# THE 1,4-DITHIIN RING OPENING IN 1,4-DITHIINODIQUINOLINES AS A ROUTE TO QUINOLINE CROWN THIOETHERS*

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Abstract - Quinoline crown thioethers (**7**) and (**8**) with 8-, 9-, 10-, 11-, 12-, 18-, 20-, 21- and 24-membered macrocyclic thiacrown ring were obtained by the 1,4-dithiin ring opening in 1,4-dithiinodiquinolines (**1**) and (**2**) with divalent sulfur nucleophiles followed by *S*-alkylation with divalent alkylating agents. Thiacrowns (**7**) and (**8**) contain two or four quinoline units.

## INTRODUCTION

The chemistry of thioether macrocycles has received considerable attention during the past years. The ability of these multidentate compounds to complex transition and heavy metal ions and potential application in catalysis, in sequestration or biological delivery of heavy metal ions are responsible for the interest in this research.[1-3] Synthesis of some crown thioethers is attended with difficulty because starting materials are often hard to handle.[2-4] There are only a few examples of azacyclophane crown thioethers most often containing stable 2-pyridinomethylene units.[5-6] The 1,4-dithiin ring opening reactions in 1,4-dithiinodiquinolines (thioquinanthrene (**1**) - easy to obtain by sulfurization of quinoline with elemental sulfur[7], and isothioquinanthrene (**2**) - easy to obtain from dithiin (**1**) by ring opening - ring closure reactions[8]) with sulfur nucleophiles proceeded as a cleavage of only one $C_{4\text{-quinolinyl}}$- S bond to form alkali metal salts of 4-substituted 3'-mercapto-3,4'-diquinolinyl sulfide, which under some reaction conditions underwent the unprecedented S→ S type of the Smiles rearrangement to form alkali metal salts of 4-substituted 4'-mercapto-3,3'-diquinolinyl sulfide. The final products were isolated after *S*-alkylation with alkyl halides as 3',4-dialkyltio-3,4'-diquinolinyl sulfides and 4,4'-dialkyltio-3,3'-diquinolinyl sulfides.[8-10] These dialkylthiodiquinolinyl sulfides may be regarded as polythioethers, possessing three sulfur atoms separated by two-carbon units. It prompted us to use the 1,4-dithiin ring opening reactions in 1,4-dithiinodiquinolines (**1**) and (**2**) with se-

lected sulfur nucleophiles as a route to quinoline thiacrowns. No less important is study of the Smiles rearrangement of sodium salt of new 4-substituted 3'-mercapto-3,4'-diquinolinyl sulfides.

## RESULTS AND DISCUSSION

We found previously 4,4'-dichloro-3,3'-diquinolinyl sulfide to be an excellent substrate to built heterocyclodiquinolines in the reactions with divalent nucleophiles.[11] Attempts of synthesis of quinoline crown thioethers in the reactions with alkanedithiols or their disodium salts in anhydrous ethanol or DMSO failed. For this reason we started to work out synthesis of thiacrowns *via* 1,4-dithiin ring opening in 1,4-dithiinodiquinolines (**1**) and (**2**).

To elaborate a route to synthesis of quinoline thiacrowns we have chosen divalent sulfur nucleophiles - sodium $\alpha,\omega$-alkanedithiolates (ethane-1,2-dithiolate, propane-1,3-dithiolate, 3-oxapentane-1,5-dithiolate and 3-thiapentane-1,5-dithiolate) and divalent alkylating agents - $\alpha,\omega$-alkylene dihalides and ditosylates (1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, diethylene glycol ditosylate and tetraethylene glycol ditosylate). Since the Smiles rearrangement observed during reactions of dithiin (**1**) and (**2**) with sulfur nucleophiles is dependent on the nature of reagent and reaction conditions,[9,10] we started our synthesis in standard conditions: 1.2 equivalent of nucleophile, DMSO, 70°C, *S*-alkylation after pouring the reaction mixture into three volume of 15% aqueous sodium hydroxide. This procedure appeared to be ineffective because of low solubility of the resulted sodium alkanebis(quinolinylthioquinolinethiolates) (**5A-7A**), containing four quinoline units, in the DMSO-water mixture. For this reason the *S*-alkylation stage was performed directly in DMSO neat and crude quinoline thiacrowns were separated after pouring the solution into three volume of 15% aqueous sodium hydroxide.

