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

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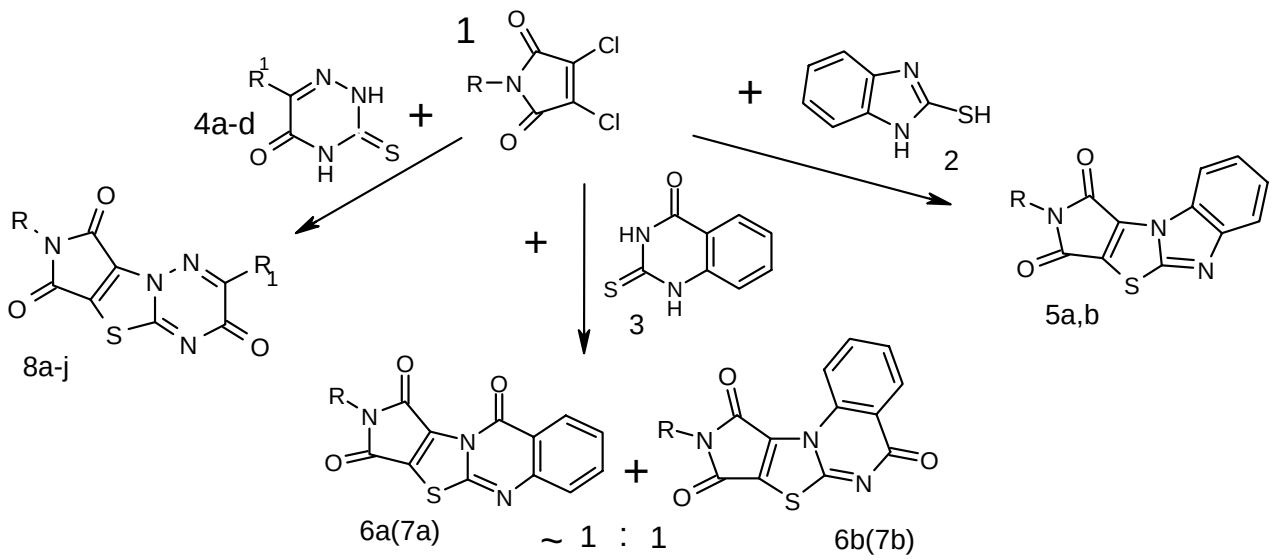
**Abstract** - Reaction of *N*-substituted 3,4-dichloromaleimides (**1**) with α-mercaptoazaheterocycles, 2-mercapto-*1H*-benzo[*d*]imidazole (**2**) and 3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazin-5-ones (**4**) in the presence of triethylamine, led to the formation of condensed thiazole ring resulting in 2,3-dihydro-*1H*-benzo[4,5]imidazo[2,1-*b*]pyrrolo[3,4-*d*][1,3]thiazole-1,3-diones (**5**) and 7,8-dihydro-*2H*,*6H*-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-*7H*-[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-*1H*,*5H*-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-*1H*-

