Derivatives of Some Cyclic 3,4-Quinolinediyl Bis-sulfides with *N*,*N*-Dimethylcarbamoyl and *N*-Methyl-*N*-formylaminomethyl Substituents in the 2-Quinolinyl Position#

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Reactions of hydrogen sulfates of quino- and diquino-annelated 1,4-dithiins **11** and **2** with DMF/hydroxylamine-*O*-sulfonic acid/Fe^{++} ion system took place at the α-quinolinyl positions and led to *N*,*N*-dimethylcarbamoyl and *N*-methyl-*N*-formylaminomethyl derivatives **6**, **8**, **12** and **7**, **9**, **13**, respectively. The ^1H and ^{13}C NMR spectra of *N*-methyl-*N*-formylaminomethyl derivatives **7**, **9**, **13** showed the presence of rotational isomers *E* and *Z* regarding to the *N*-methyl-*N*-formylaminomethyl substituent. The spectra of **6**, **7**, **8**, **12** and **13** were completely assigned with the use of 1D and 2D NMR techniques. In the case of rotational isomers **7a** and **7b**, the crucial correlations came from the NOE interaction between the methylene and methyl protons from $CH_2N(CH_3)CHO$ groups and benzene-rings protons. Synthesis of 2,3-dihydro-1,4-dithiino[6,5-*c*]quinoline 4-oxide **14** was presented as well.

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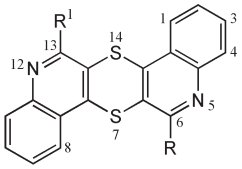
Introduction.

The reactions of protonated azines with the DMF/hydroxylamine-*O*-sulfonic acid/Fe^{++} ion system led to α- and or γ-substituted azines with *N*,*N*-dimethylcarbamoyl and (or) *N*-methyl-*N*-formylaminomethyl substituents [1-4]. The same reaction course was observed also for thioquinanthrene (1,4-dithiino[2,3-*c*:5,6-*c*']diquinoline) **1** as shown in Scheme 1. Compound **1**, a 3,4-bisubstituted quinoline, underwent substitution with radicals formed from DMF in α-quinolinyl positions. The reaction led to both monosubstitution products **2** and **3**, but from three possible α,α'-disubstitution products only 6,13-bis(dimethylcarbamoyl) derivative **4** was isolated [5-7]. To evaluate the structural requirements for the reaction mentioned above, further cyclic **5**, **11** and open-chain 3,4-quinolinediyl bis-sulfides **15** were subjected to the reaction with DMF/hydroxylamine-*O*-sulfonic acid/Fe^{++} ion system.

Scheme 1

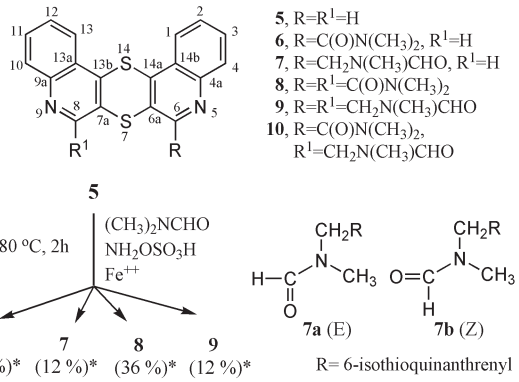


1, R=R^1=H
2, R=C(O)N(CH$_3$)$_2$, R^1=H
3, R=CH$_2$N(CH$_3$)CHO, R^1=H
4, R=R^1=C(O)N(CH$_3$)$_2$

Results and Discussion.

Isothioquinanthrene **5**, (*i.e.* 1,4-dithiino[2,3-*c*:6,5-*c*']-diquinoline), as the close structural analog of **1**, was chosen as the first compound for the present study. The reaction was performed in the same manner as that for **1**, [5] treating the molecule of bis-hydrogen sulfate of azine **5** in DMF with hydroxylamine-*O*-sulfonic acid/Fe^{++} ion system. The reaction gave (Scheme 2) both 6-monosubstitution products **6** and **7**, as well as 6,8-bis(dimethylcarbamoyl) derivative **8** and 6,8-bis(*N*-methyl-*N*-formylaminomethyl) derivatives **9** as α,α'-disubstitution products. (We did not find the derivative **10**).

