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NITROTHIOQUINANTHRENES AND THEIR *S*-OXIDES

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Abstract - The reaction of dithiinodiquinolines (**1**) or (**5**) with an excess of nitrating mixture at 0-5 °C led within 3 days to the mixtures of nitrothioquinanthrene *S*-oxides (**3a-d**) or nitroisothioquinanthrene *S*-oxides (**7a**, **b**). Sulfoxides (**3a-d**) were reduced to sulfides (**4a**, **b**) with KI / aq. HCl system. Sulfides (**4a, b**) were reoxidised to sulfoxides (**3a-d**) with nitrating mixture. Structure of compounds (**3a, 4a, b, 7b**) was assigned by means of 1D and 2D ^{1}H and ^{13}C NMR spectral techniques. The structural conclusions were supported by an X-Ray analysis of 8-nitrothioquinanthrene 7-oxide (**3a**).

INTRODUCTION

3,4-Functionalization of quinoline leading to 1,4-dithiino[2,3-c;5,6-c']diquinoline, i.e. thioquinanthrene (**1**) (64%) [1] could be achieved in a *one-pot* process by sulfurization of quinoline with elemental sulfur (240 °C, 48 h). The nucleophilic splitting of 1,4-dithiin ring in compound (**1**) gave numerous 4-substituted 3-thioquinolines or 1-alkyl-4-substituted 1,4-dihydro-3-thioquinolines including sulfides, sulfoxides and sulfonamides.[2] The most interesting biologically active quinolines are the ones substituted at benzene ring.[3-6] However, attempted sulfurization of benzene-ring substituted quinolines with elemental sulfur gave poor results.[7]

Benzene-ring substituted quinolines are usually prepared by cyclization of appropriate benzene derivatives or, less commonly, by electrophilic substitution reaction. Using the latter strategy attempts were made to prepare benzene-ring substituted thioquinanthrenes, like **3**, **4** in the reaction of thioquinanthrene (**1**) with nitrating mixture (0-5 °C, 1.5 h). However, it proceeded as *S*-oxidation to form thioquinanthrene 7-oxide (**2**) instead of the expected nitrothioquinanthrenes.[8] On the other hand further

studies described in this paper have shown that extending the reaction time from 1.5 h up to 3-5 days led to the mixture of nitrothioquinanthrene-7-oxides (**3a-d**).

RESULTS AND DISCUSSION

In order to carry out the reaction of thioquinanthrene (**1**) or isothioquinanthrene (**5**) with nitrating mixture, the quinoline base was dissolved in conc. sulfuric acid (0-5 °C) and treated, as quinolinium salt, with the nitrating mixture.[8,9] After the addition of the first drop of the nitrating mixture, the color of the reaction mixture became deep green. It then turned to yellow when the addition of 1 molar equivalent of nitric acid was complete. Dilution of the reaction mixture with water gave thioquinanthrene-*S*-oxide (**2**) or isothioquinanthrene-*S*-oxide (**6**) with high yield (91 % and 93 %, respectively).[8,9]

As oxidation of aryl sulfides including thianthrene derivatives proceeds through the stage of intensively colored sulfur cation-radicals, one would expect the formation (or occurrence) of this type species in the course of reaction of thioquinanthrene (**1**) and isothioquinanthrene (**5**) with nitrating mixture. In fact, an ESR spectral study showed the presence of radical species (single broad line with a g-value of 2.0081) when the solution of thioquinanthrene (**1**) in sulfuric acid was treated up to 1 molar equivalent of nitric acid (in the form of nitrating mixture). Very similar behavior was also observed in the case of isothioquinanthrene (**5**) producing a species with a g-value of 2.0078. In both cases the signal of radical disappeared when 1 molar equivalent of nitric acid was added. No ESR spectral signals of the solution of thioquinanthrene or isothioquinanthrene in sulfuric acid were observed.

Similar ESR spectral data were observed for the thianthrene radical cation with a g-value of 2.0081.[10] The g-values of the radicals formed from dithiins (**1)** and (**5**) were close to those of the cationic radicals formed from substituted thianthrenes and diaryl sulfoxides in concentrated sulfuric acid (2.008-2.009).[11] Our results concerning the reaction of dithiins (**1**) and (**5**) with nitrating mixture indicated the presence of the sulfur cation radicals.

