

REACTION OF *N*-SUBSTITUTED 3,4-DICHLOROMALEIMIDES WITH α -MERCAPTOAZAHETEROCYCLES

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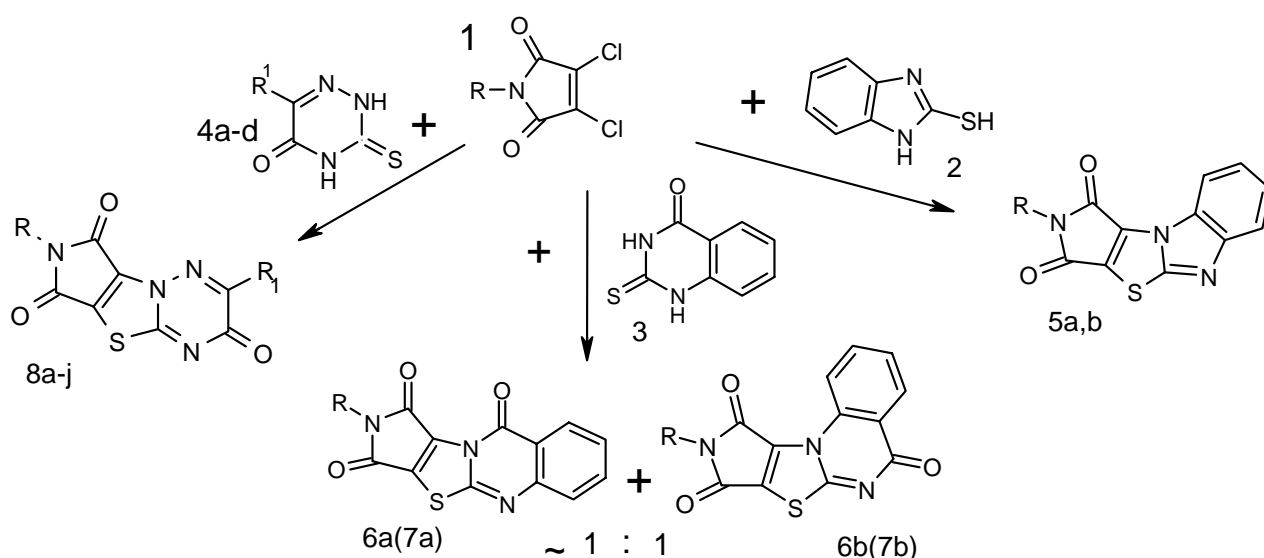
Abstract - Reaction of *N*-substituted 3,4-dichloromaleimides (**1**) with α -mercaptoazaheterocycles, 2-mercapto-1*H*-benzo[*d*]imidazole (**2**) and 3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazin-5-ones (**4**) in the presence of triethylamine, led to the formation of condensed thiazole ring resulting in 2,3-dihydro-1*H*-benzo[4,5]imidazo[2,1-*b*]pyrrolo[3,4-*d*][1,3]thiazole-1,3-diones (**5**) and 7,8-dihydro-2*H*,6*H*-pyrrolo[3',4':4,5][1,3]thiazolo[3,2-*b*][1,2,4]triazine-2,6,-8-triones (**8**), respectively. Refluxing of **8** in aqueous dioxane-triethylamine produced derivatives of 7-oxo-7*H*-[1,3]thiazolo[3,2-*b*][1,2,4]triazine-2-carboxamides (**9**) by destruction of maleimide ring with decarboxylation. The structure of **9i** was confirmed by X-Ray analysis. **1** reacted with 2-thioxo-1,2,3,4-tetrahydro-4-quinazolinone (**3**) with cyclization at N-1 and N-3 positions.

Katritzky *et al.* in 1988-89 reported the formation of pyrrolo[3,4-*d*]thiazole structure in the reaction of 3,4-dichloro-*N*-phenylmaleimide with thioamides (thiourea, thioacetamide, dithiooxamide).^{1,2} Later Matsuoka *et al.* described the formation of another product, 2,6-diphenyl-2,3,6,7-tetrahydro-1*H*,5*H*-pyrrolo[3',4':5,6][1,4]dithiino[2,3-*c*]pyrrole-1,3,5,7-tetraone, in a reaction with dithiooxamide.³ Katritzky *et al.* reconsidered results of previous research in 1993 having concluded that only minor amounts of pyrrolo[3,4-*d*]thiazoles were actually obtained in the reaction of thioamides with dichloromaleimides.⁴ The principal product was indeed the structure proposed by Japanese authors.³ We have studied the reaction of *N*-substituted 3,4-dichloromaleimides (**1**) with α -mercaptoazahetero-cycles: 2-mercapto-1*H*-

benzo[*d*]imidazole (**2**), 2-thioxo-1,2,3,4-tetrahydro-4-quinazolinone (**3**), and 6-substituted 3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazin-5-ones (**4a-c**). The process does not stop at the stage of *S*-monosubstitution even under mild reaction conditions, and reaction proceeds further resulting in annelation of thiazole on side [*c*] of maleimide.

