Oligomers with Four 3,4-Quinolinediyl Units and α,ω-Bis (4-chloro-3-quinolinylthio)alkanes [1]

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Starting from the reaction of thioquinanthrene **1** with sodium methoxide followed by the reaction with α,ω-dihalogenoalkanes, title bis-methoxy oligomers **4a-c** with four 3,4-quinolinediyl units were prepared (40-91%). Acid catalysed hydrolysis of methoxy groups in **4a-c** gave tetramers **5a-c** (46-94%) with two 4(1*H*)-quinolinone functions. The reactions of bis-quinolinones **5a-c** with phosphoryl chloride in DMF run as deoxo-chlorination and afforded title dichlorotetramers **6a-c** (51-66%) with 4-chloroquinolinyl groups. The treatment of bis-methoxy tetramers **4a-c** with boiling phosphoryl chloride led to title α,ω-bis(4-chloro-3-quinolinylthio)alkanes **7a-c** (52-56%) and thioquinanthrene (65-70%).

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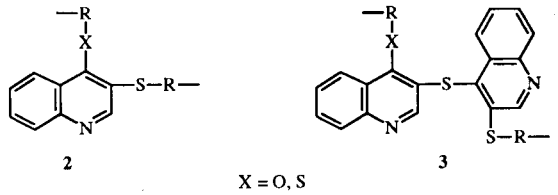
Introduction.

Reactions of thioquinanthrene **1** (*i.e.* 1,4-dithiino-[2,3-*c*:5,6-c']diquinoline) with alkoxides and alkanethiolates open way to the preparation of bifunctional compounds containing 4-substituted-3-quinolinylthio- **2** or 4-substituted-3'-thio-3,4'-diquinolinyl sulfide **3** units [2,3,4]. The later may be formally used in the construction of polymeric or macrocyclic compounds with 3,4-quinolinediyl moieties. As a source of the unit **2** or **3** could be used 3- or 3'-quinolinethiolates of type **2a** or type **3a** being primary products of the reactions of thioquinanthrene with nucleophiles mentioned above. β-Quinolinethiolates **2a** or **3a** were usually trapped and characterized by means of *S*-alkylation with simple alkylating agents as 3- or 3'-alkylthio derivatives of type **2b** or **3b**.

Scheme 1



2 X = O, S **3**

2a, X = O or S, -S-R- = SNa
2b, X = O or S, -R = alkyl
2c, X = O, -R- = alkyl-
2d, -R-X = alkyl-O, -S-R- = SNa

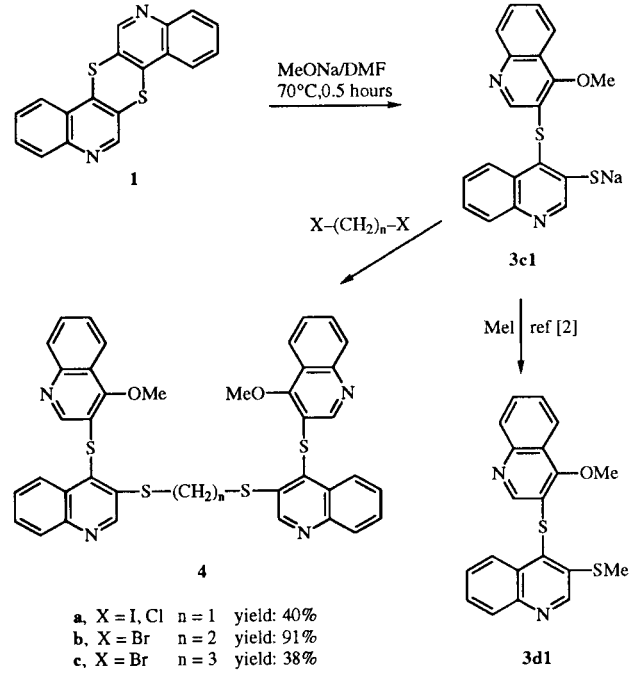
3a, X = O or S, -S-R- = SNa
3b, X = O or S, -R = alkyl
3c, -R-X = alkyl-O, -S-R- = Na-S
3d, -R-X = alkyl-O, -R-S = alkyl-S)
3e, -R-X = Cl, -R-S = alkyl-S)

Treatment of 3'-quinolinethiolates of type **3a** with α,ω-dihalogenoalkanes linked simultaneously two molecules of **3** and afforded oligomeric compounds of type **4** with four 3,4-quinolinediyl units (see Scheme 2). Compounds **4** were then hydrolysed to bis-quinolinones **5**. Further reactions of **5** with phosphoryl chloride/DMF system gave 4,4-dichloro-tetramers **6** but those of **5** or **6** with boiling phosphoryl chloride afforded title α,ω-bis(4-chloro-3-quinolinylthio)alkanes **7** (Scheme 3).

