Reaction of 4-Thioxo-1,3-benzothiazines with Thiocarbohydrazine: Synthesis and Reactivity of 1,3,4-Triazolo[3,2-*c*]quinazoline Derivatives

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2-Aryl-4-thioxo-1,3-benzothiazines react with thiocarbohydrazide to give the new mesoionic compounds anhydro 1-amino-5-aryl-2-mercapto-1,3,4-triazolo[3,2-*c*]quinazolin-4-ium hydroxides. These compounds react with methyl iodide, aldehydes and phenacyl bromides to give 1-amino-5-aryl-2-methylthio-1,3,4-triazolo-[3,2-*c*]quinazolin-4-ium iodides, 4-arylidenamino-3-(*o*-aroylamino)phenyl-1*H*-1,2,4-triazolin-5-thiones and 3-(*o*-aroylamino)phenyl-6-aryl-7*H*-1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazines, respectively. These latter compounds by sequential treatment with methyl trifluoromethanesulphonate and triethylamine lead to 3-(*o*-aroylamino)-phenyl-6-aryl-1-methyl-7-mercapto-1*H*-pyrazolo[5,1-*c*]-1,2,4-triazoles.

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In connection with our investigations on the preparation of fused mesoionic compounds we have reported [1] the reaction of 3-amino-2-phenyl-4-thioxo-3,4-dihydroquinazoline with alkyl and aryl isothiocyanates to give 1,3,4-triazolo[3,2-*c*]quinazoline derivatives which display mesoionic character. We report now a convenient synthesis of anhydro 1-amino-5-aryl-2-mercapto-1,3,4-triazolo[3,2-*c*]-quinazolin-4-ium hydroxides **2** by reaction of 2-aryl-4-thioxo-1,3-benzothiazines **1** readily available from 2-aryl-3,1-benzoxazin-4-ones [2] and phosphorus pentasulfide, with thiocarbohydrazide [3].

Compounds **1** react with thiocarbohydrazide in ethanol in the presence of triethylamine at reflux temperature to yield the new mesoionic compounds anhydro 1-amino-5-aryl-2-mercapto-1,3,4-triazolo[3,2-*c*]quinazolin-4-ium hydroxides [2] as crystalline solids in high yields (Table I). In the monocyclic series anhydro 1-amino-2-mercapto-1,3,4-triazolium hydroxides have been prepared from hydrazides by sequential treatment with carbon disulfide, sodium chloroacetate and hydrazine [4] or by isomerization of 1,3,4-triazolium-2-benzylidenehydrazinides [5]. The present method is thus a useful addition to the existing ones in the monocyclic series due to its simplicity, general availability of starting materials and high yields.

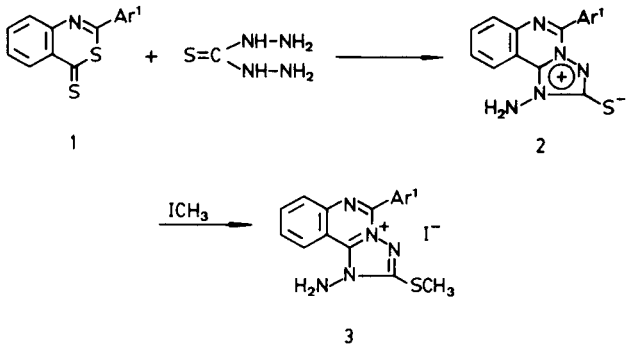
Compounds **2** react with methyl iodide to give the corresponding *S*-methyl derivatives **3** in good yields (Table I). Support for the formulation **2** and **3** is clearly provided by their analytical and spectral data. The ir spectra of compounds **2** show absorption at 1379 cm^{-1} attributable to C=S stretching vibration which may be compared in position with the thione stretching in the monocyclic anhydro 2-mercapto-1,3,4-triazolium hydroxides [6], in addition compounds **2** show two absorption bands at 3300 and 3205