Reaction of dichloromaleimide (**1**) with symmetric 2-mercaptobenzimidazole (**2**) in the presence of 2 eq. of triethylamine led to the formation of 2,3-dihydro-1*H*-benzo[4,5]imidazo[2,1-*b*]pyrrolo[3,4-*d*][1,3]thiazole-1,3-dione (**5a,b**) (Scheme 1).

Scheme 1



A rigid heterocyclic system is formed where the hydrogen in position 9 is spatially close to carbonyl group of maleimide. Deshielding effect of carbonyl results in the low-field shift of 9-H signal in ^1H NMR spectrum of compounds (**5a,b**) (8.14 ppm, d, $J = 6.9$ Hz (**5a**), $J = 7.2$ Hz (**5b**)). The chemical shifts for remaining aromatic protons are observed in the region 7.3-7.8 ppm. Two bands of carbonyl groups of maleimide are observed in IR spectrum at 1775-1770 (asymmetric) and 1710 (s) cm^{-1} , lower-frequency band being more intense.

There are three different nucleophilic centers in the molecule of 2-thioxo-1,2,3,4-tetrahydro-4-quinazolinone (**3**): sulfur atom and nitrogens in positions 1 and 3 of quinazolinone. As expected, two competitive directions of cyclization at N-1 and N-3 quinazolinone positions were realized in the reaction of compound (**3**) with dichloromaleimide (**1**). Reaction product was obtained as ~1:1 mixture of isomers (**6a,b**) and (**7a,b**) (Scheme 1). The isomers (**6a,7a,7b**) were successfully isolated by crystallization. The lowest-field signal in proton NMR spectrum of isomer (**6a**) (8.31 ppm, d, $J = 8.1$ Hz) and (**7a**) (8.29 ppm, d, $J = 8.1$ Hz) corresponds to proton in position 9. Proton H-1 in isomer (**6b,7b**) is subject to even stronger deshielding effect of carbonyl group, and its resonance is shifted to lower field (9.11 ppm (**6b**); 9.08 ppm(**7b**)) than that of H-9 proton of **6a,7a**. Availability of ^1H NMR spectrum of individual isomer

(6a) allowed to make signal assignments for protons of isomer (6b) in the spectrum of isomeric mixture. Two bands of carbonyl groups of maleimide are observed in IR spectrum of isomer (6a,7a,7b) at 1785-1770 (as) and at 1720-1715 (s) cm^{-1} , and carbonyl group of quinazolone at 1700 cm^{-1} (6a,7a) and 1650 cm^{-1} (7b).

Reaction of dichloromaleimides (1) with 6-substituted 3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazin-5-ones (4a-c) resulted in the formation of only one possible isomer (8a-j), product of cyclization at nitrogen atom in position 2 of triazine (Scheme 1). IR spectra of 7,8-dihydro-2*H*,6*H*-pyrrolo[3',4':4,5][1,3]thiazolo[3,2-*b*][1,2,4]triazine-2,6,8-triones (8a-j) show asymmetric and symmetric bands of maleimide carbonyl groups in the region 1785-1770 and 1730-1710 cm^{-1} , respectively. The bands of carbonyl group of triazine of 8a-j are observed at 1670-1640 cm^{-1} .

Table 1. Physical and analytical data for 5a,b; 6a; 7a,b; 8a-j.

Compd	Formula	Calcd %				Found %				mp °C
		C	H	N	S	C	H	N	S	
5a	C ₁₈ H ₁₁ N ₃ O ₂ S	64.85	3.33	12.60	9.62	64.87	3.30	12.72	9.58	193-194
5b	C ₁₇ H ₇ N ₃ O ₂ Cl ₂ S	52.59	1.82	10.82	8.26	52.51	1.85	10.91	8.42	201-202
		Cl 18.26				Cl 18.18				
6a	C ₁₉ H ₁₁ N ₃ O ₃ S	63.15	3.07	11.63	8.87	63.22	3.09	11.57	8.68	245-246
7a	C ₁₉ H ₁₁ N ₃ O ₄ S	60.47	2.94	11.13	8.50	60.43	2.99	11.19	8.54	279-280
7b	C ₁₉ H ₁₁ N ₃ O ₄ S	60.47	2.94	11.13	8.50	60.46	2.86	11.25	8.46	234-235
8a	C ₁₃ H ₆ N ₄ O ₃ S	52.35	2.03	18.78	10.75	52.40	2.00	18.96	10.80	233-234
8b	C ₁₃ H ₅ N ₄ O ₃ ClS	46.93	1.51	16.84	9.64	46.88	1.55	16.98	9.51	256-257
		Cl 10.66				Cl 10.50				
8c	C ₁₄ H ₈ N ₄ O ₃ S	53.84	2.58	17.94	10.27	53.83	2.61	18.03	10.19	232-233
8d	C ₁₅ H ₁₀ N ₄ O ₃ S	55.21	3.09	17.17	9.82	55.43	3.07	17.24	9.97	205-206
8e	C ₁₅ H ₁₀ N ₄ O ₃ S	55.21	3.09	17.17	9.82	55.33	3.06	17.34	10.00	253-254
8f	C ₁₅ H ₁₀ N ₄ O ₄ S	52.63	2.94	16.37	9.37	52.61	2.95	16.55	9.30	228-229
8g	C ₁₄ H ₇ N ₄ O ₃ ClS	48.49	2.03	16.16	9.25	48.51	2.04	16.08	9.32	185-186
		Cl 10.22				Cl 10.07				
8h	C ₁₄ H ₇ N ₄ O ₃ ClS	48.49	2.03	16.16	9.25	48.52	2.01	16.27	9.29	238-239
		Cl 10.22				Cl 10.29				

