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REACTIONS OF THIOQUINANTHRENE WITH DISODIUM SALTS OF GLYCOLS [1]

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Abstract - Reactions of thioquinanthrene **(1)** with disodium salts of 1,3-propylene, l ,4-butylene and diethylene glycol in DMF at 70 °C followed by *S*-methylation of thiolate **(2-A)** in aqueous sodium hydroxide afforded 4-(ω-hydroxyalkoxy)-3'-methylthio-3,4'-diquinolinyl sulfides **(2)**. *S*-Methylation of **2-A** performed directly in DMF solution provided three types of the products **(2)**, **(3)** and **(4)** which yield depended on the type of the disodium salt of glycol reacted. Reaction of **1** with disodium salt of ethylene glycol in DMF at 70 °C gave 4-(2-hydroxyethoxy)-3'-methylthio-3,4'-diquinolinyl sulfide **(2d)** in low yield. The same reaction carried out in DMSO afforded the quinolones **(5)** and **(7)** as dealkylated products.

INTRODUCTION

It has been reported that the functionalization of quinoline in the positions 3 and 4 can be efficiently carried out by the reaction of thioquinanthrene **(1)** with alkoxides.[2-6] These reactions performed in DMSO or DMF solution at 70 °C ran by cleavage of one 4-quinolinyl-sulfur bond in 1,4-dithiin ring of **1** to form sodium 4-(4-alkoxy-3-quinolinylthio)-3-quinolinylthiolates **(2-A)** as primary products which were next alkylated in aqueous solution with alkyl halides to give 4-alkoxy-3'-methylthio-3,4'-diquinolinyl sulfides **(2)**.[2] The 4-quinolinyl-sulfur bond of **2** exhibited greater susceptibility to alkoxides than that of the 1,4-dithiin ring of **1** . The cleavage of the 4-quinoline-sulfur bond in sulfides **(2)** proceeded at 20 °C and led to 4-alkoxy-3-(alkylthio)quinolines **(4)** after *S*-alkylation. Treatment of **1** with an excess of alkoxide in DMF followed by the addition of two moles of an alkylating agent run as one-pot process gave directly 4-alkoxy-3-(alkylthio)quinolines **(4)**.[3] When α,ω-dibromoalkanes were used as bifunctional alkylating agents along the lines of the one-pot procedure mentioned above, thioquinanthrene **(1)** may be converted to the

oligomers with four 3,4-quinolinediyl units of the type of α,ω-bis[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]alkanes.[4] This process proceeds through 4-alkoxy-3'-(ω-haloalkylthio)-3,4'-diquinolinyl sulfides, as an intermediate products. It was found that the different behavior of this product under the reaction conditions determined the yield of the oligomers.[6] These results prompted us to further study on the reaction of **1** with disodium salts of glycols as bifunctional nucleophiles as a potential method for the construction of polymeric or macrocyclic compounds containing 3,4-quinolinediyl moieties.

In this paper we wish to report the result of our study on the reaction of **1** with disodium salts of glycols which are used as α,ω-bisnucleophiles.

RESULTS AND DISCUSION

The reactions of **1** with disodium salts of glycols (1.5 equiv) were performed in DMF or DMSO solution under nitrogen at 70 °C and led to the formation of disodium salts **(2-A)**. The latter ones were then methylated afier dilution oft he reaction mixture with aqueous sodium hydroxide (procedure A) or directly in DMF or DMSO solution (procedure B) at 20 °C by the addition of methyl iodide. The products were isolated from aqueous sodium hydroxide by extraction and separated by column chromatography. The results obtained for disodium salts of 1,3-propylene, 1,4-butylene, diethylene and ethylene glycol used in the present investigation are collected in Table 1 .

Table 1 . The Results of the Reactions of Thioquinanthrene **(1)** with Disodium Salts of Glycols in DMF at 70 °C .

