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Tautomerism of Azacycles: III.[1] Molecular and Crystal Structures of 3*H*- and 2-Phenyl-1*H*,4*H*-4,5-dihydro-1,2,4-triazole-5-thiones

B. I. Buzykin, E. V. Mironova, A. T. Gubaidullin, I. A. Litvinov, and V. N. Nabiullin

Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, Tatarstan, 420088 Russia
e-mail: katy@iopc.knc.ru

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Abstract—Compounds capable of tautomerism: sulfanyl-1,2,4-triazole, its *C*-phenyl derivative, and the crystal hydrate of the latter, were studied by single crystal X-ray diffraction. In the crystals they exist in the form of 3-R-1(*H*),4(*H*)-4,5-dihydro-1,2,4-triazole-5-thione with a considerable contribution of the bipolar structure. Published data on the tautomerism of sulfanyl-1,2,4-triazoles and their N-substituted analogs and on the correlation between the spectral characteristics and structures of sulfanyl-1,2,4-triazoles capable of tautomerism are discussed.

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Sulfhydryl derivatives of 1,2,4-triazole are widely used in chemistry, biology, medicine, and agriculture. The use of these compounds substituted at the sulfur atom was discussed in detail in the first papers of this series [1, 2] (see also reviews [3–6]). 3(5)-Sulfhydryl-1,2,4-triazoles unsubstituted at the S and N atoms are also successfully used in the organic synthesis for preparing annelated 1,2,4-triazoles [3–11] and macrocycles [12], iron nitrosyl complexes [13], and compounds with biological activity (antimicrobial [14], antituberculous [15], antifungal [16], antidepressant [17], pesticide [18], and other kinds of biological activity [11, 16]). 3(5)-Sulfanyl-1,2,4-triazoles substituted at one of nitrogen atoms and capable of tautomerism are also widely used. 4-N-Substituted sulfanyl-1,2,4-triazoles, especially 4-amino-3(5)-sulfanyl-1,2,4-triazole and its derivatives [3–6], are studied in considerably more detail than their 1(2)-N-substituted analogs.

In the first communication we discussed in detail the problems of intracyclic tautomerism of N-unsubstituted 1,2,4-triazoles and especially alkylsulfanyl-1,2,4-triazoles [2]. In the second paper, along with the annular tautomerism {by the example of 3-(hydroxyethylsulfanyl)-5-R-1,2,4-triazoles, analogs of compounds with tuberculostatic activity [8, 14, 15]}, we discussed the possibilities of the ring–chain tautomerism involving the side fragment and also the tautomerism of the 1,2,4-triazolium salts [1]. Here we report on a single crystal X-ray diffraction study of sulfanyl-1,2,4-triazole **I**, its *C*-phenyl derivative **II**, and its crystal hydrate **III**. These compounds do not contain substituents at the N and S atoms. The data obtained are necessary for discussing the aspects of the thiol–thione tautomerism of 3(5)-sulfanyl-5(3)-R-1,2,4-triazoles and of the relationships between the spectral characteristics and structures of sulfanyl-1,2,4-triazoles capable of tautomerism.

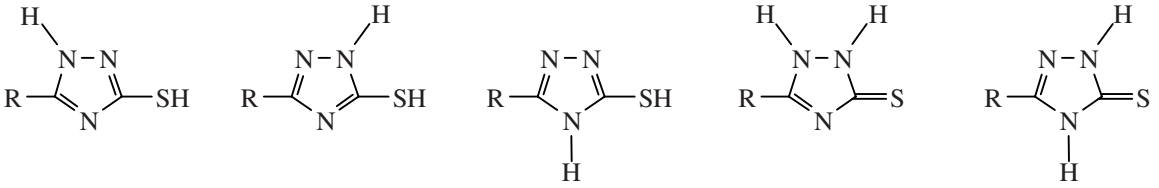
The structures of N,S-unsubstituted sulfanyl-1,2,4-triazoles were discussed superficially. In the basic review [19], they were not mentioned at all. The problem was not duscussed in the subsequent reviews [3–6], either. For example, in the review [6] specially devoted to thiol–thione tautomerism of sulfanylazoles,

[1] For communication II, see [1].

among 1,2,4-triazoles only the 1-N- and 4-N-substituted analogs, which can be considered only as sulfanyltriazole tautomeric forms partially fixed at the N^1 or N^4 atom, were briefly considered. Analysis of the IR spectra of sulfanyltriazole and its N-methyl-substituted analogs (mainly of the band at 1200–1280 cm^{-1}, which was assigned to $\nu_{C=S}$ vibrations) led Blacman and Polya [20] to a conclusion that these compounds have a thione structure in the crystals. The same conclusion was also made in other papers dealing with UV, vibration, and NMR spectra of sulfanyltriazole and its N-methyl-substituted analogs [21, 22]. However, Krishnakumar and Xavier [23], returning to the analysis of the IR and Raman spectra of sulfanyltriazole and using also calculations, revised these data and made a conclusion (in our opinion, insufficiently reasoned) that this compound exists in crystals in the thiol form, i.e., as 3-sulfanyl-1*H*-1,2,4-triazole. We found no data about studies of tautiomeric equilibria between various forms of sulfanyl-1,2,4-triazoles by instrumental methods, although Shklyarenko et al. [24] believe, without serious reasoning, that there occur fast mutual transformations of 1*H*-3-*SH* and 1*H*-5-*SH* tautomers of unsubstituted sulfanyl-1,2,4-triazole with prevalence of the former tautomer.

The prevalence of a particular tautomeric form of 4-N-substituted 1,2,4-triazoles was judged in [25] on the basis of a linear correlation between the dissociation constants and Hammett constants of substituents (log *K* 1.06, σ_x 11.01). It was concluded that the thione form of 3,4-diaryl-5-sulfanyl-1*H*-1,2,4-triazoles is realized in solutions.

The scarcity of data and inconsistency of conclusions on the thio–thione tautomerism are due to specific properties of the thioamide fragment, giving rise to certain problems in studying this tautomerism for any class of organic compounds: thioamides, thiohydrazides, and 3-sulfanylheterocycles of various nature, e.g., 3-sulfanylpyridine [26], 3-sulfanylhydrazidines, and 3-sulfanylformazans [27, 28]. The history of elucidating the structure of the well-known analytical reagent Dithizone and its analogs is instructive in this respect. In most cases, the use of spectroscopic methods is complicated by ambiguous interpretation of their results, even in the method of fixed structures. For example, thioacetamide and *N*-phenylthiobenzamide, for which the thioamide structure was confirmed, exhibit even longer-wavelength UV absorption than do the *S*-methyl derivatives of their thiol forms (267 and 230 nm for the first, and 317 and 296 nm for the second pair, respectively) [27]. Therefore, conclusions about the structure of such compounds, based on a single spectroscopic method, should be treated with caution.

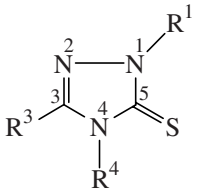


Usually five possible tautomeric forms of N,S-unsubstituted sulfanyl-1,2,4-triazoles, **A–E**, are considered in the literature (see, e.g., [21–25]). In articles, patents, and reports, virtually all the forms are represented, but in the overwhelming majority of cases this is done without due reasoning. Even in the Beilstein electronic database the data on triazoles **I** and **II** are given under the formulas of four tautomeric forms **A–D** of each compound [29], and in all the cases the actual structure is not proved and the data on the properties of the tautomers partially duplicate each other.

It is known that the sulfhydryl group is an electron acceptor. The inductive constant σ_I for the unsubstituted SH group is estimated at 0.18 to 0.41 [30]. In view of this fact and of the conclusion we made previously [2] that the major tautomeric form of N-unsubstituted 1,2,4-triazoles is the 3-R_A-5-R_D-1*H* form,[2] among thiol tautomers **A–C** of N,S-unsubtituted sulfanyl-1,2,4-triazoles form **A** should be preferred. However, actually this structure was and is given in relevant papers less frequently [3, 23, 24, 31] than the structures of tautomers **C** [3H-3(5)-*SH* tautomer] [10, 31–34] and especially **B** (1*H*-5-*SH* tautomer) [35–41].

[2] R_A and R_D are substituents with acceptor and donor properties, respectively.

