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Heterocyclic Thiones and Their Analogs in 1,3-Dipolar Cycloaddition Reactions: II.* Reactions of Benzothiazole-2-thione with Nitrilimines

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Abstract—Benzothiazole-2-thione reacted with C,N-disubstituted nitrilimines to give the corresponding bis-[2-(1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfides. In some cases, α-(1,3-benzothiazol-2-ylsulfanyl)-(α-R)-alkanone arylhydrazones were formed as by-products. The structure of the isolated compounds was proved by X-ray analysis.

Reactions of thioketones with classical 1,3-dipolar systems have been well documented [2, 3]. Various acyclic and heterocyclic thioamides also react with 1,3-dipolar reagents [4–5]. We previously showed that 1,2-dithiophthalides containing an exocyclic thioketone moiety react with nitrilimines to give benzothiophene-spiro-thiadiazoles [1]. However, there are only fragmentary published data on the behavior in 1,3-dipolar cycloaddition reactions of compounds whose molecules contain a secondary amino group in the α-position with respect to the thione group [7, 8].

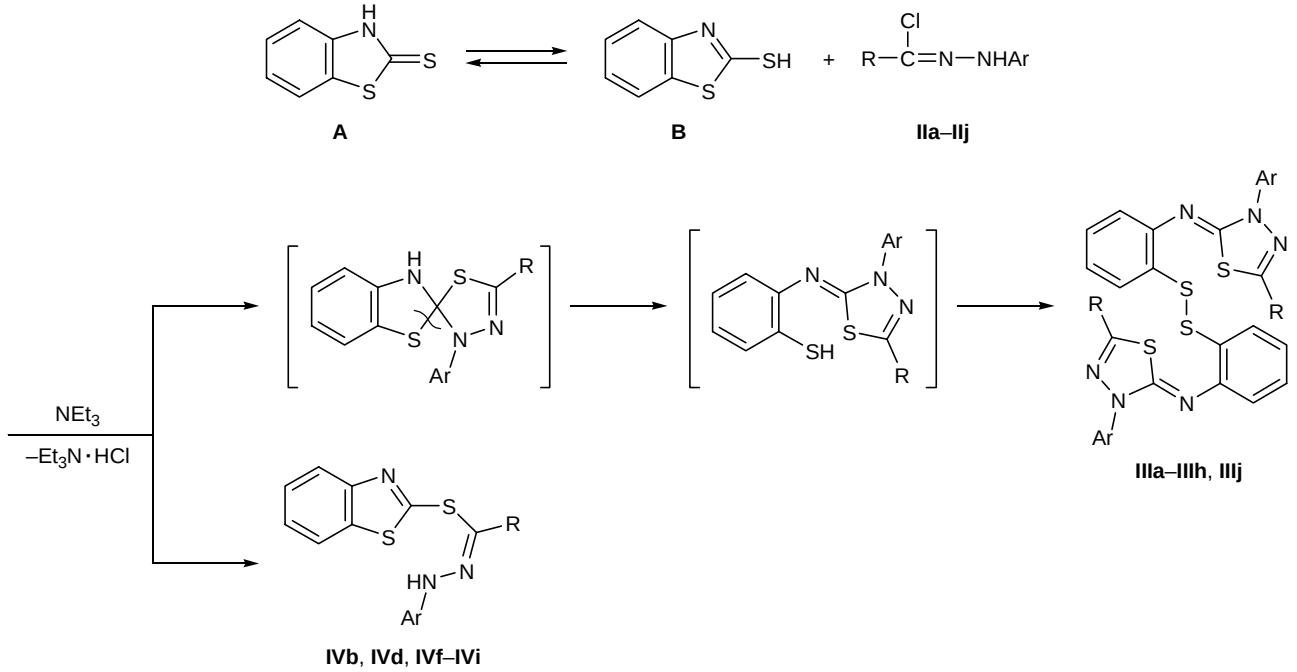
The present article reports on the results of studying the reaction of benzothiazole-2-thione with C,N-disubstituted nitrilimines which were generated *in situ* from the corresponding *N*-aryl carbohydrazonoyl chlorides **IIa**–**IIj** by the action of triethylamine. Benzothiazole-2-thione possesses an ambident HN–C=S moiety which is capable of undergoing tautomeric transformation. Depending on the solvent polarity and basicity, benzothiazole-2-thione can exist as two tautomers, thione **A** or thiol **B** [9]; therefore, it could give rise to two series of derivatives with participation of the NH or SH functionality; furthermore, 1,3-dipolar cycloaddition involving the exocyclic thione group is possible [10–12].

Presumably, the initial stage in the reaction of benzothiazole-2-thione (**I**) with C,N-disubstituted nitrilimines is [3+2]-cyclization with participation of the thione C=S bond (tautomer **A**). The subsequent opening of the thiazole ring in the benzothiazole-spiro-thiadiazole structure thus formed, followed by dimerization of intermediate thiol, leads to formation of bis[2-(1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfides **IIIa**–**IIIh** and **IIIj** (Scheme 1). In some cases, we detected α-(1,3-benzothiazol-2-ylsulfanyl)-(α-R)alkanone arylhydrazones **IVb**, **IVd**, and **IVf**–**IVi** which were formed as a result of nucleophilic substitution of the halogen atom in the carbohydrazonoyl chloride by the thiol tautomer (**B**) of initial benzothiazole-2-thione. In the reactions of benzothiazole-2-thione with *C*-ethoxycarbonyl-*N*-arylnitrilimines having an *ortho* substituent in the benzene ring, compounds **IVh** and **IVi** were the major products. It should be noted that hydrazones **IVb**, **IVd**, and **IVf**–**IVi** can exist as *E* and *Z* isomers. We succeeded in separating the *E* and *Z* isomers of arylhydrazone **IVh**, while compound **IVi** was isolated exclusively as the *E* isomer. In all other cases, mixtures of isomers were examined.

All the isolated products are crystalline substances which are stable on exposure to air for a long time. The ^{1}H NMR spectra of bis[2-(1,3,4-thiadiazole-2-ylideneamino)phenyl] disulfides **IIIa**–**IIIh** and **IIIj** contained

* For communication I, see [1].

Scheme 1.



II, R = MeCO (**a**–**c**), MeOCO (**d**, **e**), EtOCO (**f**–**i**), Ph (**j**); Ar = C_6H_5 (**a**, **f**, **j**), *p*-$MeOC_6H_4$ (**e**), *p*-BrC_6H_4 (**d**), *o*-ClC_6H_4 (**c**, **i**), *m*-ClC_6H_4 (**b**, **g**), *o*-$O_2NC_6H_4$ (**h**); **III**, R = MeCO (**a**–**c**), MeOCO (**d**, **e**), EtOCO (**f**–**h**), Ph (**j**); Ar = Ph (**a**, **f**, **j**), *p*-$MeOC_6H_4$ (**e**), *p*-BrC_6H_4 (**d**), *o*-ClC_6H_4 (**c**), *m*-ClC_6H_4 (**b**, **g**), *o*-$O_2NC_6H_4$ (**h**); **IV**, R = MeCO (**b**), MeOCO (**d**), EtOCO (**f**–**i**); Ar = Ph (**f**), *p*-BrC_6H_4 (**d**), *o*-ClC_6H_4 (**i**), *m*-ClC_6H_4 (**b**, **g**), *o*-$O_2NC_6H_4$ (**h**).

signals typical of substituents at the carbon and nitrogen atoms of the initial nitrilimine, as well as signals from aromatic protons. The ^{13}C NMR spectra of **IIIa**–**IIIh** and **IIIj** were consistent with the assumed structures. The formation of disulfides **III** was also confirmed by the mass spectra which contained the molecular ion peaks and peaks from ions formed by cleavage of the S–S bond. Further fragmentation pattern is fairly complex.