Scheme 2



5, R=R^1=H
6, R=C(O)N(CH$_3$)$_2$, R^1=H
7, R=CH$_2$N(CH$_3$)CHO, R^1=H
8, R=R^1=C(O)N(CH$_3$)$_2$
9, R=R^1=CH$_2$N(CH$_3$)CHO
10, R=C(O)N(CH$_3$)$_2$, R^1=CH$_2$N(CH$_3$)CHO

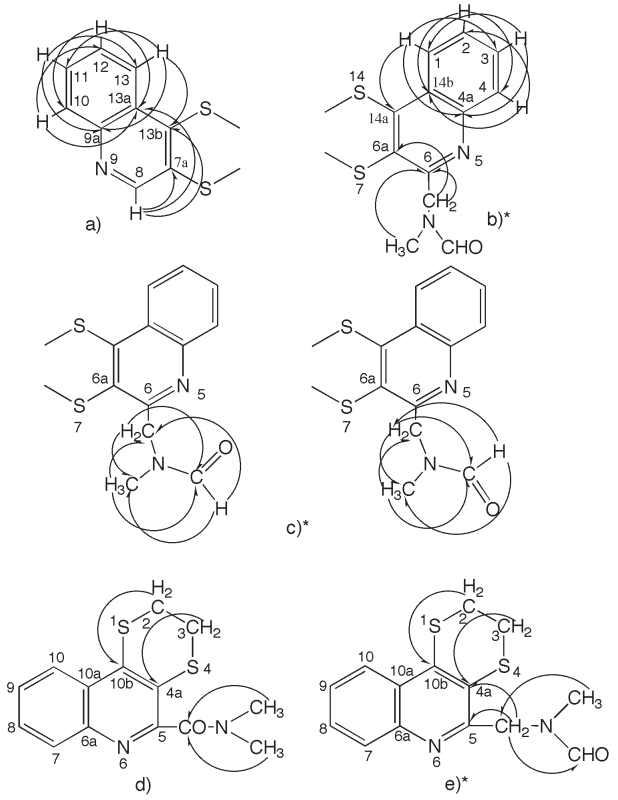
* yield based on amount of substrate **5** reacted, (*ca.* 58 %)

The structure of *N*,*N*-dimethylcarbamoyl derivatives **6** and **8** was completely assigned by ^1H and ^{13}C NMR studies performed in the same manner as described for **2** and **4** [5,7]. Analytical steps used in NMR assignment of **6** and **8** are the same as those presented below for **7**.

^1H and ^{13}C NMR spectra of **7** show resonances of the same functional groups of two species, having the same intensities and very similar coupling patterns. As presented below, this observation could be explained in terms of the presence of the E and Z rotational isomers **7a** or **7b**.

Scheme 3

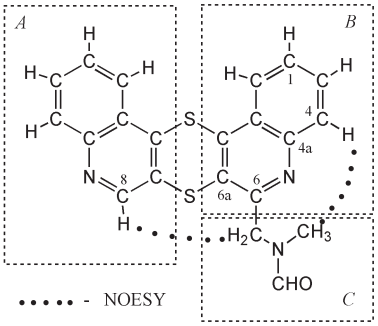
Sets of long-range proton-carbon correlations for analysis of **6**, **7**, **8**, **9**, **10**, **12**, **13**.



* Other long-range proton-carbon correlations between the members of *N*-methyl-*N*-formylaminomethyl substituents of **7a** and **7b** or **13a** and **13b** are presented in Table 1 and in the experimental part, respectively.

Following analytical steps were used for the complete ^{1}H and ^{13}C NMR assigment of **7a** or **7b** occurring simultanously in $CDCl_3$ solution: i) A COSY ^{1}H-^{1}H experiment allowed for segregation of sixteen benzene ring protons into four ABMX systems of quinolinyl type. ii) Long-range proton-carbon correlations (Scheme 3) show connectivities between the carbon and proton atoms as depicted by areas A, B or C (Scheme 4). The NOESY experiments with *N*-CH_3 and *N*-CH_2 protons proved **7a** to be conformer E and **7b** to be conformer Z. iii) Connectivities between areas A, B and C for both rotamers **7a** and **7b** could be deduced from NOESY experiments (Figure 1) indicating the interaction of the methylene group protons with H8 proton and the methyl group protons with H4 proton (see Scheme 4 and Figure 2).

Scheme 4



The NOESY experiments prove that similarly to rotamers **3a** and **3b** [7] the distances between methylene group protons with H8 proton and methyl group protons with H4 proton are within the limit required for the occurrence of NOE., *i.e.* 4.5 Å [8], which is likely due to the folded shape of the molecules of **7a** and **7b** (see Figure 2) . In fact, the calculation by means of AM1 and PM3 methods [9] show that the H8/CH_2 distances are 4.17 Å or 4.31 Å for **7a** and 4.16 Å or 4.18 Å for **7b** but those for H4/CH_3 are of the magnitude of 3.71 Å or 3.50 Å for **7a** and 3.58 Å or 3.42 Å for **7b**.