Table I

Mesoionic Compounds **2** and Their *S*-Methyl Derivatives **3**

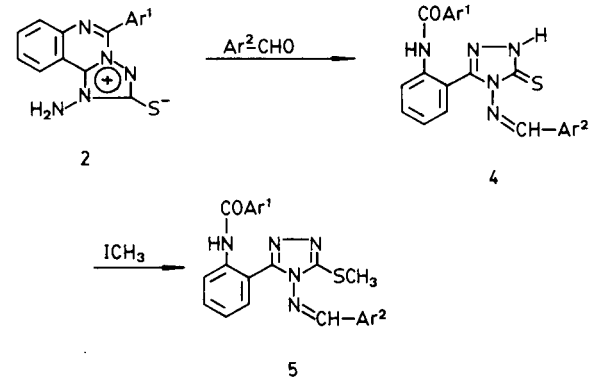
Compound No.	Ar[1]	Yield (%)	Mp (°C)	Appearance Solvent	Reaction Time (hours)	Molecular Formula	Analyses (%) Calcd. C	H	N	Found C	H	N
2a	C_6H_5	76	240-242	brown prisms benzene	5	$C_{15}H_{11}N_5S$ 293.35	61.42	3.78	23.87	61.58	3.52	23.65
2b	4-H_3C-C_6H_4	78	234-236	brown prisms EtOH/$CHCl_3$	4	$C_{16}H_{13}N_5S$ 307.37	62.52	4.26	22.78	62.58	4.17	22.64
2c	4-Cl-C_6H_4	75	247-248	brown prisms EtOH/$CHCl_3$	4	$C_{15}H_{10}ClN_5S$ 327.79	54.96	3.07	21.36	55.07	3.16	21.51
2d	4-H_3CO-C_6H_4	73	254-256	brown prisms EtOH/C_6H_6	18	$C_{16}H_{13}N_5OS$ 323.37	59.43	4.05	21.65	59.52	3.97	21.63
3a	C_6H_5	85	165-166	yellow prisms EtOH	2	$C_{16}H_{14}N_5IS$ 435.28	44.15	3.24	16.08	44.32	3.41	16.21
3b	4-H_3C-C_6H_4	88	155-156	yellow prisms $CHCl_3$	2	$C_{17}H_{13}ClN_5IS$ 449.31	45.44	3.58	15.58	45.53	3.61	15.63
3c	4-Cl-C_6H_4	82	144-146	yellow prisms $CHCl_3$	2	$C_{16}H_{13}ClN_5IS$ 469.25	40.95	2.79	14.92	41.06	2.84	14.75
3d	4-H_3CO-C_6H_4	86	156-157	white needles $CHCl_3$	3	$C_{17}H_{16}N_5IOS$ 465.31	43.88	3.46	15.05	43.70	3.32	15.23

cm^{-1} respectively, attributable to the primary amino group. Mass spectra of **2** show the expected molecular ion peaks, the base peak appears at m/e 205, peaks are also found at M^+-16, M^+-32 and the characteristic M^+-NCS. The proton nmr spectra of **3** show among others a singlet at δ 2.9 ppm corresponding to the S-CH_3 group. The simple relationship between **2** and **3** is shown by the appearance of the M^+ of **2** as the molecular ion in the mass spectra of **3**, in addition an important peak of **3** corresponding to the fragment at m/e 142 (ICH_3) (Table II).



Scheme 1

On the other hand, compounds **2** react with aromatic aldehydes in ethanol in the presence of hydrochloric acid to give 4-arylideneamino-1,2,4-triazoline-5-thiones **4**, which react with methyl iodide to give the corresponding *S*-methyl derivatives **5** in good yields (Table III). The proton nmr spectra of **5** show among others a singlet at δ 2.8 ppm corresponding to the *S*-methyl group and a singlet near to δ 9.0 ppm due to the aldiminic proton; mass spectra show the molecular ion peak and the fragment ion Ar^1-CO^+ is the base peak (Table IV).



Scheme 2

Compounds **2** also react with phenacyl bromides to give 3-(*o*-aroylamino)phenyl-6-aryl-7*H*-1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazines **6** as crystalline solids in high yields