Results and Discussion.

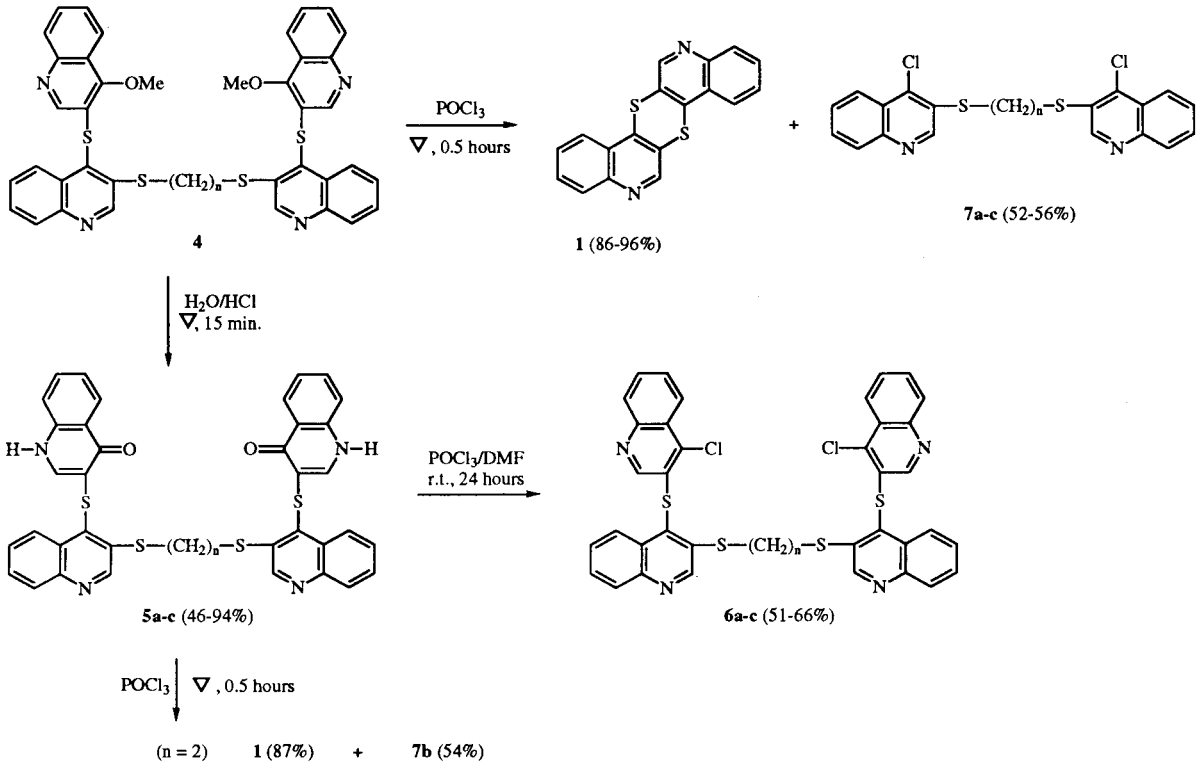
As it was demonstrated previously [2,3], the reactions of thioquinanthrene **1** with sodium alkoxides performed in DMSO or DMF solutions run by the cleavage of the γ-quinolinyl sulfur bond in 1,4-dithiin ring of thioquinanthrene with alkanolate anion to form sodium 4-(4-alkoxy-3-quinolinylthio)-3-quinolinylthiolates **3c** (-R-X = alkyl-O, -RS = Na-S). The later ones were then alkylated after dilution of the reaction mixture with aqueous sodium hydroxide or also directly in DMF solution to 4-alkoxy-3'-alkylthio-3,4'-diquinolinyl sulfides **3d** (-R-X = alkyl-O, -R-S = alkyl-S). The same procedures applied to the compounds **3d** (as γ-quinolinyl sulfides) resulted in 4-alkoxy-

