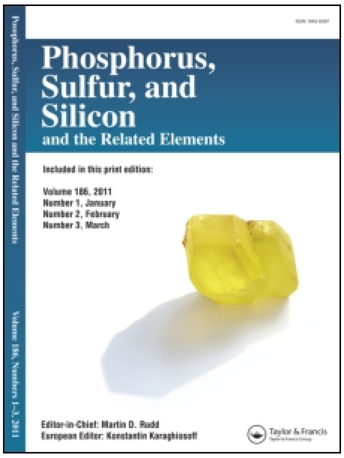

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Studies on Quinazolines. Part III. Synthesis of Some Fused-Ring Cationic and Mesoionic Derivatives of the 1,3-Thiazolo[3,2-c]quinazoline Ring System

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STUDIES ON QUINAZOLINES. PART III. SYNTHESIS OF SOME FUSED-RING CATIONIC AND MESOIONIC DERIVATIVES OF THE 1,3-THIAZOLO[3,2-c]QUINAZOLINE RING SYSTEM

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4-Allylthio-2-arylquinazolines ***4a–c*** *undergo cyclization by action of bromine to furnish 5-aryl-3-bromomethyl-2,3-dihydrothiazolo[3,2-c]quinazolin-4-ium bromide* ***5a–c****. Compounds* ***5a–c*** *undergo ring opening by action of water under acid catalysis to afford the corresponding dibromide derivatives* ***6a–c****. Bromination of 3-allyl-2-aryl-4(3*H*)quinazolinethiones* ***7a–c*** *leads to 5-aryl-2-bromomethyl-2,3-dihydrothiazolo[3,2-c]quinazolin-4-ium bromides* ***8a–c****. However, 5-aryl-1,3-thiazolo[3,2-c]quinazolinium-3-olate* ***10a–c*** *were prepared by the cyclodehydration of the corresponding thioglycolic acids* ***9a–c*** *with* Ac_2O.

Keywords: Annelated quinazoline derivatives; fused cationic and mesoionic heterocycles; 1,3-thiazolo[3,2-c]quinazoline derivatives

We previously reported[1] the synthesis of bridgehead nitrogen heterocycles of neutral character which contain the quinazoline moiety, e.g., 3-oxo-2*H*-imidazo[1,2-c]- and 4-oxo-2*H*,3*H*-pyrimido[1,2-c]quinazolines. In this context we communicate here the synthesis of some new cationic or mesoionic annelated derivatives of the thiazolo[3,2-c]quinazoline ring system based on quinazoline-4(3*H*)-thione. In continuation of our studies on phenomena of a thione ⇌ thiol tautomeric equilibrium in heterocyclic diazines, in particular, in the quinazoline-4(3*H*)-thione[1] and pyrimidine-2(1*H*)-thione[2] series, we have now investigated for the first time the behavior of the quinazoline-4(3*H*)-thione derivatives **3a–c** toward unsaturated alkylating reagents under different reaction conditions in order to obtain more precise information about the course of the reaction. We also have prepared the S- and N-unsaturated alkyl

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derivatives with the aim of using them as starting material for the synthesis of the title compounds.

Accordingly, three representative members of quinazoline-4(3*H*)-thiones[3] **3** (R = benzyl, 2-chlorophenyl, 2-naphthyl) were selected for the present investigation and these were conveniently prepared by heating of the corresponding 4*H*-3,1-benzothiazine-4-thiones[4] **2**, readily available from direct thionation of 3,1-benzoxazin-4-one derivatives[5] **1**, with formamide at 150°C. Now we report in this paper the synthesis of otherwise not available cationic derivatives of the thiazolo[3,2-c]quinazoline ring system. It has been briefly mentioned,[6,7] that thiazolo[3,2-c]quinazolinum cations are intermediates in the preparation of 2-(o-aminophenyl)-thiazoles from 2-(4-quinazolinylthio)acetophenones and perchloric acid or phosphoryl chloride.

It is worth mentioning that the rational approach for the preparation of thiazolo[3,2-c]quinazolinium cations is based on the cyclization of S- and N-allyl derivatives **4a–c** and **7a–c** of quinazoline-4(3*H*)-thiones **3a–c**. In this type of compounds the allylic side-chain can provide a secondary carbenium ion at a carbon center appropriately located for an attack at N-3 or at the exocyclic sulfur to form the thiazole ring.