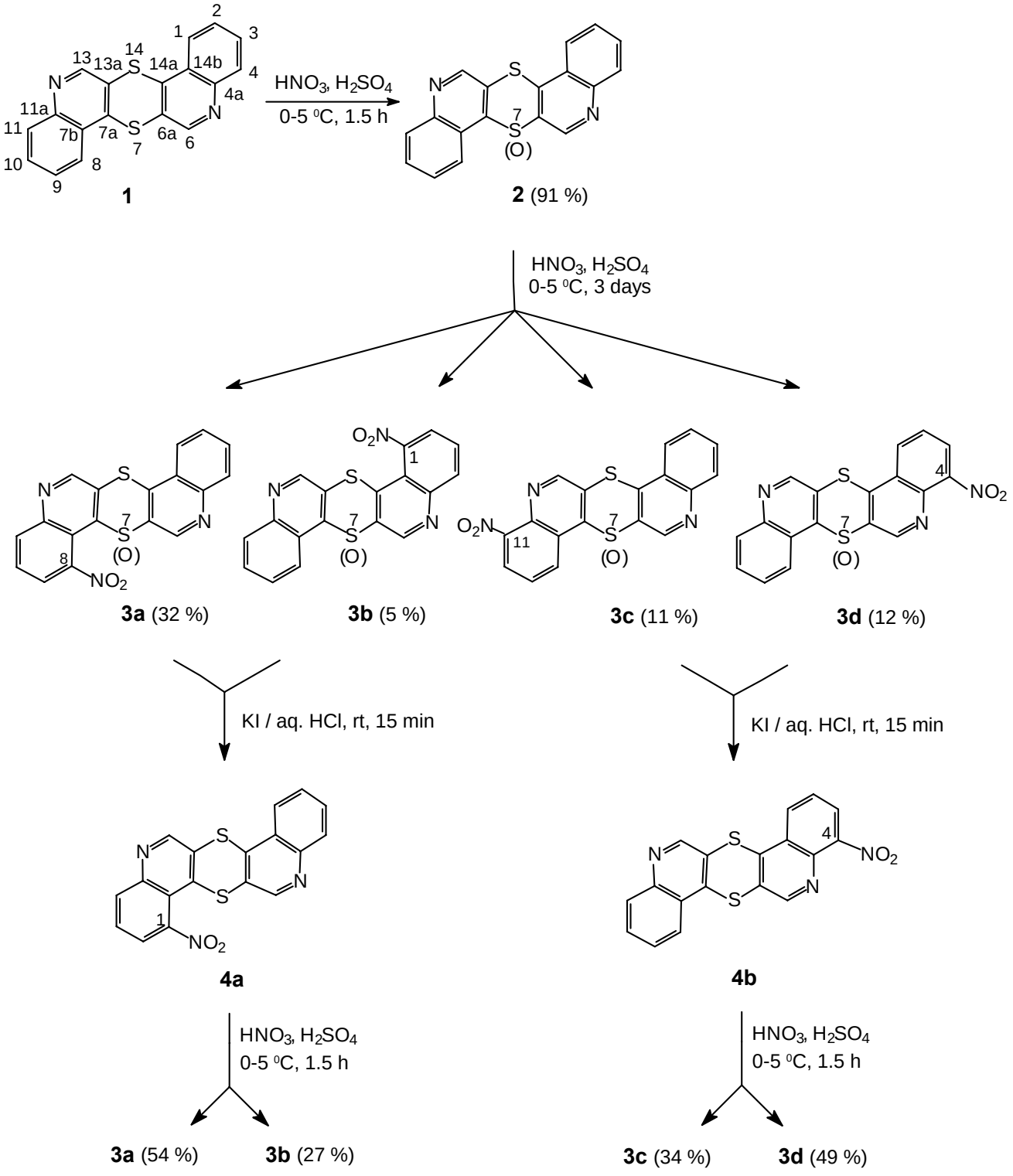
Reactions of thioquinanthrene (**1**) and isothioquinanthrene (**5**), even in the presence of an excess of nitrating mixture (0-5 °C, 1-3 h) led to the sulfoxides (**2**) and (**6**) as the only products. However, when the reaction mixture formed from **1** was left for 3 days, dithiin *S*-oxide (**2**) was accompanied by nitrothioquinanthrene *S*-oxides (**3a-d**)(Scheme 1) but in the case of that formed from **5,** dithiin *S*-oxide (**6**) was accompanied by nitroisothioquinanthrene *S*-oxides (**7a)** and (**7b**).

The composition of **3a**–**d** mixtures was deduced from the ^{1}H NMR spectra and from quantitative TLC data. Compound (**3a**) was isolated by recrystallization of mixture of **2** and **3a-d** from methanol or DMF, isomers (**3c, d**) were obtained by preparative TLC (SiO_2, CCl_4 : acetone 4:1 v/v) but the minor isomer (**3b**) in the pure state was isolated only from reoxidation products of **4a**.

For analytical purposes nitrosulfoxides (**3a-d**) presented below were reduced with aqueous hydrogen