Table 1. Bond lengths (*d*, Å) in the triazole ring of compounds **I–III** and their structural analogs **IV–XIV**



Comp. no.	R^1	R^3	R^4	N^1–N^2	N^2–C^3	C^3–N^4	N^4–C^5	C^5–N^1	C^5–S	Reference
I	H	H	H	1.379(6)	1.284(8)	1.371(8)	1.354(8)	1.337(8)	1.683(6)	–[a]
IIa	H	Ph	H	1.39(2)	1.32(2)	1.33(1)	1.38(1)	1.34(2)	1.69(1)	–[a]
IIb	H	Ph	H	1.35(2)	1.33(2)	1.34(1)	1.37(1)	1.35(2)	1.68(1)	–[a]
IIc	H	Ph	H	1.38(2)	1.31(2)	1.35(1)	1.34(1)	1.35(2)	1.68(1)	–[a]
IId	H	Ph	H	1.39(2)	1.32(2)	1.37(2)	1.37(2)	1.32(2)	1.68(1)	–[a]
IIIa[b]	H	Ph	H	1.374(3)	1.306(3)	1.375(3)	1.352(3)	1.333(3)	1.690(2)	–[a]
IIIb[b]	H	Ph	H	1.364(3)	1.308(3)	1.371(3)	1.352(3)	1.335(3)	1.684(2)	–[a]
IV	H	Bn	Ph	1.372(2)	1.296(2)	1.381(2)	1.379(2)	1.338(2)	1.672(2)	[57]
Va	H	4-Py	4-Tol	1.367(3)	1.295(3)	1.376(3)	1.389(3)	1.333(3)	1.663(2)	[58]
Vb	H	4-Py	4-Tol	1.377(3)	1.300(3)	1.378(3)	1.382(3)	1.339(3)	1.660(3)	[58]
VI	H	*n*-Pr	NMe_2	1.384(2)	1.304(2)	1.377(2)	1.372(2)	1.332(2)	1.686(2)	[59]
VII	H	Et	–N=CHR[c]	1.383(4)	1.295(4)	1.379(4)	1.387(4)	1.330(4)	1.681(4)	[60]
VIII	H	Furyl-2	4-ClC_6H_4	1.374(2)	1.311(2)	1.384(2)	1.383(2)	1.346(2)	1.677(2)	[61]
IX	H	Bn	4-ClC_6H_4	1.381(2)	1.307(2)	1.387(2)	1.379(2)	1.333(2)	1.688(2)	[62]
X	H	H	–N=CHPh	1.370(2)	1.287(2)	1.367(2)	1.381(2)	1.340(2)	1.673(2)	[63]
XI	H	NHNHBz	NH_2	1.390(3)	1.317(3)	1.345(3)	1.368(3)	1.333(3)	1.668(3)	[64]
XII	CH_2Morf[d]	4-Py	$CH_2CH=CH_2$	1.372(2)	1.301(2)	1.371(1)	1.373(2)	1.353(2)	1.668(1)	[65]
XIII	Me	SMe	–N=C(Ph)CH_2SR[e]	1.383	1.293	1.375	1.382	1.346	1.665	[66]
XIV[f]	Ph	Ph[f]	Ph	1.379(3)	1.328(3)	1.413(3)	1.346(3)	1.323(3)	1.681(2)	[73]

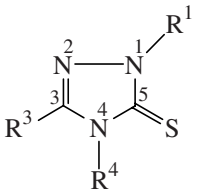
[a] This study. [b] Crystal hydrate, [c] R = 2-Furyl. [d] Morf = morpholin-4-yl. [e] R = 2-phenyl-4-methyl-6-methylsulfanylpyrazolo[5,1-*c*]1,2,4-triazol-3-yl. [f] 1,4,5-Triphenyl-1,2,4-triazolium-3-thiolate.

Sometimes, related compounds are presented in the form of different tautomers (see, e.g., [31]). Many authors, often also without reasoning and without references to [20–22], present the structures of N,S-unsubstituted sulfanyl-1,2,4-triazoles in the form of thione tautomers **D** and **E** (sometimes in the form of a general formula with N-substituted analogs) [17, 42, 43]. In these cases, 1*H*,5*H*-5-thione tautomer **E** [4–6, 9, 11, 12, 16, 18, 20, 21, 44–46] is preferred over 1*H*,2*H*,3-thione tautomer **D** [7, 8, 14, 15–17].

3(5)-Sulfanyl-1,2,4-triazoles with the substituent at one of the N atoms of the ring can be considered as partially fixed analogs of the corresponding tautomers **A–F**. Some authors used this approach when discussing the tautomerism of these compounds [20–22]. The structures of 1N-substituted 3(5)-sulfanyl-1,2,4-triazoles are most frequently presented in the thione form, and also without reasoning [4, 5, 15, 18, 43, 47, 48]. In both these cases (sulfanyl group in the 3- or 5-position), two tautomers are posible, but usually the tautomer with the hydrogen localization in position 4 of the ring (analog of tautomer **E**) is shown. With more extensively studied 4N-substituted 3(5)-sulfanyl-1,2,4-triazoles, the pattern is more similar to that observed with N,S-unsubstituted sulfanyl-1,2,4-triazoles.

These compounds are presented with equal probability in the form of thiol and thione tautomers (see, e.g., [3, 5, 34, 49–52] and [4–6, 15, 18, 25, 48, 53–56]), including general formulas [17, 42]. Many representatives of this group of sulfanyl-1,2,4-

Table 2. Bond angles (ω, deg) in the triazole rings **I–III** and their structural analogs **IV–XIV**[a]



Comp. no.	R^1	R^3	R^4	$N^2N^1C^5$	$N^1N^2C^3$	$N^2C^3N^4$	$C^3N^4C^5$	$N^4C^5N^1$
I	H	H	H	112.5(4)	104.4(4)	110.6(5)	108.5(5)	103.6(5)
IIa	H	Ph	H	112(1)	104(1)	111(1)	109.0(9)	103.9(9)
IIb	H	Ph	H	114(1)	104(1)	110(1)	110.6(9)	101.6(9)
IIc	H	Ph	H	113(1)	104(1)	110(1)	110.8(9)	102.8(9)
IId	H	Ph	H	114(1)	103(1)	111(1)	108(1)	104(1)
IIIa[b]	H	Ph	H	112.5(2)	104.6(2)	110.0(2)	108.5(2)	104.4(2)
IIIb[b]	H	Ph	H	113.0(2)	104.6(2)	109.7(2)	108.9(2)	103.8(2)
IV	H	Bn	Ph	114.0(1)	104.2(1)	110.8(1)	108.1(1)	102.9(1)
Va	H	4-Py	4-Tol	114.2(2)	103.8(2)	111.8(2)	107.0(2)	103.2(2)
Vb	H	4-Py	4-Tol	114.0(2)	103.5(2)	111.8(2)	107.4(2)	103.3(2)
VI	H	*н*-Pr	NMe_2	114.0(2)	103.7(2)	110.6(2)	108.7(2)	103.0(2)
VII	H	Et	–N=CHR[c]	114.6(3)	103.1(3)	111.9(3)	107.6(3)	102.8(3)
VIII	H	R[c]	4-ClC_6H_4	113.8(1)	103.9(1)	111.2(1)	107.7(1)	103.4(1)
IX	H	Bn	4-ClC_6H_4	113.9(2)	103.9(1)	110.7(2)	107.9(1)	103.6(2)
X	H	H	N=CHPh	114.5(2)	103.0(2)	112.6(2)	107.4(2)	102.5(2)
XI	H	NHNHBz	NH_2	113.8(3)	102.5(3)	111.6(3)	109.2(3)	103.6(3)
XII	CH^2Morf[d]	4-Py	$CH_2CH{=}CH_2$	112.54(9)	104.48(9)	111.5(1)	107.67(9)	103.8(1)
XIII	Me	SMe	–N=C(Ph)CH_2SR[e]	113.8	103.6	111.7	108.0	102.6
XIV[f]	Ph	Ph[f]	Ph	112.1(3)	105.6(2)	107.9(2)	108.2(2)	106.2(2)

[a] For references, see Table 1. [b] Crystal hydrate. [c] R = Furyl-2. [d] Morf = morpholin-4-yl. [e] R = 2-phenyl-4-methyl-6-methylsulfanylpyrazolo [5,1-*c*]1,2,4-triazol-3-yl. [f] 1,4,5-Triphenyl-1,2,4-triazolium-3-thiolate.

triazoles, in contrast to 1N-substituted 3(5)-sulfanyl-1,2,4-triazoles, have been studied by single crystal X-ray diffraction (e.g., **IV–XIII**, Tables 1, 2 [57–66]. It was shown that they exist in crystals exclusively in the form of thione tautomers (analogs of tautomer **E**) [52–59], and we found no examples of tautomeric equilibria except an assumption made in [24] about its occurrence.