Reactions of dithiins (**1**) with sodium alkanedithiolates proceeded as a cleavage of only one $C_{4\text{-quinolinyl}}$- sulfur bond in two molecules of dithiin with both sides of the divalent sulfur nucleophile. Symmetrical structure of thiacrowns (**7a**, **7b** and **7d**) possessing the pairs of the identical alkylene group (showing four identical quinoline units) and the identity with thiacrowns obtained from dithiin (**2**) manifest the Smiles rearrangement of the intermediates. Initially formed disodium salt of 4-($\omega$-mercaptoalkylthio)-3'-mercapto-3,4'-diquinolinyl sulfide (**3A**) underwent two transformations: the Smiles rearrangement and reaction with another molecule of dithiin (**1**) in optional sequence (**3A** → **4A**→ **6A** → **7A** and/or **3A**→ **5A**→ **6A**→ **7A**) giving after *S*-alkylation thiacrowns (**7a-d**). Because of formation of quinolinethiones, quinolinethiols and their sodium salts (**3A-7A**), insoluble and non-melting polymeric products and some side-products (connected with higher susceptibility of the $C_{4'\text{-quinolinyl}}$ - $SC_{3\text{-quinolinyl}}$ bond for the cleavage with sulfur nucleophile than the $C_{3'\text{-quinolinyl}}$ - $SC_{3\text{-quinolinyl}}$ and $C_{4\text{-quinolinyl}}$ - $SC_{alkyl}$ bonds)[10,12] the yields of thiacrowns (**7a-d**) did not exceed 20% (Table 1).

Table 1. Reactions of dithiins (**1**) and (**2**) with selected sulfur nucleophiles

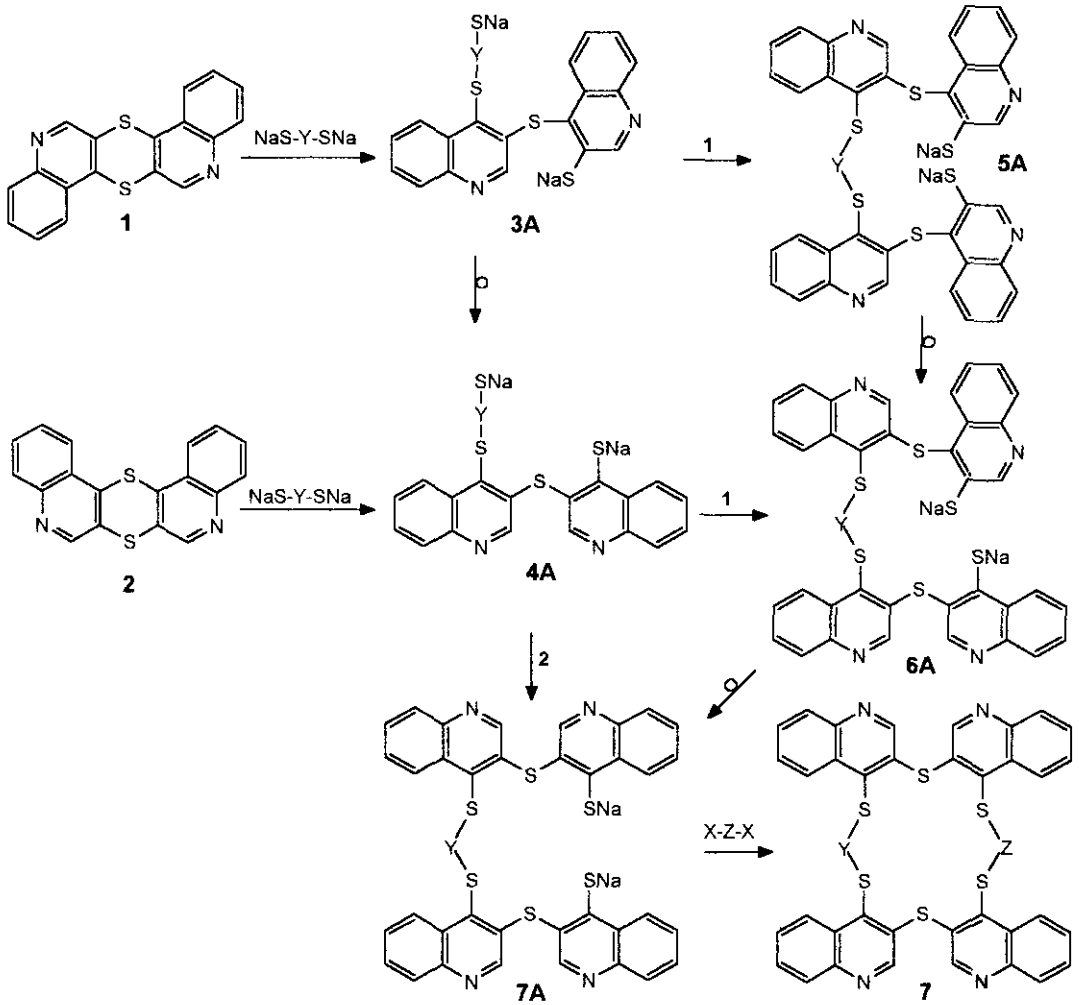
| No | Dithiin | Nucleophile NaS-Y-SNa | Alkylating agent X-Z-X | Products (%) |
|---|---|---|---|---|
| 1 | **1** | $NaSCH_2CH_2SNa$ | $BrCH_2CH_2Br$ | **7a** (20) |
| 2 | **1** | $NaSCH_2CH_2CH_2SNa$ | $BrCH_2CH_2CH_2Br$ | **7b** (17) |
| 3 | **1** | $NaSCH_2CH_2SCH_2CH_2SNa$ | $BrCH_2CH_2Br$ | **7c** (14) |
| 4 | **1** | $NaSCH_2CH_2OCH_2CH_2SNa$ | $TsO(CH_2CH_2O)_2Ts$ | **7d** (15) |
| 5 | **2** | $NaSCH_2CH_2SNa$ | $BrCH_2CH_2Br$ | **7a** (52) |
| 6 | **2** | $NaSCH_2CH_2CH_2SNa$ | $BrCH_2CH_2CH_2Br$ | **7b** (67) |
| 7 | **2** | $NaSCH_2CH_2SCH_2CH_2SNa$ | $BrCH_2CH_2Br$ | **7c** (54) |
| 8 | **2** | $NaSCH_2CH_2OCH_2CH_2SNa$ | $TsO(CH_2CH_2O)_2Ts$ | **7d** (70) |
| 9 | **2** | $[CH_2SC(NH_2)NH_2^+Cl^-]_2$ [a] | $BrCH_2CH_2Br$ | **7a** (36) |
| 10 | **2** | $CH_2[CH_2SC(NH_2)NH_2^+Cl^-]_2$ [a] | $BrCH_2CH_2CH_2Br$ | **7b** (43) |
| 11 | **2** | $Na_2S$ | $ICH_2I$ | **8a** (63) |
| 12 | **2** | $Na_2S$ | $BrCH_2CH_2Br$ | **7a** (21), **8b** (66) |
| 13 | **2** | $Na_2S$ | $BrCH_2CH_2Br$ [b] | **7a** (13), **9a** (19), **2** (16) |
| 14 | **2** | $Na_2S$ | $BrCH_2CH_2CH_2Br$ | **7b** (35), **8c** (30) |
| 15 | **2** | $Na_2S$ | $BrCH_2CH_2CH_2CH_2Br$ | **8d** (31), **9b** (21) |
| 16 | **2** | $Na_2S$ | $TsO(CH_2CH_2O)_2Ts$ | **7d** (50), **8e** (26) |
| 17 | **2** | $Na_2S$ | $TsO(CH_2CH_2O)_4Ts$ | **8f** (16) |