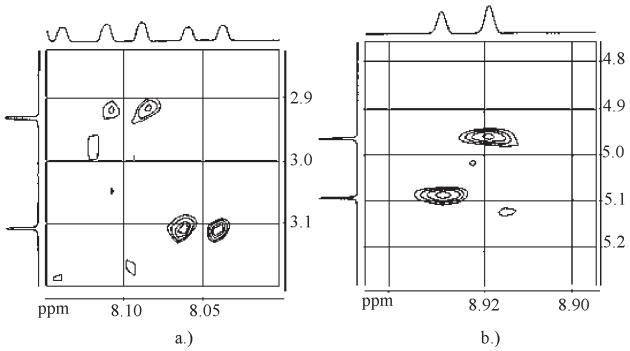


Figure 1. The NOESY spectra (500 MHz, $CDCl_3$, τmix= 0.5 s) for rotational isomers **7a** and **7b**: a) interactions of methyl group protons (2.93 ppm, 3.10 ppm) with H4 protons (8.10 ppm, 8.07 ppm), b) interactions of methylene group protons (4.97 ppm, 5.09 ppm) with H8 protons (8.92 ppm, 8.93 ppm).

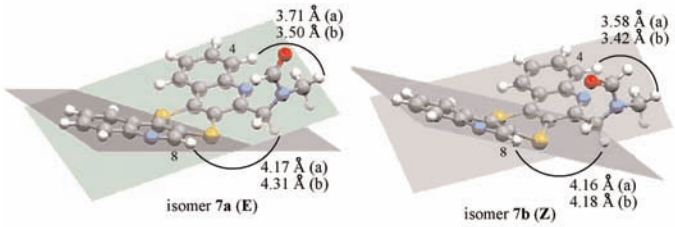


Figure 2. Views of the structure of 6-(*N*-methyl-*N*-formylaminomethyl)-isothioquinanthrene rotamers **7a** (isomer **E**) and **7b** (isomer **Z**) optimized by means of PM3 method. Distances between H8/CH_2 and H4/CH_3 protons were calculated by means of (a) AM1 and (b) PM3 methods.

We tried to extend the methodology presented above for the analysis of ^{1}H and ^{13}C NMR spectra of **9**. They revealed the presence of 36 carbon signals and furthermore, as deduced from the long-range proton-carbon correlations, also the presence of four non-identical *N*-methyl-*N*-formylaminomethyl groups in the ratio I:II:III:IV = 2:3:2.5:3 (Table 2). The NOE experiments prove that I and

Table 1

Summary of the ^1H and ^{13}C NMR data including the values of δ_H and δ_C, and HSQC and HMBC correlations for compound **7**.

	7a (conformer **E**)			**7b** (conformer **Z**)		
Position	Proton δ_H [ppm]	Carbon δ_C [ppm]	Proton-carbon long range coupling	Proton δ_H [ppm]	Carbon δ_C [ppm]	Proton-carbon long range coupling
1	8.54	123.6	143.2 (C14a), 146.3 (C4a), 130.5 (C3)	8.52	123.6	142.5 (C14a), 146.3 (C4a), 130.5 (C3)
2	7.72	128.1	126.8 (C14b), 130.0 (C4)	7.66	127.7	126.7 (C14b), 129.9 (C4)
3	7.79	130.6	123.6 (C1), 146.3 (C4a)	7.76	130.5	123.6 (C1), 146.3 (C4a)
4	8.10	130.5	126.8 (C14b), 128.1 (C2)	8.07	129.9	126.7 (C14b), 127.7 (C2)
4a		146.3			146.3	
6		152.4			152.2	
6a		128.5			128.7	
7a		128.0			128.2	
8	8.92	148.2	142.4 (C13b), 147.3 (C9a), 128.0 (C7a), 130.1 (C10)	8.93	148.4	142.3 (C13b), 147.3 (C9a), 128.2 (C7a), 130.1 (C10)
9a		147.3			147.3	
10	8.16	130.1	126.9 (C13a), 128.1 (C12)	8.14	130.1	127.0 (C13a), 128.0 (C12)
11	7.80	130.3	147.3 (C9a), 123.6 (C13)	7.78	130.3	147.3 (C9a), 123.6 (C13)
12	7.73	128.1	126.9 (C13a), 130.1 (C10)	7.70	128.0	127.0 (C13a), 130.1 (C10)
13	8.51	123.6	130.3 (C11), 147.3 (C9a), 142.4 (C13b)	8.50	123.6	130.3 (C11), 147.3 (C9a), 142.3 (C13b)
13a		126.9			127.0	
13b		142.4			142.3	
14a		143.2			142.5	
14b		126.8			126.7	
CH_3	2.93	30.2	54.1 (CH_2), 164.0 (CHO)	3.10	35.1	48.7 (CH_2), 162.9 (CHO)
CH_2	4.97	54.1	30.2 (CH_3), 164.0 CHO 128.5 (C6a), 152.4 (C6)	5.09	48.7	35.1 (CH_3), 162.9 (CHO) 128.7 (C6a), 152.2 (C6)
CHO	8.52	164.0	30.2 (CH_3), 54.1 (CH_2)	8.31	162.9	35.1 (CH_3). 48.7 (CH_2)