Our studies show that N,S-unsubstituted sulfanyl-1,2,4-triazoles **I** and **II** and crystal hydrate **III** also exist in the crystals in the thione form. Crystals of **I** were grown from water. Molecule **I** (Fig. 1) in the crystal occurs in a special position on the symmetry plane *m*.

The realization of 1*H*,4*H*-thione tautomer **E** of **I** was inferred from the positions of hydrogen atoms revealed at the N^1 and N^4 atoms of the ring. The geometric parameters of the triazole ring in thione **I** are close to those in the other thione derivatives of 1,2,4-

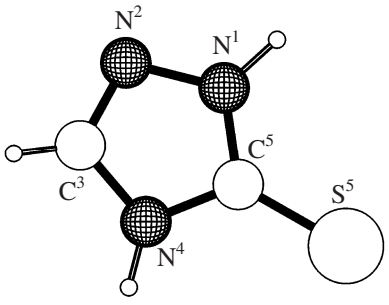


Fig. 1. Molecular geometry of **I** in the crystal.

triazole (**II**–X**III**) (Tables 1, 2). In going from aromatic 1,2,4-triazole ring (geometric parameters of the ring in 3(5)-mono-, 3,5-di-, 1,3,5-tri-, and 3,4,5-trisubstituted 1,2,4-triazoles and 1,2,4-triazolium salts, see [1, 2] and references therein) to the 4,5-dihydrothione ring do not lead to significant changes in the geometric parameters of the ring (for bond lengths and bond angles, see Tables 1 and 2). The bond alternation is also preserved. There is no bond length averaging in the triazole ring of **I**, although the N^4–C^5 and C^5–N^1 bonds in the amidine fragment are equal within the experimental error [1.348 (7) and 1.345 (7) Å, respectively]. The N^1–N^2 and C^3–N^4 bond lengths are close to the mean lengths of these bonds in 3-R_D-5-R_D-1,2,4-triazoles and their salts [1, 2]. The N^2–C^3 bond is somewhat shortened, whereas the N^4–C^5 and C^5–N^1 bond lengths are close to the mean values for the above-mentioned analogs.

The bond angles in the triazole ring of thione **I**, as in other thiones **II**–**XIII** (Table 2), are closer to those in molecules of 1,2,4-triazolium salts [1] than in nonprotonated 1,2,4-triazoles. As compared to 3(5)-mono-3,5-di-, 1,3,5-tri-, and 3,4,5-trisubstituted 1,2,4-triazoles, in triazolinethione the endocyclic angles at the N^1 and N^4 atoms somewhat increase (by 4°–8°), and those at the C^3 and C^5 atoms decrease (by 4°–7°).

The $N^1N^2C^3$ bond angle (102°–105°) in all the three groups of triazole derivatives varies to the least extent. In triazolinethiones **I**–**XIII** (and others), the differences between the $C^3N^4C^5$ and $N^1C^5N^4$ angles are more pronounced than in triazolium salts (cf. data in [1]).

Apparently, passing from the 1,2,4-triazolium system to the 4,5-dihydro-1,2,4-triazole-5-thione system, as in the pyridine series [26], does not alter essentially the ring aromaticity. This assumption is also confirmed by the fact that the triazole rings in molecules of **I** participate only in the π–π interactions stabilizing the crystal packing: The distance between the centers of the triazole ring is d_c = 3.616(2) Å, and the dihedral angle α between them is 0°; the shortest distance between these rings is $d\perp$ = 3.22 Å.

Via hydrogen bonds N^1–$H^1\cdots D^5$ and N^4–$H^4\cdots N^2$ (Table 3), the molecules in the crystal of **I** are combined in infinite chains arranged parallel to each other along the 0a axis of the crystal (Fig. 2), i.e., the 1D structure is realized. The crystalline forms of the phenyl derivative of thione **I** are determined by the nature of the solvent. A slight change in the solvent polarity leads to changes in the crystal structure. For example, thione **II** crystallizes from water; its hydrate **III**, from a water–ethanol mixture; and a third form, whose sturcture we have not yet determined, from acetonitrile. From the viewpoint of X-ray diffraction analysis, compound **II** appeared to be a more complex object than thione **I**. In the asymmetric part of the unit

Table 3. Short contacts (distances, Å; angles, deg) in the crystals of **I**–**III**

D–H···A	D–H	H···A	D···A	DHA	Symmetry codes
4,5-Dihydro-1*H*-1,2,4-triazole-5-thione (**I**)					
N^1–$H^1\cdots S^5$	0.99 (7)	2.32 (7)	3.251 (5)	155 (6)	–1 + *x*, *y*, *z*
N^4–$H^4\cdots N^2$	0.95 (5)	2.00 (5)	2.916 (6)	164 (4)	1 + *x*, *y*, *z*
3-Phenyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (**II**)					
N^{1a}–$H^{1a}\cdots S^{5d}$	0.86	2.47	3.28 (1)	159	–1/2 + *x*, 1/2 + *y*,
N^{1c}–$H^{1c}\cdots S^{5b}$	0.86	2.46	3.29 (1)	162	1/2 + *x*, –1/2 + *y*, *z*
N^{4b}–$H^{4b}\cdots S^{5c}$	0.86	2.46	3.29 (1)	162	–1/2 + *x*, 1/2 + *y*, *z*
N^{4d}–$H^{4d}\cdots S^{5a}$	0.86	2.43	3.27 (1)	165	–1/2 + *x*, 1/2 + *y*, *z*
N^{1b}–$H^{1b}\cdots S^{5c}$	0.86	2.46	3.29 (1)	161	–
N^{1d}–$H^{1d}\cdots S^{5a}$	0.86	2.47	3.30 (1)	160	–
N^{4a}–$H^{4a}\cdots S^{5d}$	0.86	2.43	3.27 (1)	164	–
N^{4c}–$H^{4c}\cdots S^{5b}$	0.86	2.45	3.28 (9)	164	–
C^{11a}–$H^{11a}\cdots N^{2a}$	0.93	2.54	2.88 (2)	102	–
C^{11b}–$H^{11b}\cdots N^{2b}$	0.93	2.53	2.87 (2)	102	–
C^{11c}–$H^{11c}\cdots N^{2c}$	0.93	2.56	2.87 (2)	100	–
C^{11d}–$H^{11d}\cdots N^{2d}$	0.93	2.52	2.86 (2)	102	–

Table 3. (Contd.)