No .	Disodium Salt of Glycol	Reaction Time [h]	Methylation Procedure	Products (Yields %)
1	$NaO(CH_2)_3ONa$	0.5	A[a]	**2a** (71)
2	$NaO(CH_2)_3ONa$	0.5	B[b]	**3a** (62), **4a** (28)
3	$NaO(CH_2)_4ONa$	0.5	A	**2b** (68)
4	$NaO(CH_2)_4ONa$	0.5	B	**2b** (46), **3b** (18), **4b** (21)
5	$NaO(CH_2)_2O(CH_2)_2ONa$	0.5	A	**2c** (62)
6	$NaO(CH_2)_2O(CH_2)_2ONa$	0.5	B	**2c** (41), 3**c** (14), **4c** (17)
7	$NaO(CH_2)_2ONa$	0.5	A	**2d** (26), **I** (65)
8	$NaO(CH_2)_2ONa$	2	A	**2d** (34), **I** (42)

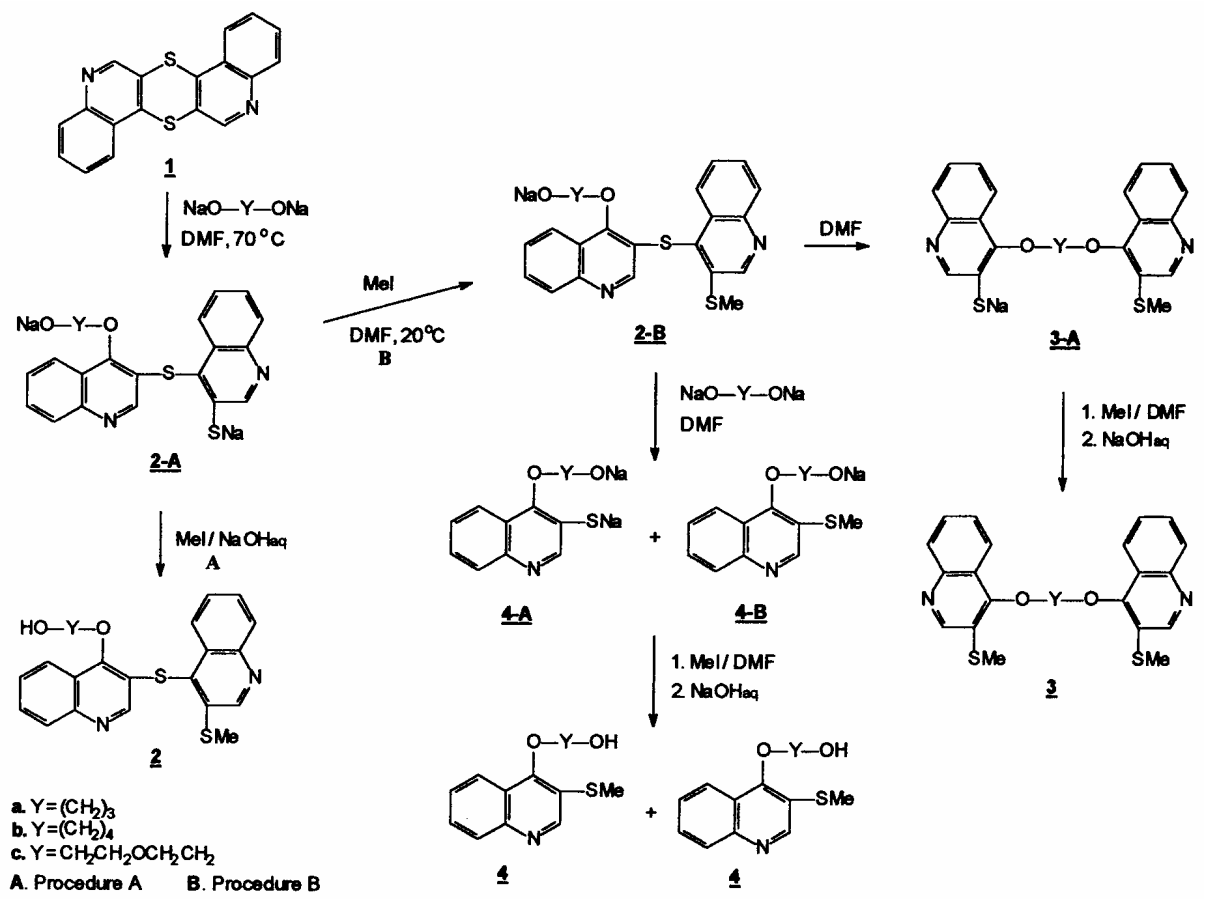
a - methylation of disodium salts **(2-A)** in aqueous sodium hydroxide (procedure A)

b - methylation of disodium salts **(2-A)** in DMF or DMSO solution (procedure B)

The reaction of **1** with disodium salt of propylene glycol performed in DMF solution followed by *S*-methylation according to the procedure A gave sulfide **(2a)** as a sole product. The same reaction performed

according to the procedure B afforded a mixture of two compounds, which were separated by column chromatography and identified as etheral products **(3a)** and **(4a)**. Thioquinanthrene **(1)** reacted with disodium salts of butylene glycol and diethylene glycol (procedure A) gave sulfides **(2b)** and **(2c)** in 68 and 62 % yields, respectively. If the same reactions were carried out according to the procedure B the mixtures of three compounds were obtained **(2b), (3b), (4b)** and **(2c), (3c), (4c),** respectively, which were successfuly separated by column chromatography. The formation of products **(3)** and **(4)** can be accounted by the reaction pathways outlined in Scheme 1 .