The structure of bis[2-(5-ethoxycarbonyl-3-phenyl-2,3-dihydro-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (**IIIf**) was proved by X-ray analysis. The molecular structure is shown in Fig. 1 (hereinafter, the atom numbering given in the corresponding figure is

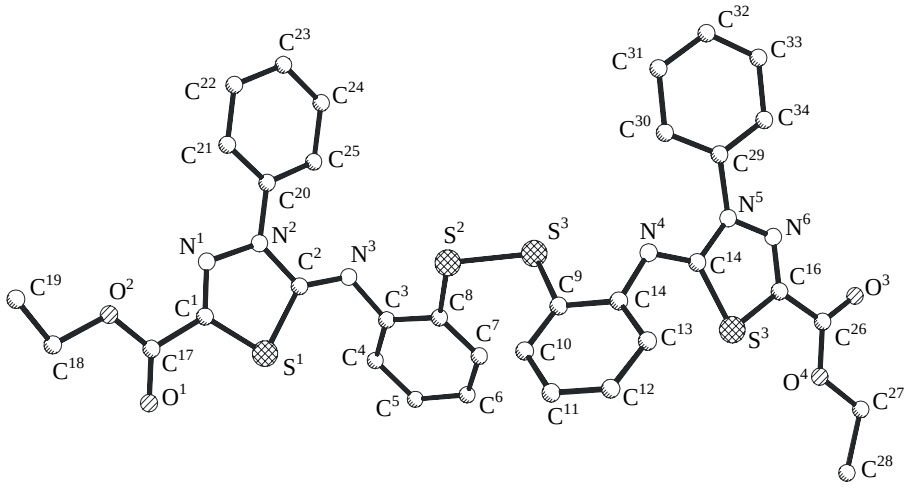


Fig. 1. Structure of the molecule of bis[2-(5-ethoxycarbonyl-3-phenyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (**IIIf**) according to the X-ray diffraction data. Hydrogen atoms are not shown.

used while describing the X-ray diffraction data). A unit cell of **IIIf** includes two independent molecules (major *A* and minor *B*) which slightly differ from each other in mutual arrangement of the ethoxycarbonyl groups and benzene rings. A second-order pseudoaxis was revealed. It passes through points with approximate coordinates of [1/3, 1/3, 1/2]. The bond angles and bond lengths in the right part of the molecule slightly differ from those in the left part (Table 1). The torsion angles $C^8S^2S^3C^9$ are 86.9 and 82.7° for molecules *A* and *B*, respectively. The thiadiazole rings are planar: the maximal deviations from the $C^1N^1N^2C^2S^1$ plane are 0.03 and 0.06 Å, and from the $C^{15}N^5N^6C^{16}S^4$ plane, 0.02 and 0.04 Å, respectively, for molecules *A* and *B*. However, the N^3 and N^4 atoms deviate from the thiadiazole ring planes; the deviations of N^3 from the $C^1N^1N^2C^2S^1$ plane are 0.15 and 0.13 Å, and of N^4 from the $C^{15}N^5N^6C^{16}S^4$ plane, 0.12 and 0.17 Å, respectively, for molecules *A* and *B*. Table 2 contains the dihedral angles between different planes in molecule **IIIf**.

As noted above, α-(1,3-benzothiazol-2-ylsulfanyl)-(α-R)alkanone arylhydrazones **IV** exist as *E* and *Z* isomers. Apart from signals typical of substituents at the carbon and nitrogen atoms of the initial nitrilimine, the ^{1}H NMR spectra of compounds **IV** contained a singlet from proton of the hydrazone moiety at δ 12.95–14.05 (*E* isomers) and 9.80–12.9 ppm (*Z* isomers). The ^{13}C NMR spectra of **IVb**, **IVd**, and **IVf**–**IVi** were consistent with the assumed structures. Compounds **IVb**, **IVd**, and **IVf**–**IVi** showed in the mass spectra the corresponding molecular ion peaks and peaks from ions formed by cleavage of the thiol C–S bond. As with compounds **III**, further fragmentation pattern of **IV** was fairly complex.

The structure of compounds **IVf** and **IVh** was proved by X-ray analysis (Figs. 2, 3). The X-ray diffraction data for compound **IVf** showed formation of intramolecular hydrogen bond $O^1\cdots H(N^3)$ which stabilizes the *E* isomer. The hydrogen bond parameters are as follows: N^3–H 0.841, $O^1\cdots H(N^3)$ 1.967, $O^1\cdots N^3$

Table 1. Bond lengths (*d*, Å) and bond angles (ω, deg) in molecules *A* and *B* of bis[2-(5-ethoxycarbonyl-3-phenyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (**IIIf**)[a]

Bond	*d*		Bond	*d*	
	molecule *A*	molecule *B*		molecule *A*	molecule *B*
S^1–C^1	1.722(5)	1.738(5)	N^5–N^6	1.359(5)	1.367(5)
S^1–C^2	1.771(5)	1.764(5)	N^5–C^{15}	1.397(5)	1.393(5)
S^2–C^8	1.783(4)	1.783(4)	N^5–C^{29}	1.444(6)	1.434(6)
S^2–S^3	2.0314(16)	2.0296(15)	N^6–C^{16}	1.282(6)	1.279(6)
S^3–C^9	1.785(4)	1.787(4)	C^1–C^{17}	1.487(7)	1.486(7)
S^4–C^{16}	1.734(5)	1.732(5)	C^3–C^4	1.390(6)	1.391(6)
S^4–C^{15}	1.778(5)	1.771(4)	C^3–C^8	1.393(6)	1.393(6)
O^1–C^{17}	1.195(6)	1.191(6)	C^4–C^5	1.385(7)	1.390(7)
O^2–C^{17}	1.311(6)	1.336(7)	C^5–C^6	1.372(7)	1.374(7)
O^2–C^{18}	1.460(6)	1.475(6)	C^6–C^7	1.389(6)	1.387(6)
O^3–C^{26}	1.194(6)	1.197(6)	C^7–C^8	1.382(6)	1.385(6)
O^4–C^{26}	1.323(6)	1.317(6)	C^9–C^{10}	1.381(6)	1.381(5)
O^4–C^{27}	1.461(5)	1.468(6)	C^9–C^{14}	1.392(6)	1.397(5)
N^1–C^1	1.278(6)	1.276(6)	C^{10}–C^{11}	1.397(7)	1.393(6)
N^1–N^2	1.369(5)	1.370(5)	C^{11}–C^{12}	1.363(7)	1.371(7)
N^2–C^2	1.398(5)	1.412(6)	C^{12}–C^{13}	1.393(7)	1.390(6)
N^2–C^{20}	1.437(5)	1.434(6)	C^{13}–C^{14}	1.394(6)	1.396(6)
N^3–C^2	1.257(5)	1.259(5)	C^{16}–C^{26}	1.489(7)	1.486(7)
N^3–C^3	1.415(5)	1.417(5)	C^{18}–C^{19}	1.435(8)	1.480(8)
N^4–C^{15}	1.266(5)	1.265(5)	C^{27}–C^{28}	1.493(8)	1.409(8)
N^4–C^{14}	1.411(5)	1.408(5)			

Table 1. (Contd.)