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-*1H*-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 $^1$H 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 crystalization. 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 $^1$H 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-*2H*,*6H*-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** | $C_{18}H_{11}N_3O_2S$ | 64.85 | 3.33 | 12.60 | 9.62 | 64.87 | 3.30 | 12.72 | 9.58 | 193-194 |
| **5b** | $C_{17}H_7N_3O_2Cl_2S$ | 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** | $C_{19}H_{11}N_3O_3S$ | 63.15 | 3.07 | 11.63 | 8.87 | 63.22 | 3.09 | 11.57 | 8.68 | 245-246 |
| **7a** | $C_{19}H_{11}N_3O_4S$ | 60.47 | 2.94 | 11.13 | 8.50 | 60.43 | 2.99 | 11.19 | 8.54 | 279-280 |
| **7b** | $C_{19}H_{11}N_3O_4S$ | 60.47 | 2.94 | 11.13 | 8.50 | 60.46 | 2.86 | 11.25 | 8.46 | 234-235 |
| **8a** | $C_{13}H_6N_4O_3S$ | 52.35 | 2.03 | 18.78 | 10.75 | 52.40 | 2.00 | 18.96 | 10.80 | 233-234 |
| **8b** | $C_{13}H_5N_4O_3ClS$ | 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** | $C_{14}H_8N_4O_3S$ | 53.84 | 2.58 | 17.94 | 10.27 | 53.83 | 2.61 | 18.03 | 10.19 | 232-233 |
| **8d** | $C_{15}H_{10}N_4O_3S$ | 55.21 | 3.09 | 17.17 | 9.82 | 55.43 | 3.07 | 17.24 | 9.97 | 205-206 |
| **8e** | $C_{15}H_{10}N_4O_3S$ | 55.21 | 3.09 | 17.17 | 9. 82 | 55.33 | 3.06 | 17.34 | 10.00 | 253-254 |
| **8f** | $C_{15}H_{10}N_4O_4S$ | 52.63 | 2.94 | 16.37 | 9.37 | 52.61 | 2.95 | 16.55 | 9.30 | 228-229 |
| **8g** | $C_{14}H_7N_4O_3ClS$ | 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** | $C_{14}H_7N_4O_3ClS$ | 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** | $C_{19}H_{10}N_4O_3S$ | 60.96 | 2.69 | 14.97 | 8.56 | 61.02 | 2.73 | 15.03 | 8.66 | 225-226 |
| **8j** | $C_{19}H_9N_4O_3BrS$ | 50.35 | 2.00 | 12.36 | 7.07 | 50.43 | 2.04 | 12.44 | 7.12 | 252-253 |
| | | Br 17.63 | | | | Br 17.75 | | | | |

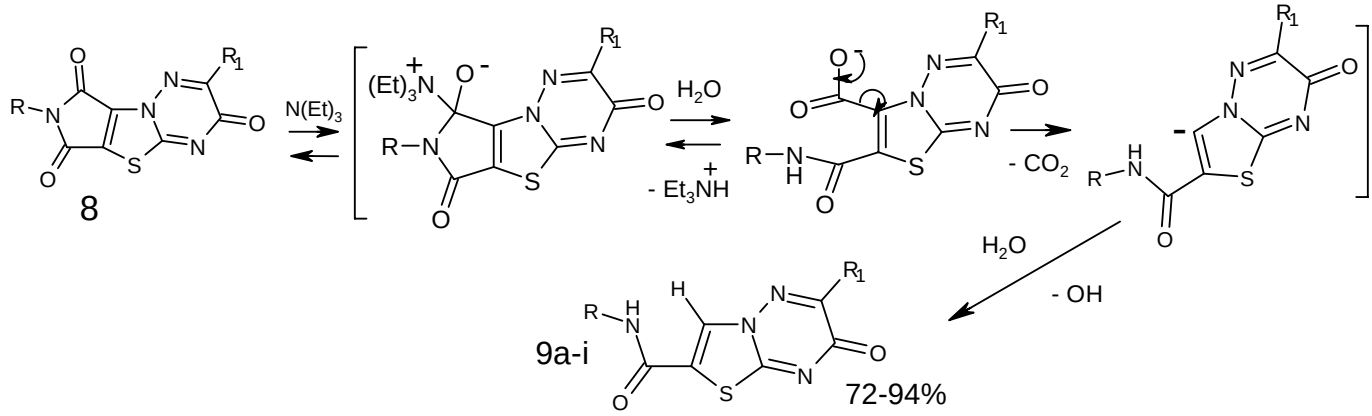
Table 2. Yield and $^1$H-NMR chemical shifts of derivatives (**5a,b; 6a,b; 7a,b; 8a-j**).

