral analogs [1]. The average $C^3N^4C^5$ angle in neutral triazoles is considerably smaller than in the triazolium cations in salts **IVA**, **IVB**, and **V** and is 101.7° [**IVA**, 105.9(9)°; **IVB**, 106.0(8)°; **V**, 105.4(7)°]. The corresponding angle in other protonated triazoles (**VI**–**XXIII**) [23, 32,

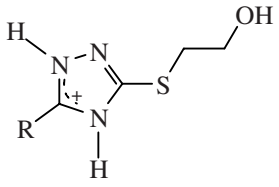
43–57] is appreciably larger than in the free bases; it ranges from 105.7(4) to 107(1)° (Table 4, cf. [1]).

Analysis of the data in Tables 3 and 4 led us to conclude that 1,2,4-triazoles having no substituent on the nitrogen atom and their 1-substituted analogs always undergo protonation at the nitrogen atom in position *4*. This conclusion is consistent with the results of theoretical calculations of 1,2,4-triazole molecule, according to which the largest electron density is localized just on the N^4 atom [33, 59] (see also references given in [1]). On the other hand, the site of proton addition (N^4) is not necessarily the site of localization of the positive charge in the ring. Tables 3 and 4 contain sometimes contradictory views of authors of the original articles and CSD compilers on preferential structure of cationic species given therein. The structures of cations **IVe** and **Ve** with probable charge localizations are shown below.



The structures of 1,2,4-triazolium cations assumed in [23, 32, 43–57] were substantiated insufficiently. In some cases, cation structure was represented as a set of canonical structures in terms of the resonance theory [57] or as complete charge delocalization over the ring [26], which are difficult to match with the experimental data. We give preference to structures **IVc** and **Vc**; however, taking into account bond length alternation in the triazole ring and simultaneous bond leveling in the amidine fragment, structures like **IVe** and **Ve** with partial charge delocalization seem to be the most probable.

In order to draw a final conclusion on charge localization in 1,2,4-triazolium cations **IV** and **V** and other related systems, quantum-chemical calculations



IVe, Ve

and precise X-ray diffraction studies are likely to be necessary to analyze electron density distribution in 1,2,4-triazolium cations.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from films, dispersions in mineral oil,

KBr pellets, and solutions in carbon tetrachloride ($c \approx 10^{-4}$ M). The ^{1}H and ^{13}C NMR spectra were measured on Bruker MSL-400 (400.13 MHz for ^{1}H and 100 MHz for ^{13}C) and Avance 600 spectrometers (600.00 MHz for ^{1}H and 150.864 MHz for ^{13}C) using tetramethylsilane as internal reference or acetone-d_6 as external reference. The mass spectra (electron impact) were obtained on a Trace MS GC–MS system (solvent ethanol). The melting points were determined on a Boetius type melting point apparatus or standard PTP instrument.

2-(1*H*-1,2,4-Triazol-3-ylsulfanyl)ethanol (I). A solution of 20.9 g of potassium hydroxide in 300 ml of methanol was added to 27.82 g of 2,3-dihydro-1*H*-1,2,4-triazole-3-thione, the mixture was heated for 30 min under reflux, 27.0 g of 2-chloroethanol was added, and the mixture was heated for 3 h under reflux. The mixture was cooled, the precipitate of potassium chloride was filtered off, and the filtrate was evaporated. The residue, 45 g, was a syrup-like material which was dissolved in propan-2-ol, and the solution was passed through a column charged with aluminum oxide to remove residual KCl. After prolonged evacuation, we obtained about 37 g (91%) of a syrupy material which did not crystallize over several months. After storage for more than a year, a few colorless crystals were formed, but we failed to separate them from the oily material because of ready solubility in most organic solvents. IR spectrum, ν, cm^{-1}: film: 3300 and 3100 v.br, 1646, 1514, 1277, 1242, 1178, 1067, 1046, 1014, 974; CCl_4 ($c \approx 10^{-4}$ M): 3458, 3300. The ^{1}H and ^{13}C NMR spectra are given in Tables 1 and 2. Mass spectrum, *m*/*z* (I_{rel}, %): $[M]^{+\cdot}$ 145 (9), 144 (2), 128 (3), 126 (8), 116 (7), 115 (99), 114 (46), 102 (14), 101 (100), 82 (10), 74 (17), 71 (13), 70 (43), 60 (10), 46 (15), 45 (53), 44 (17), 43 (47), 42 (36). Found, %: C 32.87, 32.94; H 4.56, 4.39; N 28.59, 29.68; S 21.78, 21.89. $C_4H_7N_3OS$. Calculated, %: C 33.09; H 4.86; N 28.94; S 22.08.

