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SYNTHESIS AND RECYLIZATION OF 2,3,9,10-TETRAHYDRO-8*H*-[1,4]DIOXINO[2,3-*f*]-[1,3]THIAZINO[3,2-*a*]BENZIMIDAZOLIUM SALTS

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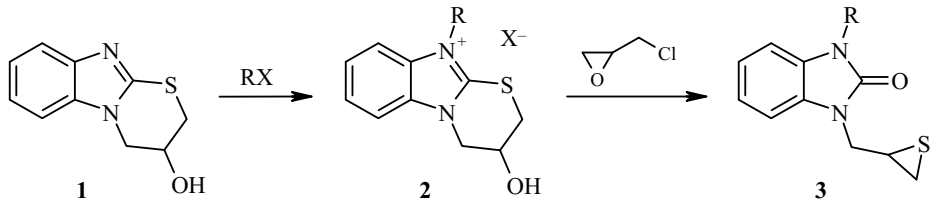
A series of [1,3]thiazino[3,2-a]benzimidazolium salts modified in the benzene ring by a condensed 1,4-dioxane ring has been prepared. Reaction with epichlorohydrin occurs with recyclization to form derivatives of 3-(2,3-epithiopropyl)benzimidazol-2-one.

Keywords: 3-(2,3-epi-thiopropyl)-1,3,6,7-tetrahydro-2*H*-[1,4]dioxino[2,3-*f*]benzimidazol-2-ones, 2,3,9,10-tetrahydro-8*H*-[1,4]dioxino[2,3-*f*][1,3]thiazino[3,2-*a*]benzimidazolium salts, thiiranes, recyclization.

A proposed in the paper [1] method for the preparation of 3-(2,3-epithiopropyl)benzimidazol-2-ones **3** from the condensed thiazinium salts **2** *via* their recyclization in excess epichlorohydrin allowed to synthesize a series of derivatives containing various substituents at position 1 of the imidazolone ring, and this method proved convenient for working with small amounts of materials.



R = $PhCOCH_2$, 4-$BrC_6H_4COCH_2$, (piperidin-1-yl)$COCH_2$, $EtOCOCH_2$, (morpholin-4-yl)$COCH_2$, $MeOCOCH_2$

Since compounds **2** and **3**, substituted in the benzene ring, were unknown it was of interest to prepare such derivatives with the aim of searching for novel biologically active structures (particularly antitumor medications with a thiirane ring [2]). It should be noted that there are only isolated examples in the literature of structural analogs of compound **1** [3-7] (which is the precursor in the synthesis of compounds **2** and **3**), despite the continuing interest in compounds containing a thiirane ring [8-12].

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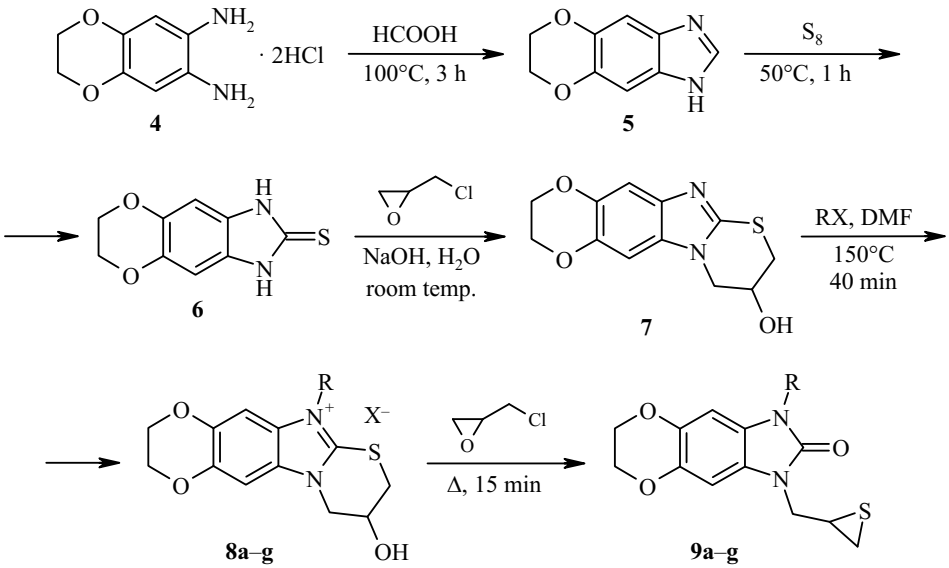
We selected the alkoxy groups of a condensed [1,4]benzodioxane ring as the substituent in the benzene ring and its introduction can lead to derivatives of the condensed heterocyclic system 2,3,9,10-tetrahydro-8*H*-[1,4]dioxino[2,3-*f*][1,3]thiazino[3,2-*a*]benzimidazole **7**. On its basis we proposed a synthesis of the salts **8a**-**g** and the 3-(2,3-epithiopropyl)imidazol-2-ones **9a**-**g**.