Table 2

Proton-carbon Correlations in *N*-Methyl-*N*-formylaminomethyl Substituents of the Rotamers of Compound **9**

Entry	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	conformation*
I	NCH_3 (δ=3.14)	NCH_3 (δ=35.4)	NCH_2 (δ=5.12)	NCH_2 (δ=48.7)	C*H*O (δ=8.31)	*C*HO (δ=163.0)	Z
II	NCH_3 (δ=3.09)	NCH_3 (δ=35.0)	NCH_2 (δ=5.10)	NCH_2 (δ=49.0)	C*H*O (δ=8.29)	*C*HO (δ=163.9)	Z
III	NCH_3 (δ=2.91)	NCH_3 (δ=30.3)	NCH_2 (δ=4.97)	NCH_2 (δ=54.2)	C*H*O (δ=8.46)	*C*HO (δ=162.8)	E
IV	NCH_3 *(δ=2.91)*	NCH_3 (δ=30.0)	NCH_2 (δ=5.03)	NCH_2 (δ=54.3)	C*H*O (δ=8.61)	*C*HO (δ=164.4)	E

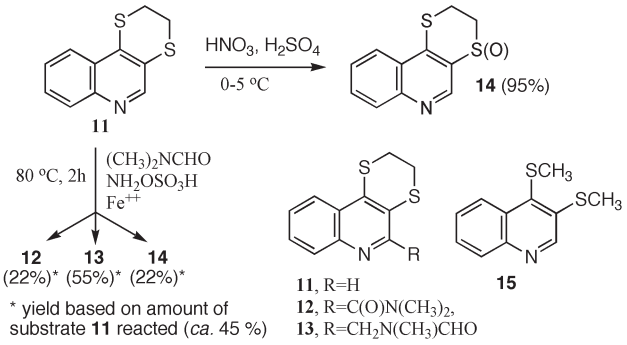
* The Z/E assignment was deduced from the magnitude of deshielding effect of carbonyl oxygen relative to the methyl group protons.

II are conformers Z and III and IV are conformers E, respectively. However, we were not able to find connectivity between the protons of the ABMX systems as the spectral lines of the hydrogen multiplets are very close.

Next we studied the behaviour of 2,3-dihydro-1,4-dithiino[6,5-*c*]quinoline **11** and its open-chain analog 3,4-dimethylthioquinoline **15** after treatment with DMF/hydroxylamine-*O*-sulfonic acid/Fe^{++} ion system. The reaction with dithiin **11** afforded two products **12** and **13** containing the substituents formed from DMF but they were accompanied by sulfoxide **14**. Sulfoxide **14** was also obtained by oxidation of dithiin **11** with nitrating mixture according to the procedure reported for the same transformation of β-quinolinyl sulfides [10-11].

The presence of an ethylene bridge in the molecules of **12** and **13** facilitate the ^1H and ^{13}C NMR assignment for compounds **12** and **13** using long-range proton-carbon correlations presented in Scheme 3. It reveals also that the both *Z* and *E* rotational isomers **13a** and **13b** exist in the spectra of *N*-methyl-*N*-formylaminomethyl derivative in $CDCl_3$ solutions.

Scheme 5



Conclusions.

Cyclic 3,4-quinolinediyl bis-sulfides **5** and **11** underwent homolytic substitution in α-quinolinyl positions with radicals formed from DMF under the Minisci reaction conditions. No reaction was observed for 3,4-dimethylthioquinoline **15**, which may be due to the steric arrangement of **15**. Because, as deduced from NMR study (in chloroform solution) and X-ray-examination, 3-methylthio group in the molecule of **15** is almost coplanar with the H-2 atom and it may cause steric hindrance at position 2 and prevent the reaction of **15** with radicals formed from DMF.

E and Z *N*-methyl-*N*-formylaminomethyl substituents influenced the parent quinoline moiety non-identically, therefore the spectral lines of two quinoline fragments were observed in nmr spectra of the respective *N*-methyl-*N*-formylaminomethyl derivatives **7** and **13**. This effect is also transmitted through the 1,4-dithiin ring in dithiinodiquinolines **3** [5,7] and **7** to the second (the "left" one) quinoline moiety. Fortunately, due to the folded shape of dithiinodiquinolines **2** [6], **4** [12] as well as and *N*-methyl-*N*-formylaminomethyl derivatives **3** [5,7] and **7**, the correlation between the parts of the molecules of **7** could be detected by means of NOE experiments.