2-(5-Methyl-1*H*-1,2,4-triazol-3-ylsulfanyl)ethanol (II). A solution of 4.2 g of sodium hydroxide in 8 ml of water was added under stirring to a suspension of 11.5 g of 5-methyl-2,3-dihydro-1*H*-1,2,4-triazole-3-thione in 75 ml of propan-2-ol, the mixture was heated until it became homogeneous, 10 ml of 2-chloroethanol was added. and the mixture was heated for 3 h under reflux and left overnight. The solvent was removed under reduced pressure (water-jet pump) on heating on a water bath, and the residue was treated with chloroform (two layers were formed). Propan-2-ol was added until the mixture became homogeneous, and the resulting solution was passed through a column charged with aluminum oxide. The column was additionally washed with a small amount of propan-2-ol. The elueate were combined and evaporated under reduced pressure, the residue was treated with chloroform, and the crystals were filtered off, washed with chloroform and a small amount of acetone, and dried in air. Yield 9.6 g (49.4%), snow-white fine crystals, mp 74–76°C (capillary, PTP), 77.5–79°C (Boetius apparatus). IR spectrum, ν, cm^{-1}: mineral oil: 3128 v.br, 1556, 1333,1292, 1263, 1223, 1205, 1165, 1117, 1078, 1056, 1016, 950, 779, 719, 701; CCl_4 ($c \approx 10^{-4}$ M): 3457, 3300. Mass spectrum, *m*/*z* (I_{rel}, %): $[M]^{+\cdot}$ 159 (7), 158 (2), 142 (3), 140 (7), 129 (100), 128 (38), 116 (9), 115 (99), 114 (46), 99 (17), 96 (12), 84 (35), 74 (22), 59 (15), 58 (22), 57 (16), 56 (59), 46 (12), 45 (44), 43 (26), 42 (84). The ^{1}H and ^{13}C NMR spectra are given in Tables 1 and 2. Found, %: C 37.67, 37.64; H 5.51, 5.49; N 26.53, 26.48; S 19.78, 19.86. $C_5H_9N_3OS$. Calculated, %: C 37.72; H 5.70; N 26.39; S 20.14.

2-(5-Phenyl-1*H*-1,2,4-triazol-3-ylsulfanyl)ethanol (III). A solution of 0.73 g of potassium hydroxide in 25 ml of methanol was added to 1.77 g of 5-phenyl-1*H*-1,2,4-triazole-3-thiol, the mixture was heated for 0.5 h, 0.98 g of 2-chloroethanol was added, and the mixture was heated for 3 h under reflux. The mixture was cooled, the precipitate of potassium chloride was filtered off, and the filtrate was evaporated under reduced pressure. The residue was dissolved in 10 ml of boiling methylene chloride, 15–20 ml of aluminum oxide was added until a free-flowing material was obtained, and the latter was placed into a separatory funnel and washed with 50 ml of methylene chloride. The eluate was cooled, white crystals of triazole **III**, 0.1 g, were filtered off, and the filtrate was evaporated. The residue, 0.7 g, was a thick syrupy material which crystallized in storage for 5 days. The crystalline material was ground with a small amount of methylene chloride, and the crystals were separated. We thus isolated an additional 0.4 g of triazole **III** as white crystals with mp 103–105°C (Boetius apparatus). The overall yield of the pure product was 23%. The yield may be considerably improved by repeating the procedure for isolation from the mother liquor. IR spectrum, ν, cm^{-1}: KBr: 3210 and 3132 br, 3075, 2793, 2670, 1611 w, 1561, 1492, 1418, 1334, 1282, 1268, 1181, 1145, 1123, 1065, 1022, 1010, 980; mineral oil: 3210, 3131, 3074, 2750, 2660, next the same as in

KBr. The ^{1}H and ^{13}C NMR spectra are given in Tables 1 and 2. Mass spectrum, *m*/*z* (I_{rel}, %): $[M]^{+\cdot}$ 221 (15), 220 (2), 204 (2), 202 (5), 192 (12), 191 (98), 190 (23), 178 (12), 177 (95), 161 (11), 158 (18), 146 (18), 119 (13), 118 (41), 104 (100), 103 (54), 91 (29), 77 (52), 76 (26), 74 (16), 63 (13), 51 (22), 45 (30), 43 (15). Found, %: C 54.40, 54.35; H 4.91, 4.82; N 19.11, 19.06; S 14.02, 14.31. $C_{10}H_{11}N_3OS$. Calculated, %: C 54.28; H 5.01; N 18.99; S 14.49.