D–H···A	D–H	H···A	D···A	DHA	Symmetry codes
3-Phenyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione crystal hydrate (**III**)					
N^{1a}–H^{1a}···O^{1}	0.83 (2)	1.97 (2)	2.774 (3)	162 (2)	–1/2 + *x*, 1/2 – *y*, –1/2 + *z*
N^{1b}–H^{1b}···O^{2}	0.87 (3)	1.89 (3)	2.743 (3)	167 (3)	*x*, *y*, 1 + *z*
N^{4a}–H^{4a}···S^{5b}	0.86 (2)	2.45 (2)	3.306 (2)	177 (2)	–1/2 + *x*, 1/2 – *y*, –1/2 + *z*
N^{4b}–H^{4b}···S^{5a}	0.83 (2)	2.45 (2)	3.276 (2)	175 (2)	1/2 + *x*, 1/2 – *y*, 1/2 + *z*
O^{1}–H^{11}···N^{2b}	0.81 (3)	2.14 (3)	2.933 (3)	169 (3)	1/2 + *x*, 1/2 – *y*, –1/2 + *z*
O^{1}–H^{12}···S^{5a}	0.91 (3)	2.47 (3)	3.367 (2)	170 (3)	1/2 – *x*, 1/2 + *y*, 1/2 – *z*
O^{2}–H^{21}···S^{5b}	0.79 (3)	2.57 (3)	3.340 (2)	164 (3)	1 – *x*, –*y*, 1 – *z*
C^{7a}–H^{7a}···S^{5b}	0.93 (3)	2.81 (3)	3.696 (2)	158 (3)	–1/2 + *x*, 1/2 – *y*, –1/2 + *z*
C^{7b}–H^{7b}···S^{5a}	0.95 (3)	2.85 (3)	3.644 (3)	141 (3)	1/2 + *x*, 1/2 – *y*, 1/2 + *z*
O^{2}–H^{22}···N^{2a}	0.69 (5)	2.38 (5)	2.972 (3)	146 (5)	–
C^{11a}–H^{11a}···N^{2a}	0.92 (3)	2.57 (3)	2.902 (3)	102 (2)	–
C^{11b}–H^{11b}···N^{2b}	0.91 (3)	2.62 (3)	2.927 (3)	101 (2)	–

Table 4. Some torsion angles (τ, deg) in the molecules of triazoles **II** and **III**

Angle	**IIa**	**IIb**	**IIc**	**IId**	**IIIa**	**IIIb**
$N^{2}C^{3}C^{6}C^{11}$	–8(2)	4(2)	–2(1)	5(2)	10.1(4)	14.2(4)
$N^{4}C^{3}C^{6}C^{11}$	176(1)	178(1)	–178(1)	–179(1)	–170.3(3)	–163.3(3)
$N^{2}C^{3}C^{6}C^{7}$	174(1)	–176(1)	180(1)	–174(1)	–168.7(3)	–166.4(3)
$N^{4}C^{3}C^{6}C^{7}$	–3(2)	–2(1)	4(2)	1(1)	10.9(4)	16.1(4)

cell of its crystal, there are four independent molecules. All of them are thione tautomers and have virtually equal planar conformation (the torsion angles are given in Table 4). The dihedral angles between the planes of the heterorings and phenyl substituents in molecules **IIa–IId** are 7.0(7)°, 3.3(7)°, 2.2(7)°, and 5.0(7)°, respectively.

Figure 3 shows the general view of these molecules in the crystal. The planar configuration of the molecules is favorable for the π–π conjugation of the aromatic phenyl and triazolinethione rings.

The bond lengths and bond angles in molecules **IIa–IId** and **I** are the same within the experimental error (Tables 1, 2).

Owing to hydrogen bonding, a 1D supramolecular structure is realized in the crystal of phenyl thione **II** (for parameters, see Table 3), with two types of V-shaped ribbons, one of which contains only molecules **IIa** and **IId** (Fig. 4), and the other, **IIb** and **IIc** (Fig. 5). The ribbons are not linked to each other and are packed in the crystal in the mutually perpendicular

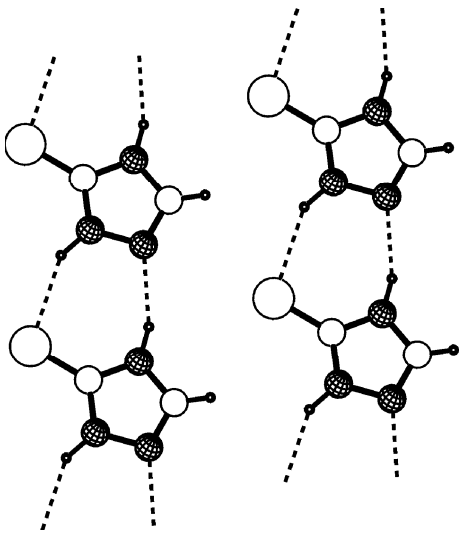


Fig. 2. System of hydrogen bonds in the crystal of triazole **I**.

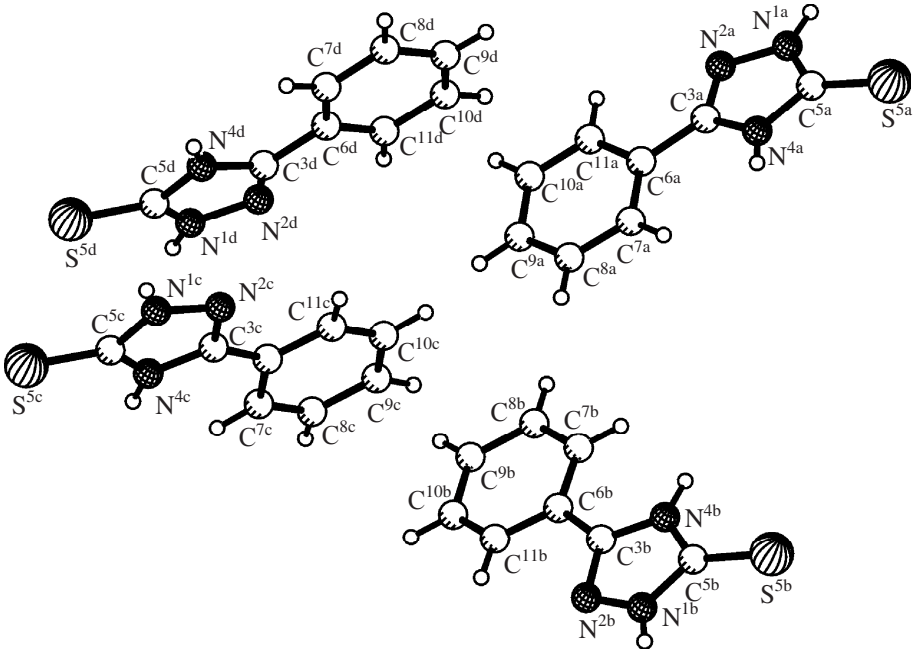


Fig. 3. Molecular geometry of phenyl thione **II** in the crystal.

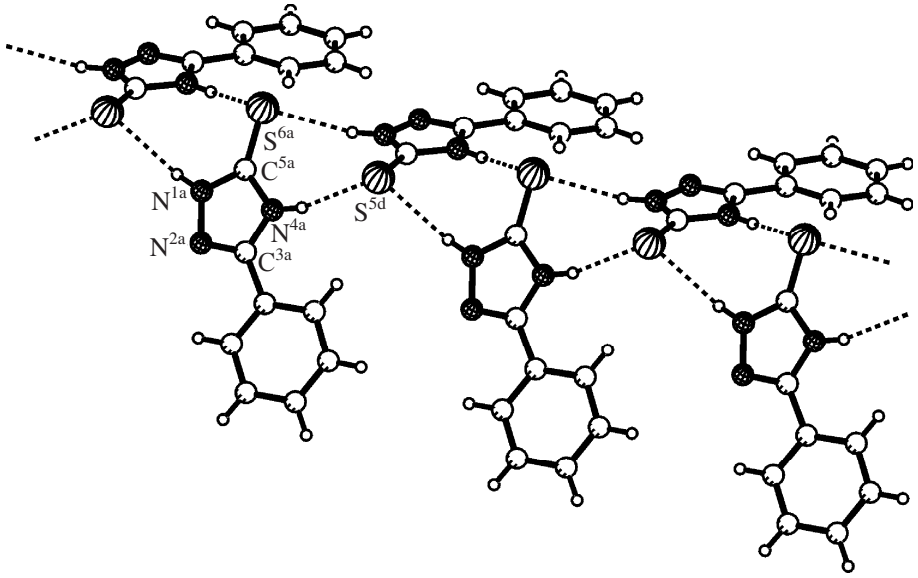


Fig. 4. System of hydrogen bonds between molecules **IIa** and **IId** in the crystal.

directions (110) and (–110) (Fig. 6). The dihedral angle between the molecular planes in ribbons of molecules **IIa** and **IId** is 119.4°, and in ribbons of molecules **IIb** and **IIc**, 117.2°.

It should be noted that in the crystal of phenyl thione **II** there are numerous π–π interactions between the triazole and phenyl rings. The distance between the ring centers d_c varies within 3.950(8)–4.029(7) Å. The dihedral angle between the corresponding planes α vareis from 0.8° to 5.8°, and the shortest distance between the planes $d_\perp$ is 3.38 Å. These interactions lead to the formation of molecular stacks in the crystal (Fig. 6).