| Com-pd | Substituent | | $^1$H NMR spectra ( 300 MHz ), δ , ppm, DMSO-$d_6$ , *J* (Hz) | Yield % |
|---|---|---|---|---|
| | R | $R_1$ | | |
| **5a** | 4-$CH_3$Ph | | 8.14 (d, 1H, *J*=6.9, HC(9)), 7.81 (d, 1H, *J*=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, *J*=7.2, HC(9)), 7.86 (d, 1H, *J*=7.8, HC(6)), 7.82 (s, 1H, Ph(6')-H), 7.8 (d, 1H, *J*=8.7, Ph(3')-H), 7.72 (dd, 1H, $^3J$=7.8, $^4J$=2.7, Ph(4')-H), 7.46-7.56 (m, 2H, HC(7,8)) | 61 |
| **6a** | 4-$CH_3$Ph | | 8.31 (d, 1H, *J*=8.1, HC(9)), 7.95 (t, 1H, *J*=8.1, HC(7)), 7.72 (d, 1H, *J*=8.1, HC(6)), 7.62 (t, 1H, *J*=8.1, HC(8)), 7.35 (d, 2H, *J*=7.8, Ph(2',6')-H), 7.29 (d, 2H, *J*=8.1, Ph(3',5')-H), 2.38 (s, 3H, $CH_3$) | 23 |
| **6b** | 4-$CH_3$Ph | | 9.11 (d, 1H, *J*=9, HC(1)), 8.26 (d, 1H, *J*=7.8, HC(4)), 8.0 (t, 1H, *J*=8.1, HC(2)), 7.75 (t, 1H, *J*=8.1, HC(3)), 7.37 (d, 2H, *J*=7.8, Ph(2',6')-H), 7.26 (d, 2H, *J*=8.2, Ph(3',5')-H), 2.40 (s, 3H, $CH_3$) | |
| **7a** | 4-$OCH_3$Ph | | 8.29 (d, 1H, *J*=8.1, HC(9)), 7.94 (t, 1H, *J*=7.8, HC(7)), 7.70 (d, 1H, *J*=7.8, HC(6)), 7.61 (t, 1H, *J*=8.1, HC(8)), 7.34 (d, 2H, *J*=8.7, Ph(2',6')-H), 7.09 (d, 2H, *J*=9, Ph(3',5')-H), 3.82 (s, 3H, $CH_3$) | 11 |
| **7b** | 4-$OCH_3$Ph | | 9.08 (d, 1H, *J*=9, HC(1)), 8.22 (d, 1H, *J*=8.1, HC(4)), 7.98 (t, 1H, *J*=8.4, HC(2)), 7.72 (t, 1H, *J*=8.1, HC(3)), 7.39 (d, 2H, *J*=7.8, Ph(2',6')-H), 7.13 (d, 2H, *J*=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, *J*=8.7, Ph(2',6')-H), 7.46 (d, 2H, *J*=8.7, Ph(3',5')-H) | 73 |
| **8c** | 4-$CH_3$Ph | H | 8.27 (s, 1H, HC(3)), 7.36 (d, 2H, *J*=9, Ph(2',6')-H), 7.28 (d, 2H, *J*=9, Ph(3',5')-H), 2.37 (s, 3H, $CH_3$) | 76 |
| **8d** | 4-$CH_3$Ph | $CH_3$ | 7.35 (d, 2H, *J*=8.4, Ph(2',6')-H), 7.29 (d, 2H, *J*=8.4, Ph(3',5')-H), 2.38 (s, 3H, $CH_3$), 2.34 (s, 3H, $CH_3$) | 79 |

| | | | | |
|---|---|---|---|---|
| **8e** | $CH_2Ph$ | $CH_3$ | 7.3-7.4 (m, 5H, Ph-H), 4.75 (s, 2H, $CH_2$), 2.35 (s, 3H, $CH_3$) | 73 |
| **8f** | 4-$OCH_3Ph$ | $CH_3$ | 7.33 (d, 2H, *J*=9, Ph(2',6')-H), 7.09 (d, 2H, *J*=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, *J*=7.5, Ph(4')-H), 7.53-7.56 (m, 2H, Ph(2',5')-H), 7.42 (dd, 1H, $^3J$=7.8, $^4J$=1.8, Ph(6')-H), 2.35 (s, 3H, $CH_3$) | 68 |
| **8h** | 4-ClPh | $CH_3$ | 7.64 (d, 2H, *J*=8.7, Ph(2',6')-H), 7.46 (d, 2H, *J*=8.7, Ph(3',5')-H), 2.34 (s, 3H, $CH_3$) | 65 |
| **8i** | Ph | Ph | 8.1 (dd, 2H, $^3J$=7.5, $^4J$=2.1, Ph(2'',6'')-H), 7.44-7.62 (m, 8H, Ph-H) | 79 |
| **8j** | 4-BrPh | Ph | 8.1 (d, 2H, *J*=7.5, Ph(2'',6'')-H), 7.78 (d, 2H, *J*=9, Ph(2',6')-H), 7.52 (m, 3H, Ph(3'',4'',5'')-H), 7.42 (d, 2H, *J*=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