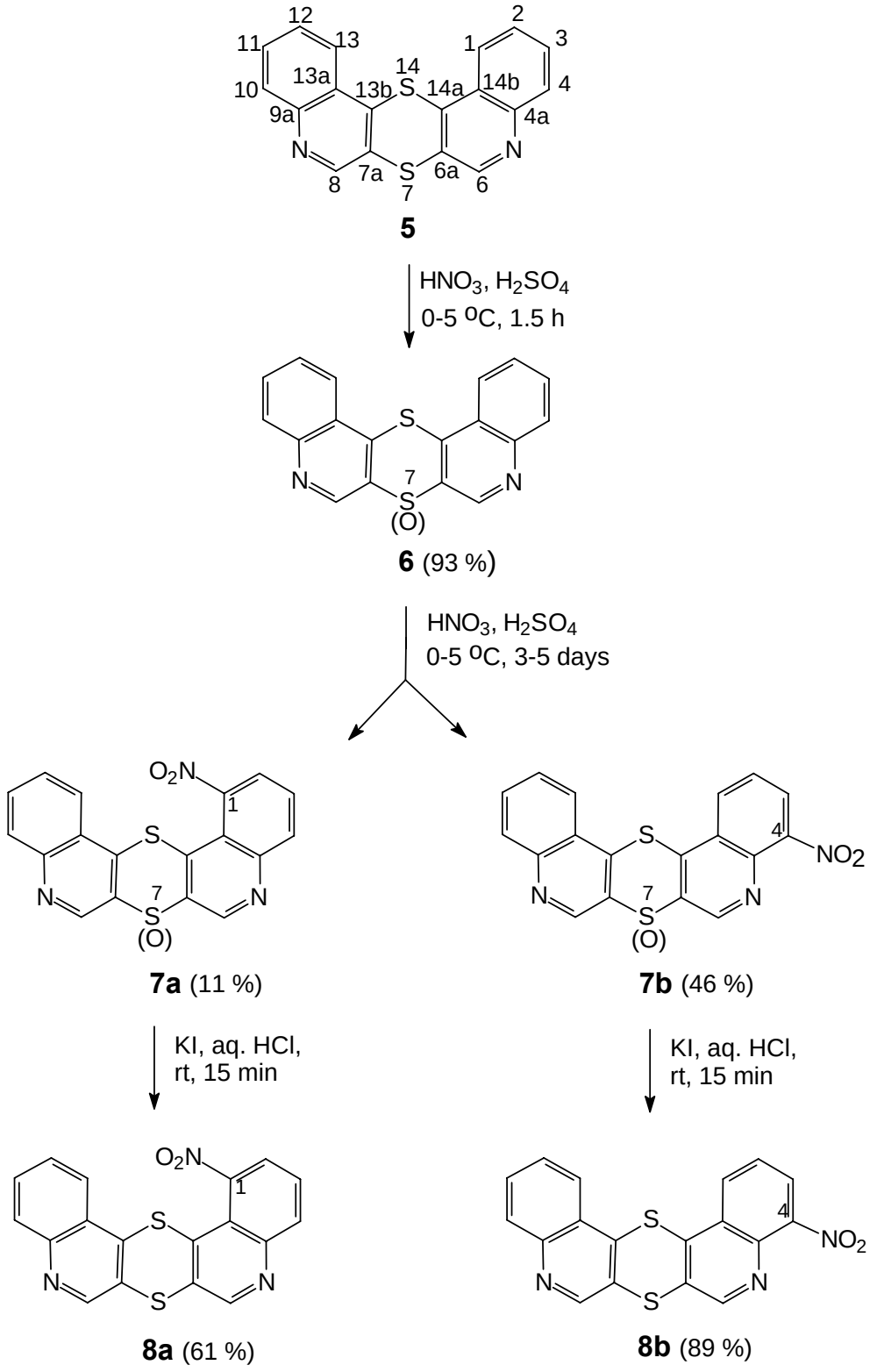
iodide (generated from potassium iodide and hydrochloric acid) to nitrothioquinanthrenes (**4**). Reoxidation of compounds (**4a**) with nitrating mixtures led to sulfoxides (**3a, b**) but the same treatment of **4b** afforded sulfoxides (**3c, d**) (see Scheme 1).

Scheme 1



The same reactions of isothioquinanthrene (**5**) with nitrating mixture (Scheme 2) led to *S*-oxide (**6**) which was then nitrated to nitro-*S*-oxides (**7a, b**).

Scheme 2



Structure assignment of compounds (**3a-d**) and (**4a, b**)

Elemental analysis and MS spectral data have shown that compounds (**3**) and (**7**) were formed by introduction of one nitro group into the molecules of sulfoxides (**2**) or (**6**). The IR spectra of all new synthesized compounds have shown strong bands due to aromatic nitro groups at 1310-1350 cm^{-1} and

1500-1565 cm^{-1}. In the case of nitrosulfoxides (**3**) and (**7**) strong bands in sulfoxide region [13] at $\nu_{S=O}$ = 1025-1055 cm^{-1} were also observed.

As a starting point in the structure analysis of nitrosulfoxides (**3a-d**) we considered to simplify the analytical steps by eliminating of sulfinyl group spectroscopic effects. For this purpose, nitro sulfoxide (**3a**) was reduced by KI / aq. HCl system to nitrothioquinanthrene (**4a**). The same reduction of **3c** and **3d** species led to nitrothioquinanthrene (**4b**). Treatment of nitrothioquinantrenes (**4a**, **4b**) with nitrating mixture (0 °C, 1.5 h) follows as *S*-monooxidation to gave the mixture of **3a**, **b** for **4a** or the mixture of **3c**, **d** for isomer (**4b**) (see Scheme 1)

The ^{1}H NMR spectrum of **4a** as well as of **4b** reveals two singlets from α-quinolinyl protons (H6 and H13) and multiplets from seven benzene-ring protons. The latter could be divided into ABX and ABMX systems, based on the multiplicity of the proton signals.