8i	C ₁₉ H ₁₀ N ₄ O ₃ S	60.96	2.69	14.97	8.56	61.02	2.73	15.03	8.66	225-226
8j	C ₁₉ H ₉ N ₄ O ₃ BrS	50.35	2.00	12.36	7.07	50.43	2.04	12.44	7.12	252-253
		Br 17.63				Br 17.75				

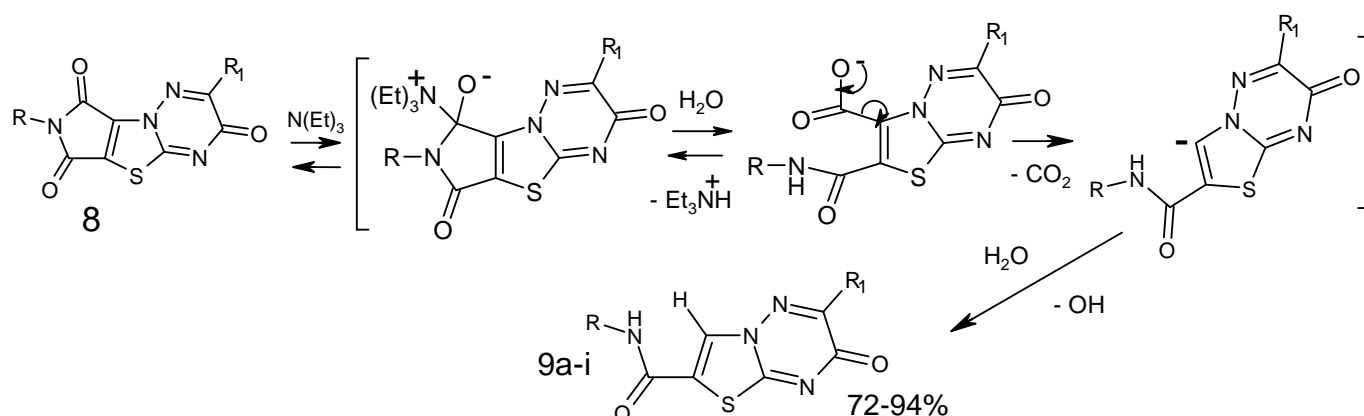
Table 2. Yield and ¹H-NMR chemical shifts of derivatives (**5a,b**; **6a,b**; **7a,b**; **8a-j**).