[a] In the presence of sodium hydroxide. [b] The reverse variant of alkylation with an excess of 1,2-dibromoethane.

In order to obtain thiacrowns (**7a-d**) with satisfactory yields we studied the synthesis starting with dithiin (**2**) in the same reaction conditions. We observed a cleavage of one $C_{4\text{-quinolinyl}}$ - sulfur bond in two molecules of dithiin (**2**) with one molecule of the nucleophile. The resulting intermediate (**4A**) was stable and did not undergo either the Smiles rearrangement or the C-S cleavage. In our opinion this fact is a reason that the yields of thiacrowns (**7a-d**) were relatively good 52-70%.

To avoid working with odorous alkanedithiols and their sodium salts an alternative method was proposed. The dithiin ring opening in dithiin (**2**) was achieved using *S,S*-alkylenebis(isothiouronium) salts (alkylene = 1,2-ethylene and 1,3-propylene) in the presence of sodium hydroxide giving sodium alkanedithiolates *in situ* in the reaction mixture. Thiacrowns (**7a-d**) were obtained in this manner in lower yields (36 and 43%, respectively) than in the case of using sodium alkanedithiolates prepared separately.

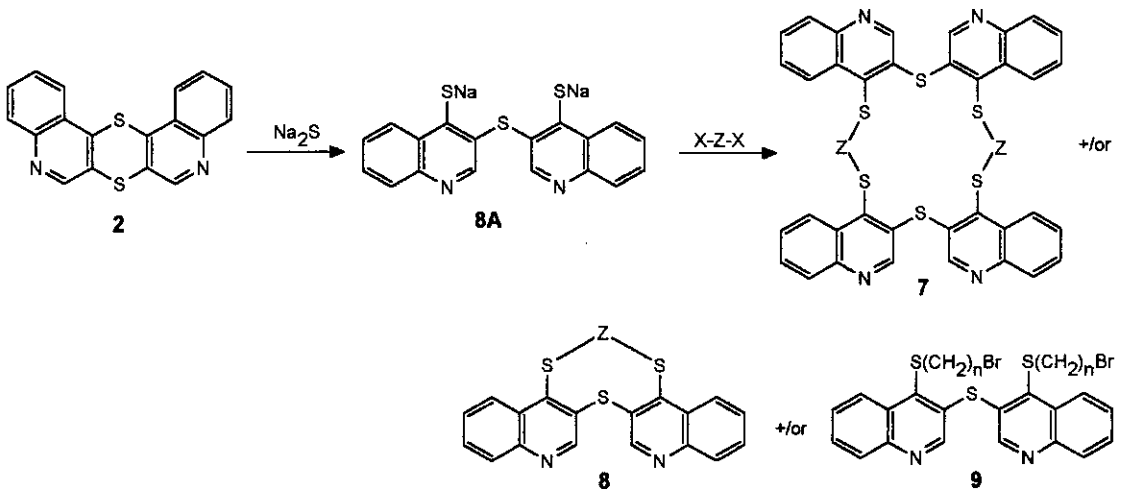
Scheme 1




Reaction of dithiin (**2**) with sodium sulfide led to disodium 3,3'-thiobis(4-quinolinethiolate) (**8A**), which were alkylated with α,ω-alkylene dihalides and ditosylates to form thiacrowns (**7**) and (**8**), and sulfides (**9**), depending on alkylating agents and conditions of alkylation (Table 1). In the reverse variant of alkylation with an excess of 1,2-dibromoethane we observed formation of sulfide (**9a**), being a result of dialkylation, instead of thiacrown (**8b**). The presence of dithiin (**2**) (16%) in the reaction products is a result of recycli-

zation of some intermediates as the 1,4-dithiin ring opening stage proceeded in 100% yield (a yellow suspension of highly insoluble dithiin (**2**) changed into a transparent red solution in the end of this stage).

Scheme 2




**2** **8A** **7** **8** **9**

The obtained thiacrowns (**7**) and (**8**) possess two or four quinoline moieties. The central crown thioether rings contain 3 (3S), 4 (3S1O), 6 (6S and 3S3O), 7 (7S) and 8 (6S2O) heteroatoms built in 8-, 9-, 10-, 11-, 12-, 18-, 20-, 21- and 24-membered macrocycles. The longest alkylene units in two types of alkylene and oxaalkylene chains (1,4-butylene and 3,6,9-trioxaundecan-1,12-ylene) favors the formation of thiacrown (**8**), being a result of intramolecular *S*-alkylation of disodium 3,3'-thiobis(4-quinolinethiolate) (**8A**). Thiacrowns (**7**) and (**8**) show interesting $^1$H NMR properties. Whereas the signals of the $H_{5\text{-quinolinyl}}$ protons are dependent on the kind of the 4-substituent