Reactions of Thioquinanthrene with Sodium Alkanethiolates. The Smiles Rearrangement of Diquinolinyl Sulfides*

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Reactions of thioquinanthrene **1** with sodium alkanethiolates or *S*-alkylisothiouronium salts (in the presence of sodium hydroxide) at 70° in DMSO or DMF yielded 4,4'-dialkylthio-3,3'-diquinolinyl sulfides **3**, which were results of the S–S type of the Smiles rearrangement of primary reaction products - sodium 3-quinolinethiolates **6**. When the reactions were carried out at 20° the products were 3',4-dialkylthio-3,4'-diquinolinyl sulfides **2**.

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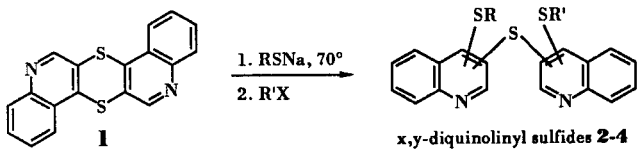
Introduction.

We have previously reported on the opening of the 1,4-dithiin ring in 1,4-dithiino[2,3-*c*:5,6-*c*']diquinoline **1** (a "thioquinanthrene" - the main product of the sulfuration reaction of quinoline [1-5]) with S-, O-, N- and C-nucleophiles [6-10]. The reactions were carried out most often in DMSO at 70°. The primary products (as appropriate quinolinethiolates) were alkylated in aqueous DMSO solution by alkyl halides or sulfates. The product of the reaction of dithiin **1** with sodium methanethiolate was identified by ^{1}H nmr and mass spectra as 3',4-dimethylthio-3,4'-diquinolinyl sulfides **2a** [7]. The spectroscopic equality of both *S*-methyl groups might be fortuitous or sulfide **2a** has symmetrical structure. In this paper we wish to report the results of the systematic investigation on the reactions of dithiin **1** with sodium alkanethiolates.

Results and Discussion.

The reaction of ring opening in dithiin **1** with sodium alkanethiolates or *S*-alkylisothiouronium salts (in the presence of alkali) were carried out in the same condition as mentioned above (70°, DMSO). The use of *S*-alkylisothiouronium salts allowed to avoid working with very odorous alkanethiols. All the products had two quinoline moieties linked by sulfur atom and represented one of *ortho,ortho'*-dialkylthiodiquinolinyl sulfide structures **2**, **3** or **4**.

Scheme 1



1

x,y-diquinolinyl sulfides **2-4**

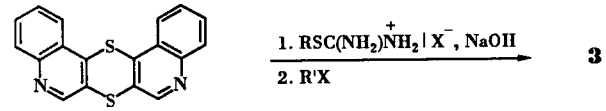
x,y		R	R'
2 3,4'	**a**	Me	Me
3 3,3'	**b**	Et	Et
4 4,4'	**c**	$PhCH_2$	$PhCH_2$
	d	allyl	allyl
	e	Me(Et)	Et(Me)

The ^{1}H nmr spectra of the products alkylated by alkyl halides possessing the same alkyl group as the nucleophile **a-d** showed one two-fold signal of both *S*-alkyl groups and one two-fold signal of both the H-2 protons. The ^{13}C nmr spectra of the products showed the identity of both alkyl groups and both C-2 atoms as well. But the ^{1}H nmr spectrum of the product alkylated by other alkyl halide (the alkyl groups in the nucleophile and in alkyl halide were different) showed two signals of the H-2 protons. What is more the ^{1}H nmr spectrum of the ethylated product of the reaction of dithiin **1** with sodium methanethiolate was identical with the spectrum of the methylated product of reactions of dithiin **1** with sodium ethanethiolate **e** (melting points and tlc data were identical as well). We came to the conclusion that the products of the reaction of dithiin **1** with sodium alkanethiolates at 70° were symmetrical sulfides, *i.e.* 4,4'-dialkylthio-3,3'-diquinolinyl sulfides **3** or 3,3'-dialkylthio-4,4'-diquinolinyl sulfides **4**.