Table II

Spectral Data of Compounds **2** and **3**

Compound No.	IR (cm^{-1})	^{1}H-NMR (δ ppm) [a]	MS m/e (%)
2a	3300, 3205, 1577, 1561, 1542, 1493, 1477, 1379, 774, 757, 691, 654	8.9-7.2 (m, aromatics) [A]	293 (M^+, 25), 278 (40), 277 (43), 261 (13), 235 (25), 205 (100), 129 (23), 121 (20), 103 (40), 102 (64), 77 (74), 76 (43)
2b	3271, 3191, 1655, 1584, 1559, 1502, 1371, 1193, 1043, 830, 776, 760, 722	8.5 (1H, d), 8.6-7.4 (9H, m), 2.6 (3H, s) [A]	308 (M^+ + 1, 21), 307 (100), 292 (39), 291 (42), 275 (31), 249 (22), 219 (34), 91 (4)
2c	3284, 1653, 1588, 1563, 1464, 1398, 1376, 1166, 1090, 1013, 835, 778, 761, 722	9.6 (1H, dd), 8.8-7.7 (9H, m) [A]	329 (M^+ + 2, 41), 328 (21), 327 (M^+, 100), 314 (10), 313 (16), 312 (27), 311 (27), 297 (11), 295 (28), 271 (7), 269 (20), 241 (11), 239 (30)
2d	3313, 3194, 1654, 1605, 1560, 1541, 1465, 1373, 1260, 1181, 1022, 784, 759, 625	9.6 (1H, dd), 8.7-7.2 (9H, m), 4.10 (3H, s) [A]	324 (M^+ + 1, 22), 323 (M^+, 100), 308 (47), 307 (47), 291 (87), 290 (22), 265 (30), 236 (17), 235 (54), 192 (21)
3a	3300, 3205, 1618, 1575, 1548, 1522, 1445, 1322, 1195, 942, 882, 777, 701, 694, 683, 655	8.7-7.8 (9H, m), 7.55 (2H, s), 2.9 (3H, s) [B]	293 (M^+-ICH_3, 8), 292 (36), 291 (20), 277 (8), 254 (88), 247 (13), 205 (38), 142 (54), 128 (7), 127 (100), 103 (9), 102 (38), 77 (38)
3b	3240, 3115, 1642, 1613, 1585, 1523, 1460, 1274, 1189, 820, 786, 775, 724	9.7 (1H, dd), 8.6-7.5 (9H, m), 2.9 (3H, s), 2.6 (3H, s) [A]	307 (M^+-ICH_3, 22), 306 (100), 305 (52), 291 (27), 254 (67), 142 (52), 128 (11), 127 (44)
3c	3222, 1638, 1587, 1561, 1518, 1460, 1092, 1000, 854, 760, 723	9.6 (1H, dd), 8.7-7.6 (9H, m), 2.9 (3H, s) [A]	341 (7), 329 (6), 328 (18), 327 (18), 326 (45), 311 (5), 254 (35), 239 (10), 142 (52), 127 (33), 85 (74), 83 (100)
3d	3211, 3115, 1636, 1603, 1582, 1558, 1507, 1468, 1311, 1272, 1179, 1019, 850, 766, 760, 697	9.5 (1H, dd), 8.6-7.16 (9H, m), 4.07 (3H, s), 2.95 (3H, s) [A]	323 (M^+-ICH_3, 17), 322 (75), 321 (26), 307 (28), 277 (9), 254 (100), 235 (26), 192 (10), 142 (11), 127 (30)

[a] Measured solvents: [A] Deuteriochloroform-trifluoroacetic acid; [B] DMSO-d_6.

Table III

4-Arylidenamino-1,2,4-triazolin-5-thiones **4** and Their *S*-Methyl Derivatives **5**

Compound No.	Ar^1	Ar^2	Yield (%)	Mp (°C)	Molecular Formula	Analyses (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
4a	C_6H_5	4-H_3C-C_6H_4	78	211-213	$C_{23}H_{19}N_5OS$ 413.47	66.81	4.63	16.94	66.62	4.75	17.12
4b	C_6H_5	4-H_3CO-C_6H_4	60	194-196	$C_{23}H_{19}N_5O_2S$ 429.5	64.36	4.46	16.30	64.57	4.32	16.20
4c	C_6H_5	2-H_3CO-C_6H_4	62	206-207	$C_{23}H_{19}N_5O_2S$ 429.5	64.36	4.46	16.30	64.60	4.62	16.12
4d	C_6H_5	3,4$(H_3CO)_2C_6H_3$	78	217-218	$C_{24}H_{21}N_5O_3S$ 459.53	62.73	4.60	15.24	62.91	4.58	15.50
4e	4-H_3CO-C_6H_4	4-H_3C-C_6H_4	72	167-170	$C_{24}H_{21}N_5O_2S$ 443.53	64.99	4.77	15.78	65.11	4.80	15.62
5a	C_6H_5	2-H_3CO-C_6H_4	85	213-215	$C_{24}H_{21}N_5O_2S$ 443.53	64.99	4.77	15.78	65.12	4.89	15.52
5b	C_6H_5	3,4$(H_3CO)_2C_6H_3$	83	162-164	$C_{25}H_{23}N_5O_3S$ 473.56	63.40	4.89	14.79	63.61	5.00	14.63