EXPERIMENTAL

The ^{1}H and ^{13}C nmr spectra were recorded at 303 K for *ca.* 0.1 mol dm^{-3} $CDCl_3$ solutions on a Bruker MSL 500 spectrometer operating at 500.133/125.769 MHz for ^{1}H/^{13}C nuclei. All δ_X were referenced to internal tetramethylsilane (TMS). The COSY experiments were performed on a 1024 × 1024 matrix (F_1, F_2) with 4-6 scans per t_1 increment, using the pulse program *cosygp*. SW's were 1-4.5 kHz (F_1) and 1-4.5 kHz (F_2), The ^{1}H pulses (P1) 6.7-9.2 and 14.0-15.0 μs, the 90°, and AQ of 0.16-0.57 s. The HSQC experiments were performed using a 8192 × 2048 data matrix (F_1, F_2) with 2 scans per t_1 increment, using the gradient selection pulse sequence *invietgs*. Spectral widths (SWs) were 19-25 kHz in the ^{13}C evolution dimension (F_1) and 3.3-4.5 kHz in the ^{1}H acquisition dimension (F_2), 90 and 180° ^{1}H pulses (P1, P2) 6.6-9.2 μs and 13.3-18.4 μs, 90 ^{13}C pulses (P3) 13.0 μs, acquisition times (AQ) 0.23-0.34 s, and the *garp* composite-pulse-decoupling (^{13}C) sequence applied during the acquisition. The HMBC experiments were performed on using a 16384 × 2048 matrix (F_1, F_2) with 4-8 scans per t_1 increment, using the pulse program *inv4gplplrnd* that includes a low-pass *J* filter to suppress one-bond cross-peaks. SW's were 19-23 kHz (F_1) and 3.5-4.5 kHz (F_2), 90 and 180° ^{1}H pulses (P1, P2) 6.7-7.5 and 13.2-15.1 μs, the 90° ^{13}C pulse (P3) 13.0 μs, and AQ of 0.23-0.29 s. The NOESY experiments were performed using a 2048 × 2048 matrix (F_1, F_2) with 8 scans per t_1 increment, using the pulse program *cosygp*. The time mixing for NOE build up was 0.5 s, spectral width (SW) was 3.5 kHz, pulse (P1) 7.2 μs, acquisition time (AQ) 0.49 s. Low- and high- resolution electron-impact mass spectra (MS) were taken on an AMD 604 spectrometer (70 eV). IR spectra were recorded with a Magma – IR 500 (Nicolet) spectrometer in potassium bromide pellets. Compounds **5** and **11** were prepared as described previously [13-14].

Reactions of Dithiinoquinolines **5** and **11** with DMF/Hydroxylamine-*O*-sulfonic Acid/Fe^{++} ion System.

Reaction of **5**.

The reaction was performed under a nitrogen atmosphere at 80 °C as described previously for thioquinanthrene **1** [5]. A solution of isothioquinanthrene **5** (0.95 g, 3 mmoles) in 3 ml of conc. sulfuric acid, 250 ml of DMF containing 2 ml of water, ferrous sulfate (6 mmoles, 0.83 g) and hydroxylamine–*O*-sulfonic acid (6 mmoles, 0.68 g) were used. The mixture was then concentrated to 30 ml by vacuum distillation. The residue was poured into 200 ml of water. The solid formed was collected by filtration, washed with water, and air dried to give yellow solid containing four new products with spots of R_f value R_f=0.60 for **6**, R_f=0.58 for **7**, R_f=0.50 for **8**, R_f=0.43 for **9** R_f=0.41 for **5** (chloroform/ethanol 19:1, SiO_2). Composition of the mixture determined by quantitative thin layer chromatography indicated **6** - 23%, **7** - 7%, **8** – 21%, **9** – 7% accompanied by *ca.* 42% of unreacted isothioquinanthrene **5**. The products were separated by tlc using the chromatographic system mentioned above. All products were finally recrystallized from ethanol.

6-(*N,N*-Dimethylcarbamoyl)isothioquinanthrene (**6**).