As shown earlier,[2h,16] the connectivity link between the pyridine and benzene parts of quinoline moieties in 3,4'-diquinolinyl sulfides could be established by long-range proton-carbon correlations between bridged quaternary carbon atoms of both aromatic rings and the respective protons. In the case of compound (**4a**) and (**4b**) it should be the correlations of carbon C4a with H1, H3 and H6 or C11a with H8, H10 and H13, respectively.

The analysis of the "right hand" quinoline fragments, i.e. β,γ-disubstituted quinoline moieties of **4a** and **4b** were performed according to the reported methodology.[2h] It confirmed the spectral position of the singlets from H-6 protons and showed the position of the second singlet, i.e. that from H-13 proton. Spectra of ABX group (i.e. in trisubstituted quinoline unit) of **4a** and **4b** isomers are composed of three double doublets, two with one *ortho* and one *meta* couplings and one with two *ortho* couplings. It indicates that the nitro substituent in **4a** and **4b** are located at the C-1 or C-4 carbon atom i.e. in *5- or 8-quinolinyl-type* position. Double doublets with two *ortho* coupling may be assigned for proton H-2 (in the case of 4-nitro isomer (**4b**)) or for proton H-3 (for 1-nitro isomer (**4a**)). The distinction between H-1 and H-4 protons could be achieved owing to long - range proton – carbon correlations, as shown in Scheme 3.

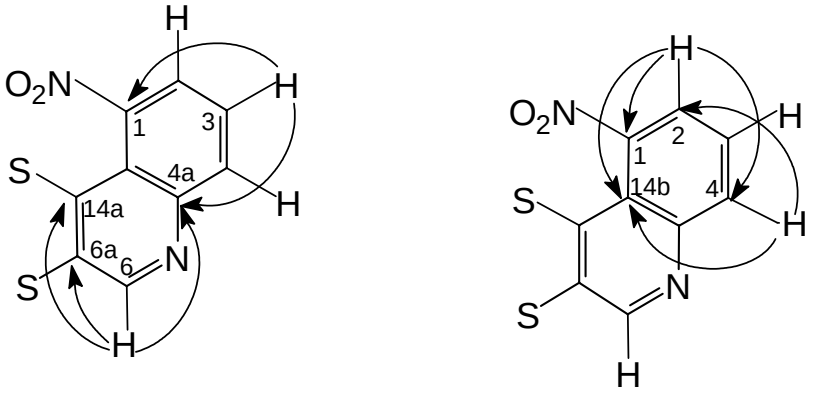
In the case of compound (**4a**) the three - bond $^3J_{CH}$ correlations between H-3 proton and C1 and C4a carbon atoms and those of the H-6 proton with the C4a, C6a and C14a carbons confirm the connectivity link between the members of the aromatic rings in the trisubstituted quinoline unit. Thus, the nitro group must be located on position 1. This conclusion is in full agreement with long-range proton-carbon correlations of H2 / C1, C4, C14b and H4 / C2, C14b (see Table 1).

Crucial data in the structure assignment of isomer (**4b**) come from the three - bond $^3J_{CH}$ correlations between H-1 proton and C3, C4a and C14a; H-3 proton and C1, C4 and C4a, as well as those of the H-6 proton and C4a, C6a and C14a. Thus, the nitro group must be located in position 4. This conclusion is in full agreement with long-range proton-carbon correlations of H2 with C4 and C14b.

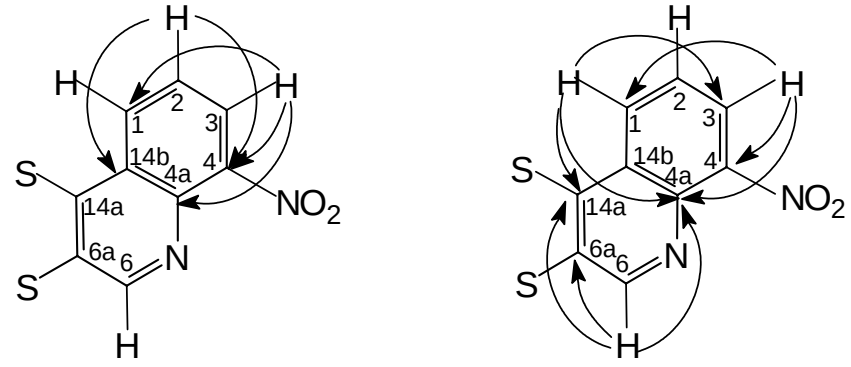
Scheme 3

Sets of long-range proton-carbon correlation in 1-nitrothioquinanthrene (**4a**) and 4-nitrothioquinanthrene (**4b**)

for **4a**



for **4b**



The deoxygenation of nitrosulfoxides (**3a**) and (**3b**) led to 1-nitrothioquinanthrene (**4a**) but that of nitrosulfoxides (**3c**) and (**3d**) to 4-nitrothioquinanthrene (**4b**) (Scheme 1). This means that nitro group in compounds (**3a**) and (**3b)** is located on the *5-quinolinyl* positions, i.e. 1 or 8 according to the numbering of thioquinanthrene. In compounds (**3c**) and (**3d**) it is located in *8-quinolinyl* positions, i.e. 4 or 11 according to the numbering of thioquinanthrene.