Scheme 2



a, X = I, Cl n = 1 yield: 40%
b, X = Br n = 2 yield: 91%
c, X = Br n = 3 yield: 38%

Scheme 3



3-(alkylthio)quinolines **2c** (-R-X = alkyl-O, -R-S- = alkyl-S-) and sodium 4-alkoxy-3-quinolinethiolates **2d** (-R-X = alkyl-O, -S-R- = SNa). Removal of the neutral compounds **2c** by extraction followed by *S*-alkylation of remaining thiolates **2d** gave two molecules of 4-alkoxy-3-(alkylthio)quinolines **2c**. Furthermore, both γ-quinolinyl-sulfur bond cleavage steps and both *S*-alkylation ones could be combined, and treatment of thioquinanthrene **1** with an excess of alkoxide in DMF followed by addition of two moles of an alkylating agent run as four stage (alkoxidative cleavage of the 4-quinolinyl-sulfur bond in thioquinanthrene → *S*-alkylation of 3-quinolinethiolates **3c** formed → alkoxidative cleavage of the 4-quinolinyl-sulfur bond in 4-alkoxy-3'-alkylthio-3,4'-diquinolinyl sulfides **3d** → *S*-alkylation of 3-quinolinethiolates **2d** formed) but one-pot procedure directly to 4-alkoxy-3-(alkylthio)quinolines **2c** [3]. One would therefore expect that when a double alkylating agent, such as α,ω-dihalogenoalkane is used along the lines of the one-pot procedure mentioned above, thioquinanthrene **1** ought to be converted to α,ω-bis(4-methoxy-3-quinolinylthio)alkanes **9** (X = X = OMe) as a result of the *S*-alkylation of sodium 4-alkoxy-3-quinolinethiolates **2d1** (R = Me). However, the reaction has been discontinued at the stage of *S*-alkylation of **3d** (-R-X = alkyl-O, -R-S = alkyl-S) and gave mainly the oligomers with four 3,4-quinolinediyl units of type α,ω-bis[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]alkanes **4**.

It indicates that compounds **4** did not react with an excess of sodium methoxide, *i.e.* that the second γ-quinolinyl-sulfur bond derived from thioquinanthrene remains unsplitted. In fact, though 4-methoxy-3'-methylthio-3,4'-diquinolinyl sulfide **3d1** (-R-X = methyl-O, -R-S = methyl-S) is completely consumed in the reaction with sodium methoxide at 20° for 30 minutes, oligomers **4** are completely stable toward the action of sodium methoxide in DMF at 70° for 4 hours. In the case of the reactions with methylene chloride and propylene bromide, oligomers **4a** and **4c** were accompanied with some amounts of 4-methoxy-3'-(ω-halogenoalkylthio)-3,4'-diquinolinyl sulfides **3d2**. They were detected by the reaction with silver nitrate reagents as well as by spectral analysis. However we could not isolate them in a pure state.

The spectral properties of the bis-methoxy tetramers **4** are very close to those of 4-alkoxy-3'-alkylthio-3,4'-diquinolinyl sulfides **3d** as the signals of α-quinolinyl protons of 4-methoxyquinoline fragments in **4a-c** were observed at δ_H 8.06-8.09 ppm versus δ_H 8.11 ppm for 4-methoxy-3'-methylthio-3,4'-diquinolinyl sulfide **3d1** [2,5], and the signals of α-quinolinyl protons of 3,4-quinolinediyl bis-sulfide fragments were recorded at 8.83 ppm [2,5] for the reference compound **3d1** and at 8.71-8.91 ppm for **4a-c**. Also the chemical shift values of the 4-methoxy groups and benzene rings protons of **4a-c** fit well those of 4-methoxy-3'-methylthio-3,4'-diquinolinyl sulfide **3d1** [2,5].

