3',4-DIALKYLTHIO-3,4'-DIQUINOLINYL SULFIDES WITH NON-IDENTICAL ALKYL GROUPS [1]

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Abstract - 3',4-Dialkylthio-3,4'-diquinolinyl sulfides (**6**) were obtained by three methods in the reaction of thioquinanthrene (**1**) with sodium hydrosulfide followed by sequential *S*-alkylation of the 3- and 4-thiolate functions. Competitive *S*-alkylation of 3- and 4-quinolinethiolates (**4**) and (**10**) in DMSO showed three times greater susceptibility of the 3-thiolate function to the alkylating agent than the 4-thiolate function. 4-Quinolinethiolates (**3**) were converted into 4(1*H*)-quinolinethiones (**8**).

INTRODUCTION

Ortho,ortho'-disubstituted 3,4'-diquinolinyl sulfides show unusual conformations and ^{1}H and ^{13}C NMR spectra being the results of donor-acceptor interactions of the heteroatoms.[2-6] The conformational properties, which could not be predicted from the properties of diphenyl and dipyridinyl sulfides,[7-9] explain unexpected type of the Smiles rearrangement of 3,4'-diquinolinyl sulfides to 3,3'-diquinolinyl sulfdes.[10-11] Syntheses of 3,4'-diazinyl sulfides (azinyl = pyridinyl, quinolinyl) are extremely seldom owing to relatively unreactive position 3. Leaving our methodology out of account there is only one report concerning the synthesis of unsubstituted 3,4'-dipyridinyl sulfide.[12] *Ortho,ortho'*-disubstituted 3,4'-diquinolinyl sulfides are easily available from quinoline according to our methodology consisted of two main reactions: sulfurization of quinoline with elemental sulfur to thioquinanthrene (**1**) *(i.e.,* 1,4-dithiino[2,3-*c*;5,6-*c'*]diquinoline)[13] and the reaction of thioquinanthrene with nucleophiles.[10-11,14-16] In the reaction with sodium sulfide and with sodium hydrosulfide (70 °C, DMSO, 1 h)[10] only one γ-quinolinyl-sulfur bond in the 1,4-dithiin ring