As already noted, compound **III**, in contrast to phenyl thione **II**, is a crystal hydrate (Fig. 7).

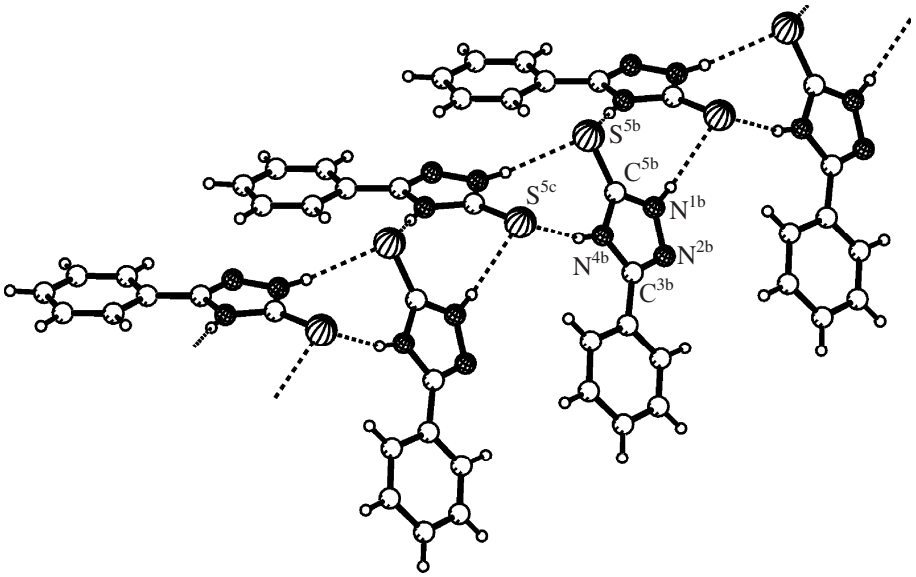


Fig. 5. System of hydrogen bonds between molecules **IIb** and **IIc** in the crystal.

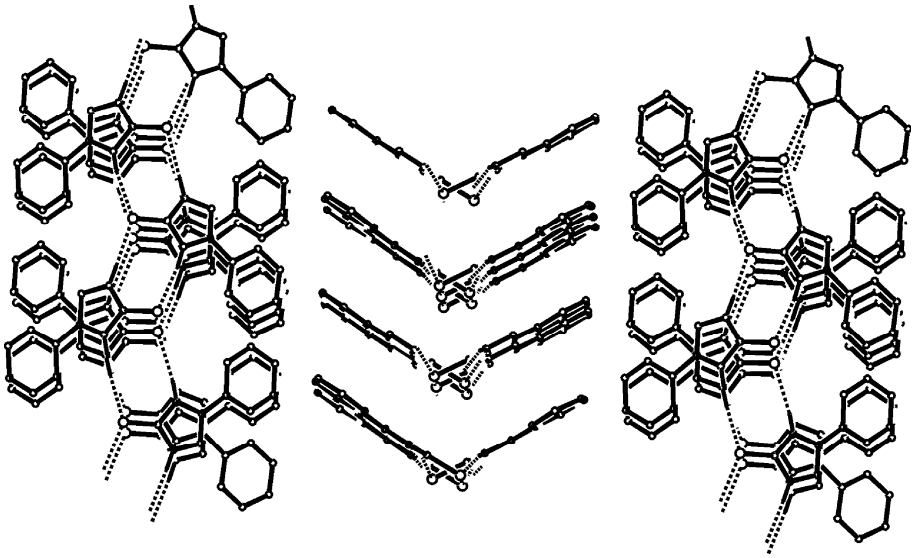


Fig. 6. Packing of ribbons in crystal **II**.

The asymmetric part of the unit cell of crystal hydrate **III** contains two molecules of **IIIa** and **IIIb** and two water molecules. The dihedral angles between the planes of the phenyl ring and heteroring in **IIIa** and **IIIb** are 10.3(2)° and 15.5(2)°, respectively. These values noticeably exceed the corresponding values in **IIa–IId**. Thus, in contrast to **II**, the core of the whole molecule **IIIa** or **IIIb** is appreciably nonplanar. The other geometric parameters of molecules **IIIa** and **IIIb** coincide within the experimental error with those for triazolinethiones **I** and **IIa**–**IId** and their structural analogs **IV–XIII** (Tables 1, 2).

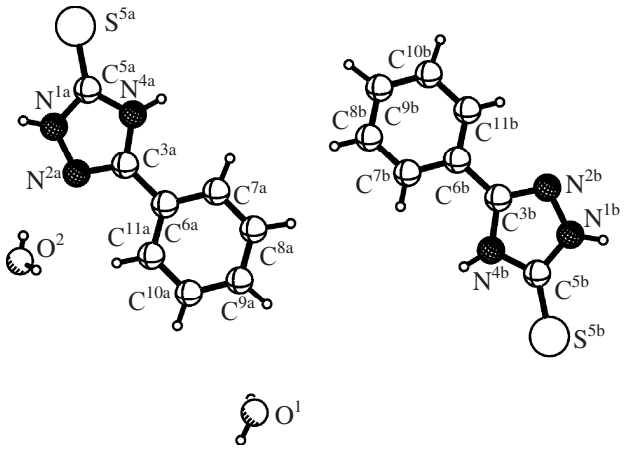


FIg. 7. Molecular geometry of **III** in the crystal.

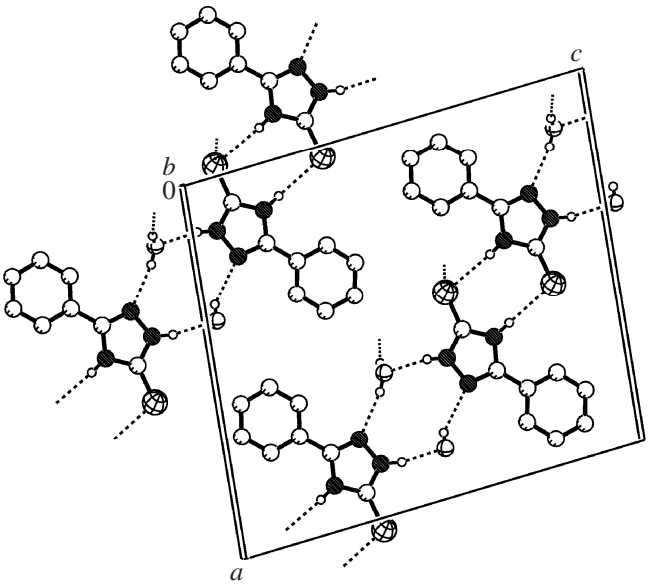


Fig. 8. Molecular chains in the crystal hydrate of **III**, formed by hydrogen bonds.

The differences in the number and nature of substituents in 1,2,4-triazolinethione molecules affect the molecular packing considerably more strongly than their geometric parameters. For example, in contrast to triazolinethiones **I** and **II** in which a 1D supramolecular structure is formed in the crystals owing to a system of hydrogen bonds, crystals of N-monosubstituted analogs **IV–X** (for geometries, see Tables 1, 2) are characterized by formation of closed H-dimeric 0D associated owing to N^1–$H^1 \cdots S$ hydrogen bonds. Exceptions are compound **V** and 4-amino-3-benzoylhydrazino-4,5-dihydro-1,2,4-triazole-5-thione **XI** whose molecules in the crystals are arranged in infi-nite chains in a different fashion compared to **I** and **II**.

In crystals of thione **V**, owing to the presence of the pyridine ring, the infinite chains of monomeric molecules are formed by hydrogen bonding involving the substituent and not the triazoline ring [N^1–$H^- \cdots N$ (Py) type] [58], and in crystals of thione **XI** the initially formed H dimers are arranged in infinite chains [59].