$^1$H 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 $D_2O$. 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, $R_1$ = 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)$^o$ and 0.4(8)$^o$, respectively).

Repulsion between the H(1) and H(4) atoms (distance is 2.20 Å, van der Waals radii sum is 2.32 Å[5]), 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 substitutent 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.

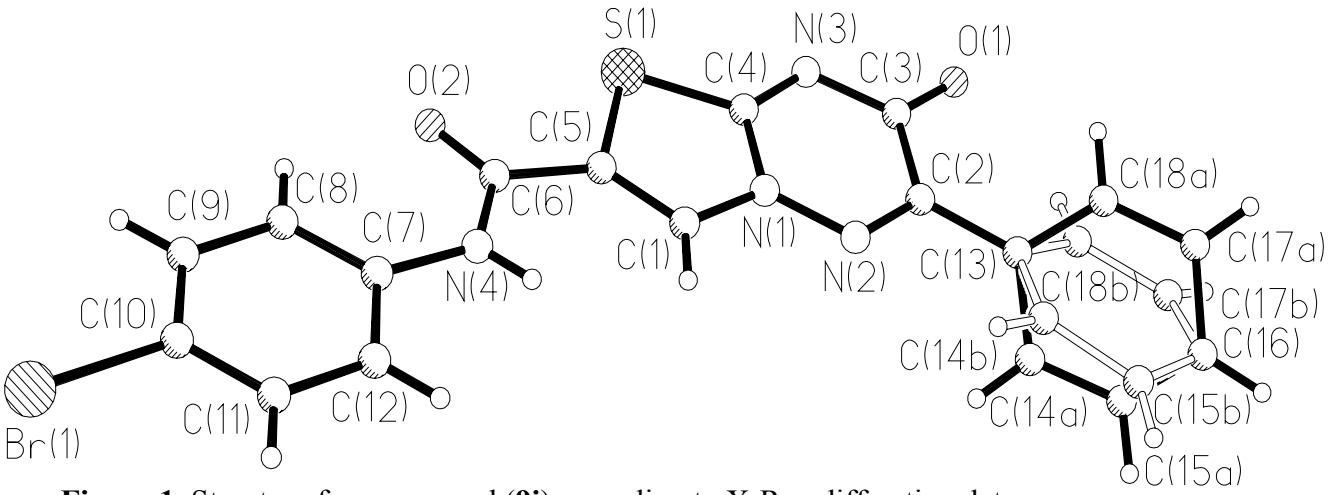



**Figure 1.** Structure for compound (**9i**) according to X-Ray diffraction data.

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

| Compd | Formula | Calcd % | | | | Found % | | | | mp °C |
|---|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | S | C | H | N | S | |
| **9a** | $C_{12}H_8N_4O_2S$ | 52.94 | 2.96 | 20.58 | 11.77 | 53.07 | 3.01 | 20.70 | 11.84 | 299-300 |
| **9b** | $C_{13}H_{10}N_4O_2S$ | 54.54 | 3.52 | 19.57 | 11.20 | 54.60 | 3.47 | 19.63 | 11.15 | > 300 |
| **9c** | $C_{12}H_7N_4O_2ClS$ | 46.99 | 2.30 | 18.27 | 10.45 | 46.83 | 2.32 | 18.35 | 10.62 | > 300 |
| | | Cl 11.56 | | | | Cl 11.65 | | | | |
| **9d** | $C_{14}H_{12}N_4O_2S$ | 55.99 | 4.03 | 18.65 | 10.67 | 56.02 | 4.00 | 18.60 | 10.72 | > 300 |
| **9e** | $C_{14}H_{12}N_4O_2S$ | 55.99 | 4.03 | 18.65 | 10.67 | 56.03 | 3.95 | 18.54 | 10.69 | 295-296 |
| **9f** | $C_{14}H_{12}N_4O_3S$ | 53.16 | 3.82 | 17.71 | 10.13 | 53.25 | 3.88 | 17.74 | 10.28 | > 300 |
| **9g** | $C_{13}H_9N_4O_2ClS$ | 48.68 | 2.83 | 17.47 | 10.00 | 48.72 | 2.85 | 17.46 | 9.88 | > 300 |
| | | Cl 11.05 | | | | Cl 10.94 | | | | |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **9h** | $C_{13}H_9N_4O_2ClS$ | 48.68 | 2.83 | 17.47 | 10.00 | 48.60 | 2.79 | 17.38 | 9.96 | > 300 |
| | | Cl 11.05 | | | | Cl 11.16 | | | | |
| **9i** | $C_{18}H_{11}N_4O_2BrS$ | 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 $^1$H-NMR chemical shifts of derivatives (**9a-i**).

| Compd | Substituent | | $^1$H NMR spectra ( 300 MHz ), δ , ppm, DMSO-$d_6$ , $J$ (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, *J*=8.1, Ph(2',6')-H), 7.38 (t, 2H, *J*=8.1, Ph(3',5')-H), 7.15 (t, 1H, *J*=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, *J*=6.9, Ph(2',6')-H), 7.19 (d, 2H, *J*=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, *J*=9, Ph(2',6')-H), 7.46 (d, 2H, *J*=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, J=6.9, Ph(2',6')-H), 7.18 (d, 2H, *J*=7.2, Ph(3',5')-H), 2.28 (s, 6H, $CH_3$) | 90 |