Table IV

Spectral Data of Compounds **4** and **5**

Compound No.	IR (cm^{-1})	^{1}H-NMR (δ ppm) [a]	MS m/e (%)
4a	3273, 3140, 3070, 1695, 1618, 1594, 1556, 1498, 1306, 1177, 812, 763, 740, 692, 630	10.3 (1H, s), 9.5 (1H, s), 8.3-7.2 (14H, m), 2.45 (3H, s) [A]	413 (M^+, 2), 296 (7), 278 (64), 277 (53), 220 (16), 205 (22), 117 (28), 116 (17), 105 (100), 77 (64)
4b	3290, 3140, 3050, 1686, 1596, 1540, 1517, 1307, 1260, 1165, 1027, 833, 766, 699	10.5 (1H, s), 9.55 (1H, s), 8.4-7.1 (14H, m), 4.0 (3H, s) [A]	429 (M^+, 3), 296 (3), 378 (3), 263 (2), 205 (4), 134 (10), 133 (100), 118 (12), 105 (28), 104 (13), 103 (40), 90 (48), 77 (17)
4c	3300, 3130, 3070, 1690, 1615, 1595, 1537, 1498, 1300, 1270, 1010, 745, 730, 730	10.15 (1H, s), 9.05 (1H, s), 8.2-7.0 (14H, m), 3.95 (3H, s) [A]	429 (M^+, 4), 296 (5), 278 (4), 263 (5), 205 (7), 134 (10), 133 (100), 105 (73), 104 (82), 103 (24), 90 (45), 77 (25)
4d	3220, 3090, 3030, 1687, 1591, 1543, 1464, 1358, 1306, 1271, 1023, 754, 743, 704, 641	10.2 (1H, s), 9.25 (1H, s), 8.25-7.10 (13H, m), 4.05 (6H, s) [A]	459 (M^+, 2), 296 (4), 278 (4), 263 (3), 205 (16), 164 (48), 136 (76), 150 (15), 137 (38), 105 (48), 103 (12), 102 (22), 77 (100)
4e	3358, 3335, 3120, 1680, 1609, 1592, 1511, 1303, 1265, 1189, 1031, 972, 840, 765, 757, 745	10.4 (1H, s), 9.45 (1H, s), 8.8-7.2 (13H, m), 4.1 (3H, s), 2.55 (3H, s) [A]	427 (M^+-16, 3), 326 (34), 308 (100), 307 (50), 268 (14), 250 (5), 235 (17), 135 (12), 117 (82), 116 (34), 90 (7)
5a	3120, 3080, 1675, 1630, 1585, 1470, 1439, 1253, 1165, 1017, 775, 733, 708	9.7 (1H, s), 9.3 (1H, s), 8.15-6.9 (13H, m), 3.85 (3H, s), 2.85 (3H, s) [A]	443 (M^+, 5), 415 (2), 396 (2), 366 (3), 310 (6), 282 (3), 233 (16), 205 (8), 134 (4), 133 (3), 105 (100), 77 (49)
5b	3130, 3070, 1681, 1589, 1511, 1441, 1271, 1145, 1028, 767, 706	9.0 (1H, d), 8.55 (1H, s), 8.0-6.9 (12H, m), 4.05 (6H, s), 2.8 (3H, s) [B]	473 (M^+, 4), 445 (2), 426 (2), 396 (3), 310 (8), 282 (3), 233 (16), 205 (6), 164 (8), 163 (17), 105 (100), 77 (41)

[a] Measured solvents: [A] Deuteriochloroform-trifluoroacetic acid; [B] Deuteriochloroform.

(Table V). Support for the formulation **6** is provided by elemental analysis and spectral data. The ir spectra of **6** show absorption at 1655 cm^{-1} due to the C=O stretching vibration; the proton nmr spectra show a singlet at δ 4.3 ppm due to the *S*-linked methylene protons; mass spectra show the molecular ion peak in low abundance and the base peak is due to the fragment Ar^1-CO^+ (Table VI).

The conversions **2** → **4** and **2** → **6** show the high reactivity at position 2 of the pyrimidine ring in fused 1,3,4-triazolo[3,2-*c*]quinazoline derivatives [7].

Compounds **6** react with methyl trifluoromethanesulphonate in dry dichloromethane to give the corresponding 3-(*o*-aroylamino)phenyl-6-aryl-1-methyl-7*H*-1,2,4-triazolo-[3,4-*b*]-1,3,4-thiadiazin-3-ium trifluoromethanesulphonates **7** as crystalline solids in excellent yields (Table V). The ir spectra of compounds **7** show a strong absorption in the region 1693-1659 cm^{-1} due to the C=O stretching vibration; in the proton nmr spectra the chemical shifts of N-CH_3 and S-CH_2- groups are characteristic at δ 4.15-4.05 ppm and δ 4.45-4.30 ppm respectively (Table VI).