Scheme 1

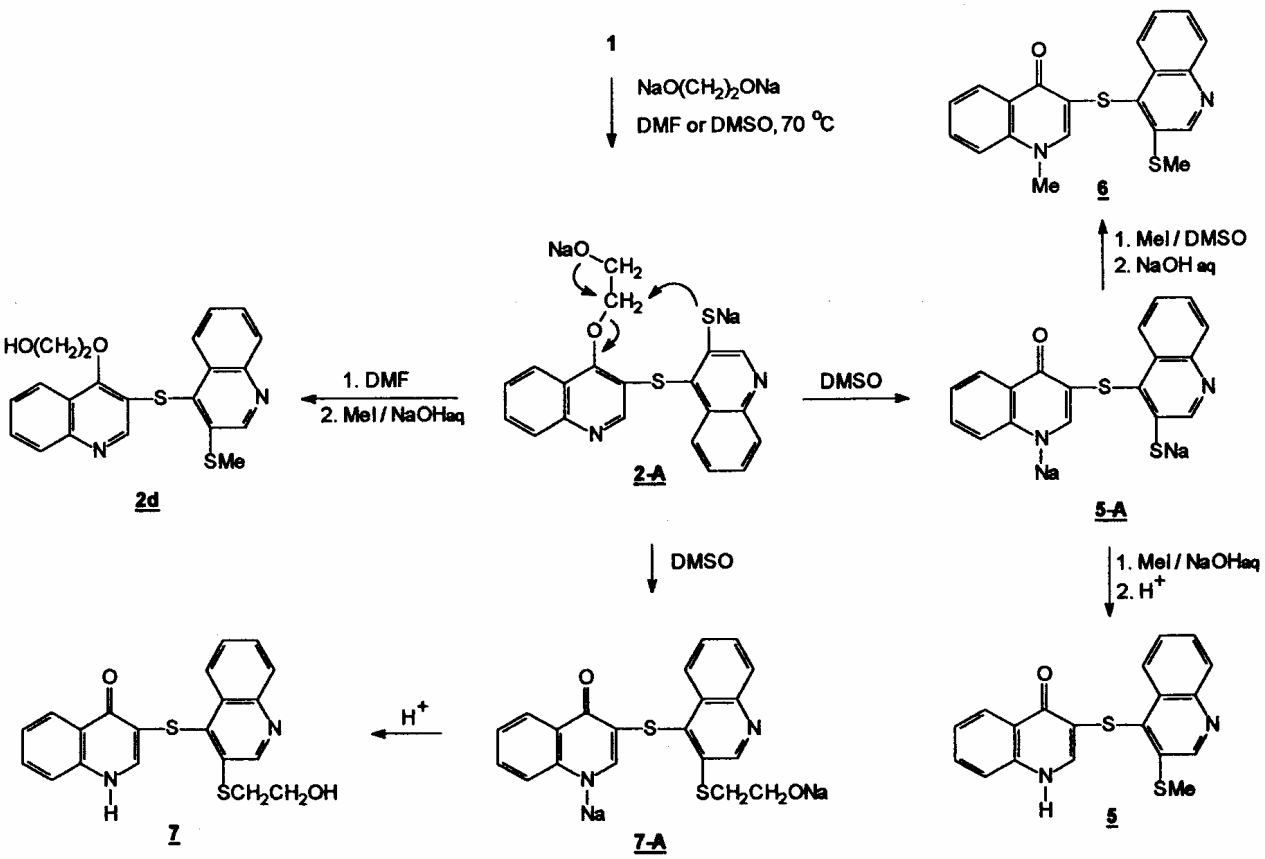


The reaction of **1** with disodium salt of mentioned above glycols proceeded with cleveage of the 4-quinolinyl-sulfur bond and led to disodium salt **(2-A)** which was alkylated with MeI in DMF solution giving sodium salt **(2-B)**. Cleveage of the 4-quinolmyl-sulfur bond in **2-B** may lead to salt **(3-A)**. This one after *S*-methylation in DMF solution would produce product **(3)**. Monosodium salt **(2-B)** may also react with other molecule of disodium salt of giycol to form disodium salt **(4-A)** and sodium salt **(4-B)** which after *S*-methylation by methyl iodide in 10%, aqueous sodium hydroxide gave sulfides **(4)**. We have also observed that the reaction of **1** with monosodium salts of giycol practically does not occur. For example,