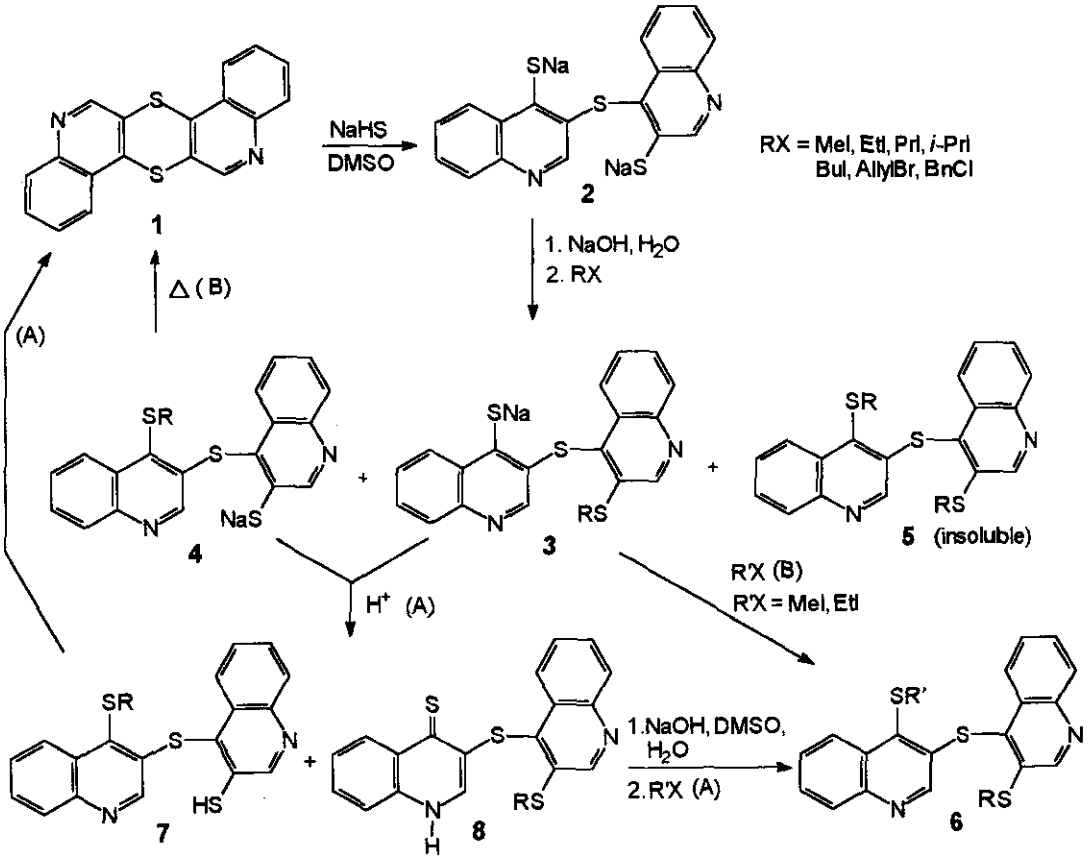
of dithiin (**1**) was cleaved to give disodium salt of 3',4-dimercapto-3,4'-diquinolinyl sulfide (**2**). It was then alkylated to 3',4-dialkylthio-3,4'-diquinolinyl sulfides (**5**) possessing the same alkyl groups.[10] In the reaction of dithiin (**1**) with alkanethiolate anions (prepared from alkanethiols) the formation of sodium salt of 3'-mercapto-4-alkylthio-3,4'-diquinolinyl sulfides (**4**) was observed. They could be alkylated to 3',4-dialkylthio-3,4'-diquinolinyl sulfides (**5**) and (**6**) having the same or different alkyl groups.[10,11] The latter sulfides turned out to be excellent substrates to obtain 4-substituted 3-alkylthioquinolines in the clevage of the 4'-quinolinyl-sulfur bond.[11,16] Owing to further study of quinolinyl sulfides as models in the oxidation of the sulfide function according to the sulfur attachment to the quinoline ring and the nature of the alkyl substituent, there was need to obtain sulfides (**6**) with non-identical alkyl groups.[17] For this purpose three methods of synthesis of sulfides (**6**) were studied without use of stench sodium alkanethiolates. As the key compound, mentioned above, easily available disodium salt (**2**) was chosen.

RESULTS AND DISCUSSION

The 1,4-dithiin ring opening in thioquinanthrene (**1**) by the reaction with sulfur nucleophiles [sodium sulfide, hydrosulfide (at 70 °C) and alkanethiolates (at 20 °C)] in DMSO led to disodium salt (**2**) or monosodium salt (**4**).[10,11,16] Under more rigorous conditions (DMSO, 70 °C or 140 °C, DMSO-water, 137 °C, resp.) primarily formed salts (**2**) and (**4**) underwent subsequent transformation to monosodium salt of 4'-mercapto-4-alkylthio-3,3'-diquinolinyl sulfides or disodium salt of 3,4-dimercaptoquinoline and disodium salt of 4,4'-dimercapto-3,3'-diquinolinyl sulfide.[10,11,14] A solution of disodium salt (**2**) in DMSO was usually diluted with threefold volume of 15% aqueous sodium hydroxide and alkylated with two equivalents of alkylating agent to give sulfides (**5**) possessing the same *S*-alkyl groups.[10] In order to obtain sulfides (**6**) possessing different *S*-alkyl groups, we decided to alkylate disodium salt (**2**) with only one equivalent of alkylating agent (RX). We obtained a mixture of the monoalkylated products (**3**) and (**4**), and the dialkylated product (**5**) (Scheme 1). Alkali insoluble sulfide (**5**) was easily removed by filtration. The separation of monosodium salts (**3**) and (**4**) was then studied based on cyclization ability of salt (**4**) to the starting dithiin (**1**).

Transformation of salt (**4**) (procedure A) was performed by acidification of aqueous alkali solution of salts (**3**) and (**4**) with 20% sulfuric acid to a mixture of thiol (**7**) and 1,4-dihydro-3'-alkylthio-4-thioxo-3,4'-diquinolinyl sulfide (**8**), followed by cyclization of thiol (**7**) to dithiin (**1**). The mixture of dithiin (**1**) and thione (**8**) was then basified, insoluble dithiin (**1**) was filtered off, the filtrate containing mainly salt (**3**) was treated with a different kind of alkylating agent (RX') to give sulfide (**6**). Cyclization of salt (**4**) (procedure B) was also performed by heating an aqueous alkali solution of salts (**3**) and (**4**), resulting dithiin (**1**) was filtered off and the remaining solution of salt (**3**) was alkylated to diquinolinyl sulfide (**6**).