Synthesis of the condensed thiazine **7** was performed from the 2,3-dihydro-1,4-benzodioxine-6,7-diamine dihydrochloride (**4**) according to the scheme below. The salt **4** was prepared from 1,4-benzodioxane according to the reported method [13]. Compound **6** has been synthesized previously [14] by the reaction of diamine **4** with alkyl xanthogenates and it has also been mentioned in the study [15] where its melting point (around 300ºC) was given but the preparation method and spectroscopic parameters were not reported.



4 **5** **6** **7** **8a–g** **9a–g**

8, **9** **a** R = 4-$ClC_6H_4COCH_2$, **b** R = 4-$BrC_6H_4COCH_2$, **c** R = 4-$MeC_6H_4COCH_2$, **d** R = 4-$MeOC_6H_4COCH_2$, **e** R = 4-$MeC_6H_4CH_2$, **f** R = 4-$FC_6H_4CH_2$, **g** R = $PhCH_2$; **8** **a**,**b**,**e**–**g** X = Cl, **c**,**d** X = Br

The alkylation of compound **7** using phenacyl and benzyl halides in DMF gives 41-77% yields of the salts **8a**-**g**. Heating the latter in excess epichlorohydrin as in the case of salt **2** [1] led to recyclization and the formation of the 3-(2,3-epithiopropyl)benzimidazol-2-ones **9a**-**g** in 75-88% yields.

The ^{1}H NMR spectra of the intermediate compounds **5**, **6** show characteristic signals for the dioxane fragment methylene groups at 4.21-4.23 ppm, the *meso*-proton of imidazole **5** at 8.03 ppm, and the NH protons of the imidazolethione **6** at 12.20 ppm. In the ^{1}H NMR spectra of the salts **8a**-**g**, the 1,4-benzodioxane OCH_2CH_2O fragment gives a singlet at 4.32-4.33 ppm. For the thiiranes **9a**-**g** it is shifted upfield (4.17-4.19 ppm) as a result of the change in molecular charge. Characteristic for the salts **8a**-**g** [1, 16] are the signals of the OH group protons at 6.05-6.26 ppm, those for the thiazine ring (3.48-3.66 ppm for the CH_2S group, 4.25-4.46 ppm for the NCH_2 group, and 4.64-4.74 ppm for the CHOH proton), and also for the substituent methylene group at 5.50-5.57 ppm in the benzyl or 6.10-6.19 ppm in the phenacyl derivatives. There are a characteristic thiirane multiplet (2.46-2.54 ppm) and doublet (2.57-2.59 ppm) for the 2,3-epithiopropyl fragment in compounds **9a**-**g** due to geminal and vicinal proton splittings as well as two double doublets for the NCH_2 fragment at 3.93-4.11 ppm and a CHS proton multiplet at 3.19-3.29 ppm.

Hence, we have developed a method for the preparation of 6-substituted [1,3]thiazino[3,2-*a*]benzimidazolium salts and 3-(2,3-epithiopropyl)benzimidazol-2-ones modified in the benzene ring by a condensed 1,4-dioxane fragment.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker Avance II 400 spectrometer (400 MHz) using DMSO-d_6 with TMS as internal standard. Elemental analysis for C, H, and halogen was carried out by combustion in an oxygen stream and analysis for nitrogen by the Dumas method. Melting points were determined on a Boetius PHMK 05 block and are not corrected. TLC was performed on Merck Silica Gel 60 F_{254} plates with $CHCl_3$–MeOH (10: 1) as eluent and developed using UV light.