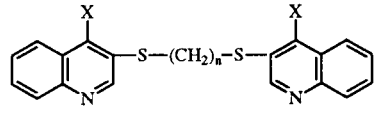
As in the case of previously reported 4-alkoxy-3-quinolinyl sulfides **2c** and 4-alkoxy-3'-alkylthio-1,4'-diquinolinyl sulfides **3d** [6], 4-alkoxyquinolinyl substituent in α,ω-bis-methoxy oligomers **4** could be easily hydrolysed (41-94%) in aqueous acidic medium to form 4(1*H*)-quinolinone fragments of bis-quinolinones **5**. Their ^{1}H nmr spectral data also are very close to those of 1,4-dihydro-4-oxo-3-(methylthio)-3,4'-diquinolinyl sulfide **8**, as the signals of α-quinolinonyl protons of 4-quinolinone fragments in **5a-c** were observed at δ_H 7.64 ppm versus δ_H 7.73 ppm for 3,4'-diquinolinyl sulfide **8** [2], and the signals of α-quinolinyl protons of 3,4-quinolinediyl bis-sulfide fragments were recorded at 8.85 ppm [2] for reference compound **8** and at 9.01 ppm for **5a-c**.

For purpose of the preparation of dimers with two potentially reactive 4-chloroquinolinyl substituents, the methoxy-oligomers **4a-c** and bis-quinolinone ones **5a-c** were treated with phosphoryl chloride as reported previously [6]. The reactions of **4a-c** and **5a-c** with boiling phosphoryl chloride led to α,ω-bis(4-chloro-3-quinolinyl) alkanes **7a-c** in quite good yields (50-56%) and thioquinanthrene (65-70%). On the other hand, when compounds **4a-c** or **5a-c** were treated with the phosphoryl chloride/DMF system at 20°, α,ω-bis[4-(4-chloro-3-quinolinylthio)-3-quinolinylthio]alkanes **6a-c** were obtained in yields of 51-66%.

Thus, the reactions of tetramers **4a-c** and **5a-c** with phosphoryl chloride occur in both cases as those reported for respective 4-substituted-3,4'-diquinolinyl sulfides [6].

Final Conclusions.

Reactions of thioquinanthrene **1** with sodium methoxide followed by treatment with α,ω-dihalogenoalkanes X-$(CH_2)_n$-X are a source of α,ω-bis(4-substituted-3-quinolinylthio)alkanes **4**, **5**, **6** and **7**. Transformation of **4** to **5** and **5** to **6** occur by internal changes in or as replacement of 4- and 4'- substituents remaining common skeleton of **4**, **5** and **6** unaffected.



4, X = X = 4-Methoxy-3-quinolinylthio-
5, X = X = 1,4-dihydro-4-oxo-3-quinolinylthio-
6, X = X = 4-Chloro-3-quinolinylthio-
7, X = X = Cl
9, X = X = OMe

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 (300 MHz) spectrometer in deuteriochloroform or DMSO-d_6 solvents with tetramethylsilane as the internal standard and chemical shifts reported in ppm (δ) and J values in Hz. EI mass spectra were run on a LKB GC 2091 spectrometer at 70 eV i 15 eV. FAB mass spectra were recorded on Finnigan MAT 95 spectrometer in FAB mode (Cs^+, 13 keV, nba).

Thin layer chromatography was performed on silica gel 60 254F plates (Merck) using a mixture of chloroform and ethanol (20:1, v/v) as an eluent.

Thioquinanthrene **1** was obtained by exhaustive sulfurization of quinoline with elemental sulfur [7].

Reactions of Sodium 4-(4-Methoxy-3-quinolinylthio)-3-quinolinylthiolate **3c** with α,ω-Dihalogenoalkane: (previously reported [2,3] procedure for the preparation of thiolate **3c** was used). (Details concerning α,ω-dihalogenoalkanes applied are presented in Scheme 2).

A suspension of thioquinanthrene **1** (3.18 g, 10 mmoles), sodium methoxide (30 mmoles) and dry DMF (35 ml) was stirred at 70° for 30 minutes, *i.e.* up to dissolution of **1**. Clear solution was then cooled down to 20° and α,ω-dihalogenoalkane (12 mmoles) as an alkylating agent was added dropwise at 20° during 30 minutes. The reaction mixture was stirred for 30 minutes and then poured into 150 ml of 5% aqueous sodium hydroxide. The solid was filtered off, washed with water and air-dried.