Angle	ω		Angle	ω	
	molecule *A*	molecule *B*		molecule *A*	molecule *B*
$C^1S^1C^2$	88.4(2)	88.8(3)	$C^7C^8S^2$	124.6(4)	125.1(3)
$C^8S^2S^3$	105.02(15)	106.45(15)	$C^3C^8S^2$	114.9(3)	114.4(3)
$C^9S^3S^2$	106.48(15)	105.12(14)	$C^{10}C^9C^{14}$	120.7(4)	121.1(4)
$C^{16}S^4C^{15}$	88.4(2)	87.7(2)	$C^{10}C^9S^3$	124.9(3)	124.9(3)
$C^{17}O^2C^{18}$	116.1(4)	117.4(5)	$C^{14}C^9S^3$	114.4(3)	114.0(3)
$C^{26}O^4C^{27}$	116.4(4)	116.1(4)	$C^9C^{10}C^{11}$	118.8(4)	119.2(4)
$C^1N^1N^2$	110.9(4)	111.5(4)	$C^{12}C^{11}C^{10}$	121.2(4)	120.1(4)
$N^1N^2C^2$	115.8(4)	115.6(4)	$C^{11}C^{12}C^{13}$	120.2(5)	121.2(4)
$N^1N^2C^{20}$	116.6(3)	117.0(4)	$C^{14}C^{13}C^{12}$	119.5(4)	119.3(4)
$C^2N^2C^{20}$	127.2(4)	127.1(4)	$C^{13}C^{14}C^9$	119.6(4)	119.1(4)
C^2-N^3-C^3	122.7(4)	122.5(4)	$C^{13}C^{14}N^4$	122.9(4)	123.8(4)
$C^{15}N^4C^{14}$	121.0(4)	122.4(4)	$C^9C^{14}N^4$	117.3(4)	116.9(4)
$N^6N^5C^{15}$	116.7(4)	115.5(4)	$N^4C^{15}N^5$	124.6(4)	123.7(4)
$N^6N^5C^{29}$	116.5(4)	116.5(4)	$N^4C^{15}S^4$	128.3(3)	127.9(3)
$C^{15}N^5C^{29}$	126.8(4)	127.6(4)	$N^5C^{15}S^4$	107.1(3)	108.3(3)
$C^{16}N^6N^5$	111.1(4)	111.1(4)	$N^6C^{16}C^{26}$	120.9(5)	123.2(5)
$N^1C^1C^{17}$	123.1(5)	120.8(5)	$N^6C^{16}S^4$	116.6(3)	117.1(4)
$N^1C^1S^1$	117.2(4)	116.5(4)	$C^{26}C^{16}S^4$	122.5(4)	119.7(4)
$C^{17}C^1S^1$	119.7(4)	122.7(5)	$O^1C^{17}O^2$	126.4(5)	125.6(5)
$N^3C^2N^2$	124.3(4)	122.6(4)	$O^1C^{17}C^1$	121.9(5)	125.2(7)
$N^3C^2S^1$	128.1(4)	129.8(4)	$O^2C^{17}C^1$	111.7(5)	109.2(5)
$N^2C^2S^1$	107.5(3)	107.5(3)	$C^{19}C^{18}O^2$	107.5(5)	107.2(5)
$C^4C^3C^8$	119.5(4)	119.8(4)	$C^{25}C^{20}N^2$	121.3(4)	119.2(5)
$C^4C^3N^3$	123.5(4)	123.2(4)	$C^{21}C^{20}N^2$	118.1(4)	121.9(5)
$C^8C^3N^3$	116.7(4)	116.7(4)	$O^3C^{26}O^4$	125.3(5)	126.3(5)
$C^5C^4C^3$	119.4(5)	119.2(4)	$O^3C^{26}C^{16}$	124.6(5)	122.5(5)
$C^6C^5C^4$	121.1(5)	120.9(5)	$O^4C^{26}C^{16}$	110.1(5)	111.2(5)
$C^5C^6C^7$	119.8(4)	120.1(5)	$O^4C^{27}C^{28}$	107.1(4)	107.7(5)
$C^8C^7C^6$	119.6(4)	119.5(4)	$C^{30}C^{29}N^5$	121.2(4)	118.2(5)
$C^7C^8C^3$	120.5(4)	120.4(4)	$C^{34}C^{29}N^5$	118.0(4)	120.8(4)

[a] Hereinafter, the bond lengths and bond angles in the benzene rings are not given, for they have their standard values.

2.622 Å; $\angle N^3HO^1$ 133.9°. The benzothiazole ring is planar: the maximal deviation of atoms from the mean-square plane is 0.008 Å; the maximal deviation of atoms from the $HN^3N^2C^{14}C^{15}O^1$ plane arising from hydrogen bonding is 0.03 Å. The S^2 atom appears in both the benzothiazole ring and $HN^3N^2C^{14}C^{15}O^1$ planes. The existence of conjugation between the $C^{14}=N^2$ double bond, lone electron pair on the N^3 atom, and C^8–C^{13} benzene ring may be presumed: the angle between the benzene ring and $HN^3N^2C^{14}C^{15}O^1$ planes is as small as 6.8°. The bond lengths and bond angles in molecule **IVf** are listed in Table 3.

Ethyl 2-(1,3-benzothiazol-2-ylsulfanyl)-2-(*o*-nitrophenylhydrazono)acetate (**IVh**) in crystal also has *E* configuration of the hydrazone fragment (Fig. 3), which is stabilized by intramolecular hydrogen bond $O^1\cdots H(N^3)$ and weak intramolecular hydrogen bond $O^4\cdots H(N^3)$ with the following parameters: $O^1\cdots H(N^3)$: N^3–H 0.820, O^1–$H(N^3)$ 2.11, O^1–N^3 2.640 Å; $\angle N^3HO^1$ 122.2°; $O^4\cdots H(N^3)$: N^3–H 0.820, O^4–$H(N^3)$ 1.94,

Table 2. Dihedral angles between planes *x* and *y* in molecules *A* and *B*[a] of bis[2-(5-ethoxycarbonyl-3-phenyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (**IIIf**)

Plane *x*	Plane *y*		
	$C^1N^1N^2C^2S^1$	$C^{15}N^5N^6C^{16}S^4$	C^3–C^8
$O^1C^{17}O^2$	5.8 (12.2)	–	–
C^{20}–C^{25}	12.9 (11.1)	–	–
C^3–C^8	57.2 (54.6)	–	–
$O^3C^{26}O^4$	–	4.3 (12.7)	–
C^{29}–C^{34}	–	23.1 (11.6)	–
C^9–C^{14}	–	56.4 (58.1)	77.2 (71.9)

[a] In parentheses.