and rotation around the $C_{4\text{-quinolinyl}}$ - substituent bond, the signals of the $H_{2\text{-quinolinyl}}$ protons are less influenced by the 4-substituent or even the 3-sulfide group but are influenced mainly by rotation of two quinoline rings around the central C-S-C bonds. The peri effect being a through-space interaction of the $H_{5\text{-quinolinyl}}$ atoms with the 4-substituent induces deshielding of the $H_{5\text{-quinolinyl}}$ protons in comparison with the $H_{5\text{-quinolinyl}}$ proton in quinoline (7.78 ppm[13]). The value of this effect is dependent on the conformation of the macrocyclic ring. We observed quite similar chemical shifts of the $H_{5\text{-quinolinyl}}$ protons (8.46-8.54 ppm, the peri effect $\Delta\delta$ = +0.68-0.76 ppm) in nearly all thiacrowns (**7**) and (**8**) except thiacrowns (**8a**) and (**8b**) (8.29 and 8.25 ppm respectively, $\Delta\delta$ = +0.47-0.51 ppm), which reflect a similar influence of the 4-*S*-alkyl groups as that in sulfides (**9a**) and (**9b**) (both 8.55 ppm, $\Delta\delta$ = +0.77 ppm). The peri effect is the greatest when the 4-*S*-alkyl group is perpendicular to the quinoline moiety, enabling the greatest interaction of the lone electron of the sulfur atom with the $H_{5\text{-quinolinyl}}$ atom.[14] The

X-Ray examination of thiacrown (**8e**) showed trans-perpendicular orientation of the 4-$SCH_2CH_2$ groups with respect to the central C-S-C bonds.[15] The smallest peri effects in thiacrowns (**8a**) and (**8b**), representing the smallest rings, is an evidence for some steric constrains in the central macrocyclic rings, causing different rotation around the $C_{4\text{-quinolinyl}}$ -S bond.

The chemical shifts of the $H_{2\text{-quinolinyl}}$ protons are found in the region of 8.38-8.92 ppm, which in comparison with the same proton in quinoline (8.81 ppm[13]) shows both shielding and deshielding. The extreme values were observed for the smallest crown thioethers (**8a**) (8.92 ppm) and (**8b**) (8.38 ppm). In the case of thiacrowns (**7a-d**) the $H_{2\text{-quinolinyl}}$ protons signals were found in the region of 8.46-8.57 ppm.

Whereas the molecular ion in FABMS is a basic peak or at a least significant peak in thiacrowns (**8a-f**), in thiacrowns (**7a-d**), being dimeric in relation to thiacrowns (**8**), the molecular ion is insignificant (1-24% intensity). Both thiacrowns show a fragmentary ion of m/z = 319, being the M+1 peak of the dithiin (**2**) moiety ($C_{18}H_{10}N_2S_2$ +1).

Using the reactions of 1,4-dithiinodiquinolines (**1**) and (**2**) with divalent sulfur nucleophiles followed by *S*-alkylations with divalent alkylating agents we enlarged the central dithiin ring into 8-24-membered crown thioether macrocycles.