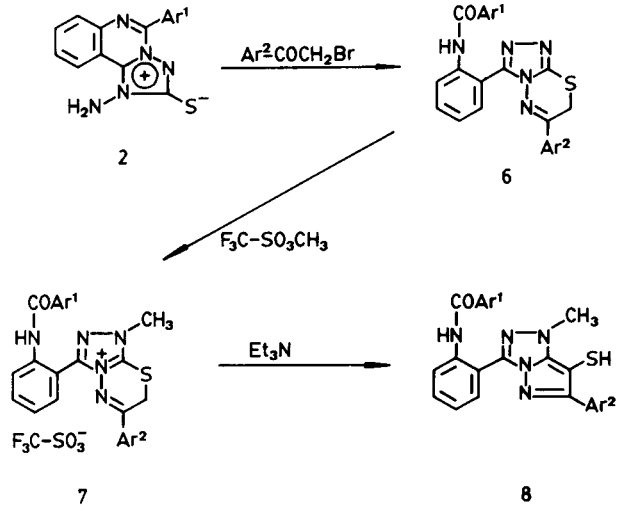
Table V

7*H*-1,2,4-Triazolo[3,4-*b*]-1,3,4-thiadiazine Derivatives **6** and **7**

Compound No.	Ar¹	Ar²	Yield (%)	Mp (°C)	Reaction Time (hours)	Molecular Formula	Analyses (%) Calcd. C	H	N	Found C	H	N
6a	C_6H_5	C_6H_5	65	230-232	12	$C_{23}H_{17}N_5OS$ 411.49	67.13	4.16	17.02	67.02	4.22	16.90
6b	C_6H_5	4-Br-C_6H_4	60	254-255	15	$C_{23}H_{16}BrN_5OS$ 490.39	56.33	3.29	14.28	56.47	3.38	14.50
6c	C_6H_5	4-Cl-C_6H_4	68	245-247	15	$C_{23}H_{16}ClN_5OS$ 445.93	61.95	3.62	15.70	62.07	3.71	15.79
6d	C_6H_5	4-H_3CO-C_6H_4	63	265-266	12	$C_{24}H_{19}N_5O_2S$ 441.51	65.29	4.34	15.86	65.40	4.51	15.63
6e	C_6H_5	4-C_6H_5-C_6H_4	73	225-227	12	$C_{29}H_{21}N_5OS$ 487.58	71.44	4.34	14.36	71.64	4.61	14.13
6f	4-H_3CO-C_6H_4	4-Cl-C_6H_4	75	240-242	20	$C_{24}H_{18}ClN_5O_2S$ 475.95	60.56	3.81	14.71	60.71	3.60	14.83
6g	4-H_3CO-C_6H_4	4-Br-C_6H_4	67	246-248	24	$C_{24}H_{18}BrN_5O_2S$ 520.41	55.39	3.49	13.46	55.21	3.33	13.70
7a	C_6H_5	C_6H_5	75	237-240	2	$C_{25}H_{20}F_3N_5O_4S_2$ 575.6	52.17	3.50	12.16	52.30	3.63	12.15
7b	C_6H_5	4-Br-C_6H_4	78	251-253	2	$C_{25}H_{19}BrF_3N_5O_4S_2$ 654.5	45.88	2.92	10.70	45.63	3.11	10.52
7c	C_6H_5	4-Cl-C_6H_4	82	260-262	2	$C_{25}H_{19}ClF_3N_5O_4S_2$ 610.04	49.22	3.14	11.48	49.41	3.19	11.30
7d	C_6H_5	4-H_3CO-C_6H_4	95	257-258	2	$C_{26}H_{22}F_3N_5O_5S_2$ 605.63	51.56	3.66	11.56	51.63	3.50	11.49
7e	4-H_3CO-C_6H_4	4-Cl-C_6H_4	82	224-226	1	$C_{26}H_{21}ClF_3N_5O_5S_2$ 640.07	48.78	3.31	10.94	48.90	3.27	11.07

When compounds **7** are treated with triethylamine undergo ring-contraction to give the corresponding pyrazolo[5,1-*c*]-1,2,4-triazole derivatives **8** as crystalline solids in excellent yields (Table VII). We believe that this conversion is conceptually similar to the previously reported [8] for the reaction of 1-methyl-3-methylthio-6-aryl-7*H*-1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazin-3-ium bromides with triethylamine to give a mixture of 1-methyl-3-methylthio-6-aryl-7-[1-methyl-3-methylthio-5-thioxo-1,2,4-1*H*-triazol-4-ylimino methylen(phenyl)methylthio]pyrazolo[5,1-*c*]-1,2,4-triazole and 1-methyl-3-methylthio-6-arylpyrazolo[5,1-*c*]-1,2,4-triazol-3-yl disulfide.