after reaction of **1** with monosodium salt of propylene glycol at 70 °C in DMF solution, followed by *S*-methylation in aqueous solution the product **(2a)** in 8 % yield was isolated and unreacted **1** (87 %) was recovered. This would suggest that probably the monoanion of glycol as nucleophile is deactivated through solvation by free hydroxyl group deriving from glycol.

The reaction of **1** with disodium salt of ethylene giycol performed in DMF solution (procedure A) at 70 °C in 0.5 h resulted in giving the sulfide **(2d)** (26 %) and unreacted starting material (**1)** (65 %). The prolongation of the reaction time up to 2 h increased the yield of **2d** (34 %) with decreasing the recovery of the unreacted substrate **1** to 42%. We found that a change in solvent from DMF to DMSO gave unexpected result; from this reaction two products were isolated, which were identified as *N*-unsubstituted quinolones **(5)** and **(7)** in 62 and 11% yields, respectively. It was observed that under these conditions the thioquinanthrene **(1)** was completely consumed. The products can be readily accounted for according to the reaction pathways outlined in Scheme 2. From the structure of the products it could be assumed that this process is the result of two consecutive reactions: a nucleophilic aromatic substitution, which affords the disodium salt **(2-A)** and the nucleophilic aliphatic substitution, which is effected mainly by the alkoxide anion giving salt **(5-A)**. This one after *S*-methylation in aqueous solution gave sulfide **(5)**.

Scheme 2



Formation of the small amount of product **(7)** may be explained by the participation of the 3'-thiolate function of disodium salt **(2-A)** in the dealkylation proccss. Alkylation of disodium salt **(5-A)** directly in DMSO solution with two equivalent of methyl iodide gives the *N*-and *S*-methylated quinolone **(6)** in 58 % yield. It is interesting that under the experimental conditions employed the dealkylation process occurred very easily. This fact may suggest that this conversion, especially in alkaline solution, probably proceeds through an intramolecular nucleophilic substitution in which alkoxide anion acts as a conventional neighboring group participator.[7] The formation of **5** was previously observed in the reaction of **1** with potassium methoxide under similar conditions.[3,8] The dealkylation of aryl alkyl ethers and thioethers has been recently reported as convenient method for the synthesis of phenols and thophenols, which also includes examples of reactions carried out on quinolyl and pyidyl derivatives.[9,10] However, generally these reactions required high temperature, long reaction time and sometime autoclave conditions.[9]