O^4–N^3 2.620 Å; $\angle N^3HO^4$ 138.7°. The maximal deviations of atoms from the $HN^3N^2C^8C^9O^1$ plane formed as a result of H-bonding $O^1\cdots H(N^3)$ is 0.04 Å. The $HN^3C^{12}C^{13}N^4O^4$ ring closed via $O^4\cdots H(N^3)$ hydrogen bond is planar within 0.005 Å. The benzothiazole ring $S^1C^2C^7N^1C^1$ is also planar: the maximal deviation of atoms from that plane is 0.01 Å. The S^2 atom simultaneously lies in the plane of the benzothiazole ring and in the $HN^3N^2C^8C^9O^1$ plane. The $C^8{=}N^2$ double bond, lone electron pair on the N^3 atom, and the C^{12}–C^{17} benzene ring are likely to be involved in conjugation: the dihedral angle between the benzene ring plane and $HN^3C^{12}C^{13}O^1N^4O^4$ H-bond plane is 0.8°. The nitro group $N^4O^4O^3$ is conjugated with the benzene ring: the dihedral angle between the respective planes is 0.6°. The bond angles and bond lengths in molecule **IVh** are given in Table 4.

Thus we have found that the reactions of benzothiazole-2-thione with equimolar amounts of C,N-disubstituted nitrilimines begin with 1,3-dipolar cycloaddition at the exocyclic C=S bond to give an unstable spiro compound which readily decomposes via cleavage of the C–S bond in the thiazole ring. The subsequent dimerization of intermediate thiol results in formation of substituted bis[2-(1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide **III**. Compounds formed via replacement of the halogen atom in carbohydrazonoyl chlorides by the thiol group of benzothiazole-2-thione tautomer, α-(1,3-benzothiazol-2-ylsulfanyl)-(α-R)alkanone arylhydrazones **IV**, are as a rule, minor products.

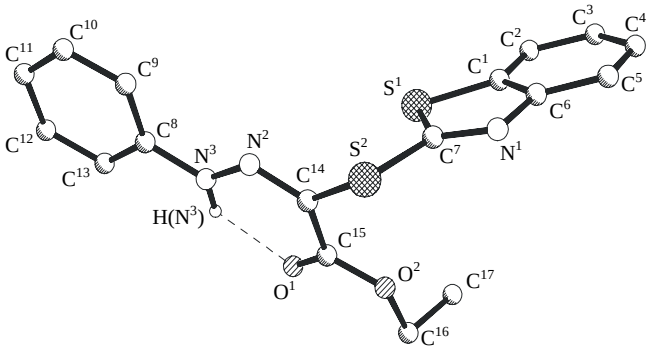


Fig. 2. Structure of the molecule of ethyl (1,3-benzothiazol-2-ylsulfanyl)(phenylhydrazono)acetate (**IVf**) according to the X-ray diffraction data. Only the hydrogen atom involved in intramolecular hydrogen bond is shown.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C) from 20% solutions in DMSO-d_6. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1321 instrument (vaporizer temperature 120°C, ion source temperature 200°C).

X-Ray analysis of single crystals of bis[2-(5-ethoxycarbonyl-3-phenyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (**IIIf**) was performed on a Syntex P-1 automatic diffractometer (CuK_α irradiation, β-filter, θ/2θ scanning in the range $2.30 \le \Theta \le 57.44°$). Monoclinic crystals, $C_{34}H_{28}N_6O_4S_4$, with the following unit cell parameters: a = 9.0270(10), b = 30.925(4), c = 24.575(4) Å; β = 95.630(10)°; V = 6827.3(16) Å^3; space group $P2_1/c$; Z = 8, d_{calc} = 1.387 g/cm^3. The structure was solved by the direct method using 7094 reflections with $\sigma > 3\sigma(I)$ in full-matrix anisotropic approximation for non-hydrogen atoms and isotropic approximation for hydrogen atoms; the final divergence factors were R = 0.0497 and R_w = 0.1084 (no correction for absorption was introduced).

X-Ray diffraction data for ethyl 2-(1,3-benzothiazol-2-ylsulfanyl)-2-(phenylhydrazono)acetate (**IVf**) were obtained on a CAD-4 automatic diffractometer (MoK_α irradiation, β-filter, θ/2θ scanning in the range $2.08 \le \Theta \le 24.97°$). Triclinic crystals, $C_{17}H_{15}N_3O_2S_2$, with the following unit cell parameters: a = 9.311(1), b = 9.540(1), c = 10.179(2) Å; α = 104.13(2), β = 95.74(2), γ = 94.84(2)°; V = 866.9(2) Å^3; space group $P1$; Z = 2; d_{calc} = 1.369 g/cm^3. The structure was solved by the direct method using 3330 reflections with $\sigma > 3\sigma(I)$ in full-matrix anisotropic approximation for non-hydrogen atoms and isotropic approximation for hydrogen atoms; the final divergence factors were R = 0.0254 and R_w = 0.0692 (no correction for absorption was introduced).

X-Ray diffraction data for ethyl 2-(1,3-benzothiazol-2-ylsulfanyl)-2-(*o*-nitrophenylhydrazono)acetate (**IVh**) were obtained on an Enraf–Nonius CAD-4 automatic diffractometer (MoK_α irradiation, β-filter, θ/2θ scanning in the range $2.48 \le \Theta \le 24.91°$). Monoclinic crystals, $C_{17}H_{14}N_4O_4S_2$, with the following unit cell parameters: a = 7.1060(10), b = 29.722(6), c = 8.5500(10) Å; β = 93.03(3)°; V = 1803.3(5) Å^3; space group $P2_1/c$; Z = 4; d_{calc} = 1.482 g/cm^3. The structure was solved by the direct method using 1200 reflections with $\sigma > 3\sigma(I)$ in full-matrix anisotropic approximation for non-hydrogen atoms and isotropic approximation for hydrogen atoms; the final diver-gence factors were R = 0.0806 and R_w = 0.1784 (no correction for absorption was introduced).

The complete sets of crystallographic coordinates of non-hydrogen and hydrogen atoms and their equivalent temperature factors are available from the authors.

Nitrilimines were generated *in situ* by the action of triethylamine on the corresponding *N*-aryl carbohydrazonoyl chlorides **IIa**–**IIj** [13].

General procedure for reactions of benzothiazole-2-thione with *C*-aryl(acetyl, methoxycarbonyl, ethoxycarbonyl)-*N*-phenylnitrilimines. To a solution of 4 mmol of benzothiazole-2-tione (**I**) in 50 ml of anhydrous toluene we added in succession 4 mmol of the corresponding *N*-aryl carbohydrazonoyl chloride **II** and 4.5 mmol of anhydrous triethylamine. The mixture was heated for 4 h under reflux, cooled, and filtered from triethylamine hydrochloride (yield 75–90%). The filtrate was evaporated under reduced pressure, and the oily residue was crystallized by grinding with diethyl ether. Products **III** and **IV** were separated by column chromatography on silica gel using chloroform as eluent. Compound **IVh** was separated into the *E* and *Z* isomers, and only the *E* isomer of **IVi** was isolated from the mixture; in the other cases, *E*/*Z* isomer mixtures were analyzed. The products were additionally recrystallized from acetone.