3-(2-Hydroxyethylsulfanyl)-1*H*,4*H*-1,2,4-triazolium hydrogen oxalate (IV). Crude syrupy triazole **I**, 45 g, was dissolved in 200 ml of ethanol, the solution was filtered, and the filtrate was added to a hot solution of 10 g of oxalic acid. The mixture was stirred for 10 min and filtered while hot to remove potassium oxalate which is almost insoluble in hot ethanol. An additional amount of oxalic acid, 25 g, was added to the filtrate, and the resulting solution was cooled in a refrigerator. The crystals were filtered off, washed with cold ethanol, and dried. Recrystallization from methanol gave 31 g (42.5%) of salt **IV** as a white crystalline powder with mp 138–140°C (PTP), which is readily soluble in water, DMSO, and DMF. The product melted at 132–136°C with partial decomposition on a Boetius type hot stage. IR spectrum (mineral oil), ν, cm^{-1}: 3199, 3113, 2665, 2611, 1751, 1651, 1559, 1528, 1421, 1306, 1240, 1188, 1174, 1138, 1058, 1023, 946. The ^{1}H and ^{13}C NMR spectra are given in Tables 1 and 2. Found, %: C 30.58; H 3.81; N 18.03; S 13.17. $C_4H_7N_3OS \cdot C_2H_2O_4$. Calculated, %: C 30.64; H 3.86; N 17.86; S 13.60.

Evaporation of the mother liquor to 1/4 of the initial volume gave an additional amount of salt **IV** which was recrystallized from alcohol (11.0 g). Overall yield 42 g (57.5%).

3-(2-Hydroxyethylsulfanyl)-5-phenyl-1*H*-1,2,4-triazole hydrochloride (V). Triazole **III**, 1.1 g, was dissolved in 50 ml of methanol, concentrated hydrochloric acid was added under stirring to the solution until pH ~1, and the mixture was stirred for 0.5 h. The solvent was removed under reduced pressure (water-jet pump), and the precipitate was recrystallized first from aqueous ethanol and then from ethanol. Yield 1.2 g (87%, calculated on the monohydrate), colorless fine needles, mp 56–59 (PTP), 50–54°C (Boetius). IR spectrum (mineral oil), ν, cm^{-1}: 3377, 3256, 3055, 2716, 2604, 2505, 1614, 1592, 1503, 1394, 1343, 1296, 1244, 1162, 1065, 1011, 985. The ^{1}H and ^{13}C NMR spectra are given in Tables 1 and 2. Found, %: C 43.52, 43.74; H 4.93, 4.81; Cl 12.53, 12.74; N 15.41,15.36; S 12.28, 12.31. $C_{10}H_{11}N_3OS \cdot HCl \cdot H_2O$. Calculated, %: C 43.56; H 5.12; Cl 12.86; N 15.24; S 11.63.

X-Ray analysis of triazolium salts IV and V. Single crystals were obtained from solutions in methanol–water (10:1). The X-ray diffraction data were acquired at room temperature (20°C) on an Enraf–Nonius CAD-4 automatic four-circle diffractometer [monochromatized MoK_α irradiation, λ = 0.71073 Å (**IV**), or CuK_α irradiation, λ = 1.54184 Å (**V**); graphite monochromator]. The unit cell parameters were determined from 25 reflections. The stability of crystals during data acquisition was checked by measuring the intensities of three control reflections every two hours, and orientation of the crystals was monitored by centering two reflections after every 200 reflections. No drop in the intensity of control reflections was observed. The unit cell parameters were determined, and preliminary processing of the experimental data was performed, using MolEN software [60]. The structures were solved by the direct method using SIR program [61]. The structures were refined first in isotropic and then in anisotropic approximation using MolEN software [60] for compound **V** and SHELX-97 [62] from WinGX [63] for compound **IV**. All structures were plotted, and intermolecular interactions were analyzed, using PLATON program [64]. The X-ray diffraction experiments were performed at the X-Ray Analysis Department (Collective Use Center, Spectral Analytical Center, Laboratory of Diffraction Methods, Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences).