This compound was obtained as yellow needless (ethanol), mp 220-223 °C; ms (70 eV, electron impact), m/z (rel. intensity): 389 (M, 45.5%), 332 (M-57, 12.6%), 318 (M-71, 100%), 285 (M-104, 10%). High resolution ms: Calcd. for $C_{21}H_{15}N_3OS_2$**:** M = 389.06566, Found: 389.06280, error: 7.3 ppm; ^{1}H nmr: δ [δ_C for carbons from single bond and / long range proton-carbon correlations]: 3.01 [(s, 3H, CH_3); 38.4 (CH_3) / 35.2 (CH_3), 166.9 (CO), 152.3 (C6)], 3.31 [(s, 3H, CH_3); 35.2 (CH_3) / 38.4 (CH_3), 166.9 (CO), 152.3 (C6)], 7.65 [(m, 1H, H12); 128.0 (C12) / 126.9 (C13a), 130.1 (C10)], 7.66 [(m, 1H, H2); 128.6 (C2) / 126.8 (C14b), 130.1 (C4)], 7.68 [(m, 1H, H11); 130.1 (C11) / 147.2 (C9a), 123.5 (C13)], 7.69 [(m, 1H, H3); 130.6 (C3) / 123.6 (C1), 145.5 (C4a)], 8.11 [(m, 1H, H4); 130.1 (C4) / 126.8 (C14b), 128.6 (C2)], 8.13 [(m, 1H, H10); 130.1 (C10) / 126.9 (C13a), 128.0 (C12)], 8.49 [(m, 1H, H13); 123.5 (C13) / 130.1 (C11), 147.2 (C9a), 142.0 (C13b)], 8.53 [(m, 1H, H1); 123.6 (C1) / 143.1 (C14a), 145.5 (C4a), 130.6 (C3)], 8.90 [(s, 1H, H8); 148.3 (C8) / 142.0 (C13b), 147.2 (C9a), 129.2 (C7a), 126.9 (C13a)], there are no correlations for C6a (127.9).

Anal. Calcd for $C_{21}H_{15}N_3OS_2$: C, 64.76; H, 3.88; N, 10.79; S, 16.46. Found: C, 64.45; H, 3.48; N, 10.46; S, 16.41.

6-(*N*-Methyl-*N*-formylaminomethyl)isothioquinanthrene (**7**).

This compound was obtained as yellow needless (ethanol); mp 221-222°C; ms (70 eV, electron impact), m/z (rel. intensity): 389 (M, 27.9%), 360 (M-29, 12 %), 332 (M-57, 100%), 300 (M-89, 19 %), 285 (M-104, 14 %). High resolution ms: Calcd. for $C_{21}H_{15}N_3OS_2$**:** M = 389.06566, Found: 389.06628, error: -1.6 ppm. For ^1H and ^{13}C nmr data – see Table 1.

Anal. Calcd for: $C_{21}H_{15}N_3OS_2$: C, 64.76; H, 3.88; N, 10.79; S, 16.46. Found: C, 64.44; H, 3.99; N, 10.49; S, 16.48.

6,8-Bis(*N,N*-dimethylcarbamoyl)isothioquinanthrene (**8**).

This compound was obtained as yellow needless (ethanol); mp 304-306 °C; ms (70 eV, electron impact), m/z (rel. intensity): 460 (M, 77.5%), 403 (M-57, 17.8%), 388 (M-70, 98.7%), 357 (M-103, 17 %), 318 (M-142, 100%). High resolution ms: Calcd. for $C_{24}H_{20}N_4O_2S_2$: 460.10277. Found: 460.10169, error: 2.3 ppm; ^1H nmr: δ [δ_C for carbons from single bond and / long range proton-carbon correlation]: 2.94 [(s, 3H, CH_3); 38.0 (CH_3) / 34.6 (CH_3), 166.9 (CO)], 3.26 [(s, 2H, CH_3); 34.6 (CH_3) / 38.0 (CH_3), 166.9 (CO)], 7.72 [(m, 2H, H2 and H12); 128.5 (C2 and C12) / 126.8 (C13a and C14b), 130.1 (C4 and C10)], 7.79 [(m, 2H, H3 and H11); 130.7 (C3 and C11) / 123.5 (C1 and C13), 146.0 (C4a and C9a)], 8.13 [(m, 2H, H4 and H10); 130.1 (C4 and C10) / 126.8 (C13a and C14b), 128.5 (C2 and C12)], 8.51 [(m, 2H, H1 and H13); 123.5 (C1 and C13), 144.5 (C14a and C13b), 146.0 (C4a and C9a), 130.7 (C3 andC11)], there are no correlations for C6/C8 (153.2) and C6a/C7a (126.2).

Anal. Calcd for $C_{24}H_{20}N_4O_2S_2$: C, 62.59; H, 4.38; N, 12.16; S, 13.92. Found: C, 62.39; H, 4.70; N, 12.39; S, 13.85.

6,8-Bis-(*N*-methyl-*N*-formylaminomethyl)isothioquinanthrene (**9**).