As alkylation in other heterocyclic thioureas with an exocyclic thiono function proceeds at the sulfur atom, similarly, 4-(allylthio)-2-benzyl-, 2-(2-chlorophenyl)- or 2-(2-naphthyl)quinazolines (**4a–c**) are obtained in excellent yields from 2-benzyl-, 2-(2-chlorophenyl)- or 2-(2-naphthyl)-4(3*H*)-quinazolinethiones (**3a–c**) and allyl bromide in the presence of triethylamine. Compounds **4a–c** undergo ring closure by action of bromine in glacial acetic acid at room temperature to furnish the corresponding 3-(bromomethyl)-5-benzyl, 5-(2-chlorophenyl)- or 5-(2-naphthyl)-2,3-dihydrothiazolo[3,2-c]-quinazolin-4-ium bromide (**5a–c**) in good yield. The conversion of **4a–c** to **5a–c** presumably involves initial formation of a bromonium ion. Subsequent cyclization by intramolecular nucleophilic attack of the N-3 of the quinazoline ring would give the corresponding 2,3-dihydrothiazolo[3,2-c]quinazolinium bromide **5a–c**.

Compounds **5a–c** undergo ring opening of the thiazole moiety by action of water under acid catalysis to furnish the corresponding 2-benzyl-, 2-(2-chlorophenyl)-, or 2-(2-naphthyl)-4-[(2,3-dibromopropyl)thio]quinazolines (**6a–c**) in moderate yields. The formation of **6a–c** proceeds via initial nucleophilic attack of water at position 3 of the 2,3-dihydrothiazole ring followed by nucleophilic attack of the bromide anion on the open-chain bromohydrine to give **6a–c**. Unfortunately, attempts to prepare the N-allyl derivatives

7a–c, by direct allylation of quinazoline-4(3*H*)-thiones **3a–c**, is impeded by the preferencial reactivity of the sulfur atom with the alkylating reagent. Therefore, we have prepared the regioisomers of **5a–c**, 3-allyl-2-benzyl-, 2-(2-chlorophenyl)- and 2-(2-naphthyl)-4(3*H*)-quinazolinethiones (**7a–c**) in good yields by the reaction of 2-benzyl-, 2-(2-chlorophenyl)- and 2-(2-naphthyl)-4*H*-3,1-benzothiazine-4-thiones (**2a–c**) with allylamine. In agreement with the previously reported results,[8] bromination of **7a–c** in acetic acid solution at room temperature gave 2-(bromomethyl)-5-benzyl-, 5-(2-chlorophenyl)- and 5-(2-naphthyl)-2,3-dihydrothiazolo[3,2-c]quinazolin-4-ium bromides (**8a–c**) in good yields.

A variety of monocyclic mesoionic compounds are known,[9] but derivatives containing fused mesoionic rings are less common, especially those with the second ring being heteroaromatic.[10] We have now attempted to synthesize some fused-ring mesoionic systems based on 4(3*H*)-quinzolinethiones. Our approach to the preparation of mesoionic 5-benzyl-, 5-(2-chlorophenyl)-, and 5-(2-naphthyl)-1,3-thiazolo[3,2-c]quinazolinium-3-olates (**10a–c**) is based on the cyclization of 2-benzyl-, 2-(2-chlorophenyl- and 2-(2-naphthyl)-4-(carboxymethylthio)quinazolines (**9a–c**).