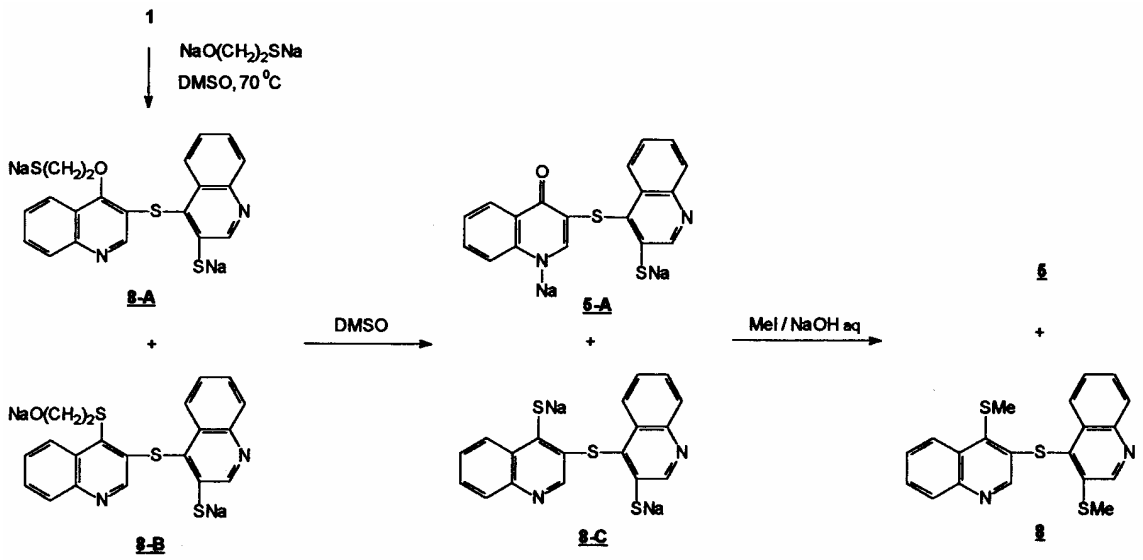
The fact that the reaction of **1** with disodium salt of ethylene glycol occurred much faster in DMSO than DMF under the same oonditions indicate that the type of solvent applied appeared to be important factor determining the reactivity of disodium salt of ethylene glycol towards **1**. It is well known that specific solvation of alkali metal cations by dipolar aprotic solvents involves great enhancement of the reactivity of the alkoxide anion as a nucleophilic agent.[11] On the other hand there was no information in the literature on the reactivity of disodium salt of glycols (as binucleophilic agent) in the dipolar aprotic solvents. We assume that the increase in the reactivity of the disodium salt of ethylene glycol may be due to the increase of free dianions formation, which increase with the solvent polarity. Therefore, the dielectric constant (ε) and a parameter of solvent dipolarity/polarizability (π*) which are higher for DMSO (ε=46.4, π*=1.0) than for DMF (ε=36.7 and π*=0.88) [11] can explain this effect and the fact that the reaction take place more rapidly in DMSO. In order to investigate the influence of the solvent some experiments with mixtures containing DMSO and DMF were performed (procedure A). The data in Table 2 illustrate that the reaction of **1** with disodium salt of ethylene glycol was very efEcient in DMSO neat. In the mixture of DMSO and DMF the conversion of **1** increases with increasing percentage of DMSO in the mixture

Table 2. The Influence of Solvent on the Reactivity of Disodium Salt of Ethylene Glycol towards Thioquinanthrene **(1)** at 70℃.

No.	Mixture of Solvent (v/v)	Products (Yields %)
1	DMSO	**5** (62), **7** (11)
2	DMF/DMSO 1 : 1	**2d** (28), **5** (24), **1**(22)
3	DMF/DMSO 3 : 1	**2d** (24), **5** (11), **1**(39)
4	DMF/DMSO 12 : 1	**2d** (24), **1** (58)
5	DMF	**2d** (26), **1** (65)

The obtained results promptod us to carry out the reaction of **1** with disodium salt of thioethylene giycol as binucleophilic agent containing two different reaction sites, i.e. *O*- and *S*-centre. The reaction was performed in DMSO solution and after *S*-methylation (procedure A) gave two products. One of them was isolated from aqueous sodium hydroxide by extraction and was identified as sulfide **(8)** (21%) The second, quinolone **(5)** (43%), was obtained from the precipitate resulting after neutralization of the aqueous layer after extraction. These results are interpreted by the mechanism described in Scheme 3 . The reaction of **1** with disodium salt of thioethylene glycol yield salts **(8-A)** and **(8-B)**, formed as a consequence of attack by *S*-centre and *O*-centre at the C-4 of thioquinanthrene **(1)**. These salts undergo dealkylation to provide the corresponding disodium salts **(5-A)** and **(8-C)** which after *S*-methylation in aqueous solution give **5** and **8**. The predominant formation of quinolone **(5)** can be explained as a result of faster *O*-dealkylation **(8-A)** than *S*-dealkylation **(8-B)** rather than the different behavior of *O*- and *S*-sites of dianion of thioethylene glycol in nucleophilic opening of the 1,4~dithiln ring in thioquinanthrene **(1)**. This result seems to be proved by the literature data indicating that ArOMe dealkylates faster than ArSMe. [10]

Scheme 3



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 spectrometer at 300 MHZ in deuteriochloroform. EI MS spectra were run on a LKB GC 2091 spectrometer. FAB MS spectra were recorded on Finnigan MAT 95 spectrometer in FAB mode (Cs^{+}, 13keV, nba). TLC was performed on silica gel 60 254F plates (Merck) using a mixture of chloroform and ethanol (15: l, v/v) as an eluant. All solvents and glycols were dried and distilled before use. Mono- and disodium salts of glycols were prepared from

corresponding glycols and sodium hydride in boiling dioxane. All reactions were performed under nitrogen. Thioquinanthrene **(1)** was obtained by exhaustive sulfurization of quinoline with elemental sulfur and recrystallized from DMF, mp 314-315 ^{o}C. [12]

General procedure for the reaction of thioquinanthrene **(1)** with mono- and disodium salts of glycols.