The appropriate 4,4'-diquinolinyl sulfides **4a-c** were synthesized by an independent way in the reactions of 3-alkylthio-4-chloroquinolines with 3-alkylthio-4-quinolinethiones and were not identical with the products obtained from dithiin **1**. It denotes that 3,3'-diquinolinyl sulfides **3** were to be the products of reaction of dithiin **1** with sodium alkanethiolates at 70° instead of the expected sulfides **2** and the Smiles rearrangement took place during the reactions.

In our first paper [5] we stated that thioquinanthrene and its isomer - isothioquinanthrene **5** have two sulfur bridges in the positions 3,4'/3',4 and 3,3'/4,4' respectively. In order to avoid an objection 3,3'-diquinolinyl sulfides **3** could be formed from thioquinanthrene possessing in fact the bridges in the positions 3,3'/4,4' [11] we carried out the reactions of isothioquinanthrene with *S*-alkylisothiouronium salts (in the presence of alkali). In all cases we obtained 3,3'-diquinolinyl sulfides **3a-c**.

Scheme 2

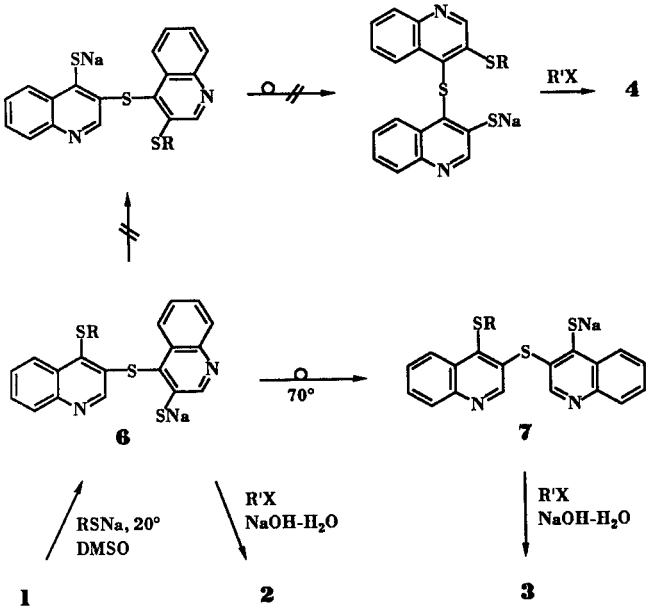


5

These results indicated that the reactions of dithiin **1** with sodium alkanethiolates proceed through a stage of the S-S type of the Smiles rearrangement.

In literature only the S-N type of the Smiles rearrangement was described for substituted azinyl sulfides [12-14] and the S-S type of this rearrangement was unknown [15-19].

Scheme 3



When the reactions of dithiin **1** with sodium alkanethiolates were carried out at 20° the products turned to be unexpectedly unchanged 3,4'-diquinolinyl sulfides **2a-c**. The ^{1}H nmr spectra showed two different signals of the *S*-alkyl groups and two different signals of the H-2 protons. These results suggest that the primary opening products - 3-quinolinethiolates **6** rearrange to 4-quinolinethiolates **7** during the reaction in DMSO.

In order to confirm this suggestion we heated sodium 3-quinolinethiolates **6a-c** at 70° in DMSO for 15 minutes. In all cases we obtained sodium quinolinethiolates **7a-c**, which were characterized by their *S*-alkyl derivatives as sulfides **3a-c**. This rearrangement does not proceed when the solution of sodium 3-quinolinethiolates **6** in DMSO is mixed with aqueous sodium hydroxide and heated at 70° for 30 minutes. In these conditions 3-quinolinethiolate **6a** recyclized to dithiin **1** in 78% yield.

The Smiles rearrangement does not proceed when the alkyl group in the nucleophile is changed into hydrogen. The reactions of dithiin **1** with sodium hydrogen sulfide or sodium sulfide at 70° gave (after alkylation) sulfides **2a-c** as the sole products.