## EXPERIMENTAL

Melting points were determined in open capillary tubes on a Boetius melting point apparatus and are uncorrected. The $^1H$ NMR spectra were recorded on a Bruker MSL 300 and a UNITYplus-300 spectrometers at 300 MHz in deuteriochloroform with tetramethylsilane as the internal standard. EIMS spectra were run on a LKB 9000S spectrometer at 15 eV. FABMS spectrum was recorded on a Finnigan MAT 95 spectrometer ($Cs^+$, 13 keV, 3-nitrobenzyl alcohol as matrix). Thin layer chromatography was performed on aluminum oxide (type E) and silica gel 60 254F plates (Merck) using methylene chloride and benzene-ethyl acetate (1:1) solutions as eluents.

Thioquinanthrene (**1**) was obtained by exhaustive sulfuration of quinoline with elemental sulfur,[7] and isothioquinanthrene (**2**) from thioquinanthrene (**1**) *via* ring opening-ring closure reactions.[8]

Disodium alkanedithiolates were prepared from commercial alkanedithiols (1,2-ethanedithiol, 1,3-propanedithiol, 3-oxapenthane-1,5-dithiol and 3-thiapenthane-1,5-dithiol) and sodium hydride (two equivalents) in boiling anhydrous benzene (48 hours) or sodium ethoxide (two equivalents) in anhydrous boiling ethanol (1 hour). The solvents were distilled off under reduced pressure and the residue was mixed with anhydrous tetrahydrofuran, filtered off, and washed with tetrahydrofuran to give the salts as white powder. *S,S*-Alkylenebis(isothiouronium) dibromides were prepared from 1,2-dibromoethane or 1,3-dibromopro-

pane and thiourea (two equivalents) in ethanol by boiling for 3 hours. After cooling down white precipitate was filtered off and washed with ethanol.

Reaction of dithiins (**1**) and (**2**) with disodium alkanedithiolates, *S,S*-alkylenebis(isothiouronium) dibromides and sodium sulfide. General procedure.

To a suspension of dithiin (**1**) or (**2**) (0.64 g, 2 mmol) in dry DMSO (20 mL) at 70 °C was added disodium alkanedithiolate (2 mmol) or *S,S*-alkylenebis(isothiouronium) dibromide (2.4 mmol) in the presence of powdered sodium hydroxide (0.40 g, 10 mmol) or sodium sulfide (0.47 g, 6 mmol). The mixture was stirred for 15 or 30 (in the case of sodium sulfide) min. The progress of the 1,4-dithiin ring opening reaction was followed by observation of a color of the reaction mixture (a change from yellow to deep red) and dissolution of dithiin into solution during the course of the reaction (being a transparent solution in the end of this stage). The mixture, cooled to rt (and decanted in the case of the reaction with sodium sulfide) was alkylated portionally by dropping diiodomethane, 1,2-dibromoethane, 1,3-dibromopropane and 1,4-dibromobutane (2.4 mmol) or solution of diethylene glycol ditosylate and tetraethylene glycol ditosylate (2.4 mmol) in DMSO (10 mL) during 60 min. The mixture was stirred for another 60 min and then was poured into 15% aqueous sodium hydroxide (threefold volume in relation to DMSO - 60 or 90 mL). The resulted solid or viscous oil was filtered off and dissolved in chloroform. Insoluble solid was filltered off and the filtrate was purified by column chromatography (silica gel, chloroform and chloroform-anhydrous ethanol as eluents) to give compounds (**7**), (**8**) and (**9**). The results of the reactions was collected in Table 1. In the reverse variant of alkylation the reaction mixture was dropped during 3 min into a solution of 1,2-dibromoethane (9 mmol) in DMSO (10 mL) and then poured into 15% aqueous sodium hydroxide (90 mL).

2,5,16,27,30,41-Hexathia-13,19,38,44-tetraazanonacyclo[40,8,0,$0^{6,15}$,$0^{7,12}$,$0^{17,26}$,$0^{20,25}$,$0^{31,40}$,$0^{32,37}$,$0^{45,50}$]pentaconta-1(42),6(15),7(12),8(9),10(11),13(14),17(26),18(19),20(25),21(22),23(24),31(40),32(37),33(34),35(36),38(39),43(44),45(50),46(47),48(49)-eicosaene (**7a**): mp 296-297 °C (ethanol). $^1$H NMR ($CDCl_3$), $\delta$: 3.25 (s, 8H, $4CH_2$), 7.68 (t, 4H, $4H_{6\text{-quinolinyl}}$), 7.79 (m, 4H, $4H_{7\text{-quinolinyl}}$), 8.12 (m, 4H, $4H_{8\text{-quinolinyl}}$), 8.46 (m, 4H, $4H_{5\text{-quinolinyl}}$), 8.52 (s, 4H, $4H_{2\text{-quinolinyl}}$). FABMS, (m/z): 757 (M+1, 1), 154 (100). *Anal. Calcd* for $C_{40}H_{28}N_4S_6$: C 62.61; H 3.32; N 7.69; S 26.39. Found: C 62.28; H 3.46; N 7.51; S 26.09.