The product was purified by column chromatography on silica gel 40 (70-230 mesh), using a mixture of chloroform and ethanol (20:1, v/v) as an eluent. The eluate (R_f value *ca.* 0.2-0.3) was evaporated to dryness and the residue was crystallized from DMF to give pure α,ω-bis[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]alkanes **4**.

Bis[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]methane (**4a**).

This compound had mp 142-143°, yield 40%; ^{1}H nmr (deuteriochloroform): δ 4.02 (s, 6H, 2 x CH_3O), 4.63 (s, 2H, SCH_2S), 7.46-8.30 (m, 16H, Ar-H), 8.06 (s, 1H, H-2), 8.96 (s, 1H, H-2'); ms: FAB (+VE) m/z (relative intensity) 713 (M^++1, 55.3%).

Anal. Calcd. for $C_{39}H_{28}N_4S_4O_2$: C, 65.71; H, 3.96; N, 7.86; S, 17.99. Found: C, 65.87; H, 3.91; N, 7.80; S, 17.85.

1,2-Bis[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]ethane (**4b**).

This compound had mp 195-196°, yield 91%; ^{1}H nmr (deuteriochloroform): δ 3.26 (s, 4H, SCH_2CH_2S), 4.14 (s, 6H, 2 x CH_3O), 7.50-8.38 (m, 16H, Ar-H); 8.06 (s, 1H, H-2), 8.91 (s, 1H, H-2'); ms: FAB (+VE) m/z (relative intensity) 727 (M^++1, 100%).

Anal. Calcd. for $C_{40}H_{30}N_4S_4O_2$: C, 66.09; H, 4.16; N, 7.71; S, 17.64. Found: C, 66.02; H, 4.11; N, 7.66; S, 17.67.

1,3-Bis[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]-propane (**4c**).

This compound had mp 133-136°, yield 38%; ^{1}H nmr (deuteriochloroform): δ 1.96 (m, 2H, $CH_2CH_2CH_2$), 3.14 (t, 4H, J = 7.1 Hz, 2 x SCH_2CH_2), 4.02 (s, 6H, 2 x CH_3O), 7.47-8.38 (m, 16H, Ar-H), 8.09 (s, 1H, H-2), 8.71 (s, 1H, H-2'); ms: FAB (+VE) m/z (relative intensity) 741 (M^++1, 92.7%).

Anal. Calcd. for $C_{41}H_{32}N_4S_4O_2$: C, 66.46; H, 4.35; N, 7.56; S, 17.31. Found: C, 66.34; H, 4.31; N, 7.76; S, 17.45.

Hydrolysis of Bis-methoxy-tetramers **3** to Bis-4-quinolinone-tetramers **5**.

A mixture of α,ω-bis[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]alkane **4** (3 mmoles) and azeotropic hydrochloric acid (20 ml) was heated at reflux for 15 minutes. The solution was then evaporated *in vacuo* to dryness. The residue was neutralized with 5% aqueous sodium bicarbonate solution (20 ml). The resultant solid was filtered off, and air-dried to give crude α,ω-bis[4-(1,4-dihydro-4-oxo-3-quinolinylthio)-3-quinolinylthio]alkane **5**, which was crystallized from DMF to yield pure **5**.

Bis[4-(1,4-dihydro-4-oxo-3-quinolinylthio)-3-quinolinylthio]-methane (**5a**).

This compound had mp 189-192° yield 72%; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 5.19 (s, 2H, SCH_2S), 7.25-8.47 (m, 16H, Ar-H), 7.72 (s, 2H, H-$2_{quinolonyl}$), 9.03 (s, 2H, H-$2'_{quinolinyl}$), 12.07 (broad singlett, 2H, 2 x N-H); ms: FAB (+VE) m/z (relative intensity) 685 (M^++1, 12.5%).

Anal. Calcd. for $C_{37}H_{24}N_4S_4O_2$: C, 64.89; H, 3.53; N, 8.18; S, 18.72. Found: C, 65.01; H, 3.61; N, 8.11; S, 18.58.

1,2-Bis[4-(1,4-dihydro-4-oxo-3-quinolinylthio)-3-quinolinylthio]ethane (**5b**).