Bis[2-(5-acetyl-3-phenyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (IIIa). Yield 75%, mp 210–211°C. ^{1}H NMR spectrum, δ, ppm: 2.59 s (3H, CH_3CO), 7.1–7.8 m (18H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 156.71 (C^2); 148.27 (C^5); 189.23 ($CH_3\mathbf{C}O$); 24.86 ($\mathbf{C}H_3CO$); 123.52, 128.41, 128.97, 138.05 (NC_6H_5); 118.23, 125.27, 126.86, 127.85, 128.68, 147.15 (C_6H_4). Mass spectrum, *m*/*z* (I_{rel}, %): 652 (40) $[M]^+$, 326 (50) $[C_{16}H_{12}N_3OS_2]^+$, 294 (10) $[C_{16}H_{12}N_3OS]^+$, 257 (40) $[C_{13}H_9N_2S_2]^+$, 225 (15) $[C_8H_5N_2S_3]^+$, 167 (40) $[C_7H_4NS_2]^+$, 154 (80) $[C_6H_4NS_2]^+$, 108 (20) $[C_6H_4S]^+$, 105 (40) $[C_6H_5N_2]^+$, 91 (70) $[C_6H_5N]^+$. Found, %: C 58.51; H 3.71; N 12.69;

Table 3. Bond lengths (*d*, Å) and bond angles (ω, deg) in the molecule of ethyl (1,3-benzothiazol-2-ylsulfanyl)-(phenylhydrazono)acetate (**IVf**)

Bond	*d*	Bond	*d*
S^1–C^1	1.7337(19)	N^2–N^3	1.314(2)
S^1–C^7	1.7411(19)	N^3–C^8	1.399(3)
S^2–C^7	1.749(2)	C^1–C^2	1.390(3)
S^2–C^{14}	1.7662(19)	C^1–C^6	1.402(3)
O^1–C^{15}	1.212(2)	C^2–C^3	1.376(3)
O^2–C^{15}	1.324(2)	C^3–C^4	1.391(4)
O^2–C^{16}	1.461(3)	C^4–C^5	1.379(3)
N^1–C^7	1.288(2)	C^5–C^6	1.389(3)
N^1–C^6	1.393(2)	C^{14}–C^{15}	1.479(3)
N^2–C^{14}	1.300(2)	C^{16}–C^{17}	1.457(4)
Angle	**ω**	**Angle**	**ω**
$C^1S^1C^7$	88.17(9)	$C^5C^6C^1$	119.8(2)
$C^7S^2C^{14}$	100.27(9)	$N^1C^6C^1$	115.12(17)
$C^{15}O^2C^{16}$	117.46(17)	$N^1C^7S^1$	117.63(14)
$C^7N^1C^6$	109.45(16)	$N^1C^7S^2$	121.20(14)
$C^{14}N^2N^3$	120.61(16)	$S^1C^7S^2$	121.17(11)
$N^2N^3C^8$	120.94(17)	$C^9C^8N^3$	122.15(19)
$C^2C^1C^6$	121.48(19)	$C^{13}C^8N^3$	117.84(18)
$C^2C^1S^1$	128.90(16)	$N^2C^{14}C^{15}$	124.59(17)
$C^6C^1S^1$	109.62(14)	$N^2C^{14}S^2$	114.75(14)
$C^3C^2C^1$	117.8(2)	$C^{15}C^{14}S^2$	120.60(15)
$C^2C^3C^4$	121.1(2)	$O^1C^{15}O^2$	124.57(18)
$C^5C^4C^3$	121.3(2)	$O^1C^{15}C^{14}$	121.94(18)
$C^4C^5C^6$	118.5(2)	$O^2C^{15}C^{14}$	113.49(16)
$C^5C^6N^1$	125.09(19)	$C^{17}C^{16}O^2$	109.6(2)

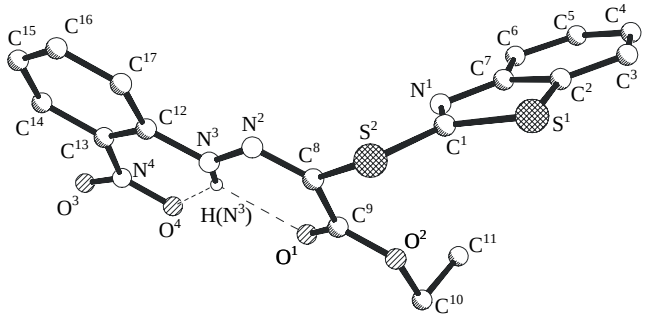


Fig. 3. Structure of the molecule of ethyl (1,3-benzothiazol-2-ylsulfanyl)(*o*-nitrophenylhydrazono)acetate (**IVh**) according to the X-ray diffraction data. Only the hydrogen atom involved in intramolecular hydrogen bonds is shown.

Table 4. Bond lengths (*d*, Å) and bond angles (ω, deg) in the molecule of ethyl (1,3-benzothiazol-2-ylsulfanyl)-(*o*-nitrophenylhydrazono)acetate (**IVh**)

Bond	*d*	Bond	*d*
S^1–C^2	1.728(11)	N^3–C^{12}	1.382(13)
S^1–C^1	1.737(10)	N^4–C^{13}	1.467(16)
S^2–C^1	1.747(10)	N^2–N^3	1.318(11)
S^2–C^8	1.761(10)	C^2–C^3	1.383(15)
O^1–C^9	1.208(12)	C^2–C^7	1.406(14)
O^2–C^9	1.307(13)	C^3–C^4	1.381(19)
O^2–C^{10}	1.462(16)	C^4–C^5	1.35(2)
O^3–N^4	1.198(12)	C^5–C^6	1.354(18)
O^4–N^4	1.214(12)	C^6–C^7	1.386(16)
N^1–C^1	1.285(12)	C^8–C^9	1.499(15)
N^1–C^7	1.383(12)	C^{10}–C^{11}	1.48(2)
N^2–C^8	1.293(12)		
Angle	**ω**	**Angle**	**ω**
$C^2S^1C^1$	89.1(5)	$C^5C^4C^3$	121.2(13)
$C^1S^2C^8$	100.0(5)	$C^4C^5C^6$	121.9(14)
$C^9O^2C^{10}$	116.0(10)	$C^5C^6C^7$	119.6(13)
$C^1N^1C^7$	110.5(8)	$N^1C^7C^2$	115.1(9)
$C^8N^2N^3$	120.1(9)	$N^1C^7C^6$	126.5(11)
$N^2N^3C^{12}$	117.5(9)	$C^2C^7C^6$	118.4(11)
$O^3N^4O^4$	122.3(12)	$N^2C^8C^9$	124.6(9)
$O^3N^4C^{13}$	119.3(12)	$N^2C^8S^2$	115.7(8)
$O^4N^4C^{13}$	118.3(10)	$C^9C^8S^2$	119.7(8)
N^1C^1-S^2	125.3(7)	$O^1C^9O^2$	125.2(10)
$N^1C^1S^1$	116.4(7)	$O^1C^9C^8$	122.4(10)
$S^2C^1S^1$	118.2(6)	$O^2C^9C^8$	112.4(9)
$C^3C^2C^7$	121.0(11)	$C^{11}C^{10}O^2$	108.4(13)
$C^3C^2S^1$	130.1(9)	$N^3C^{12}C^{13}$	121.9(11)
$C^7C^2S^1$	108.8(7)	$N^3C^{12}C^{17}$	121.6(10)
$C^4C^3C^2$	117.8(13)		

S 19.11. $C_{32}H_{24}N_6O_2S_4$. Calculated, %: C 58.82; H 3.68; N 12.87; S 19.60.