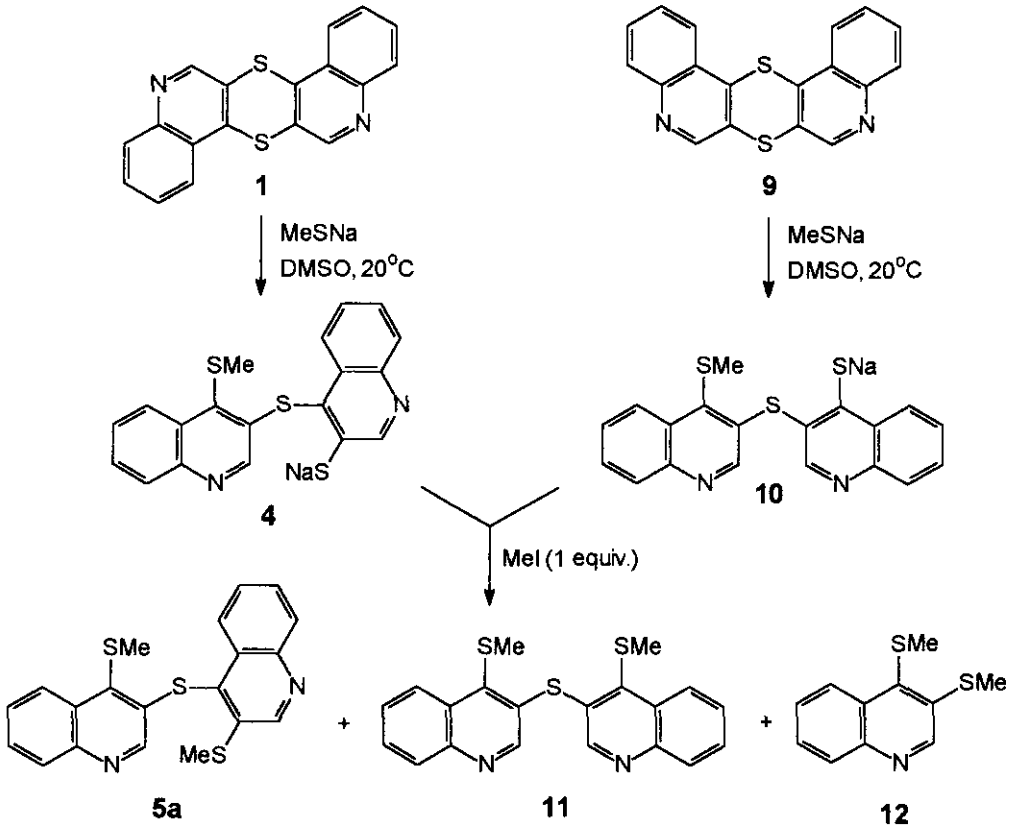
Scheme 1



Although *S*-alkylation of 3- and 4-quinolinethiolates was very efficient in the mixture of DMSO : water (1:3) containing 10% of sodium hydroxide or even in DMSO neat (for example methylation or benzylation proceeded in yield of over 90%[10,11]), relative activity of these thiolates has not been studied. As observed in procedures A and B, *S*-methylation of the 3- and 4-thiolate functions in disodium salt of 3',4-dimercapto-3,4'-diquinolinyl sulfide (**2**) in the DMSO-water mixture containing 10% of sodium hydroxide was not selective giving three products (**3**), (**4**) and (**5**).