This compound was obtained as yellow needless (ethanol), mp 225-230 °C; ms (70 eV, electron impact), m/z (rel. intensity): 460 (M, 89.9%), 403 (M-57, 100 %), 388 (M-70, 20 %), 371 (M-89, 35.6%), 360 (M-100, 26 %), 346 (M-114, 85 %), 331 (M-129, 55 %), 314 (M-146, 46 %), 299 (M-161, 28.8 %). High resolution ms: Calcd. for: $C_{24}H_{20}N_4O_2S_2$: 460.10277, Found: 460.10267, error: 0.2 ppm; ^1H nmr ($CDCl_3$): δ 2.91 (s, 3H, CH_3), 2.92 (s, 3H, CH_3), 3.09 (s, 3H, CH_3), 3.14 (s, 3H, CH_3), 4.97 (s, 2H, CH_2), 5.03 (s, 2H, CH_2), 5.10 (s, 2H, CH_2), 5.12 (s, 2H, CH_2), 7.64-7.82 (m, 16H, ArH), 8.04-8.13 (m, 8H, ArH), 8.29 (s, 1H, CHO), 8.31 (s, 1H, CHO), 8.46 (s, 1H, CHO), 8.49-8.55 (m, 8H, ArH), 8.61 (s, 1H, CHO); ^{13}C nmr ($CDCl_3$), δ 30.0, 30.6, 35.0, 35.4, 48.7, 49.0, 54.2, 54.3, 123.6*, 127.0*, 127.6, 127.9**, 128.1***, 128.2, 128.4, 129.9, 130.0, 130.1**, 130.3, 130.4, 130.6**, 162.8, 163.0, 163.0, 164.4.

*-separated signals for four carbon atoms, **-separated signals for two carbon atoms, ***- separated signals for three carbon atoms were observed in HMBC spectra.

Anal. Calcd for $C_{24}H_{20}N_4O_2S_2$: C, 62.59; H, 4.38; N, 12.16; S, 13.92. Found: C, 62.48; H, 4.98; N, 12.45; S, 13.79

Reaction of **11**.

In the case of 2,3-dihydro-1,4-dithiino[5,6-*c*]quinoline **11**, a solution of **11** (0.66 g, 3 mmoles) in 1 ml of conc. sulfuric acid, 150 ml of DMF containing 15 ml of water, ferrous sulfate (3 mmoles, 0.41 g) and hydroxylamine–*O*-sulfonic acid (3 mmole, 0.34 g) were used. When the reaction was completed, the mixture was concentrated by vacuum distillation, the residue was treated with water (100 ml) and the products were extracted with chloroform (3 x 10 ml). The extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was then stripped off. The products were separated by tlc on silica gel using a mixture of chloroform/ethanol 19:1 as an eluent. Composition of the mixture determined by quantitative thin layer chromatography indicated **12** - 22%, **13** - 55%, **14** – 22% accompanied by *ca.* 55% of unreacted 2,3-dihydro-1,4-dithiino[5,6-c]quinoline **5**.

5-(*N*,*N*-Dimethylcarbamoyl)-2,3-dihydro-1,4-dithiino[5,6-*c*]-quinoline (**12**).

This compound was obtained as an oil; ms (70 eV, electron impact), m/z (rel. intensity): 290 (M, 26%), 233 (M-57, 12%), 219 (M-71, 70%); High resolution ms: Calcd. for $C_{14}H_{14}ON_2S_2$: 290.05476, Found: 290.05502, error –0.9 ppm; ^1H nmr ($CDCl_3$): δ [δ_C for carbons from single bond and / long range proton-carbon correlation]: 2.93 [(s, 3H, CH_3), CH_3 (37.9) / CO (167.4)], 3.18 [(s, 3H, CH_3), CH_3 (34.6) / CO (167.4)], 3.29 [(m, 1H, H3), C3 (27.2) / C4a (121.1)], 3.50 [(m, 1H, H2), C2 (28.7) / C10b (138.1)], 7.53 [(m, 1H, H9), C9 (126.8) / C10a (125.8), C7 (130.0)], 7.63 [(m, 1H, H8), C8 (128.5) / C10 (121.8) C6a (143.6)], 7.96 [(m, 1H, H7), C7 (130.0) / C9 (126.8), C10a (125.8)], 8.02 [(m, 1H, H10), C10 (121.8) / C8 (128.5), C6a (143.6)], there are no correlations for C5 (149.2).

Anal. Calcd for $C_{14}H_{14}ON_2S_2$: C, 57.90; H, 4.86; N, 9.65; S, 22.08. Found: C, 57.78; H, 4.59; N, 9.81; S, 21.92.

5-(*N*-Formyl-*N*-methylaminomethyl)-2,3-dihydro-1,4-dithiino[5,6-*c*]quinoline (**13**).

This compound was obtained as an oil; ms (70 eV, electron impact), m/z (rel. intensity): 290 (M, 24%), 233 (M-57, 96%), 219 (M-71, 12%).