This compound had mp 288-289°, yield 94%; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 3.62 (s, 4H, SCH_2CH_2S), 7.36-8.54 (m, 16H, Ar-H), 7.64 (s, 2H, H-$2_{quinolonyl}$), 9.01 (s, 2H, H'-$2_{quinolonyl}$), 12.14 (broad singlett, 2H, 2 x N-H); ms: FAB (+VE) m/z (relative intensity) 699 (M^++1, 5.5%).

Anal. Calcd. for $C_{38}H_{26}N_4S_4O_2$: C, 65.32; H, 3.75; N, 8.02; S, 18.32. Found: C, 65.28; H, 3.71; N, 8.09; S, 18.28.

1,3-Bis[4-(1,4-dihydro-4-oxo-3-quinolinylthio)-3-quinolinylthio]propane (**5c**).

This compound had mp 250-252°, yield 46%; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 1.95 (m, 2H, $CH_2CH_2CH_2$), 3.33 (t, 4H, J = 7.1 Hz, 2 x SCH_2CH_2), 7.06-8.56 (m, 16H, Ar-H), 7.84 (s, 2H, H-$2_{quinolonyl}$), 8.83 (s, 2H, H-$2'_{quinolinyl}$), 12.10 (broad singlett, 2H, 2 x N-H); ms: FAB (+VE) m/z (relative intensity) 713 (M^++1, 4.8%).

Anal. Calcd. for: $C_{39}H_{28}N_4S_4O_2$: C, 65.71; H, 3.96; N, 7.86; S, 17.99. Found: C, 65.64; H, 3.90; N, 7.81; S, 17.90.

Synthesis of Bis-chloro-tetramers **6** from Bis-quinolinones **5**.

A mixture of α,ω-bis[4-(1,4-dihydro-4-oxo-3-quinolinylthio)-3-quinolinylthio]alkane **5** (2 mmoles), phosphoryl chloride (0.55 ml) and dimethylformamide (10 ml) was stirred at room temperature under nitrogen atmosphere for 24 hours and poured into the mixture of water and ice (20 ml). The mixture was then neutralized with conc. aqueous ammonia at 0°. The solid formed was filtered off, washed with water and air-dried. Crude product was then crystallized from dimethylformamide to give the compound **6** in the yields of 51-66%.

Bis[4-(4-chloro-3-quinolinylthio)-3-quinolinylthio]methane (**6a**).

This compound had mp 210-212°, yield 51%; ^{1}H nmr (deuteriochloroform): δ 4.72 (s, 2H, SCH_2S), 7.67-8.40 (m, 16H, Ar-H), 7.84 (s, 2H, H-2), 8.90 (s, 2H, H-2'); ms: FAB (+VE) m/z (relative intensity) 721 (M^++1, 6.2%).

Anal. Calcd. for $C_{37}H_{22}N_4S_4Cl_2$: C, 61.57; H, 3.07; N, 7.76; S, 17.77; Cl, 9.82. Found: C, 61.59; H, 3.12; N, 7.71; S, 17.83; Cl, 9.75.

1,2-Bis[4-(4-chloro-3-quinolinylthio)-3-quinolinylthio]ethane (**6b**).

This compound had mp 220-221°, yield 66%; ^{1}H nmr (deuteriochloroform): δ 3.30 (s, 4H, SCH_2CH_2S), 7.50-8.40 (m, 16H, Ar-H), 7.79 (s, 2H, H-2), 8.90 (s, 2H, H-2'); ms: FAB (+VE) m/z (relative intensity) 735 (M^++1, 14.9%).

Anal. Calcd. for $C_{38}H_{24}N_4S_4Cl_2$: C, 62.03; H, 3.29; N, 7.61; S, 17.43; Cl, 9.64. Found: C, 62.10; H, 3.30; N, 7.66; S, 17.39; Cl, 9.55.

1,3-Bis[4-(4-chloro-3-quinolinylthio)-3-quinolinylthio]propane (**6c**).

This compound had mp 226-230°, yield 56%; ^{1}H nmr (deuteriochloroform): δ 1.99 (m, 2H, $CH_2CH_2CH_2$), 3.19 (t, 4H, J = 6.9 Hz, 2 x SCH_2CH_2), 7.51-8.39 (m, 16H, Ar-H), 7.93 (s, 2H, H-2), 8.84 (s, 2H, H-2'); ms: FAB (+VE) m/z (relative intensity) 749 (M^++1, 4.5%).