6,7-Dihydro-1*H*-[1,4]dioxino[2,3-*f*]benzimidazole (5). HCOOH (96%, 20 ml) was added to the 2,3-dihydro-1,4-benzodioxine-6,7-diamine dihydrochloride (**4**) (20 g, 84 mmol). The mixture obtained was heated on a boiling water bath for 3 h. After cooling, 30% ammonia solution was added to an alkaline reaction. The precipitate formed was filtered off, washed with water, dried, and recrystallized from $CHCl_3$. Yield 10.3 g (70%). Colorless crystals. Mp 193-194ºC. R_f 0.33. ^{1}H NMR spectrum, δ, ppm: 4.23 (4H, s, OCH_2CH_2O); 7.01 (2H, s, H Ar); 8.03 (1H, s, H Ar). Found, %: C 61.33; H 4.60; N 15.92. $C_9H_8N_2O_2$. Calculated, %: C 61.36; H 4.58; N 15.90.

1,3,6,7-Tetrahydro-2*H*-[1,4]dioxino[2,3-*f*]benzimidazole-2-thione (6). A mixture of compound **5** (10.3 g, 58.5 mmol) and sulfur (1.9 g, 58.5 mmol) was heated at 250ºC for 1 h. After cooling, a solution of NaOH (4.0 g, 100 mmol) in water (100 ml) was added, stirred to dissolution, and activated carbon (0.5 g) was added. The mixture obtained was refluxed for 15 min, filtered, and acidified using excess AcOH. The precipitate was filtered off, washed with water and then acetone, and dried. Yield 10.1 g (83%). Colorless powder. Mp > 350ºC. R_f 0.69. ^{1}H NMR spectrum, δ, ppm: 4.21 (4H, s, OCH_2CH_2O); 6.61 (2H, s, H Ar); 12.20 (2H, s, NH). Found, %: C 51.95; H 3.90; N 13.41; S 15.37. $C_9H_8N_2O_2S$. Calculated, %: C 51.91; H 3.87; N 13.45; S 15.40.

2,3,9,10-Tetrahydro-8*H*-[1,4]dioxino[2,3-*f*][1,3]thiazino[3,2-*a*]benzimidazol-9-ol (7). Compound **6** (10.4 g, 50 mmol) was added to a solution of NaOH (2.0 g, 50 mmol) in H_2O (100 ml) and stirred at room temperature to dissolution. Stirring was continued and epichlorohydrin (3.91 ml, 50 mmol) was added. The precipitate was filtered off, washed with water, dried, and recrystallized from DMF (50 ml). Yield 7.1 g (54%). Colorless powder. Mp 284-285ºC (decomp.). R_f 0.38. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.19 (1H, dd, ^3J = 4.6, ^2J = 12.2) and 3.35 (1H, d, ^2J = 12.2, CH_2S); 3.94 (1H, d, ^2J = 13.0) and 4.12 (1H, d, ^2J = 13.0, NCH_2); 4.27 (4H, s, OCH_2CH_2O); 4.40-4.46 (1H, m, C<u>H</u>OH); 5.79 (1H, s, OH); 6.94 (2H, s, H Ar). Found, %: C 54.57; H 4.54; N 10.63; S 12.10. $C_{12}H_{12}N_2O_3S$. Calculated, %: C 54.53; H 4.58; N 10.60; S 12.13.

Synthesis of 9-Hydroxy-2,3,9,10-tetrahydro-8*H*-[1,4]dioxino[2,3-*f*][1,3]thiazino[3,2-*a*]benzimidazolium Salts 8a-g (General Method). Compound **7** (264 mg, 1.0 mmol), the alkylating agent (1.2 mmol), and DMF (0.2 ml) were mixed. The mixture was heated at 150ºC for 40 min. Once cooled the precipitate formed was filtered off, washed with DMF (0.3 ml) and Et_2O (1 ml), and dried. Recrystallization from DMF gave the salts **8a-g** as colorless powders. Yields 41-77%.

6-(4-Chlorophenacyl)-9-hydroxy-2,3,9,10-tetrahydro-8*H*-[1,4]dioxino[2,3-*f*][1,3]thiazino[3,2-*a*]benzimidazolium Chloride (8a). Yield 52%. Mp 244-245ºC (decomp.). R_f 0.06. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.51 (1H, dd, ^3J = 5.0, ^2J = 12.4) and 3.66 (1H, d, ^2J = 12.4, CH_2S); 4.32 (4H, s, OCH_2CH_2O); 4.33-4.36 (1H, m) and 4.46 (1H, dd, ^3J = 2.8, ^2J = 13.6, NCH_2); 4.67-4.73 (1H, m, C<u>H</u>OH); 6.19 (2H, s, N^+CH_2CO); 6.21 (1H, d, *J* = 3.4, OH); 7.54 (1H, s, H Ar); 7.55 (1H, s, H Ar); 7.90 (2H, d, *J* = 8.4, H Ar); 8.10 (2H, d, *J* = 8.4, H Ar). Found, %: C 53.03; H 3.97; Cl 15.59; N 6.21; S 7.11. $C_{20}H_{18}Cl_2N_2O_4S$. Calculated, %: C 52.99; H 4.00; Cl 15.64; N 6.18; S 7.07.