Bis[2-(5-acetyl-3-*m*-chlorophenyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (IIIb). Yield 59%, mp 207–208°C. ^{1}H NMR spectrum, δ, ppm: 2.6 s (3H, CH_3CO), 7.1–8.2 m (16H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 148.02 (C^2); 147.52 (C^5); 189.29 (CH_3**C**O); 24.93 (**C**H_3CO); 121.62, 122.81, 128.51, 128.81, 133.16 (NC_6H_4Cl-*m*); 118.10, 125.46, 127.03, 127.48, 130.64, 139.03 (C_6H_4). Mass spectrum, *m*/*z* (I_{rel}, %): 720 (10) $[M]^+$, 360 (50) $[C_{16}H_{11}ClN_3OS_2]^+$, 328 (10) $[C_{16}H_{11}C_6N_3OS]^+$, 256 (50) $[C_{13}H_8N_2S_2]^+$, 224 (70) $[C_8H_4N_2S_3]^+$, 167 (60) $[C_7H_4NS_2]^+$, 154 (90) $[C_6H_4NS_2]^+$, 139 (40) $[C_6H_4ClN_2]^+$, 108 (20) $[C_6H_4S]^+$, 90 (30) $[C_6H_4N]^+$. Found, %: C 53.64; H 3.60; N 10.99; S 17.77. $C_{32}H_{22}Cl_2N_6O_2S_4$. Calculated, %: C 53.21; H 3.05; N 11.64; S 17.74.

Bis[2-(5-acetyl-3-*o*-chlorophenyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (IIIc). Yield 74%, mp 127–128°C. ^{1}H NMR spectrum, δ, ppm: 2.55 s (3H, CH_3CO), 7.0–7.75 m (16H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 156.68 (C^2); 147.72 (C^5); 189.17 (CH_3**C**O); 24.86 (**C**H_3CO); 125.87, 128.86, 130.36, 131.61, 131.77 (NC_6H_4Cl-*m*); 117.80, 125.24, 128.39, 134.94, 147.15 (C_6H_4). Mass spectrum, *m*/*z* (I_{rel}, %): 720 (15) $[M]^+$, 360 (10) $[C_{16}H_{11}ClN_3OS_2]^+$, 328 (10) $[C_{16}H_{11}ClN_3OS]^+$, 256 (100) $[C_{13}H_8N_2S_2]^+$, 224 (90) $[C_8H_4N_2S_3]^+$, 167 (25) $[C_7H_4NS_2]^+$, 154 (80) $[C_6H_4NS_2]^+$, 139 (25) $[C_6H_4ClN_2]^+$, 108 (20) $[C_6H_4S]^+$, 90 (25) $[C_6H_4N]^+$. Found, %: C 52.97; H 3.00; N 11.41; S 17.98. $C_{32}H_{22}Cl_2N_6O_2S_4$. Calculated, %: C 53.21; H 3.05; N 11.64; S 17.74.

Bis[2-(3-*p*-bromophenyl-5-methoxycarbonyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (IIId). Yield 46%, mp 196–197°C. ^{1}H NMR spectrum, δ, ppm: 3.9 s (6H, C**H**$_3$O), 7.15–7.9 m (16H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 155.94 (C^2); 148.09 (C^5); 157.91 (CH_3O**C**O); 53.58 (**C**H_3O); 120.16, 124.99, 131.86, 137.34 (NC_6H_4Br-*p*); 118.13, 125.39, 127.17, 128.52, 128.74, 139.14 (C_6H_4). Mass spectrum, *m*/*z* (I_{rel}, %): 842 (10) $[M]^+$, 421 (18) $[C_{16}H_{11}BrN_3O_2S_2]^+$, 390 (10) $[C_{16}H_{11}BrN_3O_2S]^+$, 256 (100) $[C_{13}H_8N_2S_2]^+$, 224 (50) $[C_8H_4N_2S_3]^+$, 184 (10) $[C_6H_4BrN_2]^+$, 167 (15) $[C_7H_4NS_2]^+$, 154 (80) $[C_6H_4NS_2]^+$, 108 (20) $[C_6H_4S]^+$, 90 (45) $[C_6H_4N]^+$. Found, %: C 45.63; H 2.47; N 9.87; S 14.70. $C_{32}H_{22}Br_2N_6O_4S_4$. Calculated, %: C 45.61; H 2.63; N 9.97; S 15.22.

Bis[2-(5-methoxycarbonyl-3-*p*-methoxyphenyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (IIIe). Yield 84%, mp 75–76°C. ^{1}H NMR spectrum, δ, ppm: 3.89 s (6H, CH_3O), 7.1–7.8 m (16H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 156.37 (C^2); 148.22 (C^5); 158.05 (CH_3O**C**O); 53.44 (**C**H_3O); 114.01, 125.39, 128.85, 158.56 (N**C**$_6H_4OCH_3$-*p*); 118.01, 125.13, 126.71, 128.28, 130.87, 137.89 (C_6H_4). Mass spectrum, *m*/*z* (I_{rel}, %): 744 (10) $[M]^+$, 372 (10) $[C_{17}H_{14}N_3O_3S_2]^+$, 340 (20) $[C_{17}H_{14}N_3O_3S]^+$, 256 (100) $[C_{13}H_8N_2S_2]^+$, 224 (25) $C_8H_4N_2S_3]^+$, 167 (25) $[C_7H_4NS_2]^+$, 154 (20) $[C_6H_4NS_2]^+$, 135 (35) $[C_7H_7N_2O]^+$, 108 (35) $[C_6H_4S]^+$, 90 (35) $[C_6H_4N]^+$. Found, %: C 54.73; H 3.85; N 11.71; S 17.97. $C_{34}H_{28}N_6O_6S_4$. Calculated, %: C 54.82; H 3.79; N 11.30; S 17.22.

Bis[2-(5-ethoxycarbonyl-3-phenyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (IIIf). Yield 71%, mp 124–125°C. ^{1}H NMR spectrum, δ, ppm: 1.29 t (6H, C**H**$_3$CH$_2$), 4.36 q (4H, CH$_3$C**H**$_2$O), 7.1–7.9 m (18H, H$_{arom}$). ^{13}C NMR spectrum, δ, ppm: 156.38 (C^2); 148.26 (C^5); 157.49 (CH$_3$CH$_2$O**C**O); 62.79 (CH$_3$**C**H$_2$O); 13.80 (**C**H$_3$CH$_2$); 123.59, 127.84, 128.93, 138.02 (NC$_6$H$_5$); 118.16, 125.24, 126.87, 128.41, 128.77, 138.84 (C$_6$H$_4$). Mass spectrum, *m*/*z* (I_{rel}, %): 712 (30) [*M*]$^+$, 356 (45) [C$_{17}$H$_{14}$N$_3$O$_2$S$_2$]$^+$, 324 (30) [C$_{17}$H$_{14}$N$_3$O$_2$S]$^+$, 257 (50) [C$_{13}$H$_9$N$_2$S$_2$]$^+$, 225 (5) [C$_8$H$_5$N$_2$S$_3$]$^+$, 167 (25) [C$_7$H$_4$NS$_2$]$^+$, 154 (100) [C$_6$H$_4$NS$_2$]$^+$, 108 (20) [C$_6$H$_4$S]$^+$, 105 (35) [C$_6$H$_5$N$_2$]$^+$, 91 (70) [C$_6$H$_5$N]$^+$. Found, %: C 45.63; H 2.47; N 9.87; S 14.59. C$_{34}$H$_{28}$N$_6$O$_4$S$_4$. Calculated, %: C 45.61; H 2.63; N 9.97; S 15.22.