2,6,17,28,32,43-Hexathia-14,20,40,46-tetraazanonacyclo[42,8,0,$0^{7,16}$,$0^{8,13}$,$0^{18,27}$,$0^{21,26}$,$0^{33,42}$,$0^{34,35}$,$0^{47,52}$]dopentaconta-1(44),7(16),8(13),9(10),11(12),14(15),18(27),19(20),21(26),22(23),24(25),33(42),34(39),35(36),37(38),40(41),45(46),47(52),48(49),50(51)-eicosaene (**7b**): mp 239-240 °C (ethanol). $^1$H NMR ($CDCl_3$), $\delta$: 1.82 (t, J = 6.9 Hz, 4H, $2CH_2$), 3.23 (t, J = 6.9 Hz, 8H, $4CH_2$), 7.62 (m, 4H, $4H_{6\text{-quinolinyl}}$), 7.73 (m, 4H, $4H_{7\text{-quinolinyl}}$), 8.07 (m, 4H, $4H_{8\text{-quinolinyl}}$), 8.46 (m, 4H, $4H_{5\text{-quinolinyl}}$), 8.49 (s, 4H, $4H_{2\text{-quinolinyl}}$).

FABMS, (m/z): 785 (M+1, 24), 319 ($C_{18}H_{10}N_2S_2$+1, 13), 154 (100). *Anal. Calcd* for $C_{42}H_{32}N_4S_6$: C 64.25; H 4.11; N 7.14; S 24.50. Found: C 64.11; H 4.23; N 7.02; S 24.24.

2,5,8,19,30,33,44-Heptathia-16,22,41,47-tetraazanonacyclo[43,8,0,0$^{9,18}$,0$^{10,15}$,0$^{20,29}$,0$^{23,28}$,0$^{34,43}$,0$^{35,40}$,0$^{48,53}$]tripentaconta-1(45),9(18),10(15),11(12),13(14),16(17),20(29),21(22),23(28),24(25),26(27),34(43),35(40),36(37),38(39),41(42),46(47),48(53),49(50),51(52)-eicosaene (**7c**): mp 186-187 °C (ethanol). $^1$H NMR ($CDCl_3$), δ: 2.68-2.73 (m, 4H, 2$CH_2$), 3.17-3.22 (m, 4H, 2$CH_2$), 3.30 (s, 4H, 2$CH_2$), 7.55-7.77 (m, 8H, 2$H_{6\text{-quinolinyl}}$, 2$H_{6'\text{-quinolinyl}}$, 2$H_{7\text{-quinolinyl}}$, 2$H_{7'\text{-quinolinyl}}$), 8.04 and 8.07 (2m, 4H, 2$H_{8\text{-quinolinyl}}$, 2$H_{8'\text{-quinolinyl}}$), 8.39 and 8.48 (2m, 4H, 2$H_{5\text{-quinolinyl}}$, 2$H_{5'\text{-quinolinyl}}$), 8.46 and 8.57 (2s, 4H, 2$H_{2\text{-quinolinyl}}$, 2$H_{2'\text{-quinolinyl}}$). FABMS, (m/z): 817 (M+1, 18), 319 ($C_{18}H_{10}N_2S_2$+1, 46), 154 (100). *Anal. Calcd* for $C_{42}H_{32}N_4S_7$: C 61.73; H 3.95; N 6.86; S 27.46. Found: C 61.48; H 4.09; N 6.71; S 27.18.

2,8,19,30,36,47-Hexathia-5,33-dioxa-16,22,44,50-tetraazanonacyclo[46,8,0,0$^{9,18}$,0$^{10,15}$,0$^{20,29}$,0$^{23,28}$,0$^{37,46}$,0$^{38,43}$,0$^{51,56}$]hexapentaconta-1(48),9(18),10(15),11(12),13(14),16(17),20(29),21(22),23(28),24(25),26(27),37(46),38(43),39(40),41(42),44(45),49(50),51(56),52(53),54(55)-eicosaene (**7d**): mp 126-127 °C (DMF). $^1$H NMR ($CDCl_3$), δ: 3.14 (t, J = 6.2 Hz, 8H, 4$SCH_2$), 3.52 (t, J = 6.2 Hz, 8H, 4$OCH_2$), 7.65 (m, 4H, 4$H_{6\text{-quinolinyl}}$), 7.76 (m, 4H, 4$H_{7\text{-quinolinyl}}$), 8.05 (m, 4H, 4$H_{8\text{-quinolinyl}}$), 8.47 (m, 4H, 4$H_{5\text{-quinolinyl}}$), 8.53 (s, 4H, 4$H_{2\text{-quinolinyl}}$). FABMS, (m/z): 845 (M+1, 3), 319 ($C_{18}H_{10}N_2S_2$+1, 20), 154 (100). *Anal. Calcd* for $C_{44}H_{36}N_4O_2S_6$: C 62.53; H 4.29; N 6.63; S 22.76. Found: C 62.26; H 4.37; N 6.42; S 22.38.