3-(2-Hydroxyethylsulfanyl)-1*H*,4*H*-1,2,4-triazolium hydrogen oxalate (IV). Colorless transparent prisms, triclinic crystal system; $2C_4H_8N_3SO^+ \cdot 2C_2HO_4^-$, *M* 235.23. Unit cell parameters: *a* = 8.68(1), *b* = 10.804(7), *c* = 11.44(1) Å; α = 105.09(6), β = 93.47(9), γ = 109.21(7)°; *V* = 966(2) Å^3; d_{calc} = 1.62 g/cm^3; *Z* = 4; space group *P*-1 (two independent molecules); ω-scanning, 4.39° ≤ θ ≤ 25.93°. No correction for absorption was introduced (μMo = 3.43 cm^{-1}). The coordinates of hydrogen atoms on carbon atoms, except for C^{5A} and C^{5B}, were calculated on the basis of stereochemical criteria and were refined using the riding model. Hydrogen atoms on N^{1A}, N^{4A}, N^{4B}, C^{5A}, and C^{5B} were localized from difference series of electron density, and their contributions to structural amplitudes were taken into account with fixed

Table 7. Coordinates of non-hydrogen atoms in the molecule of 3-(2-hydroxyethylsulfanyl)-1*H*,4*H*-1,2,4-triazo-**5**lium hydrogen oxalate (**IV**) in crystal and their equivalent isotropic thermal parameters U_{eq} (Å^2)[a]

Atom	*x*	*y*	*z*	U_{eq}
S^{3A}	0.2814(4)	0.4736(2)	0.5692(2)	0.073(1)
O^{8A}	0.5393(8)	0.8143(6)	0.8419(6)	0.076(3)
N^{1A}	0.158(1)	0.672(1)	0.3746(7)	0.055(4)
N^{2A}	0.233(1)	0.6744(7)	0.4837(7)	0.059(3)
N^{4A}	0.1330(9)	0.4666(8)	0.3546(7)	0.048(3)
C^{3A}	0.214(1)	0.5456(9)	0.4663(8)	0.049(4)
C^{5A}	0.099(1)	0.550(1)	0.299(1)	0.051(4)
C^{6A}	0.467(2)	0.623(2)	0.665(2)	0.058(7)
C^{7A}	0.397(3)	0.708(2)	0.768(2)	0.053(8)
S^{3B}	0.6225(3)	0.7429(2)	0.3238(2)	0.065(1)
O^{8B}	0.8188(8)	1.0742(6)	0.6203(5)	0.064(3)
N^{1B}	0.4367(9)	0.9338(8)	0.1552(6)	0.052(3)
N^{2B}	0.5499(9)	0.9391(7)	0.2475(6)	0.051(3)
N^{4B}	0.404(1)	0.7280(8)	0.1412(7)	0.048(3)
C^{3B}	0.524(1)	0.8119(9)	0.2367(8)	0.042(3)
C^{5B}	0.352(1)	0.810(1)	0.0926(9)	0.050(4)
C^{6B}	0.767(1)	0.892(1)	0.4325(8)	0.067(4)
C^{7B}	0.698(1)	0.961(1)	0.5307(9)	0.076(4)
O^{9A}	1.1001(8)	0.2060(6)	0.3176(5)	0.069(3)
O^{10A}	1.0052(8)	–0.0160(6)	0.2142(5)	0.055(3)
O^{11A}	0.9335(8)	0.2497(6)	0.1318(5)	0.061(3)
O^{12A}	0.8184(8)	0.0287(6)	0.0442(5)	0.060(3)
C^{8A}	1.018(1)	0.1078(9)	0.2307(8)	0.044(3)
C^{9A}	0.919(1)	0.135(1)	0.1321(7)	0.046(3)
O^{9B}	0.6403(8)	0.5362(6)	–0.1079(6)	0.069(3)
O^{10B}	0.7357(8)	0.7584(6)	–0.0026(5)	0.063(3)
O^{11B}	0.8420(8)	0.4961(6)	0.0567(5)	0.064(3)
O^{12B}	0.9569(8)	0.7174(6)	0.1444(5)	0.059(3)
C^{8B}	0.732(1)	0.6381(9)	–0.0243(8)	0.048(4)
C^{9B}	0.846(1)	0.6106(9)	0.0651(8)	0.044(4)