Compd	Substituent		¹ H NMR spectra (300 MHz), δ , ppm, DMSO- <i>d</i> ₆ , <i>J</i> (Hz)	Yield %
	R	R ₁		
5a	4-CH ₃ Ph		8.14 (d, 1H, <i>J</i> =6.9, HC(9)), 7.81 (d, 1H, <i>J</i> =6.9, HC(6)), 7.45-7.55 (m, 2H, HC(7,8)), 7.3-7.4 (m, 4H, Ph-H), 2.39 (s, 3H, CH ₃)	63
5b	2,5-Cl ₂ Ph		8.14 (d, 1H, <i>J</i> =7.2, HC(9)), 7.86 (d, 1H, <i>J</i> =7.8, HC(6)), 7.82 (s, 1H, Ph(6')-H), 7.8 (d, 1H, <i>J</i> =8.7, Ph(3')-H), 7.72 (dd, 1H, ³ <i>J</i> =7.8, ⁴ <i>J</i> =2.7, Ph(4')-H), 7.46-7.56 (m, 2H, HC(7,8))	61
6a	4-CH ₃ Ph		8.31 (d, 1H, <i>J</i> =8.1, HC(9)), 7.95 (t, 1H, <i>J</i> =8.1, HC(7)), 7.72 (d, 1H, <i>J</i> =8.1, HC(6)), 7.62 (t, 1H, <i>J</i> =8.1, HC(8)), 7.35 (d, 2H, <i>J</i> =7.8, Ph(2',6')-H), 7.29 (d, 2H, <i>J</i> =8.1, Ph(3',5')-H), 2.38 (s, 3H, CH ₃)	23
6b	4-CH ₃ Ph		9.11 (d, 1H, <i>J</i> =9, HC(1)), 8.26 (d, 1H, <i>J</i> =7.8, HC(4)), 8.0 (t, 1H, <i>J</i> =8.1, HC(2)), 7.75 (t, 1H, <i>J</i> =8.1, HC(3)), 7.37 (d, 2H, <i>J</i> =7.8, Ph(2',6')-H), 7.26 (d, 2H, <i>J</i> =8.2, Ph(3',5')-H), 2.40 (s, 3H, CH ₃)	
7a	4-OCH ₃ Ph		8.29 (d, 1H, <i>J</i> =8.1, HC(9)), 7.94 (t, 1H, <i>J</i> =7.8, HC(7)), 7.70 (d, 1H, <i>J</i> =7.8, HC(6)), 7.61 (t, 1H, <i>J</i> =8.1, HC(8)), 7.34 (d, 2H, <i>J</i> =8.7, Ph(2',6')-H), 7.09 (d, 2H, <i>J</i> =9, Ph(3',5')-H), 3.82 (s, 3H, CH ₃)	11
7b	4-OCH ₃ Ph		9.08 (d, 1H, <i>J</i> =9, HC(1)), 8.22 (d, 1H, <i>J</i> =8.1, HC(4)), 7.98 (t, 1H, <i>J</i> =8.4, HC(2)), 7.72 (t, 1H, <i>J</i> =8.1, HC(3)), 7.39 (d, 2H, <i>J</i> =7.8, Ph(2',6')-H), 7.13 (d, 2H, <i>J</i> =8.4, Ph(3',5')-H), 3.82 (s, 3H, CH ₃)	26
8a	Ph	H	8.28 (s, 1H, HC(3)), 7.4-7.6 (m, 5H, Ph-H)	87
8b	4-ClPh	H	8.27 (s, 1H, HC(3)), 7.63 (d, 2H, <i>J</i> =8.7, Ph(2',6')-H), 7.46 (d, 2H, <i>J</i> =8.7, Ph(3',5')-H)	73
8c	4-CH ₃ Ph	H	8.27 (s, 1H, HC(3)), 7.36 (d, 2H, <i>J</i> =9, Ph(2',6')-H), 7.28 (d, 2H, <i>J</i> =9, Ph(3',5')-H), 2.37 (s, 3H, CH ₃)	76
8d	4-CH ₃ Ph	CH ₃	7.35 (d, 2H, <i>J</i> =8.4, Ph(2',6')-H), 7.29 (d, 2H, <i>J</i> =8.4, Ph(3',5')-H), 2.38 (s, 3H, CH ₃), 2.34 (s, 3H, CH ₃)	79

8e	CH ₂ Ph	CH ₃	7.3-7.4 (m, 5H, Ph-H), 4.75 (s, 2H, CH ₂), 2.35 (s, 3H, CH ₃)	73
8f	4-OCH ₃ Ph	CH ₃	7.33 (d, 2H, <i>J</i> =9, Ph(2',6')-H), 7.09 (d, 2H, <i>J</i> =9, Ph(3',5')-H), 3.81 (s, 3H, OCH ₃), 2.34 (s, 3H, CH ₃)	67
8g	3-ClPh	CH ₃	7.58 (d, 1H, <i>J</i> =7.5, Ph(4')-H), 7.53-7.56 (m, 2H, Ph(2',5')-H), 7.42 (dd, 1H, ³ <i>J</i> =7.8, ⁴ <i>J</i> =1.8, Ph(6')-H), 2.35 (s, 3H, CH ₃)	68
8h	4-ClPh	CH ₃	7.64 (d, 2H, <i>J</i> =8.7, Ph(2',6')-H), 7.46 (d, 2H, <i>J</i> =8.7, Ph(3',5')-H), 2.34 (s, 3H, CH ₃)	65
8i	Ph	Ph	8.1 (dd, 2H, ³ <i>J</i> =7.5, ⁴ <i>J</i> =2.1, Ph(2'',6'')-H), 7.44-7.62 (m, 8H, Ph-H)	79
8j	4-BrPh	Ph	8.1 (d, 2H, <i>J</i> =7.5, Ph(2'',6'')-H), 7.78 (d, 2H, <i>J</i> =9, Ph(2',6')-H), 7.52 (m, 3H, Ph(3'',4'',5'')-H), 7.42 (d, 2H, <i>J</i> =8.7, Ph(3',5')-H)	79

Refluxing of compounds (**8**) in aqueous dioxane in the presence of triethylamine (1 eq.) led to the aminolysis and destruction of maleimide with subsequent decarboxylation and formation of carboxamides (**9a-i**) (Scheme 2).