Bis[2-(3-*m*-chlorophenyl-5-ethoxycarbonyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (IIIg). Yield 67%, mp 113–114°C. ^{1}H NMR spectrum, δ, ppm: 1.35 t (6H, C**H**$_3$CH$_2$), 4.40 q (4H, CH$_3$C**H**$_2$O), 7.1–8.15 m (16H, H$_{arom}$). ^{13}C NMR spectrum, δ$_C$, ppm: 155.83 (C^2); 147.83 (C^5); 157.36 (CH$_3$CH$_2$O**C**O); 62.94 (CH$_3$**C**H$_2$O); 13.79 (**C**H$_3$CH$_2$); 121.63, 122.83, 127.45, 128.92, 130.59, 139.13 (NC$_6$H$_4$Cl-*m*); 118.03, 125.41, 127.14, 128.52, 133.07, 139.51 (C$_6$H$_4$). Mass spectrum, *m*/*z* (I_{rel}, %): 781 (10) [*M*]$^+$, 390 (40) [C$_{17}$H$_{13}$ClN$_3$O$_2$S$_2$]$^+$, 358 (10) [C$_{17}$H$_{13}$ClN$_3$O$_2$S]$^+$, 256 (50) [C$_{13}$H$_8$N$_2$S$_2$]$^+$, 224 (45) [C$_8$H$_4$N$_2$S$_3$]$^+$, 167 (40) [C$_7$H$_4$NS$_2$]$^+$, 154 (100) [C$_6$H$_4$NS$_2$]$^+$, 139 (20) [C$_6$H$_4$ClN$_2$]$^+$, 108 (20) [C$_6$H$_4$S]$^+$, 90 (25) [C$_6$H$_4$N]$^+$. Found, %: C 52.18; H 3.88; N 10.34; S 16.75. C$_{34}$H$_{26}$Cl$_2$N$_6$O$_4$S$_4$. Calculated, %: C 52.19; H 3.33; N 10.75; S 16.37.

Bis[2-(5-ethoxycarbonyl-3-*o*-nitrophenyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (IIIh). Yield 2%, mp 173–174°C. ^{1}H NMR spectrum, δ, ppm: 1.34 t (6H, C**H**$_3$CH$_2$); 4.37 q (4H, CH$_3$C**H**$_2$O), 7.35–8.3 m (16H, H$_{arom}$). ^{13}C NMR spectrum, δ$_C$, ppm: 159.22 (C^2); 151.02 (C^5); 165.00 (CH$_3$CH$_2$O**C**O); 63.06 (CH$_3$**C**H$_2$O); 13.81 (**C**H$_3$CH$_2$): 119.14, 121.07, 121.61, 128.11, 129.02, 134.19 (NC$_6$H$_4$NO$_2$-*o*); 119.07, 123.72, 126.29, 128.25, 131.92, 141.22 (C$_6$H$_4$). Mass spectrum, *m*/*z* (I_{rel}, %): 402 (5) [C$_{17}$H$_{13}$N$_4$O$_4$S$_2$]$^+$, 369 (5) [C$_{17}$H$_{13}$N$_4$O$_4$S]$^+$, 256 (75) [C$_{13}$H$_8$N$_2$S$_2$]$^+$, 224 (100) [C$_8$H$_4$N$_2$S$_3$]$^+$, 167 (20) [C$_7$H$_4$NS$_2$]$^+$, 154 (10) [C$_6$H$_4$NS$_2$]$^+$, 122 (40) [C$_6$H$_4$NO$_2$]$^+$, 108 (40) [C$_6$H$_4$S]$^+$, 90 (30) [C$_6$H$_4$N]$^+$.

Bis[2-(3,5-diphenyl-1,3,4-thiadiazol-2-ylideneamino)phenyl] disulfide (IIIj). Yield 61%, mp 189–190°C. ^{1}H NMR spectrum, δ, ppm: 7.1–8.15 m (28H, H$_{arom}$). ^{13}C NMR spectrum, δ$_C$, ppm: 156.33 (C^2); 149.31 (C^5); 122.86, 128.91, 130.53 (5-C$_6$H$_5$); 127.29, 126.17, 128.77, 139.48 (NC$_6$H$_5$); 118.42, 124.78, 126.47, 126.64, 130.37, 147.02 (C$_6$H$_4$). Mass spectrum, *m*/*z* (I_{rel}, %): 720 (10) [*M*]$^+$, 360 (60) [C$_{20}$H$_{14}$N$_3$S$_2$]$^+$, 328 (10) [C$_{20}$H$_{14}$N$_3$S]$^+$, 257 (30) [C$_{13}$H$_9$N$_2$S$_2$]$^+$, 224 (40) [C$_8$H$_4$N$_2$S$_3$]$^+$, 194 (65) [C$_{13}$H$_{10}$N$_2$]$^+$, 167 (25) [C$_7$H$_4$NS$_2$]$^+$, 154 (80) [C$_6$H$_4$NS$_2$]$^+$, 108 (5) [C$_6$H$_4$S]$^+$, 105 (35) [C$_6$H$_5$N$_2$]$^+$, 91 (100) [C$_6$H$_5$N]$^+$. Found, %: C 66.80; H 3.85; N 11.27; S 18.15. C$_{40}$H$_{28}$N$_6$S$_4$. Calculated, %: C 66.58; H 3.88; N 11.65; S 17.75.

1,3-Benzothiazol-2-yl 2-oxo-*N*-(*m*-chlorophenyl)-propanehydrazonothioate (IVb). Yield 38%, mp 191–192°C. ^{1}H NMR spectrum, δ, ppm: 2.6 s (3H, CH$_3$CO, *Z* isomer), 2.65 s (3H, CH$_3$CO, *E* isomer), 7.03–7.84 m (16H, H$_{arom}$, *E* and *Z* isomers), 11.4 s (1H, NH, *Z* isomer), 13.41 s (1H, NH, *E* isomer). ^{13}C NMR spectrum, δ$_C$, ppm: 128.22 (C^1); 163.26 (C^2); 191.61 (CH$_3$**C**O); 25.57 (**C**H$_3$CO); 114.06, 115.16, 121.29, 131.00, 133.80, 143.69 (NC$_6$H$_4$Cl-*m*); 121.71, 123.09, 124.61, 126.37, 134.87, 153.06 (C$_6$H$_4$). Mass spectrum, *m*/*z* (I_{rel}, %): 361 (15) [*M*]$^+$, 167 (35) [C$_7$H$_4$NS$_2$]$^+$, 134 (5) [C$_7$H$_4$NS]$^+$, 122 (10) [C$_6$H$_4$NS]$^+$, 108 (15) [C$_6$H$_4$S]$^+$, 90 (15) [C$_6$H$_4$N]$^+$. Found, %: C 53.24; H 3.28; N 10.28; S 17.19. C$_{16}$H$_{12}$ClN$_3$OS$_2$. Calculated, %: C 53.06; H 3.32; N 9.95; S 17.69.