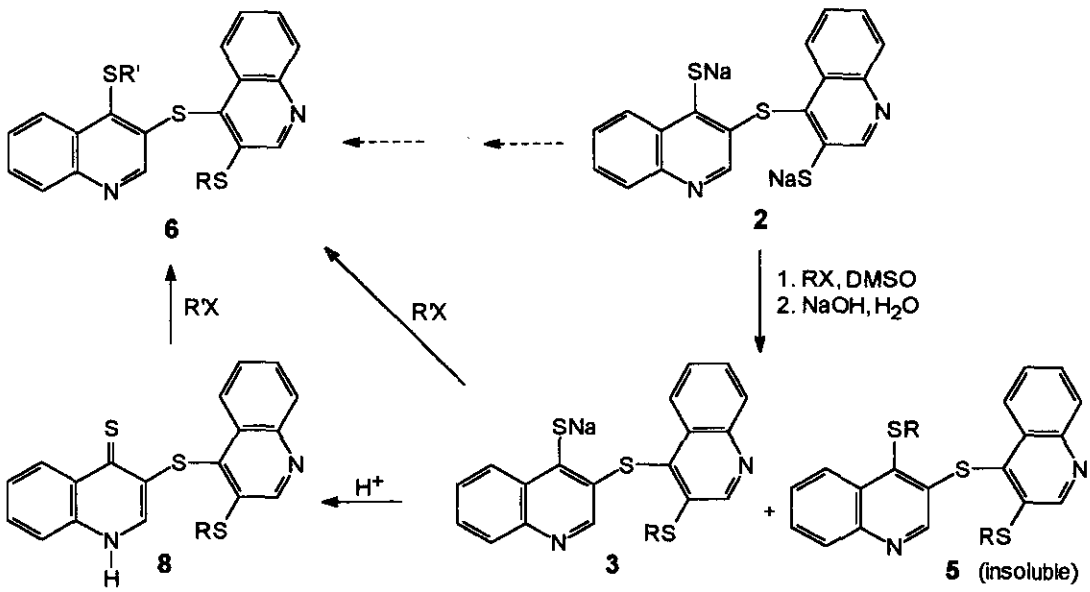
It induced us to study relative activity of these functions towards methyl iodide in DMSO neat. For this reason we carried out competitive methylation of sodium salt of 3'-mercapto-4-methylthio-3,4'-diquinolinyl sulfide (**4**) and sodium salt of 4'-mercapto-4-methylthio-3,3'-diquinolinyl sulfide (**10**) (obtained separately in the reactions of thioquinanthrene (**1**) and isothioquinanthrene (**9**)[18] with sodium methanethiolate in DMSO), representing the 3- and 4-thiolate functions, with one equivalent of methyl iodide (Scheme 2).

Scheme 2



Analysis of the methylated products based on the ^{1}H NMR spectrum (a comparison of the intensities of the singlet signals of the H-2 and *S*-methyl protons) revealed a mixture of sulfide (**5a**) (68%), 4,4'-dimethylthio-3,3'-diquinolinyl sulfide (**11**)[10] (23%) and 3,4-dimethylthioquinoline (**12**)[19] (9%). In order to prevent cyclization of salts (**4**) and (**10**)[20] to dithiins (**1**) and (**9**) in DMSO, 2 equivalents of sodium methanethiolate should be used. On the other hand, an excess of sodium methanethiolate caused breaking of the 4'-quinolinyl-sulfur bond in sulfide (**5a**) to form 3,4-dimethylthioquinoline (**12**). The observed greater susceptibility of the 3-thiolate function towards methyl iodide than the 4-thiolate function [formation of sulfides (**5a**) and (**12**) *vs* sulfide (**11**) in ratio of 3.3:1] in DMSO neat was very useful in elaborating procedure C. Alkylation of disodium salt (**2**) in procedure C was performed directly in DMSO to give monosodium salt (**3**) and dialkyl derivative (**5**). The reaction mixture was poured into 15% aqueous sodium hydroxide to remove insoluble sulfide (**5**). Alkylation of the filtrate with another alkylating agent gave sulfides (**6a - 6g**) (39-60%). Procedure C turned out the best method due to its simplicity [there is no need to recyclize to dithiin (**1**)], higher selectivity [only two primarily alkylated products (**3**) and (**5**)] and higher yields of title compounds (**6**).

Scheme 3



Furthermore, acidification of the filtrate with 10% hydrochloric acid, instead of methylation with another methylating agent, permits for the preparation of 1,4-dihydro-3'-alkylthio-4-thioxo-3,4'-diquinolinyl sulfides (**8**) in 53-54% yield. Alkylation of thiones (**8a**) and (**8b**) by alkyl iodides (methyl and ethyl) in the DMSO-water (1:3) mixture gave sulfides (**6a**) and (**6g**) in 84-86% yield.