^{1}H NMR spectra of **3a-d,** similarly to those of **4a, b**, revealed two signals of α-quinolinyl protons H-6 and H-13 and seven multiplets of benzene – ring protons. The later could be divided into ABMX and ABX systems. The shapes of multiplets of ABX groups are typical for the spectral picture of benzene ring protons in 5- or 8-substituted quinolines.

Due to sulfinyl group spectroscopic effects (see below) the role of basic reference compound for the NMR spectral assignment of nitrothioquinanthrene *S*-oxides (**3a-d**) is played by 7-thioquinanthrene *S*-oxide (**2**). To complete the ^{1}H and ^{13}C NMR spectral data of **2**, COSY, HSQC and HMBC techniques were applied. They revealed three typical features of ^{1}H NMR spectrum of **2**. As compared to starting

Table 1. ^{1}H and ^{13}C chemical shifts δ [ppm]of compounds (**2, 3a, 4a** and **4b**) (DMSO-d_6)

	2			**3a**			**4a**			**4b**		
	δ_H	δ_C	HMBC	δ_H	δ_C	HMBC	δ_H	δ_C	HMBC	δ_H	δ_C	HMBC
1	8.53	124.6	3, 4a,14a	8.56	124.3	3, 4a,14a		146.3		8.63	127.4	3,4a,14a
2	7.94	129.4	4,14b	7.96	129.1	4,14b	8.34	126.0	1, 4,14b	7.95	127.8	4a,14b
3	8.06	133.2	1,4a	8.06	132.7	1,4a	7.97	129.8	1,4a	8.38	123.8	1,4,14b
4	8.24	130.6	2,14b	8.27	130.6	2,14b	8.40	135.6	2,14b		148.2	
4a		147.6			147.1			147.3			137.4	
6	9.50	149.7	4a,6a,14a	9.40	147.6	4a, 6a,14a	9.20	151.4	4a,6a,14a	9.11	150.3	4a,6a,14a
6a		141.4			129.0			131.0			128.8	
7a		140.0			144.7			144.8			142.6	
7b		124.6			115.8			129.3			129.6	
8	8.93	123.1	7a,10,11a		144.7		8.39	124.2	7a,10,11a	8.37	125.5	7a,10,11a
9	7.96	129.8	7b,11	8.54	126.8	7b,8,11	7.82	128.9	7b,11	7.83	1385	7b,11
10	7.99	131.3	8,11a	8.07	129.5	8,11a	7.89	131.3	8,11a	7.92	130.8	8,11a
11	8.27	130.4	7b,9	8.59	136.0	7b,9	8.10	129.9	7b,9	8.13	129.5	7b,9
11a		147.1			146.7			147.0			146.5	
13	9.52	149.6	7a,11a,13a	9.72	151.3	7a,11a,13a	8.86	148.6	7a,11a,13a	9.01	148.1	7a,11a,13a
13a		124.1			138.9			126.7			125.6	
14a		124.7			139.7			143.0			144.1	
14b		124.7			124.3			118.9			126.6	

thioquinanthrene (**1**) α-quinolinyl singlets were deshielded by 0.50 ppm for proton H-6 (up to the value of 9.50 ppm) and 0.52 ppm for proton H-13 (up to the value of 9.52 ppm). Furthermore due to *peri*-sulfinyl group effect, the signal of H-8 proton was shifted by 0.55 ppm up to 8.93 ppm. These findings where of diagnostic value in the structure assignment of **3a-d**.

^{1}H NMR spectrum of **3b** exhibited a signal at 9.14 ppm close to that of 7-thioquinanthrene *S*-oxide (**2**), indicating that the nitro group must be located at the "right hand" quinoline moiety. On the other hand, ^{1}H NMR spectrum of **3a** exhibited lack of a proton being *peri*-influenced by the sulfinyl group. Thus, this position ought to be occupied by the nitro group. It points out that compound (**3a**) is a 8-nitro isomer. The complete ^{1}H and ^{13}C NMR spectral assignment of **3a** (Table 1) was performed as described for compound (**4a**). Taking into account the structural **3a**, **b** / **4a** relation (see Scheme 1) the isomer (**3b**) should be 1-nitrothioquinanthrene 7-oxide.

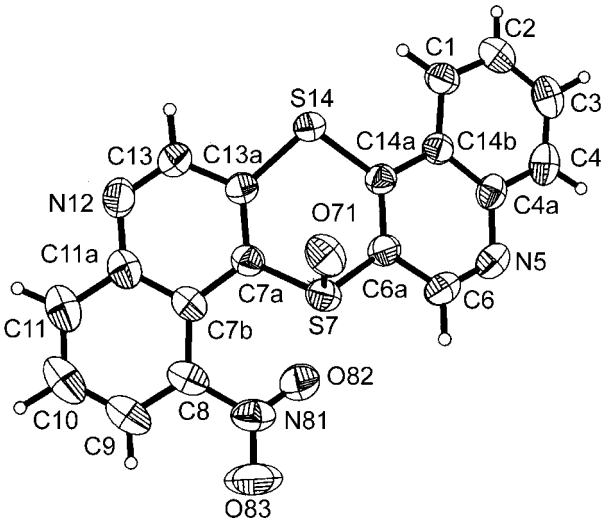
Distinction between **3c** and **3d** isomers could be made from the multiplicity of the H-8 proton, since a double doublet at δ_H = 9.19 ppm was observed for compound (**3c**) (deshielded as compared to **2** by 0.26 ppm). In the case of **3d** the H-8 proton was observed as double double doublet at 8.95 ppm.