Procedure A

A suspension of thioquinanthrene **(1)** (0.64 g, 2.0 mmol) and mono- or disodium salt of glycol (3.0 mmol) and dry DMF or DMSO (12 mL) was stirred at 70 °C for 30 min under nitrogen. The solution was then cooled down to rt and poured into 35 mL of 10 % aqueous sodium hydroxide. Possible unreacted thioquinanthrene **(1)** was filtered off and then methyl iodide (0.31g, 2.2 mmol) was added dropwise to the aqueous layer and mixture was stirred for 1 5 min. The mixture was extracted with 3 x 10 mL of chloroform. The combined organic layers were washed with water, dried with anhydrous magnesium sulfate and evaporated *in vacuo*. The crude product was separated by column chromatography (silica gel 60, 230-400 mesh, chloroform-ethanol 15 : 1 , v/v) and crystallized. The aqueous layer after extraction was neutralized with 15% hydrochloric acid. The resultant solid was filtered off, washed with water and air-dried to give crude product which was crystallized from DMF to yield pure quinolone with mp 278-280 ^{o}C, in agreement with our previously reported data.[2]

Procedure B

A suspension of thioquinanthrene **(1)** (0.64 g 2.0 mmol) and disodium salt of glycol (3 .0 mmol) and dry DMF or DMSO (12 mL) was stirred at 70 ^{o}C for 30 min under nitrogen. Clear solution was then cooled down to rt and methyl iodide (0.60 g, 4.2 mmol) was added dropwise during 30 min. The reaction mixture was stirred for **1** h and then poured into 35 mL of 10% aqueous sodium hydroxide. The mixture was extracted with 3 x 10 mL of chloroform. The combined organic layers were washed with water, dried with anhydrous magnesium sulfate and evaporated *in vacuo*. The crude product was separated by column chromatography (silica gel 60, 230-400 mesh, chloroform-ethanol 1 5 : 1 , v/v) and crystallized.

4- (3-Hydroxypropoxy)- 3'-methylthio-3,4'-diquinolinyl sulfide **(2a)**: mp 130-132 ^{o}C (ethanol).EIMS(15 eV), m/z (rel. intensity): 408(M^{+}, 100), 350(M-$CH_2CH_2CH_2O$ 16.8), 303(M-SCH_3-$CH_2CH_2CH_2O$, 49.7). ^{1}H NMR ($CDCl_3$) δ : 2.21(q, J=6.0 Hz, 2H, C**H**$_2$), 2.57(s, 3H, C**H**$_3$S), 4.05(t, J=6.0 Hz,2H,C**H**$_2$O), 4.50(t, J=6.0 Hz, 2H, C**H**$_2$O), 7.49-8.34(m, 8H, Ar-**H**), 8.00(s, 1H, **H**-2), 8.78(s, H, **H'**-2). *Anal*. Calcd for $C_{22}H_{20}N_2O_2S_2$: C 64.69, H 4.94, N 6.86, S 15.67. Found: C 64.51, H 4.83, N 7.01, S 15.86.

4- (4-Hydroxybutoxy)- 3'-methylthio-3,4'-diquinolinyl sulfide **(2b):** mp 122-123 ^{o}C (ethanol). EI MS(15 eV), m/z (rel. intensity): 422(M^{+}, 32.5), 350(M-$CH_2CH_2CH_2CH_2O$, 75.9), 303(M-SCH_3-CH_2-CH_2-CH_2 C**H**$_2$O, 100).^{1}H NMR ($CDCl_3$) δ : 1.93(m, 2H, C**H**$_2$), 2.05(m, 2H, C**H**$_2$), 2.60(s, 3H, C**H**$_3$S), 3.80(br s, 2H, C**H**$_2$O), 4.40(t, J=6.7 Hz, 2H, C**H**$_2$O), 7.46-8.38(m, 8H, Ar-**H**), 8.04(s, 1H, **H**-2), 8.82(s, H, **H'**-2). *Anal.* Calcd for $C_{23}H_{22}N_2O_2S_2$: C 65.38. H 5.25, N 6.63, S 15.17. Found: C 65. 11, H, 5.33, N 6.49, S 15.11.