Scheme 2



¹H NMR spectra of compounds (**9a-i**) showed singlet of thiazole proton at 8.42-8.88 ppm and amide proton singlet in the range 9.28-10.75 ppm; the latter disappeared after addition of D₂O. The characteristic bands of carbonyl groups of maleimide disappeared in IR spectra. The overlapping bands of amide carbonyl and carbonyl group of triazine are observed in the range 1670-1640 cm⁻¹. The band of N-H bond for compounds (**9a-i**) is observed in the region 3290-3260 cm⁻¹, and the band of thiazole C-H bond at 3100-3040 cm⁻¹. The structure of carboxamide (**9i**) (R = 4-BrPh, R₁ = Ph) was confirmed by X-Ray diffraction analysis^{5,6} (Figure 1). In the crystal phase molecules of **9i** exist as solvate with DMF(1:1). The bicyclic fragment is a planar. The amide group is coplanar to benzene ring C(7)...C(12) (the C(8)-C(7)-N(4)-C(6) and C(7)-N(4)-C(6)-O(2) torsion angles are 3.9(8)° and 0.4(8)°, respectively).

Repulsion between the H(1) and H(4) atoms (distance is 2.20 Å, van der Waals radii sum is 2.32 Å⁵), H(4) and C(1) atoms (2.59 Å, 2.87 Å) results in some turn of two planar fragments relatively each other (the C(1)-C(5)-C(6)-O(2) torsion angle is -170.6(5)°). The phenyl substituent at the C(2) atom is disordered over two positions (A and B) with equal populations due to rotation around the C(2)-C(13) bond (the N(2)-C(2)-C(13)-C(14) torsion angle is 20(1)° and -13(1)° for conformers A and B, respectively). In the crystal molecules of **9i** form the intermolecular hydrogen bonds with DMF: N(4)-H(4)...O(1S) (H...O 2.03 Å, N-H...O 172°) and C(1)-H(1)...O(1S) (H...O 2.17 Å, C-H...O 156°). The short intermolecular contact Br(1)...H(17a) 3.11 Å is detected also.

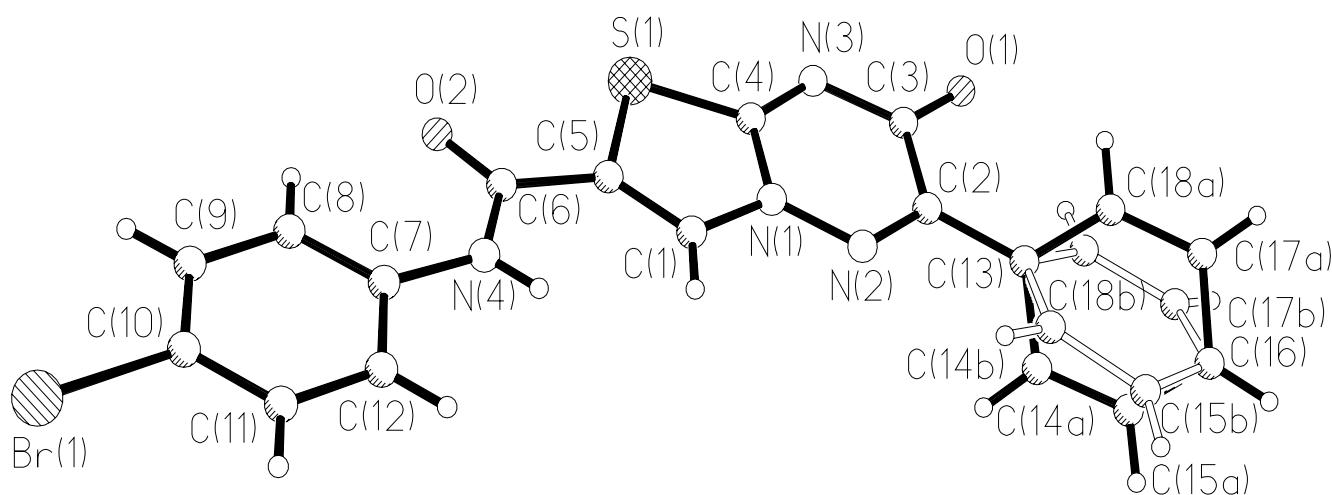


Figure 1. Structure for compound (**9i**) according to X-Ray diffraction data.

Table 3. Physical and analytical data for **9a-i**.

Compd	Formula	Calcd %				Found %				mp °C
		C	H	N	S	C	H	N	S	
9a	C ₁₂ H ₈ N ₄ O ₂ S	52.94	2.96	20.58	11.77	53.07	3.01	20.70	11.84	299-300
9b	C ₁₃ H ₁₀ N ₄ O ₂ S	54.54	3.52	19.57	11.20	54.60	3.47	19.63	11.15	> 300
9c	C ₁₂ H ₇ N ₄ O ₂ ClS	46.99	2.30	18.27	10.45	46.83	2.32	18.35	10.62	> 300
		Cl 11.56				Cl 11.65				
9d	C ₁₄ H ₁₂ N ₄ O ₂ S	55.99	4.03	18.65	10.67	56.02	4.00	18.60	10.72	> 300
9e	C ₁₄ H ₁₂ N ₄ O ₂ S	55.99	4.03	18.65	10.67	56.03	3.95	18.54	10.69	295-296
9f	C ₁₄ H ₁₂ N ₄ O ₃ S	53.16	3.82	17.71	10.13	53.25	3.88	17.74	10.28	> 300
9g	C ₁₃ H ₉ N ₄ O ₂ ClS	48.68	2.83	17.47	10.00	48.72	2.85	17.46	9.88	> 300
		Cl 11.05				Cl 10.94				