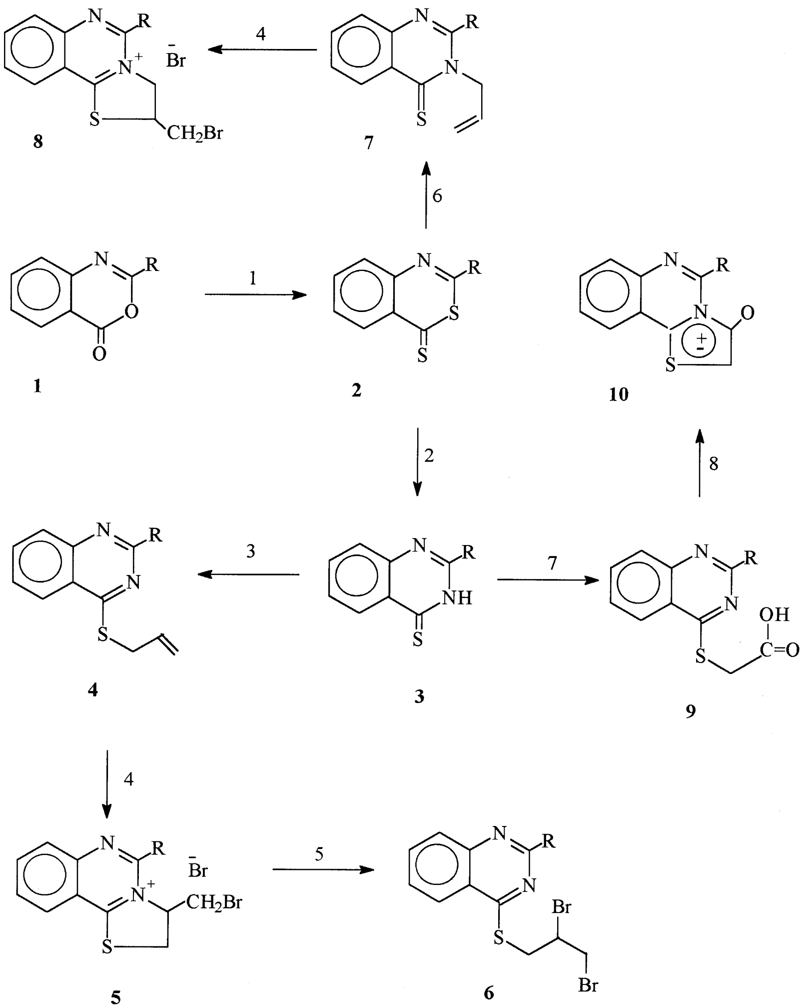
Thus, the condensation of 2-benzyl-, 2-(2-chlorophenyl)- and 2-(2-naphthyl)-4(3*H*)-quinazolinethiones (**3a–c**) with bromoacetic acid under basic condition readily gave the corresponding carboxymethylthio derivatives **9a–c** in fair yields, and these were smoothly converted into the corresponding mesoionic compounds **10a–c** by treatment with acetic anhydride in the presence or absence of triethylamine.

The structural assignments of all the compounds (Scheme 1) were based on elemental analyses and characteristic IR and ^{1}H NMR spectral data.

EXPERIMENTAL

Melting points were taken in open capillary tubes and are uncorrected. IR spectra in KBr were recorded on a Shimadzu 470 spectrophotometer and ^{1}H NMR spectra were recorded on a JEOL Fx 90 Q9 MHz (Fourier transform NMR spectrometer) using TMS as internal reference (chemical shifts are expressed as δ, ppm). Mass spectra were recorded on an HP Model MS 5988 spectrometer.

2-Benzyl-, 2-chlorophenyl- and 2-naphthyl-4*H*-3,1-benzothiazine-4-thiones (**2a–c**) were prepared from **1a–c** (0.07 mmol) and phosphorus pentasulfide (0.14 mmol) according to the literature.[4] Recrystallization from benzene furnished **2a–c**.



1, P_2S_5; 2, $HCONH_2$; 3, $CH_2{:}CHCH_2Br$; 4, $Br_2/AcOH$;
5, H_2O/H^+; 6, $CH_2{:}CHCH_2NH_2$; 7, $BrCH_2CO_2H$;
8, Ac_2O/Et_3N.

1-10	R
a	$CH_2C_6H_5$
b	$C_6H_4.Cl$-2
c	$C_{10}H_7$-2

SCHEME 1

2a: yield 5.6 g (30%), m.p. 147–149°C (lit.[4] m.p. 148°C); IR (cm^{-1}): 2910 (alkyl-H), 1620 (C=N), 1325 (C=S). Found: C, 66.92; H, 4.38; N, 5.42%. Calcd for $C_{15}H_{11}NS_2$: C, 66.88; H, 4.12; N, 5.20%.

2b: yield 8.7 g (43%), m.p. 144–146°C (lit.[4] m.p. 145°C); IR (cm^{-1}): 1615 (C=N), 1310 (C=S). Found: C, 58.30; H, 2.82; N, 4.91%. Calcd for $C_{14}H_8ClNS_2$: C, 58.02; H, 2.78; N, 4.83%.

2c: yield 10.6 g (50%), m.p. 155–157°C (lit.[4] m.p. 157°C); IR (cm^{-1}): 1610 (C=N), 1295 (C=S). Found: C, 70.84; H, 3.82; N, 4.62%. Calcd for $C_{18}H_{11}NS_2$: C, 70.79; H, 3.63; N, 4.59%.

2-Benzyl-, 2-chlorophenyl- and 2-naphthyl-4(3*H*)-quinazolinethiones (3a–c)

A mixture of **2a–c** (0.024 mmol) and formamide (1.2 ml, 0.03 mmol) was heated in an oil bath at 150°C for 4 h. The resulting solid product was cooled and crystallized from ethanol to furnish **3a–c**.