4- [2- (2-Hydroxyethoxy) ethoxy]-3 '-methylthio-3 ,4'-diquinolinyl sulfide **(2c)**: mp 157-158 ^{o}C (ethanol). EI MS (15 eV), m/z (rel. intensity): 438(M^{+}, 37.2), 378(M-OCH_2CH_2O, 46.8). ^{1}H NMR ($CDC1_3$) δ: 2.54(s, 3H, C**H**$_3$S), 3.95-4.63(m, 8H, 4 x C**H**$_2$O), 7.41-8.33(m, 8H, Ar-**H**), 8.02(s, 1H, **H**-2), 8.73(s, H, **H**'-2). *Anal*. Calcd for $C_{23}H_{22}N_2O_3S_2$: C 63.00, H 5.06, N 6.39, S 14.60. Found: C 63.22, H 4,48, N 6.45, S 14.73.

4- (2-Hydroxyethoxy)- 3'-methylthio-3 ,4'-di quinolinyl Isulfide **(2d)**: mp 161-162 ^{o}C (ethanol). EI MS (15 eV), m/z (rel. intensity): 394(M^{+}, 100), 350(M-CH_2CH_2O, 10.8), 303(M-SCH_3-CH_2CH_2O, 36.8). ^{1}H NMR ($CDC1_3$) δ: 2.59(s, 3H; C**H**$_3$S), 4.09(q, J=4.2 Hz, 2H, C**H**$_2$O), 4.51(t J=4.2 Hz, 2H, C**H**$_2$O), 7.54-8.38(m, 8H; Ar-**H**), 8.06(s, 1H, H-2), 8.82(s, H, **H**'-2). *Anal*. Calcd for $C_{21}H_{18}N_2O_2S_2$: C 63.95, H 4.60, N 7.1 1, S 16.23. Found: C 64.05, H 4.43, N 6.88, S 16.03.

l,3-Bis[4-(3-methylthioquinolinyloxy)]propane (**3a**): mp 118-119 ^{o}C (ethanol). MS FAB (+VE), m/z (rel. intensity): 423(M^{+}+1, 43.5%). ^{1}H NMR ($CDC1_3$) δ: 2.54(s, 6H, 2 x C**H**$_3$S), 2.56(q, J=6.2 Hz, 2H, C**H**$_2$), 4.63(t, J=6.2, 4H, 2 x C**H**$_2$O), 7.47-7.69(m, 4H, 2 x **H**-6 and 2 x **H**-7), 8.05-8.11(m, 4H, 2 x **H**-5 and 2 x **H**-8), 8.83(s, 2H 2 x **H**-2). *Anal*. Calcd for $C_{23}H_{22}N_2O_2S2_2$: C 65.38, H 5.25, N 6.63, S 15.17. Found: C 65.20. H 5.36, N 6.45, S 15.32.

l,4-Bis[4- (3-methylthioquinolinyloxy)] butane (**3b**): mp 97-98 ^{o}C (ethanol). EI MS (15 eV), m/z (rel. intensity): 436(M^{+}, 11.8), 422(M-CH_2, 21.8), 246(M-$C_{10}H_8NOS$, 100). ^{1}H NMR ($CDC1_3$) δ: 2.56(s, 6H, 2 x C**H**$_3$S), 2.56(q, J=6.2 Hz, 2H, C**H**$_2$), 4.63(t, J=6.2 Hz, 4H, 2 x C**H**$_2$O), 7.51-7.71(m, 4H; 2 x H-6 and 2 x **H**-7), 8.05-8.12(m, 4H, 2 x H-5 and 2 x H-8), 8.83(s, 2H, 2 x **H**-2). *Anal* .Calcd for $C_{24}H_{24}N_2O_2S_2$: C 66.04, H 5.55, N 6.42, S 14.66. Found: C 66.12, H 5.62, N 6.27 S 16.45.

l,5-Bis[4- (3-methylthioquinolinyloxy)]-3-oxapentane (**3c**): mp 63-64 ^{o}C (ethanol). EI MS (15 eV), m/z (rel. intensity): 452(M^{+}, 14.8), 437(M-CH_3, 52.5), 262(M-$C_{10}H_8NOS$, 100). ^{1}H NMR ($CDC1_3$) δ : 2.56(s, 6H, 2 x C**H**$_3$S), 4.01-4.04(m, 4H, 2 x C**H**$_2$O), 4.47-4.50(m, 4H, 2 x C**H**$_2$O), 7.43-7.67(m, 4FL 2 x **H**-6 and 2 x **H**-7), 8.03-8.24(m, 4H, 2 x **H**-5 and 2 x **H**-8), 8.82(s, 2H, 2 x **H**-2). *Anal* .Calcd for $C_{24}H_{24}N_2O_3S_2$: C 63.70, H 5.35, N 6, 19, S 14.14. Found: C 63.81, H 5.27, N 6.12, S 14.28.