Scheme 4

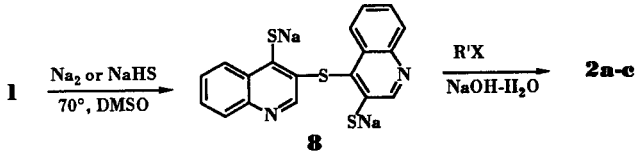


Table 1

Reactions of Dithiins **1** and **5** with *S*-Nucleophiles in DMSO

No.	Dithiin	*S*-Nucleophile	Temp. (°)	Time (minutes)	Alkyl halide	Product (Yield, % respectively)	
1	**1**	MeSNa or salt [a]	70	10	MeI	**3a**	(90), (75)
2	**1**	salt [a] [b]	70	10	MeI	**3a**	(81)
3	**1**	EtSNa or salt [c]	70	10	EtI	**3b**	(78), (56)
4	**1**	$PhCH_2SNa$ or salt [d]	70	10	$PhCH_2Cl$	**3c**	(96), (79)
5	**1**	AllylSNa	70	10	AllylBr	**3d**	(72)
6	**1**	MeSNa or salt [c]	70	10	EtI	**3e**	(80), (53)
7	**1**	EtSNa or salt [c]	70	10	MeI	**3e**	(75), (63)
8	**1**	AllylSNa	150	10	MeI	**3a**	(55)
9	**1**	MeSNa	20	60	MeI	**2a**	(91)
10	**1**	EtSNa	20	60	EtI	**2b**	(80)
11	**1**	$PhCH_2SNa$	20	60	$PhCH_2Cl$	**2c**	(86)
12	**1**	Na_2S or NaHS	70	30	MeI	**2a**	(84), (63)
13	**1**	Na_2S	70	30	EtI	**2b**	(81)
14	**1**	Na_2S	70	30	$PhCH_2Cl$	**2c**	(92)
15	**5**	salt [a]	70	10	MeI	**3a**	(78)
16	**5**	salt [c]	70	10	EtI	**3b**	(73)
17	**5**	salt [d]	70	10	$PhCH_2Cl$	**3c**	(84)

[a] *S*-methylisothiouronium sulfate + sodium hydroxide. [b] in DMF. [c] *S*-ethylisothiouronium bromide + sodium hydroxide. [d] *S*-benzylisothiouronium chloride + sodium hydroxide.

The reported reaction [7] of dithiin **1** with a significant excess of sodium sulfide gave two products: a sulfide which structure was corrected recently as **2a** [20] and 3,4-dimethylthioquinoline.

Nucleophilic aromatic substitution in quinoline compounds occurs mainly in the activated positions 2 and 4. These reactions proceed readily when the compounds possess good leaving groups, for example halogen [21] or methylsulfonyl group [22-23]. There is no report on the nucleophilic displacement of the sulfide substituent in position 3. In the rearrangement discussed anionic sulfide nucleophile in the second quinoline ring substitutes the quinolinylthio group in the position 3 in the first quinoline ring.

It is worth emphasing whereas sodium 3-quinolinethiolates **6** rearrange at 70° in DMSO, sodium quinolinethiolate **8** does not. It is evident that the anionic sulfide substituent in the position 4 in the quinoline ring prevents nucleophilic attack at the C-3 carbon. A study of the mechanism presented is now in progress. The structures of sulfides **2a**, **3a** and **4a** were confirmed by X-ray examination [20,24,25].

Makisumi [26,27] heated 4-allylthioquinoline at 200° without solvent and observed the thio-Claisen rearrangement (the S-C alkyl group migration). Sulfide **3d** heated under the same conditions did not give a thio-Claisen product but products of dealkylation and cyclization - a mixture of dithiins **5** and **1** (3:1, 51% yield). The dealkylation was also observed when dithiin **1** reacted with significant amounts sodium 2-propenethiolate at 150° in DMSO. Unexpectedly the product (after methylation) was sulfide **3a**, what means the dealkylation took place after the Smiles rearrangement of sodium 3-quinolinethiolate **6e**.