3a: yield 3.6 g (59%), m.p. 220–222°C (lit.[3] m.p. 221°C); IR (cm^{-1}): 3300–3240 (NH), 2960 (alkyl-H), 2560 (SH), 1625 (C=C), 1260 (C=S); ^1H NMR ($CDCl_3$): $\delta = 3.36$ (s, 2H, CH_2Ph), 7.11–8.74 (m, 9H, Ar-H and quinazoline ring), 9.52 (s, 1H, NHC=S, ratio 55.8), 11.14 (s, 1H, SH, ratio 44.2). Found: C, 71.48; H, 4.82; N, 11.22%. Calcd for $C_{15}H_{12}N_2S$: C, 71.40; H, 4.79; N, 11.10%.

3b: yield 3.7 g (57%), m.p. 204–206°C (lit.[3] m.p. 206°C); IR (cm^{-1}): 3340–3210 (NH), 2550 (SH), 1615 (C=C), 1255 (C=S). Found: C, 61.71; H, 3.39; N, 10.20%. Calcd for $C_{14}H_9ClN_2S$: C, 61.65; H, 3.33; N, 10.27%.

3c: yield 3.8 g (55%), m.p. 219–220°C (lit.[3] m.p. 219.5°C); IR (cm^{-1}): 3280–3170 (NH), 2570 (SH), 1618 (C=C), 1250 (C=S). Found: C, 74.87; H, 4.22; N, 9.94%. Calcd for $C_{18}H_{12}N_2S$: C, 74.97; H, 4.19; N, 9.71%.

4-Allylthio-2-benzyl-, 2-(2-chlorophenyl)- and 2-(2-naphthyl)quinazolines (4a–c)

To a solution of the appropriate thione **3a–c** (8 mmol) in benzene (50 ml), triethylamine (1.2 ml, 8.6 mmol) and allyl bromide (0.7 ml, 8.3 mmol) were added; after 4 h of heating under reflux, triethylammonium bromide was deposited. After cooling, the salt was separated by filtration and the filterate concentrated to dryness to afford a crude product which was recrystallized from ethanol to give **4a–c**.

4a: yield 2.1 g (90%), m.p. 71–73°C, yellow needles; IR (cm^{-1}): 2920, 1539, 1480, 1447, 1340, 1313, 990, 927, 860, 770, 765; ^1H NMR ($CDCl_3$): $\delta = 3.32$ (s, 2H, CH_2Ph), 4.10 (d, 2H, J = 7.1 Hz, SCH_2), 5.18–5.74 (m, 2H, $CH{=}CH_2$), 5.90–6.55 (m, 1H, $CH{=}CH_2$), 7.28–8.60 (m, 9H, Ar-H); MS (70 eV): m/z (%) = 293 ($M^+ + 1$) (18), 292(M^+) (38), 291 (100). Found: C, 73.81; H, 5.34; N, 9.62%. Calcd for $C_{18}H_{16}N_2S$: C, 73.94; H, 5.52; N, 9.58%.

4b: yield 2.2 g (88%), m.p. 64–66°C, yellow needles; IR (cm^{-1}): 1590, 1584, 1475, 1360, 1340, 1200, 1080, 1019, 960, 817, 760, 710; ^1H NMR ($CDCl_3$): $\delta = 4.22$ (d, 2H, J = 7.1 Hz, SCH_2), 5.10–5.66 (m, 2H, $CH{=}CH_2$), 5.80–6.44 (m, 1H, $CH{=}CH_2$), 7.42–8.34 (m, 8H, Ar-H); MS (70 eV): m/z (%) = 314 ($M^+ + 2$) (17), 313 (40), 312 (M^+) (36), 311 (100). Found: C, 65.20; H, 4.24; N, 8.88%. Calcd for $C_{17}H_{13}ClN_2S$: C, 65.27; H, 4.19; N, 8.96%.

4c: yield 2.3 g (87%), m.p. 85–87°C, yellow needles; IR (cm^{-1}): 1620, 1558, 1530, 1480, 1382, 1300, 1250, 1107, 990, 907, 830, 790, 755; ^1H NMR ($CDCl_3$): $\delta = 4.20$ (d, 2H, J = 7.1 Hz, SCH_2), 5.12–5.62 (m, 2H, $CH{=}CH_2$), 5.92–6.66 (m, 1H, $CH{=}CH_2$), 7.44–8.42 (m, 11H, Ar-H); MS (70 eV): m/z (%) = 329 ($M^+ + 1$) (11), 328 (M^+) (36), 327 (100). Found: C, 76.74; H, 4.68; N, 8.64%. Calcd for $C_{21}H_{16}N_2S$: C, 76.80; H, 4.91; N, 8.53%.