In the crystal hydrate of **III**, there is a fairly complex three-dimensional system of hydrogen bonds (for parameters, see Table 3). Owing to N^{4a}–$H^{4a} \cdots S^{5b}$ and N^{4b}–$H^{4b} \cdots S^{5a}$ interactions, molecules of phenyl thione **III** form H dimers which are combined in infinite chains via hydrogen bonds involving one of protons of water molecules. The chains are arranged along the diagonal of the a0c plane of the crystal (Fig. 8). The second proton of the water molecules participates in the formation of hydrogen bonds O^1–$H^{12} \cdots S^{5a}$ (for one of water molecules) and O^2–$H^{21} \cdots S^{5b}$ (for the second water molecule), which leads to mutual linking of the chains (Fig. 9) and formation of a 3D associate (Fig. 10). Intermolecular interactions C–H $\cdots$ S also stabilize such packing (for parameters, see Table 3). Intermolecular interactions C–H $\cdots$ N (for parameters, see Table 3) should also be noted.

In the crystal hydrate of phenyltriazolinethione **III**, we also revealed π–π interactions between the triazoline and phenyl rings of **IIIa** and **IIIb**. The distance between the centers of rings d_c varies within 3.579(2)–3.863(2) Å. The dihedral angle between the corresponding planes α is from 2.2° to 7.4°, and the shortest distance between the plane $d_\perp$ is 3.27 Å. However, in this case, in contrast to the crystal of thione **II**, formation of molecular stacks by the stacking effect is not observed.

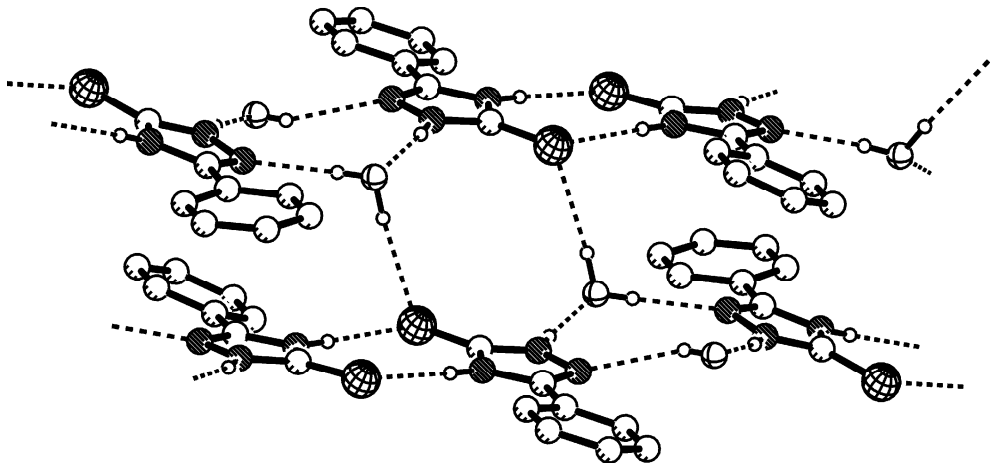
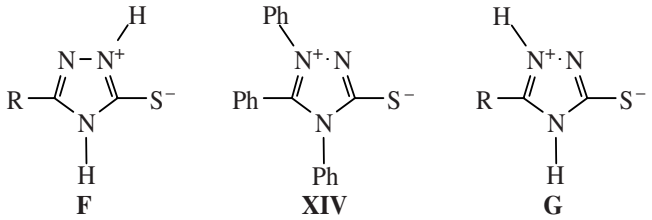


Fig. 9. Linking of molecular chains in the crystal hydrate of **III** into 3D chains owing to O–H$\cdots$S hydrogen bonding.

Analysis of the C^5–S^5 bond lengths in molecules of **I–III** (1.683–1.690 Å), as in the molecules of 4N-mono- and 1N,4N-disubstituted triazolinethiones **IV–XIII** (1.665–1.688 Å) (Table 1) and of N-substituted thioureas (1.681 Å [67]) shows that they have intermediate values between the characteristic lengths of the C–S and C=S bonds which can be taken from [67–72]. The C^5–S^5 bonds are also appreciably shorter than the C_{sp^2}–S bond lengths in molecules of alkylsulfanyl-1,2,4-triazoles and their salts, which are inthe range 1.714 –1.763 Å [1, 2]. For example, the length of the C–S single bond in aliphatic thiols is 1.808 Å, and in thioethers, 1.789–1.856 Å [67]. The C^5–S^5 bonds are even noticeably shorter than the bonds in compounds in which the sulfur atom is conjugated with π systems (1.751–1.712 Å) [67]. In the anion of sodium 4-amino-1,2,4-triazole-3-thiolate, the C–S^- bond length is 1.724(2) Å [72]. Information on the parameters of the C_{sp^2}=S bond not involved in intramolecular interactions is scarce. Allen et al. [67] report only a single value, 1.599 Å for the cyclobutanethione derivative. We were able to find only two more values in the Cambridge Structural Database, 1.613 and 1.616 Å, for thiocamphor and a thiobornane derivative [68–70]. In the thiobenzophenone derivative, it is essentially the same (1.611 Å) [67], and in the thiofluorenone derivative it increases to only 1.628 Å [71], suggesting weaker conjugation of the π systems of the C=S group and aryl rings.

When discussing the observed C_c–S bond lengths in triazolinethiones **I–XIII**, we should consider the effect of two factors: *n*–π conjugation characteristic of thioamides or significant contribution of bipolar structure **F** (naturally, the conjugation in this zwitterionic form should also be taken into account). Appreciable contribution of the second factor can also be confirmed by the fact that in the molecule of zwitterionic 1,4,5-triphenyl-1,2,4-triazolium-3-thiolate **XIV** [73] the C_c–S bond length is 1.681(2) Å, and the ring parameters are silimar to those in the molecule of thione **II** (Tables 1, 2).

The IR spectra of **I**, **II**, and other triazolinethiones always contain absorption bands at 2900–2500 cm^{-1}. Some authors assign these bands to stretching vibrations of the SH group [23, 74], and other, to stretching vibrations of the NH group [52], although they can be assigned more likely to stretching vibrations of the charged N^+H groups [75] in **F**-type structures. The stretching vibration band of the thioamide group is usually assigned to the region of ~1550 cm^{-1} [75]. Therefore, we believe that the shift of the ν(C=S) band to 1280–1160 cm^{-1}, observed in the spectra of a large number of 1,2,4-triazolinethiones, both N-alkylated and containing no substituents at the N atoms [20, 31, 76], can also be considered as an argument in favor of structure **F**.



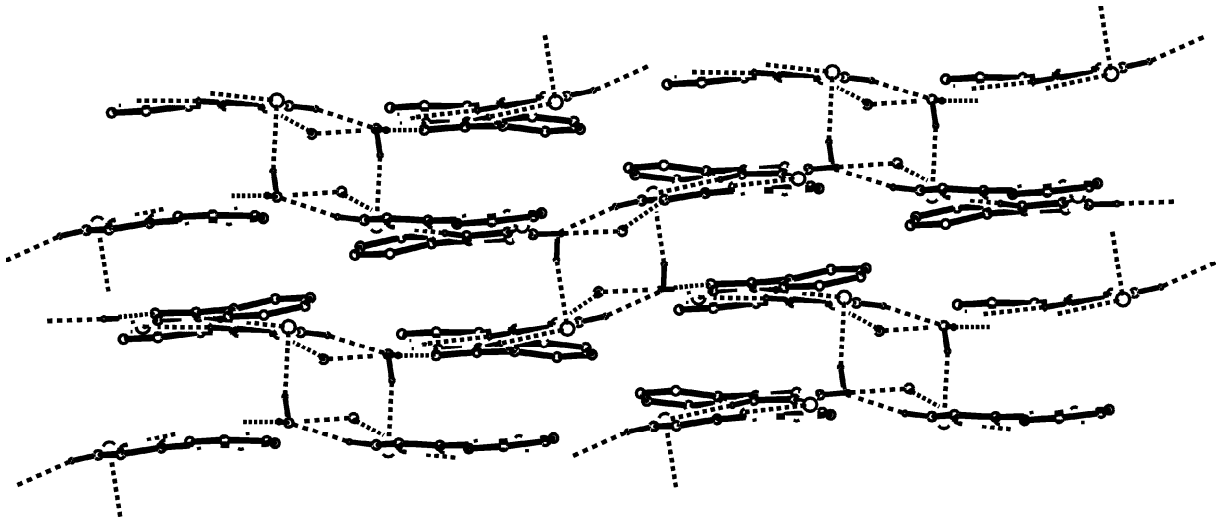


Fig. 10. Molecular packing in the crystal hydrate of **III**.