Table 1.

Product			Yield
	R	R'	[%]
6a	Et	Me	59
6b	Pr	Me	53
6c	i-Pr	Me	39
6d	Bu	Me	55
6e	Bn	Me	48
6f	allyl	Me	60
6g	Me	Et	40

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Boetius melting point apparatus and are uncorrected. The ^{1}H NMR spectra were recorded on a Bruker MSL 300 and a Varian Unity-Inova-300 spectrometers at 300 MHz in deuteriochloroform and dimethyl sulfoxide-d_6 with tetramethylsilane as the internal standard. Chemical shifts are reported in ppm (δ) and J values in Hz. The proton assignment in 3',4-dialkylthio-3,4'-diquinolinyl sulfides (**6**) was performed on the basis of the proton chemical shifts in 3',4-dimethylthio-3,4'-diquinolinyl sulfide (**5a**).[3] Electron impact MS spectra (EI MS) and high resolution MS spectra (HR MS) were run on a LKB GC 2091 and a Finnigan MAT 95 spectrometers at 15 and 70 eV.

3',4-Dialkylthio-3,4'-diquinolinyl sulfides (**6**).

Procedure A:

To a suspension of thioquinanthrene (**1**) (1.6 g, 5 mmol) in DMSO (25 mL) at 70 °C sodium hydrosulfide (NaSH · x H_2O, 0.7 g) was added. The mixture was stirred for 30 min and then cooled to rt. The mixture was poured into 15% aqueous sodium hydroxide (75 mL) and stirred with dimethyl sulfate (0.6 mL, 6.3 mmol). The solid was collected by filtration, washed with water and air-dried. The crude sulfide was purified by column chromatography (silica gel, chloroform) to give sulfide (**5a**) (0.36 g, 19%, mp 104-105 °C, lit.,[5] mp 104-105 °C). The filtrate was carefully acidified with 20% sulfuric acid to pH 3. The resulting solid was filtered off and dissolved in the mixture of DMSO (35 mL) and 15% aqueous sodium hydroxide (105 mL). The undissolved solid was filtered off, washed with water and recrystallized with ethanol to give thioquinanthrene (**1**) (0.32 g, 20%). The filtrate was stirred with ethyl iodide (0.5 mL, 6.2 mmol). The precipitate was filtered off, washed with water, air- dried and purified by column chromatography (silica gel, chloroform) to give sulfide (**6a**) (0.33 g, 17%).

Procedure B:

The reaction was carried out as in procedure A. The filtrate after collection of sulfide (**5a**) was heated at 100 °C for 1 h. After cooling down to rt the precipitate was filtered off, washed with water and recrystallized from ethanol to give thioquinanthrene (**1**) (0.25 g, 16%). The filtrate was stirred with ethyl iodide (0.5 mL, 6.2 mmol). The precipitate was filtered off, washed with water, air-dried and purified by column chromatography (silica gel, chloroform) to give sulfide (**6a**) (0.53 g, 27%).

General procedure C:

To a suspension of thioquinanthrene (**1**) (3.2 g, 10 mmol) in DMSO (60 mL) at 70 °C sodium hydrosulfide (NaSH · x H_2O, 1.4 g) was added. The mixture was stirred for 30 min and then cooled to rt. A solution of methyl or ethyl iodide (14 mmol) in DMSO (20 mL) was added dropwise during 30 min. The mixture was poured into 15% aqueous sodium hydroxide (240 mL). The solid was collected by filtration, washed

with water, air-dried and purified by column chromatography (silica gel, chloroform) to give sulfide (**5a**) (0.43 g, 11%, mp 104-105 °C, lit.,[8] mp 104-105 °C) or (**5b**) (0.42 g, 10%, mp 95-96 °C, lit.,[10] mp 95-96 °C). The filtrate was stirred with methyl, ethyl, n-propyl, isopropyl and n-butyl iodides, allyl bromide or benzyl chloride (12 mmol). The precipitate was filtered off, washed with water, air-dried and purified by column chromatography (silica gel, chloroform) to give sulfides (**6a - 6g**) (Table 1).

3'-Methylthio-4-ethylthio-3,4'-diquinolinyl sulfide (**6a**): mp 103-104 °C, lit.,[11] mp 103-104 °C.