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) or a Tesla BS 567A (100 MHz) spectrometers in deuteriochloroform solutions. The ^{13}C nmr spectra were recorded on a Bruker AC 200 (50.3 MHz) spectrometer. Mass spectra were run on a LKB spectrometer using the electron impact method. Thin layer chromatography were performed on aluminium oxide (type E) and silica gel 60 254 F plates (Merck) using methylene chloride and benzene-ethyl acetate (1:1) solution as eluents. Silica gel (100-200 mesh) Merck Kiesel gel 60 was employed for column chromatography. Sodium alkanethiolates were commercial (Aldrich Chemical Co. or Merck) or prepared from commercial alkanethiols and sodium hydride in anhydrous benzene. *S*-alkylisothiouronium salts were prepared from alkyl halides or alkyl sulfate with thiourea [28,29]. 2-Propenethiol was obtained from reaction of alkyl bromide with thiourea as described in reference [30].

Thioquinanthrene **1** was obtained by exhaustive sulfuration of quinoline with elemental sulfur [5]. Isothioquinanthrene **5** was isolated from described above reaction [5] or prepared as described in reference [31].

Reactions of Thioquinanthrene **1** with Sodium Alkanethiolates or *S*-alkylisothiouronium Salts at 70°. General Procedure.

To a suspension of thioquinanthrene **1** (1.6 g, 5 mmoles) in 20 ml of dry DMSO or DMF at 70° sodium alkanethiolate (6 mmoles) or *S*-alkylisothiouronium salt (6 mmoles) with powdered sodium hydroxide (0.48 g, 12 mmoles) was added. The mixture was stirred 10 minutes and then cooled to room temperature. The mixture was poured into 60 ml of 15% aqueous sodium hydroxide. Possibly residual dithiin **1** was filtered and the filtrate was stirred with alkyl halide (7 mmoles). The solid was collected by filtration, washed with water and air-dried. The crude sulfides **3** were purified by column chromatography (silica gel 60, chloroform, chloroform/ethanol 20:1).

4,4'-Dimethylthio-3,3'-diquinolinyl Sulfide **3a**.

This compound had mp 142-143°, lit [7] mp 142-143°; ^{1}H nmr (deuteriochloroform): δ 2.55 (s, 6H, $2SCH_3$), 7.66 (m, 2H, 2H-6), 7.73 (m, 2H, 2H-7), 8.07 (m, 2H, 2H-8), 8.55 (m, 2H, 2H-5), 8.56 (s, 2H, 2H-2), the values of aromatic coupling constants [Hz] are $J_{5,6}$ = 8.3, $J_{5,7}$ = 1.3, $J_{5,8}$ = 0.3, $J_{6,7}$ = 6.9, $J_{6,8}$ = 1.1, $J_{7,8}$ = 8.4; ^{13}C nmr (deuteriochloroform): δ 19.1 (CH_3), 125.5 (C-5), 127.8 (C-6), 129.4 (C-4a) 129.5 (C-7), 130.0 (C-8), 134.2 (C-3), 145.1 (C-4), 146.9 (C-8a), 150.7 (C-2); ms: (15 eV) m/z (relative intensity) 380 (M^+, 63.3); 333 (M-CH_3S, 100); 318 (M-$(CH_3)_2S$, 74.9).

Anal. Calcd. for $C_{20}H_{16}N_2S_3$: C, 63.12; H, 4.24; N, 7.36; S, 25.28. Found: C, 62.91; H, 4.36; N, 7.28; S, 25.04.

4,4'-Diethylthio-3,3'-diquinolinyl Sulfide **3b**.

This compound had mp 88-89°; ^{1}H nmr (deuteriochloroform): δ 1.27 (t, 6H, $2CH_3$), 3.10 (q, 4H, $2SCH_2$, J = 7.4 Hz), 7.66 (m, 2H, 2H-6), 7.73 (m, 2H, 2H-7), 8.07 (m, 2H, 2H-8), 8.59 (m, 2H, 2H-5), 8.56 (s, 2H, 2H-2), the coupling constants as above; ^{13}C nmr (deuteriochloroform): δ 15.0 (CH_3), 30.6 (CH_2), 125.9 (C-5), 127.7 (C-6), 129.4 (C-7), 130.0 (C-8), 130.3 (C-4a), 135.2 (C-3), 143.6 (C-4), 147.0 (C-8a), 150.7 (C-2); ms: (15 eV) m/z (relative intensity) 408 (M^+, 49.3), 347 (M-C_2H_5S, 100), 318 (M-$(C_2H_5)_2S$, 70.9).