6-(4-Bromophenacyl)-9-hydroxy-2,3,9,10-tetrahydro-8*H*-[1,4]dioxino[2,3-*f*][1,3]thiazino[3,2-*a*]benzimidazolium Chloride (8b). Yield 60%. Mp 250-251ºC (decomp.). R_f 0.07. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.50 (1H, dd, ^3J = 5.0, ^2J = 12.4) and 3.65 (1H, d, ^2J = 12.4, CH_2S); 4.32 (4H, s, OCH_2CH_2O); 4.34-4.37 (1H, m) and 4.46 (1H, dd, ^3J = 2.6, ^2J = 13.6, NCH_2); 4.68-4.74 (1H, m, C<u>H</u>OH); 6.18 (2H, s, N^+CH_2CO); 6.20 (1H, d, *J* = 3.4, OH); 7.54 (1H, s, H Ar); 7.55 (1H, s, H Ar); 7.89 (2H, d, *J* = 8.4, H Ar); 8.08 (2H, d, *J* = 8.4, H Ar). Found, %: C 48.30; H 3.62; Br 16.10; Cl 7.08; N 5.68; S 6.41. $C_{20}H_{18}BrClN_2O_4S$. Calculated, %: C 48.26; H 3.64; Br 16.05; Cl 7.12; N 5.63; S 6.44.

9-Hydroxy-6-(4-methylphenacyl)-2,3,9,10-tetrahydro-8*H*-[1,4]dioxino[2,3-*f*][1,3]thiazino[3,2-*a*]benzimidazolium Bromide (8c). Yield 52%. Mp 242-243ºC (decomp.). R_f 0.09. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.45 (3H, s, CH_3); 3.48 (1H, dd, ^3J = 5.1, ^2J = 12.5) and 3.64 (1H, d, ^2J = 12.5, CH_2S); 4.33 (4H, s, OCH_2CH_2O); 4.34-4.37 (1H, m) and 4.44 (1H, dd, ^3J = 2.7, ^2J = 13.7, NCH_2); 4.67-4.73 (1H, m, C<u>H</u>OH); 6.05 (1H, d, *J* = 3.4, OH); 6.14 (2H, s, N^+CH_2CO); 7.47 (2H, d, *J* = 8.4, H Ar); 7.53 (1H, s, H Ar); 7.55 (1H, s, H Ar); 8.04 (2H, d, *J* = 8.4, H Ar). Found, %: C 52.80; H 4.45; Br 16.70; N 5.90; S 6.70. $C_{21}H_{21}BrN_2O_4S$. Calculated, %: C 52.84; H 4.43; Br 16.74; N 5.87; S 6.72.

9-Hydroxy-6-(4-methoxyphenacyl)-2,3,9,10-tetrahydro-8*H*-[1,4]dioxino[2,3-*f*][1,3]thiazino[3,2-*a*]benzimidazolium Bromide (8d). Yield 41%. Mp 235-236ºC (decomp.). R_f 0.09. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.48 (1H, dd, ^3J = 4.8, ^2J = 12.4) and 3.65 (1H, d, ^2J = 12.4, CH_2S); 3.89 (3H, s, OCH_3); 4.32 (4H, s, OCH_2CH_2O); 4.33-4.36 (1H, m) and 4.42 (1H, dd, ^3J = 2.6, ^2J = 13.6, NCH_2); 4.66-4.71 (1H, m, C<u>H</u>OH); 6.05 (1H, d, *J* = 3.6, OH); 6.10 (2H, s, N^+CH_2CO); 7.17 (2H, d, *J* = 8.8, H Ar); 7.51 (1H, s, H Ar); 7.53 (1H, s, H Ar); 8.11 (2H, d, *J* = 8.8, H Ar). Found, %: C 51.16; H 4.32; Br 16.24; N 5.70; S 6.47. $C_{21}H_{21}BrN_2O_5S$. Calculated, %: C 51.12; H 4.29; Br 16.20; N 5.68; S 6.50.