Support for the formulation **8** is provided by elemental analysis and spectral data (Table VIII).



Scheme 3

EXPERIMENTAL

The melting points were determined with a Kofler hot stage microscope and were uncorrected. The ir spectra were recorded on mineral oil mulls with a Nicolet-FT 5DX instrument. The proton nmr spectra were recorded with a Varian EM-360M instrument with TMS as internal standard. Mass spectra were obtained with a Hewlet-Packard 5993C GC/MS system; compounds were introduced through the direct insertion probe. Microanalyses were performed with a Perkin-Elmer 240C instrument.

Preparation of Anhydro 1-Amino-5-aryl-2-mercapto-1,3,4-triazolo[3,2-*c*]-quinazolin-4-ium Hydroxides **2**. General Procedure.

To a solution of the appropriate 2-aryl-4-thioxo-1,3-benzothiazine **1** (10 mmoles) in ethanol (50 ml), thiocarbohydrazide (10 mmoles) and triethylamine (10 mmoles) were added. The resultant solution was stirred at reflux for 4-18 hours. After cooling, the brown precipitated solid was filtered off, dried and recrystallized from the adequate solvent to give **2** (Table I).

Table VI

Spectral Data of Compounds **6** and **7**

Compound No.	IR (cm^{-1})	^{1}H-NMR (δ ppm) [a]	MS m/e (%)
6a	3200, 3100, 1660, 1624, 1590, 1544, 1457, 1311, 968, 758, 742, 710, 681	10.0 (1H, s), 8.3-7.5 (14H, m), 4.3 (2H, s)	411 (M^+, 4), 383 (3), 334 (5), 231 (9), 222 (4), 105 (100), 104 (9), 103 (7), 77 (63)
6b	3200, 3100, 1668, 1615, 1590, 1544, 1456, 1308, 1078, 1008, 814, 759, 717, 667	9.95 (1H, s), 8.1-7.5 (13H, m), 4.23 (2H, s)	491 (M^+ +2, 3), 489 (M^+, 3), 463 (2), 461 (2), 459 (2), 457 (2), 414 (3), 412 (3), 231 (11), 222 (4), 105 (100), 102 (13), 77 (59)
6c	3200, 3070, 1660, 1619, 1591, 1545, 1455, 1308, 1098, 1013, 890, 758, 747, 713, 667	9.8 (1H, s) 8.15-7.4 (13H, m), 4.3 (2H, s)	447 (M^+ +2, 5), 445 (M^+, 14), 419 (2), 417 (7), 415 (4), 413 (11), 368 (17), 336 (5), 231 (10), 222 (7), 138 (6), 137 (5), 105 (100), 77 (50)
6d	3250, 3150, 1661, 1617, 1590, 1542, 1450, 1311, 1261, 1192, 1033, 849, 801, 757, 710, 618	10.2 (1H, s), 8.2-6.8 (13H, m), 4.2 (2H, s), 4.0 (3H, s)	441 (M^+, 5), 413 (2), 409 (2), 364 (4), 332 (3), 231 (10), 178 (7), 134 (11), 133 (9), 107 (4), 105 (100), 77 (55)