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, 4.89; N, 6.74; S, 23.31.

4,4'-Dibenzylthio-3,3'-diquinolinyl Sulfide **3c**.

This compound had 97-98°; ^{1}H nmr (deuteriochloroform): δ 4.19 (s, 4H, $2CH_2$), 7.07-7.18 (m, 10H, $2C_6H_5$), 7.59 (m, 2H, 2H-6), 7.70 (m, 2H, 2H-7), 8.05 (2H, 2H-8), 8.46 (m, 2H, 2H-5), 8.39 (s, 2H, 2H-2), the coupling constants as above; ^{13}C nmr (deuteriochloroform): δ 40.5 (CH_2), 125.8 (C-5), 127.8 (C-6), 129.4 (C-7), 129.9 (C-8), 135.5 (C-4a), 136.6 (C-3), 142.6 (C-4), 146.9 (C-8a), 150.6 (C-2) and 130.1, 128.7, 128.2 and 127.3 (C_6H_5, C_1, C_o, C_m and C_p respectively); ms: (15 eV) m/z (relative intensity) 532 (M^+, 47.8), 409 (M-$C_6H_5CH_2S$, 75.5), 310 (M-$(C_6H_5CH_2)_2S$, 56.5), 91 ($C_6H_5CH_2^+$, 100).

Anal. Calcd. for $C_{32}H_{24}N_2S_3$: C, 72.15; H, 4.54; N, 5.26; S, 18.05. Found: C, 71.76; H, 4.52; N, 4.89; S, 17.73.

4,4'-Diallylthio-3,3'-diquinolinyl Sulfide **3d**.

This compound was a viscous oil; ^{1}H nmr (deuteriochloroform): δ 3.70 (d, 4H, $2SCH_2$, J = 7.3 Hz), 4.84-4.91 (m, 4H, $2CH_2$=), 5.47-5.91 (m, 2H, 2CH=), 7.68 (m, 2H, 2H-6), 7.72 (m, 2H, 2H-7), 8.08 (m, 2H, 2H-8), 8.56 (m, 2H, 2H-5), 8.56 (s, 2H, 2H-2), the coupling constants as above; ^{13}C nmr (deuteriochloroform): δ 39.1 (CH_2), 118.1 (CH_2=), 125.9 (C-5), 127.8 (C-6), 129.4 (C-7), 130.0 (C-8), 132.7 (CH=), 150.7 (C-2); ms: (15 eV) m/z (relative intensity)

432 (M^+, 34.0), 359 (M-C_3H_5S, 47.2), 318 (M-$(C_3H_5)_2S$, 100).

Anal. Calcd. $C_{24}H_{20}N_2S_3$: C, 66.63; H, 4.66; N, 6.48; S, 22.23. Found: C, 66.25; H, 4.64; N, 6.11; S, 21.92.

4-Methylthio-4'-ethylthio-3,3'-diquinolinyl Sulfide **3e**.

This compound had mp 65-66°; ^1H nmr (deuteriochloroform): δ 1.27 (t, 3H, CH_3, J = 7.4 Hz), 2.56 (s, 3H, SCH_3), 3.10 (q, 2H, SCH_2), 7.63-7.80 (m, 4H, 2H-6, 2H-7), 8.07 and 8.08 (m, 2H, 2H-8), 8.56 and 8.58 (m, 2H, 2H-5), 8.53 and 8.56 (2s, 2H, 2H-2), the coupling constants as above; ms: (15 eV) m/z (relative intensity) 394 (M^+, 86.8), 347 (M-CH_3S, 100), 333 (M-C_2H_5S, 49.7), 318 (M-$CH_3SCH_2CH_3$, 91.1).

Anal. Calcd. for $C_{21}H_{18}N_2S_3$: C, 63.92; H, 4.60; N, 7.10; S, 24.38. Found: C, 63.61; H, 4.61; N, 7.01; S, 24.11.