3-Bromomethyl-5-benzyl-, 5-(2-chlorophenyl)- and 5-(2-naphthyl)-2,3-dihydrothiazolo[3,2-c]quinazolin-4-ium Bromide 5a–c

A solution of bromine (1 g, 6.3 mmol) in acetic acid (20 ml) was added dropwise to a well-stirred solution of the appropriate quinazoline **4a–c** (6 mmol) in the same solvent (20 ml) at room temperature. When the addition was completed, the yellow precipitate which gradually separated during the reaction, was filtered off, washed several times with diethyl ether and crystallized from ethanol to furnish **5a–c**.

5a: yield 1.7 g (64%), m.p. 192–194°C, colorless needles; IR (cm^{-1}): 2940, 1610, 1590; 1576, 1559, 1489, 1425, 1400, 1342, 1290, 1170, 1050, 960, 886, 850, 718, 660; ^1H NMR ($CDCl_3 + CF_3CO_2H$): $\delta = 3.25$–3.65 (m, with interference, 4H, CH_2Br and CH_2Ph), 4.04–4.84 (m, 2H, SCH_2), 6.25–6.85 (m, 1H, $CHCH_2Br$), 7.40–8.50 (m, 9H, Ar-H); MS (70 eV): m/z (%) = 373 ($M^+ + 2$) (6), 371 (M^+) (8), 219(100). Found: C, 47.94; H, 3.67; N, 6.28%. Calcd for $C_{18}H_{16}Br_2N_2S$: C, 47.81; H, 3.57; N, 6.19%.

5b: yield 1.7 g (62%), m.p. 176–178°C, yellow needles; IR (cm^{-1}): 2935, 1610, 1590; 1560, 1500, 1440, 1400, 1309, 1290, 1140, 1082, 1012, 950, 880, 760, 685; ^1H NMR ($CDCl_3 + CF_3CO_2H$): $\delta = 3.35$–3.68 (m, 2H, CH_2Br), 3.95–5.04 (m, 2H, SCH_2), 6.40–6.90 (m, 1H, $CHCH_2Br$), 7.28–8.45 (m, 8H, Ar-H); MS (70 eV): m/z (%) = 393 ($M^+ + 2$) (4), 391 (M^+) (5), 239 (100). Found: C, 43.42; H, 2.88; N, 5.66%. Calcd for $C_{17}H_{13}Br_2ClN_2S$: C, 43.20; H, 2.77; N, 5.93%.

5c: yield 1.7 g (60%), m.p. 223–225°C, yellow needles; IR (cm^{-1}): 2960, 1625, 1560; 1546, 1480, 1410, 1370, 1340, 1248, 1170, 1040, 990, 830, 790, 730, 625; ^1H NMR ($CDCl_3 + CF_3CO_2H$): $\delta = 3.32$–3.70 (m, 2H, CH_2Br), 3.90–4.89 (m, 2H, SCH_2), 6.30–6.78 (m, 1H, $CHCH_2Br$), 7.22–8.32 (m, 11H, Ar-H); MS (70 eV): m/z (%) = 409 (M^++2) (8), 407 (M^+) (5), 255 (100). Found: C, 51.94; H, 3.60; N, 5.88%. Calcd for $C_{21}H_{16}Br_2N_2S$: C, 51.66; H, 3.30; N, 5.74%.

2-Benzyl-, 2-(2-chlorophenyl)- and 2-(2-naphthyl)-4-[(2,3-dibromopropyl)thio]quinazolines (6a–c)

A solution of the appropriate bromide **5a–c** (2.5 mmol) in acetic acid/water (60 ml, 2:1, V/V) was stirred at room temperature for 6 h. The solution was poured into ice and the resultant precipitated solid was separated by filtration, washed with water, and recrystallized from acetone to give **6a–c**.

6a: yield 0.47 g (42%), m.p. 114–116°C, colorless needles; IR (cm^{-1}): 2950, 1618, 1558; 1544, 1480, 1442, 1344, 1318, 1255, 1190, 1030, 994, 860, 840, 772, 658; ^{1}H NMR ($CDCl_3$): $\delta = 3.34$ (s, 2H, CH_2Ph), 3.75–4.45 (m, 4H, $CH_2CHBrCH_2Br$), 4.58–5.12 (m, 1H, CHBr), 7.35–8.65 (m, 9H, Ar-H); MS (70 eV): m/z (%) = 452 ($M^+ + 2$) (7), 450 (M^+) (4), 219 (100). Found: C, 47.94; H, 3.78; N, 6.49%. Calcd for $C_{18}H_{16}Br_2N_2S$: C, 47.81; H, 3.57; N, 6.19%.