2,4,15-Trithia-12,18-diazapentacyclo[14,8,0,0$^{5,14}$,0$^{6,11}$,0$^{19,24}$]tetracosa-1(16),5(14),6(11),7(8),9(10),12(13),17(18),19(24),20(21),22(23)-decaene (**8a**): mp 278-279 °C (ethanol). $^1$H NMR ($CDCl_3$), δ: 5.30 (s, 2H, $CH_2$), 7.59 (m, 2H, 2$H_{6\text{-quinolinyl}}$), 7.73 (m, 2H, 2$H_{7\text{-quinolinyl}}$), 8.07 (m, 2H, 2$H_{8\text{-quinolinyl}}$), 8.29 (m, 2H, 2$H_{5\text{-quinolinyl}}$), 8.92 (s, 2H, 2$H_{2\text{-quinolinyl}}$). MS (15 eV), (m/z): 364 ($M^+$, 76), 318 (M-$SCH_2$, 74), 204 ($C_9H_5NS_2CH^+$, 100). FABMS, (m/z): 365 (M+1, 100). *Anal. Calcd* for $C_{19}H_{12}N_2S_3$: C 62.61; H 3.32; N 7.69; S 26.39. Found: C 62.29; H 3.49; N 7.51; S 26.06.

2,4,16-Trithia-13,19-diazapentacyclo[15,8,0,0$^{6,15}$,0$^{7,12}$,0$^{20,25}$]pentacosa-1(17),6(15),7(12),8(9),10(11),13(14),18(19),20(25),21(22),23(24)-decaene (**8b**): mp 110-111 °C (ethanol). $^1$H NMR ($CDCl_3$), δ: 3.26 (s, 4H, 2$CH_2$), 7.47 (m, 2H, 2$H_{6\text{-quinolinyl}}$), 7.67 (m, 2H, 2$H_{7\text{-quinolinyl}}$), 8.00 (m, 2H, 2$H_{8\text{-quinolinyl}}$), 8.25 (m, 2H, 2$H_{5\text{-quinolinyl}}$), 8.38 (s, 2H, 2$H_{2\text{-quinolinyl}}$). MS (15 eV), (m/z): 378 ($M^+$, 100), 318 (M-$SC_2H_4$, 30). *Anal. Calcd* for $C_{20}H_{14}N_2S_3$: C 63.46; H 3.73; N 7.40; S 25.41. Found: C 63.17; H 3.91; N 7.13; S 25.12.

2,6,17-Trithia-14,20-diazapentacyclo[16,8,0,0$^{7,16}$,0$^{8,13}$,0$^{21,26}$]hexacosa-1(18),7(16),8(13),9(10),11(12),14(15),19(20),21(26),22(23),24(25)-decaene (**8c**): mp 202-203 °C (ethanol). $^1$H NMR ($CDCl_3$), δ: 2.07 (t, J = 6.2 Hz, 2H, $CH_2$), 3.63 (t, J = 6.2 Hz, 4H, 2$CH_2$), 7.59 (m, 2H, 2$H_{6\text{-quinolinyl}}$), 7.71 (m, 2H, 2$H_{7\text{-quinolinyl}}$), 8.05 (m, 2H, 2$H_{8\text{-quinolinyl}}$), 8.51 (m, 2H, 2$H_{5\text{-quinolinyl}}$), 8.85 (s, 2H, 2$H_{2\text{-quinolinyl}}$). FABMS, (m/z): 393

(M+1, 82), 319 (M-$(CH_2)_3$S+1, 7), 154 (100). *Anal .Calcd* for $C_{21}H_{16}N_2S_3$: C 64.25; H 4.11; N 7.14; S 24.50. Found: C 64.06; H 4.22; N 7.01; S 24.22.

2,7,18-Trithia-15,21-diazapentacyclo[17,8,0,$0^{8,17}$,$0^{9,14}$,$0^{22,27}$]heptacosa-1(19),8(17),9(14),10(11),12(13),15(16),20(21),22(27),23(24),25(26)-decaene (**8d**): mp 144-145 °C (ethanol). $^1$H NMR ($CDCl_3$), $\delta$: 1.80 (m, 4H, $2CCH_2$), 3.34 (t, J = 5.8 Hz, 4H, $2SCH_2$), 7.62 (m, 2H, $2H_{6\text{-quinolinyl}}$), 7.73 (m, 2H, $2H_{7\text{-quinolinyl}}$), 8.10 (m, 2H, $2H_{8\text{-quinolinyl}}$), 8.54 (m, 2H, $2H_{5\text{-quinolinyl}}$), 8.78 (s, 2H, $2H_{2\text{-quinolinyl}}$). FABMS, (m/z): 407 (M+1, 47), 319 (M-$(CH_2)_4$S+1, 45), 154 (100). *Anal. Calcd* for $C_{22}H_{18}N_2S_3$: C 64.99; H 4.46; N 6.89; S 23.66. Found: C 64.89; H 4.52; N 6.72; S 23.41.