High resolution ms: Calcd. for $C_{14}H_{14}ON_2S_2$**:** 290.05476, Found: 290.05552, error –1.1 ppm. ^1H nmr: δ [δ_C for carbons from single bond and / long range proton-carbon correlactions]: **13a** (conformer E): 2.88 [(s, 3H, CH_3), 30.0 (CH_3) / 53.4 (CH_3), 164.0 (CHO)], 3.32 [(m, 2H, SCH_2), 27.3 (SCH_2) / 123.2 (C4a)], 3.47 [(m, 2H, SCH_2), 28.8 (SCH_2) / 138.9 (C10b)], 4.68 [(s, 2H, NCH_2), 53.4 (NCH_2) / 30.0 (CH_3), 123.2 (C4a), 151.6 (C5), 164.0 (CHO)], 7.52 [(m, 1H, H9), 126.9 (C9) / 125.7 (C10a), 129.9 (C7)], 7.62 [(m, 1H, H8), 128.9 (C8) / 121.7 (C10), 143.5 (C6a)], 7.94 [(m, 1H, H7), 129.9 (C7) / 125.7 (C10a), 126.9 (C9)], 8.03 [(m, 1H, H10), 121.7 (C10) / 128.9 (C8), 143.5 (C6a)], 8.33 [(s, 1H, CHO), 164.0 (CHO) / 30.0 (CH_3), 53.4 (NCH_2)]. **13b** (conformer Z) :3.01 [(s, 3H, CH_3), 34.9 (CH_3) / 47.9 (CH_3), 162.8 (CHO)], 3.31 [(m, 2H, SCH_2), 27.3 (SCH_2) / 123.3 (C4a)], 3.45 [(m, 2H, SCH_2), 28.7 (SCH_2) / 139.6 (C10b)], 4.81 [(s, 2H, NCH_2), 47.9 (NCH_2) / 34.9 (CH_3), 123.3 (C4a), 151.4 (C5), 162.8 (CHO)], 7.51 [(m, 1H, H9), 126.5 (C9) / 125.6 (C10a), 129.9 (C7)], 7.61 [(m, 1H, H8), 128.5 (C8) / 121.6 (C10), 143.7 (C6a)], 7.94 [(m, 1H, H7), 129.9 (C7) / 125.6 (C10a), 126.5 (C9)], 8.01 [(m, 1H, H10), 121.6 (C10) / 128.5 (C8), 143.7 (C6a)], 8.24 [(s, 1H, CHO), 162.8 (CHO) / 34.9 (CH_3), 47.9 (NCH_2)].

Anal. Calcd for $C_{14}H_{14}ON_2S_2$: C, 57.90; H, 4.86; N, 9.65; S, 22.08. Found: C, 58.11; H, 4.73; N, 9.54; S, 21.94.

Oxidation of 2,3-Dihydro-1,4-dithiino[5,6-*c*]quinoline **11** with a Nitrating Mixture.

Dithiin **11** (0.153 g, 0.7 mmole) was dissolved with stirring in 2 ml of conc. sulfuric acid. The solution was cooled down to -10 ºC. The nitrating mixture (fuming nitric acid, 0.04 ml, 0.9 mmole of nitric acid and 0.4 ml of conc. sulfuric acid) was then added dropwise. The reaction was stopped when the deep-cherry col-

ored reaction mixture turned yellow. The solution was poured on 20 g of ice and neutralized with conc. ammonia. The product was extracted with chloroform (3 x 7 ml). The extracts were treated in a typical manner to give the bright yellow solid, which was triturated with small amount of cold methanol and dried on air to afford pure sulfoxide **14** (95%) with mp 149-150 °C

2,3-Dihydro-1,4-dithiino[5,6-*c*]quinoline-4-oxide (**14**).

This compound was obtained as yellow needless (ethanol), mp 149-150 °C; ms (70 eV, electron impact), m/z (rel. intensity): 235 (M, 100%); ir (potassium bromide pellet): ν_{SO}=1033 cm^{-1}; ^1H nmr ($CDCl_3$), δ: 2.79–2.85 (m, 1H, SCH_2), 3.21-3.26 (m, 1H, SCH_2), 3.60–3.64 (m, 1H, SCH_2), 3.95–4.01 (m, 1H, SCH_2), 7.55–7.57 (m, 1H, ArH), 7.73–7.77 (m, 1H, ArH), 8.00–8.02 (m, 1H, ArH), 8.06–8.08 (m, 1H, ArH), 8.87 (s, 1H, ArH); ^{13}C nmr ($CDCl_3$), δ: 15.5, 41.6, 123.4, 125.3, 126.7, 127.4, 130.3, 131.9, 144.1, 147.8, 151.1.

Anal. Calcd for $C_{11}H_9NOS$: C, 56.15; H, 3.85; N, 5.95; S, 27.25. Found: C, 56.03; H, 4.09; N, 5.78; S, 27.01.

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