[a] The equivalent isotropic thermal parameters U_{eq} were calculated as one third of the trace of the orthogonalized tensor U_{ij}.

positional and thermal parameters in the final refinement step. The ethyl fragment in cation **IVA** was found to be disordered by two positions with populations of 0.42 and 0.58. Total of 1107 independent reflections were measured, 1045 of which were with $I \geq 2\sigma$. The final divergence factors were $R = 0.046$ and $R_w = 0.112$ [from 1045 reflections with $F^2 \geq 4\sigma(I^2)$]. The coordinates of atoms are given in Table 7. The complete set of crystallographic data was deposited to the Cambridge Crystallographic Data Center (entry no. CCDC 255381).

Table 8. Coordinates of non-hydrogen atoms in the molecule of 3-(2-hydroxyethylsulfanyl)-5-phenyl-1*H*,4*H*-1,2,4-triazolium chloride monohydrate (**V**) in crystal and their equivalent temperature factors $B = 4/3 \sum_{i=1} \sum_{j=1} (a_i,a_j)B(i,j)$ (Å^2)

Atom	*x*	*y*	*z*	B_{eq}
Cl^1	0.1348(4)	–0.3368(3)	0.5273(2)	6.04(7)
S^3	0.0634(4)	–0.1282(3)	0.7140(2)	4.28(6)
O^8	0.3059(8)	–0.0831(7)	0.8751(4)	5.8(2)
O^{15}	0.3414(8)	0.4082(6)	0.5850(4)	5.8(2)
N^1	0.2244(8)	0.1537(7)	0.5857(4)	3.1(2)
N^2	0.1626(9)	0.1148(7)	0.6578(4)	3.7(2)
N^4	0.1766(9)	–0.0555(7)	0.5725(4)	3.2(2)
C^3	0.138(1)	–0.0110(8)	0.6477(5)	2.3(2)
C^5	0.235(1)	0.0516(9)	0.5351(5)	2.5(2)
C^9	0.304(1)	0.0594(9)	0.4558(4)	2.7(2)
C^{14}	0.291(1)	–0.0516(9)	0.4078(4)	3.3(2)
C^{13}	0.357(1)	–0.051(1)	0.3332(5)	4.6(3)
C^{12}	0.432(1)	0.067(1)	0.3080(5)	5.2(3)
C^{11}	0.444(1)	0.176(1)	0.3545(5)	4.3(3)
C^{10}	0.380(1)	0.1727(9)	0.4287(5)	3.5(2)
C^6	0.038(1)	–0.0224(9)	0.7979(5)	4.3(3)
C^7	0.205(1)	0.022(1)	0.8429(5)	5.4(3)

3-(2-Hydroxyethylsulfanyl)-5-phenyl-1*H*,4*H*-1,2,4-triazolium chloride monohydrate (V). Colorless transparent prisms, monoclinic crystal system; $C_{10}H_{12}N_3SO^+ \cdot Cl^- \cdot H_2O$; *M* 275.76. Unit cell parameters: $a = 7.629(1)$, $b = 10.070(2)$, $c = 16.826(5)$ Å; $\beta = 93.86(2)°$; $V = 1289.6(5)$ Å^3; $d_{calc} = 1.42$ g/cm^3; $Z = 4$; space group $P2_1/c$; $\omega/2\theta$-scanning, $\theta \leq 57.2°$. No correction for absorption was introduced (μCu = 41.22 cm^{-1}). Hydrogen atoms were localized from difference series of electron density, and their contributions to structural amplitudes were taken into account with fixed positional and thermal parameters in the final refinement step. Total of 3400 reflections were measured, 1322 of which were with $I \geq 3\sigma$. The final divergence factors were $R = 0.060$, $R_w = 0.059$ [from 968 reflections with $F^2 \geq 3\sigma$ (I^2)]. The coordinates of atoms are given in Table 8. The complete set of crystallographic data was deposited to the Cambridge

Crystallographic Data Center (entry no. CCDC 273419).

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