9h	C ₁₃ H ₉ N ₄ O ₂ ClS	48.68	2.83	17.47	10.00	48.60	2.79	17.38	9.96	> 300
		Cl 11.05				Cl 11.16				
9i	C ₁₈ H ₁₁ N ₄ O ₂ BrS	50.60	2.59	13.11	7.50	50.71	2.54	13.20	7.36	> 300
		Br 18.70				Br 18.72				

Table 4. Yield and ¹H-NMR chemical shifts of derivatives (**9a-i**).

Compd	Substituent		¹ H NMR spectra (300 MHz), δ , ppm, DMSO- <i>d</i> ₆ , <i>J</i> (Hz)	Yield %
	R	R ₁		
9a	Ph	H	10.47 (s, 1H, N-H), 8.81 (s, 1H, HC(3)), 8.04 (s, 1H, HC(6)), 7.65 (d, 2H, <i>J</i> =8.1, Ph(2',6')-H), 7.38 (t, 2H, <i>J</i> =8.1, Ph(3',5')-H), 7.15 (t, 1H, <i>J</i> =8.1, Ph(4')-H)	88
9b	4-CH ₃ Ph	H	10.46 (s, 1H, N-H), 8.8 (s, 1H, HC(3)), 8.06 (s, 1H, HC(6)), 7.54 (d, 2H, <i>J</i> =6.9, Ph(2',6')-H), 7.19 (d, 2H, <i>J</i> =7.2, Ph(3',5')-H), 2.28 (s, 3H, CH ₃)	94
9c	4-ClPh	H	10.63 (s, 1H, N-H), 8.82 (s, 1H, HC(3)), 8.09 (s, 1H, HC(6)), 7.71 (d, 2H, <i>J</i> =9, Ph(2',6')-H), 7.46 (d, 2H, <i>J</i> =8.7, Ph(3',5')-H)	92
9d	4-CH ₃ Ph	CH ₃	10.30 (s, 1H, N-H), 8.71 (s, 1H, HC(3)), 7.52 (d, 2H, <i>J</i> =6.9, Ph(2',6')-H), 7.18 (d, 2H, <i>J</i> =7.2, Ph(3',5')-H), 2.28 (s, 6H, CH ₃)	90
9e	CH ₂ Ph	CH ₃	9.29 (t, 1H, <i>J</i> =6, N-H), 8.55 (s, 1H, HC(3)), 7.3-7.4 (m, 5H, Ph-H), 4.49 (d, 2H, <i>J</i> =6, CH ₂), 2.25 (s, 3H, CH ₃)	79
9f	4-OCH ₃ Ph	CH ₃	10.35 (s, 1H, N-H), 8.7 (s, 1H, HC(3)), 7.54 (d, 2H, <i>J</i> =9, Ph(2',6')-H), 6.93 (d, 2H, <i>J</i> =8.7, Ph(3',5')-H), 3.72 (s, 3H, OCH ₃), 2.25 (s, 3H, CH ₃)	83
9g	3-ClPh	CH ₃	10.34 (s, 1H, N-H), 8.68 (s, 1H, HC(3)), 7.78 (s, 1H, Ph(2')-H), 7.58 (d, 1H, <i>J</i> =7.8, Ph(6')-H), 7.38 (t, 1H, <i>J</i> =8.0, Ph(5')-H), 7.17 (d, 1H, <i>J</i> =8.1, Ph(4')-H), 2.29 (s, 3H, CH ₃)	91
9h	4-ClPh	CH ₃	10.44 (s, 1H, N-H), 8.71 (s, 1H, HC(3)), 7.68 (d, 2H, <i>J</i> =8.1, Ph(2',6')-H), 7.41 (d, 2H, <i>J</i> =7.2, Ph(3',5')-H), 2.28 (s, 3H, CH ₃)	77
9i	4-BrPh	Ph	10.66 (s, 1H, N-H), 8.91 (s, 1H, HC(3)), 8.07 (dd, 2H, ³ <i>J</i> =8.1, ⁴ <i>J</i> =2.1, Ph(2'',6'')-H), 7.67 (d, 2H, ³ <i>J</i> =8.7, Ph(2',6')-H), 7.5-7.6 (m, 5H, Ph(3'',4'',5'')-H + Ph(3',5')-H)	72

EXPERIMENTAL

IR spectra were recorded on a UR-20, Specord 75-I and Pye Unicam. NMR spectra were obtained on a “Varian” 300 MHz. The chemical shifts (δ) were reported in ppm downfield from tetramethylsilane.