The ^{1}H and ^{13}C NMR spectral analysis of isothioquinanthrene derivatives (**7**) and (**8**) was performed with the same analytical steps as for thioquinanthrene derivatives (**3**) and (**4**).

X-Ray diffraction analysis of compound (**3a**).

The NMR spectral conclusions concerning the structures of compounds (**3a-d**) were supported by X-Ray analysis of 8-nitrothioquinanthrene-7-oxide (**3a**). The value of O(71)-S(7)-C(7a)-C(13a) angle (52.1°) proves for the axial orientation of sulfoxide oxygen O(71). Furthermore, the O(82)·····S(7) distance (2.774 Å) is well below the sum of oxygen and sulfur van der Waals radii (3.25 Å),[17] thus indicating the

Figure 1. ORTEP representation of **3a** showing the atom labeling scheme



strong oxygen – sulfur interaction and strong attraction between *ortho* situated nitro and sulfinyl groups. The same effect was observed for methyl o-nitrophenyl sulfoxide with O·····S distance of 2.709 Å.[18]

Table 2. Selected bond lengths [Å] and angles [°] in **3a**

Bond lengths [Å]			
S(7)-O(71)	1.489(2)	S(14)-C(13a)	1.744(2)
N(81)-C(8)	1.474(3)	S(14)-C(14a)	1.749(2)
S(7)-C(6a)	1.769(2)	C(6a)-C(14a)	1.381(2)
S(7)-C(7a)	1.792(2)	C(7a)-C(13a)	1.376(2)
Bond angels [°]:			
C(6a)-S(7)-O(71)	105.96(8)	C(7a)-C(7b)-C(8)	127.29(18)
C(7a)-S(7)-O(71)	104.50(9)	S(14)-C(14a)-C(14b)	119.33(12)
C(6a)-S(7)-C(7a)	95.81(8)	S(7)-C(7a)-C(7b)	121.94(13)
C(13a)-S(14)-C(14a)	102.20(8)	C(7b)-C(1)-N(81)	120.23(18)
C(1)-C(14b)-C(14a)	123.89(16)	C(9)-C(1)-N(81)	116.14(18)
Torsion angels [°]:			
O(71)-S(7)-C(6a)-C(14a)	-54.5(2)	C(10)-C(9)-C(8)-N(81)	-168.2(2)
O(71)-S(7)-C(7a)-C(13a)	52.1(2)	C(7a)-C(7b)-C(8)-N(81)	-19.0(3)
S(7)-C(6a)-C(14a)-S(14)	-12.8(2)	C(9)-C(8)-N(81)-O(83)	-29.8(3)
S(7)-C(7a)-C(13a)-S(14)	21.8(2)	C(7b)-C(8)-N(81)-O(82)	144.7(2).

CONCLUSION

The investigated compounds - thioquinanthrene (**1**) and isothioquinanthrene (**5**) - were easily oxidised to monosulfoxides (**2**) or (**6**) when treated by a mixture of fuming nitric and concentrated sulfuric acids. No products of further oxidation were observed under these conditions. Subsequently, monosulfoxides underwent nitration yielding up to 70 % nitro derivatives. It can be seen from the described process that the presence of sulfinyl group at the β-quinolinyl position does not change characteristic orientation in electrophilic substitution reaction of quinoline leading to 5- or 8-nitro derivatives. Surprisingly high contribution of 8-nitrothioquinanthrene 7-oxide product suggests an interaction between the sulfinyl group and the nitronium ion at the initial stage of the nitration reaction.

EXPERIMENTAL

General Remarks: Melting points were taken in open capillary tubes on Digital Melting Point Apparatus IA 9000 (Electrothermal, UK). ^{1}H NMR spectra were recorded using tetramethylsilane as internal

standard for hexadeuteriodimethyl sulfoxide solutions with a Bruker AM 500 (500.13 MHz proton frequency) and Inova 300 (300.13 MHz proton frequency) spectrometers. ^{13}C and correlations NMR spectra (COSY, HSQC, HMBC) were recorded with a Bruker AM 500 spectrometer (125.76 MHz carbon frequency, hexadeuteriodimethyl sulfoxide, internal tetramethylsilane). ESR spectra (calibrated with DPPH) were measured with a Brucker EMX-10/2.7 spectrometer. IR spectra were recorded with a Magma - IR 500 (Nicolet, USA) spectrophotometer in potassium bromide pellets. LSI MS spectra (Cs^+, 15 keV, nba) and EI MS spectra (70 eV) were determined with a AMD-604 mass spectrometer. TLC analyses were performed on Merck's silica gel 60 F_{254} plates with acetone – carbon tetrachloride 1:4 (v/v) as developing system.