2,8,19-Trithia-5-oxa-16,22-diazapentacyclo[18,8,0,$0^{9,18}$,$0^{10,15}$,$0^{23,28}$]octacosa-1(20),9(18),10(15),11(12),13(14),16(17),21(22),23(28),24(25),26(27)-decaene (**8e**): mp 210-211 °C (DMF) (lit.,[15] mp 210-211 °C). $^1$H NMR ($CDCl_3$), $\delta$: 3.20 (t, J = 4.7 Hz, 4H, $2SCH_2$), 3.71 (t, J = 4.7 Hz, 4H, $2OCH_2$), 7.64 (m, 2H, $2H_{6\text{-quinolinyl}}$), 7.72 (m, 2H, $2H_{7\text{-quinolinyl}}$), 8.09 (m, 2H, $2H_{8\text{-quinolinyl}}$), 8.52 (m, 2H, $2H_{5\text{-quinolinyl}}$), 8.73 (s, 2H, $2H_{2\text{-quinolinyl}}$).[15] FABMS, (m/z): 423 (M+1, 100), 319 (M-$(CH_2)_4$OS+1, 33). *Anal. Calcd* for $C_{22}H_{18}N_2OS_3$: C 62.53; H 4.29; N 6.63; S 22.76. Found: C 62.31; H 4.34; N 6.48; S 22.39.

2,14,25-Trithia-5,8,11-trioxa-22,28-diazapentacyclo[24,8,0,$0^{15,24}$,$0^{16,21}$,$0^{29,34}$]tetratriaconta-1(26),15(24),16(21),17(18),19(20),22(23),27(28),29(34),30(31),32(33)-decaene (**8f**): mp 108-109 (DMF). $^1$H NMR ($CDCl_3$), $\delta$: 3.28 (t, J = 6.6 Hz, 4H, $2SCH_2$), 3.50 (m, 8H, $4OCH_2$), 3.68 (t, J = 6.6 Hz, 4H, $2OCH_2$), 7.69 (m, 2H, $2H_{6\text{-quinolinyl}}$), 7.79 (m, 2H, $2H_{7\text{-quinolinyl}}$), 8.09 (m, 2H, $2H_{8\text{-quinolinyl}}$), 8.54 (m, 2H, $2H_{5\text{-quinolinyl}}$), 8.57 (s, 2H, $2H_{2\text{-quinolinyl}}$). FABMS, (m/z): 511 (M+1, 100), 319 (M-$(CH_2)_8O_3$S+1, 44). *Anal. Calcd* for $C_{26}H_{26}N_2O_3S_3$: C 61.15; H 5.13; N 5.49; S 18.83. Found: C 61.01; H 5.20; N 5.21; S 18.52.

4,4'-Di(2-bromoethylthio)-3,3'-diquinolinyl sulfide (**9a**): mp 121-122 °C (ethanol). $^1$H NMR ($CDCl_3$), $\delta$: 3.47 (m, 8H, $4CH_2$), 7.73 (m, 2H, $2H_{6\text{-quinolinyl}}$), 7.78 (m, 2H, $2H_{7\text{-quinolinyl}}$), 8.12 (m, 2H, $2H_{8\text{-quinolinyl}}$), 8.55 (m, 2H, $2H_{5\text{-quinolinyl}}$), 8.57 (s, 2H, $2H_{2\text{-quinolinyl}}$). FABMS, (m/z): 565 (M+1, 25), 567 (M+3, 48), 319 (M-S$(CH_2CH_2Br)_2$+1, 48), 154 (100). *Anal. Calcd* for $C_{22}H_{18}N_2Br_2S_3$: C 46.65; H 3.20; N 4.95; S 16.98. Found: C 46.38; H 3.37; N 4.88; S 16.79.

4,4'-Di(4-bromobutylthio)-3,3'-diquinolinyl sulfide (**9b**): viscous oil. $^1$H NMR ($CDCl_3$), $\delta$: 1.73 (m, 4H, $2CCH_2$), 1.98 (m, 4H, $2CCH_2$), 3.09 (t, J = 7.1 Hz, 4H, $2CH_2Br$), 3.35 (t, J = 6.6 Hz, 4H, $2SCH_2$), 7.68 (m, 2H, $2H_{6\text{-quinolinyl}}$), 7.76 (m, 2H, $2H_{7\text{-quinolinyl}}$), 8.11 (m, 2H, $2H_{8\text{-quinolinyl}}$), 8.56 (m, 2H, $2H_{5\text{-quinolinyl}}$), 8.57 (s, 2H, $2H_{2\text{-quinolinyl}}$). FABMS, (m/z): 621 (M+1, 7), 623 (M+3, 10), 319 (M-S$(CH_2)_8Br_2$+1, 10), 154 (100). *Anal. Calcd* for $C_{26}H_{26}N_2Br_2S_3$: C 50.17; H 4.21; N 4.50; S 15.45. Found: C 50.01; H 3.48; N 4.32; S 15.29.

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