6e	3200-3100, 1671, 1584, 1546, 1455, 1305, 967, 851, 772, 760, 743, 709, 693	9.95 (1H, s), 8.3-7.4 (18H, m), 4.30 (2H, s)	487 (M^+, 8), 459 (5), 410 (6), 231 (7), 180 (6), 179 (4), 105 (100), 77 (48)
6f	3300-3150, 1665, 1617, 1590, 1516, 1459, 1307, 1270, 1179, 1092, 1031, 849, 832, 815, 751, 690	8.4-7.0 (13H, m), 4.28 (2H, s), 4.0 (3H, s)	478 (9), 477 (M^+ +2, 38), 476 (28), 475 (M^+, 88), 474 (5), 460 (11), 447 (42), 446 (10), 445 (36), 444 (28), 443 (100), 427 (20), 426 (23), 425 (32), 308 (22), 235 (8), 135 (38)
6g	3300-3170, 1651, 1621, 1608, 1592, 1517, 1459, 1325, 1260, 1175, 1019, 967, 843, 817, 765, 745, 690	9.9 (1H, s), 8.2-6.95 (12H, m), 4.28 (2H, s) 3.97 (3H, s)	522 (4), 521 (M^+ + 2, 14), 520 (4), 519 (M^+, 13), 489 (40), 487 (40), 471 (40), 469 (35), 387 (22), 385 (20), 355 (61), 353 (59), 308 (61), 307 (31), 235 (16), 135 (100)
7a	3386, 1692, 1615, 1587, 1558, 1438, 1373, 1301, 1272, 1167, 1147, 1034, 740, 702, 687, 642	9.85 (1H, s), 8.3-7.6 (14H, m), 4.45 (2H, s), 4.15 (3H, s)	394 (M^+ −32, 5), 393 (11), 316 (9), 292 (7), 291 (6), 264 (5), 205 (8), 172 (5), 122 (11), 105 (100), 103 (10), 77 (63)
7b	3384, 1693, 1613, 1589, 1541, 1442, 1278, 1258, 1166, 1034, 776, 742, 706, 640	9.80 (1H, s), 8.30-7.40 (13H, m), 4.45 (2H, s), 4.15 (3H, s)	474 (M^+ +2, 3), 473 (10), 472 (3), 471 (10), 396 (5), 394 (5), 292 (5), 291 (4), 264 (4), 222 (7), 205 (9), 183 (4), 181 (4), 122 (12), 105 (100), 77 (59)
7c	3386, 1693, 1614, 1589, 1542, 1439, 1301, 1279, 1260, 1169, 1097, 1035, 843, 740, 706, 690, 640	9.90 (1H, s), 8.3-7.5 (13H, m), 4.45 (2H, s), 4.15 (3H, s)	429 (M^+ −32, 4), 428 (15), 351 (12), 292 (8), 291 (5), 264 (4), 207 (9), 205 (7), 137 (6), 122 (11), 105 (100), 102 (8), 77 (64)
7d	3364, 1687, 1611, 1587, 1538, 1441, 1301, 1277, 1258, 1188, 1160, 1146, 1033, 848, 782, 704, 698, 641	9.75 (1H, s), 8.20-7.05 (13H, m), 4.3 (2H, s), 4.1 (3H, s), 4.0 (3H, s)	424 (M^+ −32, 4), 423 (14), 346 (13), 292 (9), 291 (6), 264 (8), 205 (7), 202 (13), 134 (14), 133 (12), 122 (14), 105 (100), 102 (10), 77 (70)
7e	3398, 1659, 1608, 1591, 1540, 1506, 1443, 1308, 1257, 1177, 1155, 1030, 837, 826, 764, 741, 639	9.45 (1H, s), 8.10-6.85 (12H, m), 4.32 (2H, s), 4.05 (3H, s), 3.90 (3H, s)	489 (M^+ −1, 2), 473 (19), 471 (52), 459 (33), 457 (100), 387 (8), 385 (20), 324 (5), 322 (21), 307 (10), 235 (7), 135 (13)