Thioquinanthrene (**1**), thioquinanthrene 7-oxide (**2**), isothioquinanthrene (**5**) and isothioquinanthrene 7-oxide (**6**) were prepared as described previously.[8,9]

General Procedure from the Treatment of Dithiinodiquinoline (**1**, **4**, **5)** with a Nitrating Mixture: Dithiin (**1**, **4** or **5**) (1 mmol) was dissolved with stirring in 96% sulfuric acid (3 mL) at 0 °C. The nitrating mixture (fuming nitric acid, d=1.50 g/mL, 0.32 mL, *ca*. 7.2 mmol of nitric acid and 0.32 mL of conc. sulfuric acid) was then added dropwise at 0-5 °C, the mixture was maintained at 0 °C for 1.5 h, and left for 3 days at 0-5 °C. It was then cautiously poured onto 40 g of ice, and neutralized at 0 °C with 25% aqueous ammonia. The solid was filtered off, washed twice with cold water and air-dried to give yellow products containing the mixture of dithiinodiquinoline S-oxides (**2**, **3a-d**) or **(6, 7a**, **b**). Sulfoxide (**2**), as well as **6** was isolated by crystallisation of products mixture from *N*,*N*-dimethylformamide. The crystallisation liquor was separated and than dry-evaporated under vacuum. The compound (**3a**) or (**7b**) was isolated from the residue by several recrystallisations from methanol. Analytical samples of all compounds synthesised were obtained by TLC chromatography (silica gel, acetone – carbon tetrachloride 1 : 4 v/v).

8-Nitrothioquinanthrene-7-oxide (**3a**): Yield 29 %. mp 239-242 ^oC (decomp). LSI MS: 380 $[M+1]^+$, 363 $[M-O]^+$. IR ν: 1058 cm^{-1} (SO), 1341, 1525 cm^{-1} (NO_2). ^1H NMR (500 MHz, DMSO-d_6), δ: 7.96 (m, 1H, ^3J = 8.3, ^3J = 7.0, ^4J = 1.4 Hz, H-2), 8.06 (m, 1H, ^3J = 8.4, ^3J = 7.0, ^{4}J = 1.4 Hz, H-3), 8.07 (dd, 1H, ^3J = 8.3, ^3J = 7.9 Hz, H-10), 8.26-8.28 (m, 1H, H-4), 8.54-8.56 (m, 1H, H-9), 8.56-8.58 (m, 1H, H-1), 8.59 (dd, 1H, ^3J = 8.3, ^4J = 1.1 Hz, H-11), 9.40 (s, 1H, H-6), 9.72 (s, 1H, H-13). *Anal.* Calcd for $C_{18}H_9N_3O_3S_2$: C 56.98; H 2.39; N 11.08; S 16.90. Found C 56.81; H 2.37; N 11.05; S 16.10.

1-Nitrothioquinanthrene-7-oxide (**3b**): mp 223-225 ^oC (decomp). EI MS (70 eV), m/z (%): 379 (5) $[M^+]$, 363 (4) $[M-O]^+$, 331 (100) $[M-SO]^+$. IR ν: 1089 (SO), 1384, 1524 cm^{-1} (NO_2). ^1H NMR (300 MHz, DMSO-d_6) δ: 7.90 (m, 1H, ^3J = 8.2, ^3J = 7.0, ^4J = 1.4 Hz, H-9), 7.96 (m, 1H, ^3J = 8.4, ^3J = 7.0, ^4J = 1.4 Hz, H-10), 8.10 (dd, 1H, ^3J = 8.4, ^3J = 7.5 Hz, H-3), 8.19-8.23 (m, 1H, H-11), 8.51 (m, 1H, ^3J = 7.5, ^4J = 1.1 Hz, H-2), 8.53 (dd, 1H, ^3J = 8.4, ^4J = 1.1 Hz, H-4), 9.12-9.16 (m., 1H, H-8), 9.28 (s, 1H, H-13), 9.51 (s, 1H, H-6). *Anal.* Calcd for: $C_{18}H_9N_3O_3S_2$: C 56.98; H 2.39; N 11.08; S 16.90. Found C 56.74; H 2.31;

N 10.98; S 16.26.

11-Nitrothioquinanthrene-7-oxide (**3c**): mp 254-255 (decomp). EI MS (70 eV), m/z (%): 379 (20) [M^+], 363 (38) [M-O]$^+$, 331 (100) [M-SO]$^+$. IR ν: 1029 (SO), 1384, 1533 cm^{-1} (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.94-7.99 (m, 1H, H-2), 8.04-8.14 (m, 2H, H-3, H-9), 8.25-8.28 (m, 1H, H-4), 8.49 (dd, 1H, ^3J = 7.6, ^4J = 1.1 Hz, H-10), 8.54-8.57 (m, 1H, H-1), 9.19 (dd, 1H, ^3J = 8.5, ^4J = 1.1 Hz, H-8), 9.52 (s, 1H, H-6), 9.67 (s, 1H, H-13). *Anal.* Calcd for $C_{18}H_9N_3O_3S_2$: C 56.98; H 2.39; N 11.08; S 16.90. Found C, 56.71; H 2.42; N 11.01; S 16.39.