3'-Methylthio-4-n-propylthio-3,4'-diquinolinyl sulfide (**6b**): mp 136-137 °C. EI MS (70 eV), (m/z): 408(M, 21.9%), 361(M-SCH_3, 42.6%), 333(M-SC_3H_7, 55.9%), 318(M-$C_3H_7SCH_3$, 100%). ^{1}H NMR ($CDCl_3$), δ: 1.10(t, *J*=7.4 Hz, 3H, CH_3); 1.76(m, *J*=7.4 and 7.5 Hz, 2H, CH_2); 2.63(s, 3H, SCH_3); 3.12(t, *J*=7.5 Hz, 3H, SCH_2); 7.56(m, 1H, **H**-6'); 7.63 and 7.64(2m, 2H, **H**-6 and **H**-7); 7.68(m, 1H, **H**-7'); 7.84(s, 1H, **H**-2); 7.95(m, 1H, **H**-8); 8.14(m, 1H, **H**-8'); 8.32(m, 1H, **H**-5'); 8.56(m, 1H, **H**-5); 8.88(s, 1H, **H**-2'); HR MS calcd for $C_{22}H_{20}N_2S_3$: MW 408.0800, found: 408.0789. *Anal.* Calcd for $C_{22}H_{20}N_2S_3$: C 64.67; H 4.93; N 6.86; S 23.54. Found: C 64.43; H 5.12; N 6.76; S 23.27.

3'-Methylthio-4-isopropylthio-3,4'-diquinolinyl sulfide (**6c**): mp 104-105 °C. EI MS (15 eV), (m/z): 408(M, 36.5%), 361(M-SCH_3, 49.9%), 333(M-SC_3H_7, 52.2%), 319(M-C_3H_6 and SCH_3, 100%), 318(M-$C_3H_7SCH_3$, 98.9%). ^{1}H NMR ($CDCl_3$), δ: 1.43(d, *J*=6.7 Hz, 6H, $2CH_3$); 2.62(s, 3H, SCH_3); 3.18(m, *J*=6.7 Hz, 1H, C**H**); 7.55(m, 1H, **H**-6'); 7.63 and 7.64(2m, 2H, **H**-6 and **H**-7); 7.68(m, 1H, **H**-7'); 7.83(s, 1H, **H**-2); 7.96(m, 1H, **H**-8); 8.14(m, 1H, **H**-8'); 8.32(m, 1H, **H**-5'); 8.55(m, 1H, **H**-5); 8.88(s, 1H, **H**-2'). HR MS calcd for $C_{22}H_{20}N_2S_3$: MW 408.0800, found: 408.0789. *Anal.* Calcd for $C_{22}H_{20}N_2S_3$: C 64.67; H 4.93; N 6.86; S 23.54. Found: C 64.39; H 5.08; N 6.71; S 23.29.

3'-Methylthio-4-n-butylthio-3,4'-diquinolinyl sulfide (**6d**): mp 121-122 °C. EI MS (15 eV), (m/z): 422(M, 37.3%), 375(M-SCH_3, 57.5%), 333 (M-SC_4H_9, 100%), 318(M-$C_4H_5SCH_3$, 98.9%). ^{1}H NMR ($CDCl_3$), δ: 0.94(t, *J*=7.2 Hz, 3H, CH_3); 1.52(m, *J*=7.2 Hz, 2H, CH_2); 1.71(m, *J*=7.3 Hz, 2H, CH_2); 2.62(s, 3H, SCH_3); 3.14(t, *J*=7.3 Hz, 2H, SCH_2); 7.55(m, 1H, **H**-6'); 7.65(2m, 2H, **H**-6 and **H**-7); 7.68(m, 1H, **H**-7'); 7.83(s, 1H, **H**-2); 7.95(m, 1H, **H**-8); 8.14(m, 1H, **H**-8'); 8.32(m, 1H, **H**-5'); 8.55(m, 1H, **H**-5); 8.88(s, 1H, **H**-2'). HR MS calcd for $C_{23}H_{22}N_2S_3$: MW 422.0945, found: 422.0930. *Anal.* Calcd for $C_{23}H_{22}N_2S_3$: C 65.37; H 5.25; N 6.63; S 22.76. Found: C 65.17; H 5.31; N 6.47; S 22.55.