Tautomeric processes are commonly considered from the viewpoint of acid–base equilibria, and it is believed that the tautomer that is a weaker acid is more stable [77, 78]. We have already noted previously that, in accordance with the conclusions made in [2] and taking into account the electronic properties of the sulfanyl group, the thiol tautomer of **I** and **II** should have form **A**. We showed in [1] that N-unsubstituted 1,2,4-triazoles are always protonated at the N^4 atom, and hence tautomer **A** as a strong acid should form zwitterion **G**. Apparently, this zwitterion is energetically unfavorable and undergoes a tautomeric transformation into isomer **E** undergoing the charge redistribution with the transformation into **F**. We discussed in detail the search for such transitions in 1,2,4-triazolinium cations in the second paper of this series. It is planned to check these assumptions by quantum-chemical calculations.

EXPERIMENTAL

The IR spectra were recorded on a Vector 22 IR Fourier spectrometer (Bruker, Germany) from KBr pellets. The NMR spectra were taken on a Bruker Avance 600 spectrometer. The melting point was determined with a standard PTP device and on a Boetius heating stage.

4,5-Dihydro-1*H*-1,2,4-triazole-5-thione (I) was prepared according to [78] and recrystallized two times from water. Colorless crystals, mp 220–222°C (PTP); published data: mp 215–216°C [79]; 221–224°C [74]. IR spectrum, ν, cm^{-1}: 3150, 3083, 2952, 2873, 2667, 2612, 2551, 1559, 1473, 1427, 1360, 1305, 1257, 1187, 1135, 1058, 945, 848, 702, 667, 625, 524.

3-Phenyl-4,5-dihydro-1*H*,4*H*-1,2,4-triazole-5-thione (II) was prepared according to [35]. After recrystallization from water, colorless crystals were obtained, mp 245–253°C (with decomposition) (PTP). On a Boetius-type heating stage, the substance recrystallized into needles at 200–210°C and decomposed in the range 245–252°C. Published data: mp 256°C [35]; 257°C [31, 76]. IR spectrum, ν, cm^{-1}: 3075, 3059, 3000, 2951, 2892, 2826, 2677, 2643, 2576, 1610 w, 1591 w, 1563, 1508, 1482, 1455, 1423, 1288, 1223, 1121, 1071, 1023, 1000, 964 s, 916, 838, 782 s, 686 s, 538. ^{1}H NMR spectrum, δ, ppm: acetone, 7.45 m (3H, Ph); 7.97 m (2H, Ph); 12.6 br.s (2H, NH + SH). DMSO-d_6, 7.40 m (3H, Ph); 7.93 m (2H, Ph).

3-Phenyl-4,5-dihydro-1*H*,4*H*-1,2,4-triazole-5-thione crystal hydrate (III) was prepared by recrystallization of **II** from a mixture of water and alcohol; colorless platelike crystals, mp 255–257°C (with decomposition) (PTP device). On a Boetius-type heating stage, the sample recrystallized at 205–210°C into rectangular plates and decomposed in the range 223–243°C. IR spectrum, ν, cm^{-1}: 3433, 3384, 3078, 3054, 3005, 2907, 2858, 2816, 2751, 2701, 2669, 2595, 2545, 1610 s, 1593 m, 1565, 1518, 1466, 1428, 1304, 1238 vs, 1155, 1138, 1081, 1014, 972 s, 918, 857, 777, 701 s, 544.

Single crystal X-ray diffraction analysis of **I–III** was performed at room temperature (20°C) on an Enraf–Nonius CAD-4 automatic four-circle diffractometer using monochromated MoK_α radiation [λ 0.71073 Å] (structure **I**) and CuK_α radiation [λ 1.54184 Å] (structures **II** and **III**). The unit cell parameters were determined from 25 reflections. The stability of the crystals in the course of the experiments was checked by measuring three control reflections every 2 h of the diffraction measurements. The crystal orienta-tion was checked by centering two reflections after taking every 200 reflections. No decrease in the intensity of the control reflections was observed.

Determination of the unit cell parameters and preliminary treatment of the experimental data were performed using MolEN software [80]. The structures were solved by the direct method using the SIR program [81]. The structures were refined first in isotropic and then in anisotropic approximations using the MolEN program package [80] for structures **I** and **II** and the SHELX-97 program [82] from the WinGX program package [83] for structure **II**. PLATON program was used for plotting all the figures and analyzing the intermolecular interactions [84].

The single crystal studies were performed at the Department of X-ray Structural Studies of the Sharing Center on the basis of the Laboratory of Diffraction Methods, Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences.

4,5-Dihydro-1*H*-1,2,4-triazole-5-thione (I). Colorless transparent prismatic crystals belonging to monoclinic system; $C_2N_3H_3S$; M 101.13; a 5.082(1), b 6.440(2), c 6.192(1) Å; β 99.82(2)°; V 199.69(9) $Å^3$, d_c 1.68 g cm^{-3}, Z 2, space group $P2_1/m$ (molecule in special position on plane m). Scanning angle $\theta < 26.3°$, ω/2θ scanning. Absorption was not taken into account (μMo 5.92 cm^{-1}). Hydrogen atoms were re-fined isotropically. A total of 888 reflections were measured, of which 322 had $I \geq$

Table 5. Coordinates of nonhydrogen atoms in the structure of **I** and their equivalent isotropic temperature factors

$$B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i, a_j) B(i, j)\ (Å^2)$$

Atom	*x*	*y*	*z*	B_{eq}
S^5	0.2430(8)	0.25	1.4441(3)	2.90 (4)
N^1	–0.2483(9)	0.25	1.1889(7)	2.5 (1)
N^2	–0.3687(8)	0.25	0.9702(7)	2.2 (1)
N^4	0.0650(8)	0.25	1.0014(8)	2.2 (1)
C^3	–0.175(1)	0.25	0.859(1)	2.8 (2)
C^5	0.019(1)	0.25	1.2096(9)	1.8 (1)

3σ. The final divergence factors were as follows: *R* 0.044 and R_W 0.042 for 305 reflections with $F^2 \geq 3\sigma(I^2)$.

3-Phenyl-4,5-dihydro-1*H*,4*H*-1,2,4-triazole-5-thione (II). Colorless transparent prismatic crystals belonging to monoclinic system; $C_8N_3H_7S$; *M* 177.24; *a* 11.164(3), *b* 11.224(2), *c* 26.638(4) Å; β 90.10(2)°; *V* 3338(1) $Å^3$, d_c 1.41 g cm^{-3}, *Z* 16, space group *Cc* (four independent molecules). Scanning angle 3.32° ≤ θ ≤ 74.18°, ω/2θ scanning. The absorption was taken into account empirically (μCu 29.78 cm^{-1}). The coordinates of the hydrogen atoms were calculated on the basis of the stoichiometric criteria and refined by the rider model. A total of 3504 unique reflections were measured, of which 2130 had $I \geq 2\sigma$. The final diverence factors were as follows: *R* 0.090 and R_W 0.215 for 2130 reflections with $F^2 \geq 4\sigma(I^2)$.