Reaction of Thioquinanthrene **1** with Sodium 2-Propenethiolate at 150°.

The reaction was carried out as mentioned above using thioquinanthrene **1** (1.6 g, 5 mmoles), sodium 2-propenethiolate (1.44 g, 15 mmoles) and methyl iodide (2.0 g, 14 mmoles).

Reaction of Thioquinanthrene **1** with Sodium Alkanethiolates at 20°. General Procedure.

To a suspension of thioquinanthrene **1** (1.6 g, 5 mmoles) in 20 ml of dry DMSO at 20° sodium alkanethiolate (10 mmoles) was added. The mixture was stirred for 60 minutes. Then the mixture was worked-up as described above to give sulfides **2a-c**.

3',4-Dimethylthio-3,4'-diquinolinyl Sulfide **2a**.

This compound had mp 104-105°, lit [7,20] mp 104-105°; ^1H nmr spectrum as in ref [32].

3',4-Diethylthio-3,4'-diquinolinyl Sulfide **2b**.

This compound had mp 95-96°; ^1H nmr (deuteriochloroform): δ 1.34 (t, 3H, CH_3, J = 7.2 Hz), 1.36 (t, 3H, CH_3, J = 7.2 Hz), 3.11 (q, 2H, CH_2), 3.15 (q, 2H, CH_2), 7.40-7.71 (m, 4H, H-6, H-6', H-7, H-7'), 7.84-8.31 (m, 3H, H-5', H-8, H-8'), 8.39-8.58 (m, 1H, H-5) 7.79 (s, 1H, H-2), 8.85 (s, 1H, H-2'); ms: (15 eV) m/z (relative intensity) 408 (M^+, 18.6), 347 (M-C_2H_5S, 100), 318 (M-$(C_2H_5)_2S$, 43.5).

Anal. Calcd. for $C_{22}H_{20}N_2S_3$: C, 64.67; H, 4.93; N, 6.86; S, 23.54. Found: C, 64.29; H, 4.86; N, 6.61; S, 23.28.

3',4-Dibenzylthio-3,4'-diquinolinyl Sulfide **2c**.

This compound had mp 122-123°; ^1H nmr (deuteriochloroform): δ 4.23 (s, 2H, CH_2), 4.26 (s, 2H, CH_2), 7.10 (s, 5H, C_6H_5), 7.12-7.29 (m, 5H, C_6H_5), 7.41-7.63 (m, 4H, H-6, H-6', H-7, H-7'), 7.71 (s, 1H, H-2), 7.85-8.40 (m, 4H, H-5, H-5', H-8, H-8'), 8.85 (s, 1H, H-2'); ms: (15 eV) m/z (relative intensity) 532 (M^+, 19.1), 409 (M-$C_6H_5CH_2S$, 100), 318 (M-$(C_6H_5)_2S$, 32.9).

Anal. Calcd. for $C_{32}H_{24}N_2S_3$: C, 72.15; H, 4.54; N, 5.26; S, 18.05. Found: C, 71.85; H, 4.49; N, 5.01; S, 17.81.

Synthesis of 3,3'-Dialkylthio-4,4'-diquinolinyl Sulfides **4**. General Procedure.

3-Alkylthio-4-chloroquinoline [8] (3 mmoles) and 3-alkylthio-4(1*H*)-quinolinethione (3 mmoles) were refluxed in chloroform (15 ml) for 15 hours. Chloroform was distilled off and the residue was mixed with 15 ml of 10% aqueous solution of sodium hydroxide. The precipitate was filtered off and crystallized from DMF.

3,3'-Dimethylthio-4,4'-diquinolinyl Sulfide **4a**.

This compound had mp 186-187°, lit [25] mp 186-187°.

3,3'-Diethylthio-4,4'-diquinolinyl Sulfide **4b**.