9-Hydroxy-6-(4-methylbenzyl)-2,3,9,10-tetrahydro-8*H*-[1,4]dioxino[2,3-*f*][1,3]thiazino[3,2-*a*]benzimidazolium Chloride (8e). Yield 75%. Mp 230-231ºC. R_f 0.08. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.28 (3H, s, CH_3); 3.50 (1H, dd, ^3J = 4.8, ^2J = 12.4) and 3.63 (1H, d, ^2J = 12.4, CH_2S); 4.25 (1H, d, ^2J = 13.2) and 4.38 (1H, dd, ^3J = 2.8, ^2J = 13.2, NCH_2); 4.32 (4H, s, OCH_2CH_2O); 4.65-4.69 (1H, m, C<u>H</u>OH); 5.50 (2H, s, $N^+C\underline{H}_2Ar$); 6.15 (1H, d, *J* = 2.8, OH); 7.20 (2H, d, *J* = 7.8, H Ar); 7.25 (2H, d, *J* = 7.8, H Ar); 7.51 (2H, s, H Ar). Found, %: C 59.38; H 5.20; Cl 8.81; N 6.89; S 7.96. $C_{20}H_{21}ClN_2O_3S$. Calculated, %: C 59.33; H 5.23; Cl 8.76; N 6.92; S 7.92.

6-(4-Fluorobenzyl)-9-hydroxy-2,3,9,10-tetrahydro-8*H*-[1,4]dioxino[2,3-f][1,3]thiazino[3,2-*a*]benzimidazolium Chloride (8f). Yield 73%. Mp 232-233ºC. R_f 0.07. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.51 (1H, dd, ^3J = 5.2, ^2J = 12.0) and 3.63 (1H, d, ^2J = 12.0, CH_2S); 4.26 (1H, dd, ^3J = 1.2, ^2J = 13.2) and 4.39 (1H, dd, ^3J = 3.2, ^2J = 13.2, NCH_2); 4.33 (4H, s, OCH_2CH_2O); 4.65-4.69 (1H, m, C<u>H</u>OH); 5.56 (2H, s, $N^+C\underline{H}_2Ar$); 6.19 (1H, d, *J* = 3.6, OH); 7.21-7.29 (2H, m, H Ar); 7.40-7.48 (2H, m, H Ar); 7.52 (1H, s, H Ar); 7.54 (1H, s, H Ar). Found, %: C 55.85; H 4.40; N 6.89. $C_{19}H_{18}ClFN_2O_3S$. Calculated, %: C 55.81; H 4.44; N 6.85.

6-Benzyl-9-hydroxy-2,3,9,10-tetrahydro-8*H*-[1,4]dioxino[2,3-*f*][1,3]thiazino[3,2-*a*]benzimidazolium Chloride (8g). Yield 77%. Mp 231-232ºC. R_f 0.08. ^{1}H NMR spectrum, δ, ppm. (*J*, Hz): 3.53 (1H, dd, ^3J = 5.2, ^2J = 12.0) and 3.65 (1H, d, ^2J = 12.0, CH_2S); 4.28 (1H, d, ^2J = 13.2) and 4.42 (1H, dd, ^3J = 2.8, ^2J = 13.2, NCH_2); 4.32 (4H, s, OCH_2CH_2O); 4.64-4.68 (1H, m, C<u>H</u>OH); 5.57 (2H, s, $N^+C\underline{H}_2Ph$); 6.26 (1H, d, *J* = 3.6, OH); 7.36-7.39 (5H, m, H Ph); 7.52 (2H, s, H Ar). Found, %: C 58.33; H 4.94; Cl 9.11; N 7.13; S 8.22. $C_{19}H_{19}ClN_2O_3S$. Calculated, %: C 58.38; H 4.90; Cl 9.07; N 7.17; S 8.20.

Synthesis of 1-Substituted 3-(2,3-Epithiopropyl)-1,3,6,7-tetrahydro-2*H*-[1,4]dioxino[2,3-*f*]benzimidazol-2-ones 9a-g (General Method). The salt **8a-g** was refluxed with a 20-fold molar excess of epichlorohydrin for 15 min. The mixture was cooled and the product was filtered off and recrystallized from epichlorohydrin. If the product was soluble (compounds **9e-g**) the epichlorohydrin was evaporated and the residue was dissolved in $CHCl_3$ and filtered through a silica gel layer. The chloroform was evaporated *in vacuo* and the material was recrystallized from ether. The thiirane products obtained are colorless powders. Yields 75-88%.