3'-Methylthio-4-benzylthio-3,4'-diquinolinyl sulfide (**6e**): mp 159-160 °C, lit.,[11] mp 159-160 °C.

3'-Methylthio-4-allylthio-3,4'-diquinolinyl sulfide (**6f**): mp 108-109 °C. EI MS (15 eV), (m/z): 406(M, 28.9%), 359(M-SCH_3, 24.8%), 333(M-SC_3H_5, 39.3%), 318(M-$C_3H_5SCH_3$, 100%). ^{1}H NMR ($CDCl_3$), δ: 2.62(s, 3H, SCH_3); 3.75(d, *J*=7.4 Hz, 2H, SCH_2); 4.96(dd, *J*=14.7 and 1.3 Hz, 2H, CH_2); 5.92-6.03(m, *J*=9.6 and 2.3 Hz, 1H, C**H**); 7.55(m, 1H, **H**-6'); 7.64 and 7.65(2m, 2H, **H**-6 and **H**-7); 7.68(m, 1H, **H**-7');

7.82(s, 1H, **H**-2); 7.94(m, 1H, **H**-8); 8.13(m, 1H, **H**-8'); 8.31(m, 1H, **H**-5'); 8.52(m, 1H, **H**-5); 8.88(s, 1H, **H**-2'). HR MS calcd for $C_{22}H_{18}N_2S_3$: MW 406.0632, found: 406.0634. *Anal.* Calcd for $C_{22}H_{18}N_2S_3$: C 64.99; H 4.46; N 6.89; S 23.66. Found: C 64.73; H 4.71; N 6.73; S 23.41.

3'-Ethylthio-4-methylthio-3,4'-diquinolinyl sulfide (**6g**): mp 134-135 °C, EI MS (70 eV), (m/z): 394(M, 13.4%), 347(M-SCH_3, 62.6%), 333(M-SC_3H_7, 55.9%), 318(M-$C_3H_7SCH_3$, 100%). ^{1}H NMR ($CDCl_3$), δ: 1.36(t, J=7.4 Hz, 3H, CH_3); 2.65(s, 3H, SCH_3); 3.14(q, J=7.4 Hz, 2H, SCH_2); 7.54(m, 1H, **H**-6'); 7.65 and 7.66(2m, 2H, **H**-6 and **H**-7); 7.68(m, 1H, **H**-7'); 7.85(s, 1H, **H**-2); 7.97(m, 1H, **H**-8); 8.14(m, 1H, **H**-8'); 8.31(m, 1H, **H**-5'); 8.55(m, 1H, **H**-5); 8.92(s, 1H, **H**-2'). HR MS calcd for $C_{21}H_{18}N_2S_3$: MW 394.0637, found: 394.0632. *Anal.* Calcd for $C_{21}H_{18}N_2S_3$: C 63.93; H 4.60; N 7.10; S 24.38. Found: C 63.83; H 4.88; N 6.88; S 24.22.

1,4-Dihydro-3'-alkylthio-4-thioxo-3,4'-diquinolinyl sulfides (**8**). General procedure:

The reaction was carried out as in procedure C. The filtrate after collection of sulfide (**5a**) or (**5b**) was carefully acidified at rt with 10% hydrochloric acid to pH 6. The resulting solid was filtered off, washed with water and dissolved in the mixture of DMSO (60 mL) and 15% aqueous sodium hydroxide (180 mL). The undissolved solid was filtered off, washed with water and recrystallized from DMF to give thioquinanthrene (**1**) (0.60 g, 19%). The filtrate was acidified with 10% hydrochloric acid to pH 6. The resulting solid was filtered off, washed with water and purified by dissolution in 10% sodium hydroxide solution in the DMSO-water mixture (1:3) and precipitation with 10% hydrochloric acid to pH 6 to give sulfide (**8a**) (1.93 g, 53%) or (**8b**) (2.06 g, 54%).