6b: yield 0.47 g (40%), m.p. 128–130°C, colorless needles; IR (cm^{-1}): 2935, 1618, 1585, 1565, 1542, 1530, 1450, 1401, 1342, 1318, 1250, 1170, 1082, 1030, 871, 792, 735, 700; ^{1}H NMR ($CDCl_3$): $\delta = 3.82$–4.28 (m, 4H, $CH_2CHBrCH_2Br$), 4.45–4.95 (m, 1H, CHBr), 7.27–8.54 (m, 8H, Ar-H); MS (70 eV): m/z (%) = 474 ($M^+ + 4$) (4), 472 ($M^+ + 2$) (8), 470 (M^+) (5), 239 (100). Found: C, 43.42; H, 2.93; N, 5.79%. Calcd for $C_{17}H_{13}Br_2ClN_2S$: C, 43.20; H, 2.77; N, 5.93%.

6c: yield 0.53 g (44%), m.p. 134–136°C, colorless needles; IR (cm^{-1}): 2970, 1625, 1560; 1540, 1501, 1456, 1349, 1262, 1160, 1020, 840, 780, 718, 685; ^{1}H NMR ($CDCl_3$): $\delta = 3.66$–4.37 (m, 4H, $CH_2CHBrCH_2Br$), 4.45–4.82 (m, 1H, CHBr), 7.39–8.66 (m, 11H, Ar-H); MS (70 eV): m/z (%) = 488 ($M^+ + 2$) (10), 486 (M^+) (7), 255 (100). Found: C, 51.88; H, 3.60; N, 5.89%. Calcd for $C_{21}H_{16}Br_2N_2S$: C, 51.66; H, 3.30; N, 5.74%.

3-Allyl-2-benzyl-, 2-(2-chlorophenyl)- and 2-(2-naphthyl)-4(3*H*)-quinazolinethiones (7a–c)

To a suspension of the appropriate 1,3-benzothiazine-4(*H*)-thione **2a–c** (8 mmol) in ethanol (50 ml), allylamine (0.7 ml, 9.4 mmol) was added. The reaction mixture was refluxed for 2 h. After cooling at 0°C the yellow precipitated solid was collected by filtration and the crude product was recrystallized from ethanol to give **7a–c**.

7a: yield 1.8 g (77%), m.p. 110–112°C, yellow needles; IR (cm^{-1}): 2965, 1575, 1520; 1470, 1350, 1330, 1210, 940, 910, 850, 760, 650; ^{1}H NMR

(CDCl$_3$): $\delta = 3.38$ (s, 2H, CH$_2$Ph), 4.70–5.60 (m, 4H, CH$_2$—CH=CH$_2$), 5.90–6.50 (m, 1H, CH=CH$_2$), 7.18–8.22 (m, 9H, Ar-H); MS (70 eV): m/z (%) = 292 (M$^+$) (25), 219 (100). Found: C, 73.80; H, 5.58; N, 9.46%. Calcd for $C_{18}H_{16}N_2S$: C, 73.94; H, 5.52; N, 9.58%.

7b: yield 2 g (80%), m.p. 115–117°C, yellow needles; IR (cm^{-1}): 1620, 1560, 1540; 1480, 1420, 1338, 1080, 1000, 990, 880, 790, 730, 690; ^{1}H NMR (CDCl$_3$): $\delta = 4.72$–5.58 (m, 4H, CH$_2$—CH=CH$_2$), 5.75–6.45 (m, 1H, CH=CH$_2$), 7.25–8.18 (m, 8H, Ar-H); MS (70 eV): m/z (%) = 314 (M$^+$ + 2) (22), 312 (M$^+$) (40), 297 (100). Found: C, 65.27; H, 4.25; N, 8.84%. Calcd for $C_{17}H_{13}ClN_2S$: C, 65.27; H, 4.91; N, 8.96%.