1-(4-Chlorophenacyl)-3-(2,3-epithiopropyl)-1,3,6,7-tetrahydro-2*H*-[1,4]dioxino[2,3-*f*]benzimidazol-2-one (9a). Yield 80%. Mp 205-206ºC. R_f 0.79. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.46-2.48 (1H, m) and 2.57 (1H, d, ^3J = 6.0, CH_2S); 3.21-3.28 (1H, m, $NCH_2C\underline{H}S$); 3.93 (1H, dd, ^3J = 6.4, ^2J = 14.8) and 4.11 (1H, dd, ^3J = 5.6, ^2J = 14.8, $NC\underline{H}_2CHS$); 4.18 (4H, s, OCH_2CH_2O); 5.41 (2H, s, NCH_2CO); 6.78 (1H, s, H Ar); 6.93 (1H, s, H Ar); 7.81 (2H, d, *J* = 8.4, H Ar); 8.02 (2H, d, *J* = 8.4, H Ar). Found, %: C 57.60; H 4.07; Cl 8.55; N 6.70; S 7.72. $C_{20}H_{17}ClN_2O_4S$. Calculated, %: C 57.62; H 4.11; Cl 8.50; N 6.72; S 7.69.

1-(4-Bromophenacyl)-3-(2,3-epithiopropyl)-1,3,6,7-tetrahydro-2*H*-[1,4]dioxino[2,3-*f*]benzimidazol-2-one (9b). Yield 83%. Mp 208-209ºC. R_f 0.78. ^{1}H NMR spectrum, δ, ppm. (*J*, Hz): 2.46-2.49 (1H, m) and 2.58 (1H, d, ^3J = 6.0, CH_2S); 3.21-3.29 (1H, m, $NCH_2C\underline{H}S$); 3.95 (1H, dd, ^3J = 6.4, ^2J = 14.8) and 4.10 (1H, dd, ^3J = 5.6, ^2J = 14.8, $NC\underline{H}_2CHS$); 4.19 (4H, s, OCH_2CH_2O); 5.42 (2H, s, NCH_2CO); 6.77 (1H, s, H Ar); 6.94 (1H, s, H Ar); 7.82 (2H, d, *J* = 8.4, H Ar); 8.01 (2H, d, *J* = 8.4, H Ar). Found, %: C 52.10; H 3.68; Br 17.36; N 6.10; S 6.91. $C_{20}H_{17}BrN_2O_4S$. Calculated, %: C 52.07; H 3.71; Br 17.32; N 6.07; S 6.95.

3-(2,3-Epithiopropyl)-1-(4-methylphenacyl)-1,3,6,7-tetrahydro-2*H*-[1,4]dioxino[2,3-*f*]benzimidazol-2-one (9c). Yield 83%. Mp 198-199ºC. R_f 0.85. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.42 (3H, s, CH_3); 2.52-2.54 (1H, m) and 2.59 (1H, d, ^3J = 6.4, CH_2S); 3.20-3.28 (1H, m, $NCH_2C\underline{H}S$); 3.95 (1H, dd, ^3J = 6.6, ^2J = 14.8) and 4.11 (1H, dd, ^3J = 5.6, ^2J = 14.8, $NC\underline{H}_2CHS$); 4.19 (4H, s, OCH_2CH_2O); 5.39 (2H, s, NCH_2CO); 6.74 (1H, s, H Ar); 6.93 (1H, s, H Ar); 7.40 (2H, d, *J* = 8.0, H Ar); 7.98 (2H, d, *J* = 8.0, H Ar). Found, %: C 63.60; H 5.06; N 7.11; S 8.05. $C_{21}H_{20}N_2O_4S$. Calculated, %: C 63.62; H 5.08; N 7.07; S 8.09.