1,4-Dihydro-3'-methylthio-4-thioxo-3,4'-diquinolinyl sulfide (**8a**): mp 267-268 °C. EI MS (70 eV), (m/z): 366(M, 14.8%), 333(M-SH, 33.8%), 318(M-CH_3SH, 100%). ^{1}H NMR (DMSO-d_6), δ: 2.69(s, 3H, CH_3); 6.87(s, 1H, **H**-2); 7.52-7.56(m, 1H, H_{arom}); 7.61-7.65(m, 1H, H_{arom}); 7.71-7.75(m, 1H, H_{arom}); 7.72-7.76 (m, 1H, H_{arom}); 8.09-8.11(m, 1H, H_{arom}); 8.13-8.16(m, 1H, H_{arom}); 8.72(m, 1H, **H**-5); 9.00(s, 1H, **H**-2'); 12.95(br, 1H, N**H**). HR MS calcd for $C_{19}H_{14}N_2S_3$: MW 366.0319, found: 366.0335. *Anal.* Calcd for $C_{19}H_{14}N_2S_3$: C 62.26; H 3.85; N 7.64; S 26.24. Found: C 62.12; H 4.04; N 7.52; S 26.11.

1,4-Dihydro-3'-ethylthio-4-thioxo-3,4'-diquinolinyl sulfide (**8b**): mp 253-254 °C. EI MS (70 eV), (m/z): 380(M, 16.8%), 347(M-SH, 57.5%), 318(M-C_2H_5SH, 100%). ^{1}H NMR (DMSO-d_6), δ: 1.29(t, J=7.3 Hz, 3H, CH_3);3.26(q, J=7.3 Hz, 2H, CH_2); 6.86(s, 1H, **H**-2); 7.52-7.56(m, 1H, H_{arom}); 7.61-7.65(m, 1H, H_{arom}); 7.70-7.74(m, 1H, H_{arom}); 7.72-7.76 (m, 1H, H_{arom}); 7.62-7.65(m, 1H, H_{arom}); 8.09-8.11(m, 1H, H_{arom}); 8.11-8.14(m, 1H, H_{arom}); 8.72(m, 1H, **H**-5); 8.72(m, 1H, **H**-5); 9.03(s, 1H, **H**-2'); 12.95(br, 1H, N**H**). HR MS calcd for $C_{20}H_{16}N_2S_3$: MW 380.0484, found: 380.0476. *Anal.* Calcd for $C_{20}H_{14}N_2S_3$: C 63.13; H 4.24; N 7.36; S 25.27. Found: C 63.01; H 4.39; N 7.25; S 25.09.

Alkylation of 1,4-dihydro-3'-alkylthio-4-thioxo-3,4'-diquinolinyl sulfide (**8**). General procedure:

A solution of sulfide (**8a**) or (**8b**) (1 mmol) in 10% solution of sodium hydroxide in DMSO-water (1:3) (20 mL) was stirred with methyl or ethyl iodide (1.2 mmol). The precipitate was filtered off, washed with water, air-dried and purified by column chromatography (silica gel, chloroform) to give sulfide (**6a**) (0.34 g, 86%) or (**6g**) (0.33 g, 84%).

Competitive alkylation of 3- and 4-quinolinethiolates.

A solution of 3-quinolinethiolate (**4**) [obtained from dithiin (**1**) (0.32 g, 1 mmol) and sodium methanethiolate (0.14 g, 2 mmol) in DMSO (10 mL) at 20 °C for 1 h] and 4-quinolinethiolate (**10**)[20] [obtained from dithiin (**9**)[18] (0.32 g, 1 mmol) and sodium methanethiolate (0.14 g, 2 mmol) in DMSO (10 mL) at 20 °C for 1 h] was stirred for 5 min and methyl iodide (0.06 mL, 1 mmol) was added. The mixture was stirred for 30 min and then poured into 15% aqueous sodium hydroxide (60 mL). The resulting solid was filtered off, washed with water and air-dried to give methylated products (0.38 g). The ^{1}H NMR spectrum in $CDCl_3$ shoved the presence of sulfide (**5a**) (68%), 4,4'-dimethylthio-3,3'-diquinolinyl sulfide (**11**) (23%) and 3,4-dimethylthioquinoline (**12**) (9%). The analysis was based on the observation of intensities of the singlet signal of the H-2 protons at 7.85 ppm (**5a**), 8.56 ppm (**11**)[10] and 8.74 ppm (**12**)[19] and selected singlet signals of the *S*-methyl protons at 2.42 ppm [the 4-SCH_3 group in (**12**)[19]], 2,55 ppm [3- and 4-SCH_3 in (**11**)[10]] and 2.62 ppm [3'-SCH_3 in (**5a**)].

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