This compound had mp 164-165°, yield 76%; ^1H nmr (deuteriochloroform): δ 1.18 (t, 6H, $2CH_3$, J = 7.2 Hz), 2.96 (q, 4H, $2CH_2$), 7.31-8.15 (m, 8H arom), 8.71 (s, 2H, 2H-2); ms: (15 eV) m/z (relative intensity) 408 (M^+, 19.3), 347 (M-C_2H_5S, 100), 318 (M-$(C_2H_5)_2S$, 46.3).

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, 4.87; N, 6.65; S, 23.32.

3,3'-Dibenzylthio-4,4'-diquinolinyl Sulfide **4c**.

This compound had mp 193-194°, yield 65%; ^1H nmr (deuteriochloroform): δ 4.06 (s, 4H, $2CH_2$), 7.13-7.23 (m, 10H, $2C_6H_5$), 7.13-8.25 (m, 8H arom), 8.64 (s, 2H, 2H-2); ms: (15 eV) m/z (relative intensity) 532 (M^+, 8.3), 409 (M-$C_6H_5CH_2S$, 100), 318 (M-$(C_6H_5CH_2)_2S$, 18.7).

Anal. Calcd. for $C_{32}H_{24}N_2S_3$: C, 72.15; H, 4.54; N, 5.26; S, 18.05. Found: C, 71.97; H, 4.49; N, 5.07; S, 17.89.

Small amounts of sulfides **4a-c** (5, 13 and 20% respectively) were obtained during synthesis of 3-alkylthio-4(1*H*)-quinolinethiones (from 3-alkylthio-4-chloroquinoline and thiourea as described in reference [8]).

Reaction of Isothioquinanthrene **5** with *S*-alkylisothiouronium Salts at 70°. General Procedure.

The reaction was carried out as described for thioquinanthrene **1**.

Reaction of Thioquinanthrene **1** with Sodium Sulfide and Sodium Hydrogen Sulfide.

To a suspension of thioquinanthrene **1** (1.6 g, 5 mmoles) in 20 ml of dry DMSO at 70° anhydrous sodium sulfide (0.8 g, 10 mmoles) or sodium hydrogen sulfide (0.56 g, 10 mmoles) was added. The mixture was stirred for 30 minutes and then cooled down to room temperature. The mixture was worked-up as described above using double amounts of alkyl halide (14 mmoles) to obtain sulfides **2a-c**.

Rearrangement of Sodium 3-Quinolinethiolates **6** to Sodium 4-Quinolinethiolates **7** in DMSO Solution.

To a suspension of thioquinanthrene **1** (1.6 g, 5 mmoles) in 20 ml of dry DMSO at 20° sodium alkanethiolate (10 mmoles) was added. The mixture was stirred for 60 minutes. Possibly residual dithiin **1** was filtered and the filtrate was divided into two halves. The first portion was worked-up as described above to give sulfides **2a-c** whereas the second portion was heated at 70° for 15 minutes. After cooling the portion was worked-up similarly to give sulfides **3a-c** (86, 75 and 86% yield, respectively).

Attempted Rearrangement of Sodium 3-Quinolinethiolate **6a** to Sodium 4-Quinolinethiolate **7a** in Aqueous DMSO Solution.

To a suspension of thioquinanthrene **1** (0.8 g, 2.5 mmoles) in 10 ml of dry DMSO at 20° sodium methanethiolate (0.35 g, 5 mmoles) was added. The mixture was stirred for 60 minutes and then poured into 30 ml of 15% aqueous sodium hydroxide. Possibly residual dithiin **1** was filtered and the filtrate was heated at 70° for 30 minutes. The resulted solid was filtered to get dithiin **1** (0.62 g, 78%).

Heating of 4,4'-Diallylthio-3,3'-diquinolinyl Sulfide **3d** at 200°.

Sulfide **3d** (0.8 g, 1.85 mmoles) was heated without solvent on an oil-bath at 200° for 1 hour. A resulting dark-brown solid was dissolved in boiling ethanol (100 ml). A dark insoluble solid was

filtered off and the ethanol solution was concentrated to 10 ml. After cooling a yellow-brown solid was filtered off (0.3 g, 51%). A mixture of dithiins **1** and **5** (*ca* 1:3) was spotted by means of tlc data in comparison with pattern compounds.

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