4- (3-Hydroxypropoxy) -3 -methylthioquinoline) (**4a**): mp 57-58^{o}C (ethanol). EI MS (15 eV),m/z(rel. intensity): 249 (M^{+}, 61.5), 191(M-$CH_2CH_2CH_2O$, 100). ^{1}H NMR ($CDC1_3$) δ: 2.18(q, J=6.0 2H, C**H**$_2$), 2.56(s, 3H, C**H**$_3$S), 4.08(t, J=6.0 Hz, 2H, C**H**$_2$O), 4.38(t, J=6.0 Hz, 2H, C**H**$_2$O), 7.51-7.69(m, 2H, **H**-6 and **H**-7), 8.04-8.09(m, 2H**,** **H**-5 and **H**-8), 8.81(s, H, **H**-2). *Anal.* Calcd for C_{13}**H**$_{15}NO_2S$:C 62.63, H 6.07, N 5.62, S 12.84. Found: C 62.81. H 6.15, N 5.54, S 12.72.

4- (3-Hydroxypropoxy) -3 -methylthioquinoline) (**4b**): mp 60-67^{o}C (ethanol). EI MS (15 eV),m/z(rel. intensity): 263 (M^{+}, 32.2), 191(M-$CH_2CH_2CH_2CH_2O$, 100). ^{1}H NMR ($CDC1_3$)δ: 1.85-2.09(m, 4H, 2 x C**H**$_2$), 2.56(s, 3H. C**H**$_3$S), 3.81(t,J=6.2 Hz, 2H, C**H**$_2$O), 4.30(t, J=6.2 Hz, 2H, C**H**$_2$O), 7.51-7.69(m, 2H, **H**-6

and **H**-7), 8.04-8.09(m, 2H, **H**-5 and **H**-8), 8.81(s, H, **H**-2). *Anal*. Calcd for $C_{14}H_{17}NO_2S$: C 63. 85,H 6.51, N 5,32, S 12.15.Found: C 63.**7212**, H 6.60, N 5.18, S 12.24,

4-[2-(2-Hydroxyethoxy) -ethoxy]-3-methylthioquinoline (**4c**): oil. EI MS (15 eV), m/z (rel.intensity): 279 (M^+, 22.2), 191(M-OCH_2CH_2O,54.4). ^{1}H NMR ($CDC1_3$) δ: 2.57(s, 3H, C**H**$_3$S), 3.68-4.49(m, 8H, 4 x C**H**$_2$O), 7.53-7.71(m, 2H, **H**-6 and **H**-7), 8.05-8,20(m, 2H, **H**-5 and **H**-8), 8.84(s, H, **H**-2). *Anal*. Calcd for $C_{14}H_{17}NO_3S$. C 60.20, H 6.14, N 5.02, S11.46. Found: C 60.03, H 6. 18, N 5. 14, S 11.61.

l ,4-Dihydro-4-oxo-3'-methylthio-3, 4'-diquinolinyl sulfide (**5**) mp 278-280 °C (DMF), lit.,[2] mp 278-280 °C

l-Methyl- 1,4-dihydro-4-oxo-3'-methylthio-3,4'-diquinolinyl sulfide (**6**) mp 241-242 °C (DMF), lit., [2] mp 241-242 °C.

l,4-Dihydro-4-oxo-3'-(2-hydroxyethylthio)- 3,4'-diquinolinyl sufide (**7**): mp 285-287 °C (DMF). FAB MS (+VE), m/z (rel.intensity): 381(M +1, 85.6). ^{1}H NMR ($CDC1_3$) δ: 3.65(q, J=6.4 Hz, 2H, C**H**$_2$O), 5.03(t, J=6.4 Hz, 2H, C**H**$_2$S), 7.38-8.48(m, 8H, Ar-**H**), 7.73(s, 1H, **H**-2), 8.94(s, H, **H**'-2), 12.04(br s, 1H; N**H**). *Anal*. Calcd for $C_{20}H_{16}N_2O_2S_2$: C 63.15, H 4.24, N 7.37, S 16.82. Found: C 63.32, FL 4.14, N 7.25, S 17.02

3' ,4-Dimethylthio-3,-4'-diquinolinyl sulfide (**8**): mp 104-l05 °C (ethanol), lit., [13,14] mp 104-105 °C.

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