| **9e** | $CH_2$Ph | $CH_3$ | 9.29 (t, 1H, *J*=6, N-H), 8.55 (s, 1H, HC(3)), 7.3-7.4 (m, 5H, Ph-H), 4.49 (d, 2H, *J*=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, *J*=9, Ph(2',6')-H), 6.93 (d, 2H, *J*=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, *J*=7.8, Ph(6')-H), 7.38 (t, 1H, *J*=8.0, Ph(5')-H), 7.17 (d, 1H, *J*=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, *J*=8.1, Ph(2',6')-H), 7.41 (d, 2H, *J*=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, $^3J$=8.1, $^4J$=2.1, Ph(2'',6'')-H), 7.67 (d, 2H, $^3J$=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, α = 102.37(3)°, β = 90.74(3)°, γ = 99.93(3)°, V = 1049.5(6) $Å^3$, Z = 2, space group Pī, d = 1.583 $g/cm^3$, μ(MoKα) = 2.092 $mm^{-1}$, F(000) = 508. All crystallographic measurements were performed at 20 °C on an automatic four-circles Siemens P3/PC difractometer (MoKα, graphite monochromator, 2θ/θ - scanning, $2\theta_{max}$ = 50°). Structure was solved by direct method using SHELX97[6] package of programs. The absorption correction was made by semiempirical method using the ψ-scans ($T_{max}$ = 1.000, $T_{min}$ = 0.358). Position of the hydrogen atoms were calculated and refined using "riding" model with $U_{iso} = 1.2U_{eq}$ 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>4σ(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 (°) 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-*1H*-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-*1H*-benzo[*d*]imidazole (**2**) and 2.02 g (20 mmol) of triethylamine in 20 mL of dry dioxane was stirred at 50-60 $^0$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-*1H,10H*-pyrrolo[3',4':4,5][1,3]thiazolo[[2,3-*b*]quinazoline-1,3,10-triones (6a,7a);**

**9,10-Dihydro-*5H,8H*-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 $^o$C. The reaction mixture was stirred at 35-45 $^o$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-*2H,6H*-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 $^o$C. The reaction mixture was stirred at 35-45 $^o$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. Precipctate 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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