3-(2,3-Epithiopropyl)-1-(4-methoxyphenacyl)-1,3,6,7-tetrahydro-2*H*-[1,4]dioxino[2,3-*f*]benzimidazol-2-one (9d). Yield 88%. Mp 214-215ºC. R_f 0.78. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.51-2.53 (1H, m) and 2.59 (1H, d, ^3J = 6.4, CH_2S); 3.19-3.27 (1H, m, $NCH_2C\underline{H}S$); 3.87 (3H, s, OCH_3); 3.94 (1H, dd, ^3J = 6.8, ^2J = 14.8) and 4.10 (1H, dd, ^3J = 5.6, ^2J = 14.8, $NC\underline{H}_2CHS$); 4.19 (4H, s, OCH_2CH_2O); 5.36 (2H, s, NCH_2CO); 6.72 (1H, s, H Ar); 6.93 (1H, s, H Ar); 7.11 (2H, d, *J* = 8.8, H Ar); 8.05 (2H, d, *J* = 8.8, H Ar). Found, %: C 61.13; H 4.84; N 6.80; S 7.72. $C_{21}H_{20}N_2O_5S$. Calculated, %: C 61.15; H 4.89; N 6.79; S 7.77.

3-(2,3-Epithiopropyl)-1-(4-methylbenzyl)-1,3,6,7-tetrahydro-2*H*-[1,4]dioxino[2,3-*f*]benzimidazol-2-one (9e). Yield 78%. Mp 107-108ºC. R_f 0.84. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.25 (3H, s, CH_3); 2.49-2.53 (1H, m) and 2.57 (1H, d, ^3J = 6.0, CH_2S); 3.20-3.26 (1H, m, $NCH_2C\underline{H}S$); 3.95 (1H, dd, ^3J = 6.4, ^2J = 14.8) and 4.10 (1H, dd, ^3J = 5.6, ^2J = 14.8, $NC\underline{H}_2CHS$); 4.17 (4H, s, OCH_2CH_2O); 4.92 (2H, s, $NC\underline{H}_2Ar$); 6.62 (1H, s, H Ar); 6.90 (1H, s, H Ar); 7.12 (2H, d, *J* = 7.6, H Ar); 7.19 (2H, d, *J* = 7.6, H Ar). Found, %: C 65.16; H 5.51; N 7.62; S 8.67. $C_{20}H_{20}N_2O_3S$. Calculated, %: C 65.20; H 5.47; N 7.60; S 8.70.

3-(2,3-Epithiopropyl)-1-(4-fluorobenzyl)-1,3,6,7-tetrahydro-2*H*-[1,4]dioxino[2,3-*f*]benzimidazol-2-one (9f). Yield 75%. Mp 143-144ºC. R_f 0.82. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.49-2.52 (1H, m) and 2.58 (1H, d, ^3J = 6.4, CH_2S); 3.22-3.28 (1H, m, $NCH_2C\underline{H}S$); 3.95 (1H, dd, ^3J = 6.8, ^2J = 15.0) and 4.10 (1H, dd, ^3J = 5.4, ^2J = 15.0, $NC\underline{H}_2CHS$); 4.17 (4H, s, OCH_2CH_2O); 4.98 (2H, s, $NC\underline{H}_2Ph$); 6.65 (1H, s, H Ar); 6.91 (1H, s, H Ar); 7.25-7.35 (5H, m, H Ph). Found, %: C 64.36; H 5.08; N 7.94; S 9.08. $C_{19}H_{18}N_2O_3S$. Calculated, %: C 64.39; H 5.12; N 7.90; S 9.05.

1-Benzyl-3-(2,3-epithiopropyl)-1,3,6,7-tetrahydro-2*H*-[1,4]dioxino[2,3-*f*]benzimidazol-2-one (9g). Yield 75%. Mp 127-128ºC. R_f 0.84. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.49-2.52 (1H, m) and 2.58 (1H, d, ^3J = 6.4, CH_2S); 3.22-3.28 (1H, m, $NCH_2C\underline{H}S$); 3.95 (1H, dd, ^3J = 6.8, ^2J = 15.0) and 4.10 (1H, dd, ^3J = 5.4, ^2J = 15.0, $NC\underline{H}_2CHS$); 4.17 (4H, s, OCH_2CH_2O); 4.98 (2H, s, $NC\underline{H}_2Ph$); 6.65 (1H, s, H Ar); 6.91 (1H, s, H Ar); 7.25-7.35 (5H, m, H Ph). Found, %: C 64.36; H 5.08; N 7.94; S 9.08. $C_{19}H_{18}N_2O_3S$. Calculated, %: C 64.39; H 5.12; N 7.90; S 9.05.

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