Crystal data for 9i: $C_{21}H_{18}N_5O_3BrS$, Mr = 500.37, triclinic, $a = 7.777(2)$, $b = 10.951(4)$, $c = 12.825(4)$ Å, $\alpha = 102.37(3)^\circ$, $\beta = 90.74(3)^\circ$, $\gamma = 99.93(3)^\circ$, $V = 1049.5(6)$ Å³, $Z = 2$, space group $P\bar{1}$, $d = 1.583$ g/cm³, $\mu(\text{MoK}\alpha) = 2.092$ mm⁻¹, $F(000) = 508$. All crystallographic measurements were performed at 20 °C on an automatic four-circles Siemens P3/PC diffractometer (MoK α , graphite monochromator, $2\theta/\theta$ - scanning, $2\theta_{\text{max}} = 50^\circ$). Structure was solved by direct method using SHELX97⁶ package of programs. The absorption correction was made by semiempirical method using the ψ -scans ($T_{\text{max}} = 1.000$, $T_{\text{min}} = 0.358$). Position of the hydrogen atoms were calculated and refined using “riding” model with $U_{\text{iso}} = 1.2U_{\text{eq}}$ for non-hydrogen atoms bonding to each hydrogen. Full-matrix least-squares refinement against F^2 (508 parameters) in anisotropic approximation using 3437 reflections was converged to $R_1=0.054$ (for 2176 reflections with $F>4\sigma(F)$), $wR_2=0.147$, $S=0.982$.

Table 5. Selected bond lengths (Å) for **9i**.

Br(1)-C(10)	1.890 (4)	C(9)-C(10)	1.367 (7)	S(1)-C(4)	1.727 (4)	C(10)-C(11)	1.376 (6)
S(1)-C(5)	1.750 (4)	C(11)-C(12)	1.382 (6)	O(1)-C(3)	1.228 (5)	C(13)-C(14B)	1.30 (2)
O(2)-C(6)	1.214 (5)	C(13)-C(18B)	1.38 (2)	N(1)-N(2)	1.350 (5)	C(13)-C(18A)	1.40 (1)
N(1)-C(4)	1.371 (5)	C(13)-C(14A)	1.44 (2)	N(1)-C(1)	1.378 (5)	C(16)-C(15A)	1.32 (4)
N(2)-C(2)	1.306 (6)	C(16)-C(15B)	1.37 (3)	N(3)-C(4)	1.303 (6)	C(16)-C(17B)	1.39 (2)
N(3)-C(3)	1.378 (6)	C(16)-C(17A)	1.41 (2)	N(4)-C(6)	1.356 (6)	C(14A)-C(15A)	1.33 (4)
N(4)-C(7)	1.413 (5)	C(17A)-C(18A)	1.36 (2)	C(1)-C(5)	1.328 (6)	C(14B)-C(15B)	1.47 (3)
C(2)-C(13)	1.482 (6)	C(17B)-C(18B)	1.43 (2)	C(2)-C(3)	1.486 (6)	O(1S)-C(3S)	1.217 (6)
C(5)-C(6)	1.482 (6)	N(1S)-C(3S)	1.304 (6)	C(7)-C(12)	1.389 (6)	N(1S)-C(2S)	1.445 (7)
C(7)-C(8)	1.393 (6)	N(1S)-C(1S)	1.462 (8)	C(8)-C(9)	1.400 (7)		

Table 6. Selected angles ($^\circ$) for **9i**.

C(4)-S(1)-C(5)	90.4 (2)	C(18B)-C(13)-C(2)	120.1 (7)	C(6)-C(5)-S(1)	116.2 (3)
N(2)-N(1)-C(1)	122.5 (3)	C(14A)-C(13)-C(2)	121 (1)	O(2)-C(6)-C(5)	119.4 (4)
C(2)-N(2)-N(1)	116.3 (3)	C(15B)-C(16)-C(17B)	120 (1)	C(12)-C(7)-C(8)	119.4 (4)
C(6)-N(4)-C(7)	126.9 (3)	C(15A)-C(14A)-C(13)	116 (2)	C(8)-C(7)-N(4)	123.9 (4)
N(2)-C(2)-C(13)	114.5 (4)	C(18A)-C(17A)-C(16)	117 (1)	C(10)-C(9)-C(8)	120.9 (4)
C(13)-C(2)-C(3)	123.2 (4)	C(13)-C(14B)-C(15B)	125 (2)	C(9)-C(10)-Br(1)	119.7 (3)
O(1)-C(3)-C(2)	122.3 (4)	C(16)-C(17B)-C(18B)	121 (1)	C(10)-C(11)-C(12)	119.3 (4)
N(3)-C(4)-N(1)	123.7 (4)	C(3S)-N(1S)-C(2S)	120.7 (5)	C(14B)-C(13)-C(18B)	120 (1)