[a] Measured solvent: Deuteriochloroform-trifluoroacetic acid.

Table VII

Pyrazolo[5,1-*c*]-1,2,4-triazole Derivatives **8**

Compound No.	Ar^1	Ar^2	Yield (%)	Mp (°C)	Molecular Formula	Analyses (%) Calcd. C	H	N	S	Found C	H	N	S
8a	C_6H_5	C_6H_5	90	213-215	$C_{24}H_{19}N_5OS$ 425.51	67.75	4.50	16.46	7.57	67.67	4.39	16.30	7.52
8b	C_6H_5	4-Br-C_6H_4	93	296-298	$C_{24}H_{18}BrN_5OS$ 504.41	57.15	3.60	13.88	6.36	57.32	3.71	13.60	6.30
8c	C_6H_5	4-Cl-C_6H_4	83	275-280	$C_{24}H_{18}ClN_5OS$ 459.95	62.67	3.94	15.23	6.97	62.60	3.84	15.12	7.06
8d	4-H_3CO-C_6H_4	4-Cl-C_6H_4	63	212-215	$C_{25}H_{20}ClN_5O_2S$ 489.98	61.28	4.11	14.29	6.54	61.39	4.03	14.40	6.39

Table VIII

Spectral Data of Compounds **8**

Compound No.	IR (cm^{-1})	^{1}H-NMR (δ ppm) [a]	MS m/e (%)
8a	3313, 1684, 1610, 1590, 1546, 1448, 1310, 774, 760, 690, 656	10.15 (1H, s), 8.7-7.10 (15H, m), 4.10 (3H, s)	393 ($M^+ - 32$, 21), 316 (14), 291 (3), 264 (4), 222 (5), 219 (11), 172 (15), 171 (9), 144 (7), 119 (20), 105 (100), 104 (34), 103 (15), 77 (62)
8b	3313, 1680, 1618, 1591, 1542, 1449, 1307, 1267, 828, 767, 704, 655	10.15 (1H, s), 8.8-7.10 (14H, m), 4.10 (3H, s)	473 ($M^+ + 2 - 32$, 2), 471 ($M^+ - 32$, 2), 396 (2), 394 (2), 391 (5), 264 (4), 221 (21), 199 (24), 197 (24), 184 (49), 183 (15), 182 (53), 181 (10), 157 (9), 155 (10), 105 (100), 77 (49)
8c	3318, 1683, 1590, 1543, 1446, 1306, 1092, 832, 762, 706, 629	10.20 (1H, s), 8.80-6.90 (14H, m), 4.10 (3H, s)	427 ($M^+ - 32$, 4), 350 (3), 291 (3), 264 (4), 222 (4), 153 (18), 138 (30), 137 (12), 111 (7), 105 (100), 77 (54)
8d	3307, 1676, 1608, 1591, 1545, 1511, 1438, 1302, 1257, 1172, 1092, 837, 764, 741, 730, 679	8.80-7.0 (14H, m), 4.20 (3H, s), 4.0 (3H, s)	459 ($M^+ + 2 - 32$, 34), 458 ($M^+ + 1 - 32$, 29), 457 ($M^+ - 32$, 100), 440 (6), 340 (27), 308 (6), 136 (14), 135 (90)

[a] Measured solvent: Deuteriochloroform-trifluoroacetic acid.

Preparation of 1-Amino-5-aryl-2-methylthio-1,3,4-triazolo[3,2-*c*]quinazolin-4-ium Iodides **3**. General Procedure.

To a suspension of mesoionic compound **2** (10 mmoles) in ethanol (50 ml), methyl iodide (20 mmoles) and hydrochloric acid (0.5 ml) were added. The reaction mixture was stirred and heated at reflux temperature for 2-3 hours. After cooling the yellow precipitated solid was filtered off, dried and recrystallized from the appropriate solvent to give **3** (Table I).

Preparation of 4-Arylidenamino-3-(*o*-aroylamino)phenyl-1*H*-1,2,4-triazoline-5-thiones **4**. General Procedure.

To a solution of mesoionic compound **2** (10 mmoles) in ethanol (20 ml), the appropriate aldehyde (10 mmoles) and hydrochloric acid (1 ml) were added. The resultant solution was stirred and heated at reflux temperature for 15 hours. After cooling, the precipitated solid was separated by filtration, dried and recrystallized from ethanol to give **4** as yellow prisms (Table III).

Preparation of 4-Arylideneamino-5-methylthio-3-(*o*-aroylamino)phenyl-1,2,4-triazoles **5**. General Procedure.

To a solution of sodium hydroxide (7 mmoles) in methanol (15 ml), the appropriate 1,2,4-triazole **4** (7 mmoles) and methyl iodide (10 mmoles) were added. The reaction mixture was stirred at reflux temperature for 3 hours. After cooling the separated solid was collected by filtration and recrystallized from chloroform gave **5** as white needles (Table III).

Preparation of 7*H*-1,2,4-Triazolo[3,4-*b*]-1,3,4-thiadiazine Derivatives **6**. General Procedure.

To a solution of the mesoionic compound **2** (1 mmole) in ethanol (20 ml), the appropriate phenacyl bromide (1 mmole) and hydrochloric acid (0.5 ml) were added. The resultant solution was stirred and heated at reflux temperature for 12-24 hours. The precipitated solid was collected by filtration and recrystallized from ethanol gave **6** as yellow prisms (Table V).

Preparation of 1*H*-Pyrazolo[5,1-*c*]-1,2,4-triazoles Derivatives **8**. General Procedure.

To a solution of 7*H*-1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazine **6** (1 mmole) in dry dichloromethane (20 ml), methyl trifluoromethanesulphonate (1.2 mmoles) was added. The reaction mixture was stirred at 40-50° for 2 hours. After cooling to room temperature, the precipitated solid was collected by filtration and recrystallized from dichloromethane gave **7** as white needles (Table V).

To a solution of **7** (0.5 mmole) in ethanol (20 ml), triethylamine (1 mmole) was added. The resultant solution was heated at reflux for 15 hours. After cooling the solid was filtered off, dried and recrystallized from ethanol gave **8** as yellow prisms (Table VII).

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