Anal. Calcd. for $C_{39}H_{26}N_4S_4Cl_2$: C, 62.47; H, 3.50; N, 7.47; S, 17.10; Cl, 9.46. Found: C, 62.50; H, 3.53; N, 7.56; S, 16.94; Cl, 9.47.

Reaction of α,ω-Bis[4-(4-methoxy-3-quinolinylthio)-3-quinolinylthio]alkanes **4** with Boiling Phosphoryl Chloride.

A mixture of bis-methoxy compound **4** (5 mmoles) and phosphoryl chloride (15 ml) was refluxed for 0.5 hour. Then the excess of phosphoryl chloride was evaporated *in vacuo*. The residue was carefully poured onto ice (30 g) and then neutralized with conc. ammonia at 0-5°. The solid was filtered off, air-dried and boiled with tetrachloromethane (20 ml). The insoluble solid was hot-filtered, air-dried and crystallized from DMF to give thioquinanthrene **1** (86-96%) with mp 310-311°, ref [7] mp 314-315°.

The tetrachloromethane filtrate was evaporated to dryness. The residue was crystallized from ethanol to give α,ω-bis(4-chloro-3-quinolinylthio)alkane **7** in yields of 52-56%.

The same procedure was applied for the transformation of bis-quinolinone **5b** to **7b** (54%) and thioquinanthrene **1** (87%) (see Scheme 3).

Bis(4-chloro-3-quinolinylthio)methane (**7a**).

This compound had mp 156-157°, yield 56%; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 5.24 (s, 2H, SCH_2S), 7.70-7.84 (m, 4H, H-6 and H-7), 8.01-8.10 (m, 4H, H-5 and H-8), 9.04 (s, 2H, H-2); ms: EI (15 eV) m/z (relative intensity) 406 (3.7, M+4), 404 (13.9, M+2), 402 (18.8, M+), 318 (72.9, M-CH_2-2Cl), 208 (100, M-C_9H_5NSCl).

Anal. Calcd. for $C_{19}H_{12}N_2S_2Cl_2$: C, 56.58; H, 3.0; N, 6.95; S, 15.90; Cl, 17.58. Found: C, 56.47; H, 3.05; N, 6.93; S, 15.97; Cl, 17.48.

1,2-Bis(4-chloro-3-quinolinylthio)ethane (**7b**).

This compound had mp 163-165°, yield 53%; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 3.26 (s, 4H, SCH_2CH_2S), 7.50-7.78 (m, 4H, H-6 and H-7), 8.0-8.1 (m, 2H, H-8), 8.4-8.5 (m, 2H, H-5), 8.90 (s, 2H, H-2); ms: EI (15 eV) m/z (relative intensity) 420 (4.0, M+4); 418 (16.1, M+2), 416 (21.7, M^+), 222 (100, M-C_9H_7NSCl), 194 (58.6, M-$C_{11}H_9NSCl$).

Anal. Calcd. for $C_{20}H_{14}N_2S_2Cl_2$: C, 57.56; H, 3.38; N, 6.71; S, 15.36; Cl, 16.99. Found: C, 57.65; H, 3.36; N, 6.67; S, 15.45; Cl, 16.87.

1,3-Bis(4-chloro-3-quinolinylthio)propane (**7c**).

This compound had mp 138-140°, yield 52%; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 2.01 (m, 2H, $CH_2CH_2CH_2$), 3.10 (t, 4H, J = 7.1 Hz, 2 x SCH_2CH_2), 7.67-7.89 (m, 4H, H-6 and H-7), 7.98-8.11 (m, 4H, H-5 and H-8), 8.98 (s, 2H, H-2); ms: EI (15 eV) m/z (relative intensity) 434 (16, M+4), 432 (66.2, M+2), 430 (85, M^+), 236 (100, M-C_9H_7NSCl), 208 (31.8, M-$C_{10}H_9NSCl$).

Anal. Calcd. for $C_{21}H_{16}N_2S_2Cl_2$: C, 58.47; H, 3.74; N, 6.49; S, 14.86; Cl, 16.44. Found: C, 58.57; H, 3.72; N, 6.58; S, 14.81; Cl, 16.32.

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