7c: yield 2 g (77%), m.p. 127–129°C, yellow needles; IR (cm^{-1}): 1618, 1570, 1557; 1470, 1365, 1342, 1210, 1118, 1030, 950, 912, 810, 762, 724, 620; ^{1}H NMR (CDCl$_3$): $\delta = 4.75$–5.52 (m, 4H, CH$_2$—CH=CH$_2$), 5.70–6.50 (m, 1H, CH=CH$_2$), 7.30–8.10 (m, 11H, Ar-H); MS (70 eV): m/z (%) = 329 (M$^+$ + 1) (12), 328 (M$^+$) (41), 327 (100). Found: C, 76.77; H, 4.67; N, 8.66%. Calcd for $C_{21}H_{16}N_2S$: C, 76.80; H, 4.91; N, 8.53%.

2-Bromomethyl-5-benzyl-, 5-(2-chlorophenyl)- and 5-(2-naphthyl)-2,3-dihydrothiazolo[3,2-c]quinazolin-4-ium bromides (8a–c)

A solution of bromine (0.9 g, 5.6 mmol) in acetic acid (15 ml) was added dropwise to a well-stirred solution of the appropriate thione **7a–c** (5 mmol) in the same solvent (25 ml) at room temperature. The reaction mixture was stirred at room temperature for 3 h and the yellow solid which gradually separated during the reaction was collected by filtration, washed with water, and recrystallized from methanol to give **8a–c**.

8a: yield 1.5 g (67%), m.p. 238–240°C, colorless needles; IR (cm^{-1}): 2954, 1618, 1590; 1560, 1480, 1350, 1300, 1245, 1029, 966, 825, 788, 727, 628; ^{1}H NMR (CDCl$_3$ + CF$_3$CO$_2$H): $\delta = 3.36$ (s, 2H, CH$_2$Ph), 3.68–4.18 (m, 2H, CH$_2$Br), 4.95–5.70 (m, 3H, =N$^+$—CH$_2$—CH), 7.38–8.54 (m, 9H, Ar-H); MS (70 eV): m/z (%) = 373 (M$^+$ + 2) (6), 371 (M$^+$) (7), 219 (100). Found: C, 47.90; H, 3.68; N, 6.25%. Calcd for $C_{18}H_{16}Br_2N_2S$: C, 47.81; H, 3.57; N, 6.19%.

8b: yield 1.48 g (63%), m.p. 281–283°C, colorless needles; IR (cm^{-1}): 2940, 1625, 1590, 1560, 1480, 1405, 1345, 1305, 1094, 1025, 826, 770, 728, 709; ^{1}H NMR (CDCl$_3$ + CF$_3$CO$_2$H): $\delta = 3.78$–4.26 (m, 2H, CH$_2$Br), 5.14–5.77 (m, 3H, =N$^+$—CH$_2$—CH), 7.40–8.56 (m, 8H, Ar-H); MS (70 eV): m/z (%) = 393 (M$^+$ + 2) (8), 391 (M$^+$) (4), 239 (100). Found: C, 43.47; H, 2.84; N, 5.69%. Calcd for $C_{17}H_{13}Br_2ClN_2S$: C, 43.20; H, 2.77; N, 5.93%.

8c: yield 1.58 g (65%), m.p. 225–227°C, colorless needles; IR (cm^{-1}): 2928, 1615, 1557; 1522, 1478, 1404, 1346, 1255, 1178, 1020, 960, 842, 775, 740, 620; ^{1}H NMR ($CDCl_3 + CF_3CO_2H$): $\delta = 3.75$–4.15 (m, 2H, CH_2Br), 4.90–5.80 (m, 3H, $=N^+-CH_2-CH$), 7.43–8.70 (m, 11H, Ar-H); MS (70 eV): m/z (%) = 409 (M^++2) (6), 407 (M^+) (7), 255 (100). Found: C, 51.90; H, 3.62; N, 5.84%. Calcd for $C_{21}H_{16}Br_2N_2S$: C, 51.66; H, 3.30; N, 5.74%.

4-Carboxymethylthio-2-benzyl-, 2-(2-chlorophenyl)- and 2-(2-naphthyl)quinazolines (9a–c)

Thiones **3a–c** (4.5 mmol) and bromoacetic acid (0.63 g, 4.5 mmol) in anhydrous benzene (50 ml) were treated with Et_3N (0.64 ml, 4.6 mmol) and stirred overnight at room temperature. The solution was filtered to remove all $Et_3N.HBr$, and the benzene was evaporated in vacuo. The products **9a–c** were finally obtained as small yellow needles by recrystallization from ethanol.