3-Phenyl-4,5-dihydro-1*H*,4*H*-1,2,4-triazole-5-thione crystal hydrate (III). Colorless transparent pris-matic crystals belonging to monoclinic system; $C_8H_7N_3S \cdot H_2O$; *M* 195.24; *a* 15.646(1), *b* 6.9097(8), *c* 17.165(3) Å; β 97.22(1)°; *V* 1841.0(4) $Å^3$, d_c 1.41 g cm^{-3}, *Z* 8, space group $P2_1/n$ (two independent molecules). Scanning angle θ < 74.3°, ω/2θ scanning. The absorption was taken into account empirically (μCu 27.80 cm^{-1}). Hydrogen atoms were refined isotropically. A total of 4250 reflections were measured, of which 2881 had $I \geq 3\sigma$. The final divergence factors were as follows: *R* 0.046 and R_W 0.056 for 2650 reflections with $F^2 \geq 3\sigma(I^2)$. The selected bond lengths and bond angles in the molecules of **I–III** are given in Tables 1 and 2; parameters of short contacts in crystals of **I–III**, in Table 3; torsion angles, in Table 4; and atomic coodinates, in Tables 5–7. The geometries of

Table 6. Coordinates of nonhydrogen atoms in the structure of **II** and their equivalent isotropic thermal parameters U_{eq} ($Å^2$)[a]

Atom	*x*	*y*	*z*	U_{eq}
S^{5a}	0.7160 (2)	0.3833 (3)	1.0076 (1)	0.0417 (9)
N^{1a}	0.5690 (9)	0.3719 (9)	1.0887 (4)	0.043 (3)
N^{2a}	0.552 (1)	0.308 (1)	1.1328 (4)	0.045 (3)
N^{4a}	0.7098 (9)	0.2433 (8)	1.0928 (3)	0.038 (3)
C^{3a}	0.640 (1)	0.2297 (9)	1.1328 (4)	0.033 (3)
C^{5a}	0.665 (1)	0.334 (1)	1.0633 (4)	0.039 (3)
C^{6a}	0.657 (1)	0.134 (1)	1.1707 (4)	0.043 (4)
C^{7a}	0.746 (1)	0.047 (1)	1.1664 (5)	0.051 (4)
C^{8a}	0.751 (2)	–0.039 (1)	1.2035 (6)	0.057 (5)
C^{9a}	0.672 (1)	–0.040 (2)	1.2437 (5)	0.058 (5)
C^{10a}	0.589 (1)	0.050 (1)	1.2483 (5)	0.056 (5)
C^{11a}	0.583 (1)	0.136 (1)	1.2121 (5)	0.045 (4)
S^{5b}	1.0076 (2)	0.5919 (3)	1.0078 (1)	0.0414 (8)
N^{1b}	0.9957 (9)	0.447 (1)	1.0906 (4)	0.044 (3)
N^{2b}	0.931 (1)	0.428 (1)	1.1328 (4)	0.046 (3)
N^{4b}	0.8657 (8)	0.5826 (8)	1.0920 (3)	0.034 (3)
C^{3b}	0.853 (1)	0.5161 (9)	1.1335 (4)	0.038 (3)
C^{5b}	0.958 (1)	0.5404 (9)	1.0632 (4)	0.035 (3)
C^{6b}	0.759 (1)	0.533 (1)	1.1709 (5)	0.044 (4)
C^{7b}	0.672 (1)	0.626 (1)	1.1683 (5)	0.054 (4)
C^{8b}	0.586 (2)	0.632 (2)	1.2056 (7)	0.069 (6)
C^{9b}	0.586 (2)	0.549 (2)	1.2449 (5)	0.060 (5)
C^{10b}	0.673 (2)	0.462 (1)	1.2458 (6)	0.063 (5)
C^{11b}	0.756 (1)	0.454 (1)	1.2106 (5)	0.047 (4)
S^{5c}	1.2587 (3)	0.3414 (3)	1.0556 (1)	0.0412 (9)
N^{1c}	1.245 (1)	0.198 (1)	0.9735 (4)	0.046 (3)
N^{2c}	1.178 (1)	0.179 (1)	0.9308 (4)	0.048 (3)
N^{4c}	1.1157 (8)	0.3337 (8)	0.9721 (3)	0.034 (3)
C^{3c}	1.101 (1)	0.266 (1)	0.9306 (4)	0.036 (3)
C^{5c}	1.206 (1)	0.2920 (9)	1.0003 (4)	0.033 (3)
C^{6c}	1.008 (1)	0.282 (1)	0.8931 (4)	0.040 (3)
C^{7c}	0.925 (1)	0.378 (1)	0.8941 (5)	0.053 (4)
C^{8c}	0.839 (1)	0.387 (2)	0.8575 (6)	0.063 (5)
C^{9c}	0.835 (2)	0.305 (2)	0.8177 (6)	0.062 (5)
C^{10c}	0.915 (2)	0.215 (2)	0.8175 (5)	0.059 (5)
C^{11c}	1.001 (1)	0.203 (1)	0.8533 (5)	0.047 (4)
S^{5d}	0.9652 (3)	0.1338 (3)	1.0550 (1)	0.0421 (8)
N^{1d}	0.820 (1)	0.1204 (9)	0.9738 (4)	0.043 (3)
N^{2d}	0.7998 (10)	0.056 (1)	0.9301 (4)	0.047 (3)
N^{4d}	0.9586 (9)	–0.0080 (9)	0.9715 (4)	0.038 (3)
C^{3d}	0.888 (1)	–0.021 (1)	0.9298 (4)	0.040 (3)
C^{5d}	0.9128 (9)	0.083 (1)	1.0000 (4)	0.034 (3)
C^{6d}	0.908 (1)	–0.117 (1)	0.8917 (4)	0.044 (4)
C^{7d}	0.997 (1)	–0.201 (1)	0.8959 (5)	0.051 (4)
C^{8d}	1.007 (2)	–0.291 (2)	0.8603 (7)	0.066 (5)
C^{9d}	0.929 (2)	–0.290 (1)	0.8189 (6)	0.062 (5)
C^{10d}	0.840 (1)	–0.206 (1)	0.8150 (5)	0.053 (4)
C^{11d}	0.829 (1)	–0.115 (1)	0.8519 (5)	0.050 (4)

[a] The equivalent isotropic thermal parameters U_{eq} were calculated as 1/3 of the trace of the orthogonalized tensor U_{ij}.

Table 7. Coordinates of nonhydrogen atoms in the structure of **III** and their equivalent isotropic temperature factors

$$B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i, a_j) B(i, j)\ (Å^2)$$

Atom	x	y	z	B_{eq}
S^{5a}	0.47177 (4)	0.2139 (1)	0.58355 (3)	3.91 (1)
N^{1a}	0.6404 (1)	0.2397 (4)	0.5624 (1)	3.22 (4)
N^{2a}	0.7219 (1)	0.2421 (3)	0.6030 (1)	3.17 (4)
N^{4a}	0.6234 (1)	0.2093 (3)	0.6825 (1)	2.93 (4)
C^{3a}	0.7100 (1)	0.2226 (4)	0.6765 (1)	2.68 (4)
C^{5a}	0.5795 (2)	0.2226 (4)	0.6097 (1)	2.91 (5)
C^{6a}	0.7788 (1)	0.2169 (4)	0.7426 (1)	2.79 (5)
C^{7a}	0.7612 (2)	0.2294 (5)	0.8194 (2)	3.52 (5)
C^{8a}	0.8270 (2)	0.2289 (5)	0.8810 (1)	3.82 (6)
C^{9a}	0.9115 (2)	0.2169 (5)	0.8663 (2)	3.90 (6)
C^{10a}	0.9295 (2)	0.2040 (6)	0.7905 (2)	4.88 (7)
C^{11a}	0.8636 (2)	0.2023 (5)	0.7283 (2)	4.30 (7)
S^{5b}	0.53125 (4)	0.1799 (1)	0.84515 (3)	3.83 (1)
N^{1b}	0.3621 (1)	0.1389 (3)	0.8635 (1)	3.13 (4)
N^{2b}	0.2822 (1)	0.1234 (3)	0.8219 (1)	3.09 (4)
N^{4b}	0.3825 (1)	0.1466 (3)	0.7441 (1)	2.98 (4)
C^{3b}	0.2960 (2)	0.1283 (4)	0.7484 (1)	2.78 (5)
C^{5b}	0.4248 (2)	0.1532 (4)	0.8178 (1)	3.00 (5)
C^{6b}	0.2291 (2)	0.1226 (4)	0.6804 (1)	2.88 (5)
C^{7b}	0.2499 (2)	0.0880 (5)	0.6051 (2)	3.84 (6)
C^{8b}	0.1862 (2)	0.0907 (5)	0.5420 (2)	4.61 (7)
C^{9b}	0.1021 (2)	0.1257 (5)	0.5525 (2)	4.48 (7)
C^{10b}	0.0808 (2)	0.1558 (5)	0.6270 (2)	4.29 (7)
C^{11b}	0.1440 (2)	0.1542 (4)	0.6908 (2)	3.61 (6)
O^1	0.1317 (1)	0.1391 (3)	0.9076 (1)	4.75 (5)
O^2	0.8709 (1)	0.3683 (4)	0.5241 (1)	5.63 (5)

the cations and the systems of short contacts in the crystals of **I**–**III** are shown in Figs. 1–10.

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