N(1)-C(4)-S(1)	109.9 (3)	C(2S)-N(1S)-C(1S)	117.0 (5)	C(14B)-C(13)-C(2)	120 (1)
C(1)-C(5)-S(1)	112.0 (3)	N(2)-N(1)-C(4)	122.7 (4)	C(18A)-C(13)-C(2)	123.0 (7)
O(2)-C(6)-N(4)	125.2 (4)	C(4)-N(1)-C(1)	114.8 (3)	C(15A)-C(16)-C(17B)	105 (1)
N(4)-C(6)-C(5)	115.3 (4)	C(4)-N(3)-C(3)	117.3 (4)	C(15A)-C(16)-C(17A)	118 (1)
C(12)-C(7)-N(4)	116.7 (4)	C(5)-C(1)-N(1)	112.8 (4)	C(16)-C(15A)-C(14A)	128 (2)
C(7)-C(8)-C(9)	118.7 (4)	N(2)-C(2)-C(3)	122.2 (4)	C(17A)-C(18A)-C(13)	125 (1)
C(9)-C(10)-C(11)	120.6 (4)	O(1)-C(3)-N(3)	120.0 (4)	C(16)-C(15B)-C(14B)	114 (2)
C(11)-C(10)-Br(1)	119.7 (3)	N(3)-C(3)-C(2)	117.6 (4)	C(13)-C(18B)-C(17B)	118 (1)
C(11)-C(12)-C(7)	121.0 (4)	N(3)-C(4)-S(1)	126.4 (3)	C(3S)-N(1S)-C(1S)	122.3 (6)
C(18A)-C(13)-C(14A)	116 (1)	C(1)-C(5)-C(6)	131.8 (4)	O(1S)-C(3S)-N(1S)	126.4 (5)

2,3-Dihydro-1*H*-benzo[4,5]imidazo[2,1-*b*]pyrrolo[3,4-*d*][1,3]thiazole-1,3-diones (**5a,b**)

The mixture of 10 mmol of appropriate dichloromaleimide (**1**), 2.25 g (15 mmol) of 2-mercapto-1*H*-benzo[*d*]imidazole (**2**) and 2.02 g (20 mmol) of triethylamine in 20 mL of dry dioxane was stirred at 50-60 °C for 3 h. Precipitate was collected by filtration, washed with dioxane and water, dried and recrystallized from dioxane. The yields of products (**5a,b**) were 63%, 61%.

2,3-Dihydro-1*H*,10*H*-pyrrolo[3',4':4,5][1,3]thiazolo[[2,3-*b*]quinazoline-1,3,10-triones (**6a,7a**);

9,10-Dihydro-5*H*,8*H*-pyrrolo[3',4':4,5][1,3]thiazolo[3,2-*a*]quinazoline-5,8,10-triones (**6b,7b**)

To a solution of 10 mmol of appropriate dichloromaleimide (**1**) and 1.78 g (10 mmol) of 2-thioxo-1,2,3,4-tetrahydro-4-quinazolinone (**3**) in 25 mL of dry dioxane 1.52 g (15 mmol) of triethylamine was added dropwise with stirring at 30-40 °C. The reaction mixture was stirred at 35-45 °C for 4 h and then at rt for 8 h. Precipitate was collected by filtration, washed with dioxane and water. Crystalline product was obtained as mixture of isomers (**6a,b**) (~1:1); **7a,b** (~1:1). The total yields of the mixture of isomers were 55 % (**6a,b**); 67 % (**7a,b**). The individual isomers (**6a**) (23%), (**7a**) (26%), (**7b**) (11%) were isolated by crystalization from dry dioxane.

7,8-Dihydro-2*H*,6*H*-pyrrolo[3',4':4,5][1,3]thiazolo[3,2-*b*][1,2,4]triazine-2,6,8-triones (**8a-j**)

To a solution of 10 mmol of appropriate dichloromaleimide (**1**) and 10 mmol of 6-substituted 3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazin-5-one (**4a-c**) in 20 mL of dry dioxane 1.52 g (15 mmol) triethylamine was added dropwise with stirring at 30-40 °C. The reaction mixture was stirred at 35-45 °C for 5 h. The product precipitated during the reaction. After cooling, the product was collected by filtration, washed with dioxane and water, dried and recrystallized from dry dioxane. The yields of products (**8a-j**) were 65-87 %.

7-oxo-7H-[1,3]thiazolo[3,2-b][1,2,4]triazine-2-carboxamides (9a-i)

The mixture of 3 mmol of appropriate compound (**8**), 0.303 g (3 mmol) of triethylamine and 1 mL of water (55 mmol) in 10 mL of dioxane was refluxed for 1 h and then stirred at rt for 8 h. Precipitate was collected by filtration, washed with dioxane and water, and recrystallized from DMF. The yields of products (**9a-i**) were 72-94 %.

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