9a: yield 1 g (72%), m.p. 176–178°C; IR (cm^{-1}) (br) 3500–3400, 1710, 1620, 1542, 1464, 1420, 1320, 1090, 980, 920, 845, 770, 690; ^{1}H NMR (Me_2SO-d_6): $\delta = 3.41$ (s, 2H, CH_2Ph), 4.46 (s, 2H, SCH_2CO), 7.40–8.55 (m, 9H, Ar-H); MS (70 eV): m/z (%) = 310 (M^+) (18), 266 (22), 219 (100). Found: C, 65.55; H, 4.29; N, 9.22%. Calcd for $C_{17}H_{14}N_2O_2S$: C, 65.79; H, 4.55; N, 9.03%.

9b: yield 1 g (70%), m.p. 161–163°C; IR (cm^{-1}) (br) 3540–3425, 1715, 1618, 1590, 1572, 1470, 1365, 1320, 1210, 1180, 1002, 980, 828, 750, 680; ^{1}H NMR (Me_2SO-d_6): $\delta = 4.37$ (s, 2H, SCH_2CO), 7.35–8.62 (m, 8H, Ar-H); MS (70 eV): m/z (%) = 330 (M^+) (22), 286 (42), 239 (100). Found: C, 58.33; H, 3.53; N, 8.62%. Calcd for $C_{16}H_{11}ClN_2O_2S$: C, 58.10; H, 3.35; N, 8.47%.

9c: yield 1 g (68%), m.p. 182–184°C; IR (cm^{-1}) (br) 3560–3414, 1705, 1628, 1590, 1530, 1490, 1381, 1310, 1270, 1100, 982, 910, 840, 780, 750, 690; ^{1}H NMR (Me_2SO-d_6): $\delta = 4.40$ (s, 2H, CH_2), 7.28–8.48 (m, 11H, Ar-H); MS (70 eV): m/z (%) = 346 (M^+) (25), 302 (19), 255 (100). Found: C, 69.44; H, 4.32; N, 8.22%. Calcd for $C_{20}H_{14}N_2O_2S$: C, 69.35; H, 4.10; N, 8.10%.

Mesoionic Ring Formation: 5-Benzyl-, 5-(2-chlorophenyl)- and 5-(2-naphthyl)-1,3-thiazolo[3,2-c]quinazolinium-3-olate (10a–c)

The thioglycolic acids **9a–c** (2 mmol) were added to a mixture of Ac_2O (3 ml) and Et_3N (3 ml). After the mixture was stirred for 15 min, anhydrous ether was added (20 ml). The dark red solids of **10a–c** recrystallized from chloroform/cyclohexane, giving dark red needles.

10a: yield 0.38 g (65%), m.p. 286–288°C; IR (cm^{-1}): 1648s (polarized CO), 1620, 1602, 1562, 1545, 1489, 1420, 1347, 1338, 1310, 1245, 1170, 1040, 990, 835, 791, 730, 622; ^1H NMR (Me_2SO-d_6): $\delta = 3.51$ (s, 2H, CH_2Ph), 7.30–8.66 (m, 10H, Ar-H); MS (70 eV): m/z (%) = 292 (M^+) (22), 219 (100). Found: C, 69.62; H, 4.22; N, 9.61%. Calcd for $C_{17}H_{12}N_2OS$: C, 69.84; H, 4.14; N, 9.58%.

10b: yield 0.39 g (63%), m.p. 269–271°C; IR (cm^{-1}): 1654s (polarized CO), 1625, 1598, 1582, 1557, 1471, 1360, 1340, 1206, 1088, 1016, 961, 822, 769, 720; ^1H NMR (Me_2SO-d_6): $\delta = 7.22$–8.64 (m, 9H, Ar-H); MS (70 eV): m/z (%) = 314 ($M^+ + 2$) (6), 312 (M^+) (12), 239 (100). Found: C, 61.62; H, 2.82; N, 8.76%. Calcd for $C_{16}H_9ClN_2OS$: C, 61.44; H, 2.90; N, 8.96%.

10c: yield 0.38 g (58%), m.p. 292–294°C; IR (cm^{-1}): 1659s (polarized CO), 1619, 1597, 1552, 1529, 1352, 1304, 1207, 1185, 1145, 991, 975, 835, 816, 769, 719, 645; ^1H NMR (Me_2SO-d_6): $\delta = 7.45$–8.62 (m, 12H, Ar-H); MS (70 eV): m/z (%) = 330 ($M^+ + 2$) (8), 328 (M^+) (14), 255 (100). Found: C, 73.30; H, 3.78; N, 8.64%. Calcd for $C_{20}H_{12}N_2OS$: C, 73.15; H, 3.68; N, 8.53%.

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