Methyl (1,3-benzothiazol-2-ylsulfanyl)(*p*-bromophenylhydrazono)acetate (IVd). Yield 35%, mp 154–155°C. ^{1}H NMR spectrum, δ, ppm: 3.8 s (3H, CH$_3$O, *Z* isomer), 3.95 s (3H, CH$_3$O, *E* isomer), 7.2–7.9 m (16H, H$_{arom}$, *E* and *Z* isomers), 11.3 s (1H, NH, *Z* isomer), 13.7 s (1H, NH, *E* isomer). ^{13}C NMR spectrum, δ$_C$, ppm: 130.70 (C^1); 164.62 (C^2); 163.88 (CH$_3$O**C**O); 53.36 (**C**H$_3$O); 115.12, 117.33, 131.01, 132.00, 140.68 (NC$_6$H$_4$Br-*p*); 120.14, 123.04, 124.67, 126.32, 134.86, 152.37 (C$_6$H$_4$). Mass spectrum, *m*/*z* (I_{rel}, %): 423 (10) [*M*]$^+$, 256 (10) [C$_9$H$_8$N$_2$O$_2$Br]$^+$, 167 (80) [C$_7$H$_4$NS$_2$]$^+$, 134 (10) [C$_7$H$_4$NS]$^+$, 122 (25) [C$_6$H$_4$NS]$^+$, 108 (40) [C$_6$H$_4$S]$^+$, 90 (50) [C$_6$H$_4$N]$^+$. Found, %: C 45.94; H 3.22; N 9.77; S 15.49. C$_{16}$H$_{12}$BrN$_3$O$_2$S$_2$. Calculated, %: C 45.46; H 2.85; N 9.94; S 15.15.

Ethyl (1,3-benzothiazol-2-ylsulfanyl)(phenylhydrazono)acetate (IVf). Yield 0.05%.

Ethyl (1,3-benzothiazol-2-ylsulfanyl)(*m*-chlorophenylhydrazono)acetate (IVg). Yield 26%, mp 169–170°C. ^{1}H NMR spectrum, δ, ppm: 1.34 t (3H, C**H**$_3$CH$_2$, *Z* isomer), 1.44 t (3H, C**H**$_3$CH$_2$, *E* isomer), 4.29 q (2H, CH$_3$C**H**$_2$O, *Z* isomer), 4.41 q (2H, CH$_3$C**H**$_2$O, *E* isomer), 6.98–7.91 m [16H, H$_{arom}$, *E* and *Z* isomers), 11.3 s (1H, NH, *Z* isomer), 13.65 s (1H,

NH, *E* isomer). ^{13}C NMR spectrum, δ_C, ppm: 130.09 (C^1); 162.83 (C^2); 160.75 ($CH_3CH_2O\mathbf{C}O$); 61.99 ($CH_3\mathbf{C}H_2O$); 14.06 ($\mathbf{C}H_3CH_2O$); 113.76, 115.27, 121.29, 129.91, 133.47, 143.78 (NC_6H_4Cl-*m*); 121.17, 122.48, 124.28, 125.83, 135.01, 153.18 (C_6H_4). Found, %: C 52.18; H 3.88; N 10.70; S 16.75. $C_{17}H_{14}ClN_3O_2S_2$. Calculated, %: C 52.10; H 3.60; N 10.72; S 16.36.

Ethyl (1,3-benzothiazol-2-ylsulfanyl)(*o*-nitrophenylhydrazono)acetate (IVh). Yield 55% (*E* isomer), 30% (*Z* isomer); mp 167–168°C (*E* isomer), 78–79°C (*Z* isomer). ^{1}H NMR spectrum, δ, ppm: 1.12 t (3H, $C\mathbf{H}_3CH_2$, *E* isomer), 1.26 t (3H, $C\mathbf{H}_3CH_2$, *Z* isomer), 4.30 q (2H, $CH_3C\mathbf{H}_2O$, *E* isomer), 4.08 q (2H, $CH_3C\mathbf{H}_2O$, *Z* isomer), 7.13–8.15 m (8H, H_{arom}, *Z* isomer), 7.23-8.24 m (8H, H_{arom}, *E* isomer), 12.9 s (1H, NH, *Z* isomer), 14.05 s (1H, NH, *E* isomer). ^{13}C NMR spectrum, δ_C, ppm: *E* isomer: 126.56 (C^1); 166.63 (C^2); 160.38 ($CH_3CH_2O\mathbf{C}O$); 62.59 ($CH_3\mathbf{C}H_2O$); 13.58 ($\mathbf{C}H_3CH_2$); 115.86, 124.98, 125.87, 135.13, 136.56, 138.14 ($NC_6H_4NO_2$-*o*); 121.66, 122.63, 125.87, 126.46, 133.57, 152.66 (C_6H_4). Mass spectrum, *m*/*z* (I_{rel}, %): 402 (50) $[M]^+$, 167 (80) $[C_7H_4NS_2]^+$, 134 (30) $[C_7H_4NS]^+$, 122 (20) $[C_6H_4NS]^+$, 108 (30) $[C_6H_4S]^+$, 90 (15) $[C_6H_4N]^+$. Found, %: C 51.02; H 3.80; N 13.33; S 16.32. $C_{17}H_{14}N_4O_4S_2$. Calculated, %: C 50.69; H 3.48; N 13.91; S 15.90.

Ethyl (1,3-benzothiazol-2-ylsulfanyl)(*o*-chlorophenylhydrazono)acetate (IVi). Yield 80% (*E* isomer), mp 106–107°C; traces of the *Z* isomer were also detected. ^{1}H NMR spectrum, δ, ppm: 1.15 t (3H, $C\mathbf{H}_3CH_2$, *E* isomer), 1.36 t (3H, $C\mathbf{H}_3CH_2$, *Z* isomer), 4.30 q (2H, $CH_3C\mathbf{H}_2O$, *E* isomer), 4.32 q (2H, $CH_3C\mathbf{H}_2O$, *Z* isomer), 7.12–7.84 m (8H, H_{arom}, *E* isomer), 7.02–7.85 m (8H, H_{arom}, *Z* isomer), 9.85 s (1H, NH, *Z* isomer), 12.95 s (1H, NH, *E* isomer). ^{13}C NMR spectrum, δ_C, ppm: *E* isomer: 128.97 (C^1); 166.11 (C^2); 161.96 ($CH_3CH_2O\mathbf{C}O$); 62.29 ($CH_3\mathbf{C}H_2O$); 13.61 ($\mathbf{C}H_3CH_2$); 114.84, 118.83, 126.45, 128.65, 129.65, 137.74 (NC_6H_4Cl-*o*); 121.46, 121.83, 124.58, 124.68, 134.86, 152.90 (C_6H_4). Mass spectrum, *m*/*z* (I_{rel}, %): 391 (20) $[M]^+$, 225 (15) $[C_{10}H_{11}ClN_2O_2]^+$, 167 (60) $[C_7H_4NS_2]^+$, 134 (10) $[C_7H_4NS]^+$, 122 (15) $[C_6H_4NS]^+$, 108 (35) $[C_6H_4S]^+$, 90 (35) $[C_6H_4N]^+$. Found, %: C 53.12; H 3.63; N 10.66; S 16.74. $C_{17}H_{14}ClN_3O_2S_2$. Calculated, %: C 52.05; H 3.57; N 10.71; S 16.33.

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