4-Nitrothioquinanthrene-7-oxide (**3d**): mp >225 °C (decomp). EI MS (70 eV), m/z (%): 379 (28) [M^+], 363 (18) [M-O]$^+$, 331 (100) [M-SO]$^+$. IR ν: 1058 (SO), 1349, 1563 cm^{-1} (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.98-8.03 (m, 2H, H-9, H-10), 8.08 (dd, 1H, ^3J = 8.6, ^3J = 7.5 Hz, H-2), 8.28-8.31 (m, 1H, H-11), 8.56 (dd, 1H, ^3J = 7.5, ^4J = 1.1 Hz, H-3), 8.81 (dd, 1H, ^3J = 8.6, ^4J = 1.1 Hz, H-1), 8.93-8.96 (m, 1H, H-8), 9.56 (s, 1H, H-13), 9.61 (s, 1H, H-6).

1-Nitroisothioquinanthrene 7-oxide (**7a**): mp >225 °C (decomp). EI MS (70 eV), m/z (%): 379 (5) [M^+], 363 (100) [M-O]$^+$, 331 (49) [M-SO]$^+$. IR ν: 1091 (SO), 1384 and 1533 cm^{-1} (NO_2). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.88 (m, 1H, ^3J = 8.2, ^3J = 7.1, ^4J = 1.1 Hz, H-12), 7.97 (m, 1H, ^3J = 8.1, ^3J = 7.0, ^4J = 1.4 Hz, H-11), 8.07 (dd, 1H, ^3J = 8.4, ^3J = 7.6 Hz, H-3), 8.17-8.19 (m, 1H, H-10), 8.25-8.28 (m, 1H, H-13), 8.45 (dd, 1H, ^3J = 7.6, ^4J = 1.0 Hz, H-2), 8.51 (dd, 1H, ^3J = 8.4, ^4J = 1.0 Hz, H-4), 9.22 (s, 1H, H-8), 9.37 (s, 1H, H-6). *Anal.* Calcd for $C_{18}H_9N_3O_3S_2$: C 56.98; H 2.39; N 11.08; S 16.90. Found: C 56.72; H 2.39; N 10.82; S 16.45.

4-Nitroisothioquinanthrene-7-oxide (**7b**): mp >225 °C (decomp). EI MS (70 eV), m/z (%): 379 (5) [M^+], 363 (20), [M-O]$^+$, 331 (100) [M-SO]$^+$. IR ν: 1081 (SO), 1334, 1534 cm^{-1} (NO_2). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.95 (m, 1H, ^3J = 8.2, ^3J = 7.0, ^4J = 1.0 Hz, H-12), 8.05 (m, 1H, ^3J = 8.2, ^3J = 7.0, ^4J = 1.2 Hz, H-11), 8.08 (dd, 1H, ^3J = 8.3, ^3J = 7.5, H-2), 8.24-8.26 (m, 1H, H-10), 8.53 (dd, 1H, ^3J = 7.5, ^4J = 1.0 Hz, H-3), 8.66-8.68 (m, 1H, H-13), 8.95 (dd, 1H, ^3J = 8.3, ^4J = 1.0 Hz, H-1), 9.42 (s, 1H, H-8), 9.51 (s, 1H, H-6). ^{13}C NMR (500 MHz, DMSO-d_6) δ: 124.5 (C-2), 124.8 (C-8a, C-13a), 124.9 (C-13), 125.9 (C-3), 128.8 (C-1), 129.5 (C-12), 130.5 (C-10), 130.9 (C-7a), 133.1 (C-6a), 132.9 (C-11), 137.6 (C-13b, C-14b), 138.6 (C-4a), 139.1 (C-14a), 145.8 (C-8), 148.8 (C-4), 149.5 (C-6).). *Anal.* Calcd for $C_{18}H_9N_3O_3S_2$: C 56.98; H 2.39; N 11.08; S 16.90. Found C 56.87; H 2.35; N 11.06; S 16.31.

Reduction of dithiinoquinoline 7-oxides (**3**) or (**7**) to dithiinoquinolines (**4**) or (**8**): Potassium iodide (0.4 g, 2.4 mmol) was added to a solution of sulfoxides **3** or **7** (1 mmol) in 3.5 mL of conc. hydrochloric acid. The mixture was stirred at 20 °C for 15 min. Saturated aqueous sodium thiosulfate was then added portionwise up to complete consumption of iodine. The solid was filtered off, washed with water and triturated with saturated aqueous sodium hydrogen carbonate. The solid was filtered off, washed with

cold water and then three times with hot water. It was then air-dried and twice recrystallised from *N*,*N*-dimethylformamide. For analytical purposes, compounds (**4**) or (**8**) were purified by TLC chromatography.

1-Nitrothioquinanthrene (**4a**): Yield 90%. mp 244-245 ^{o}C. Yield 90%. EI MS.(70 eV), m/z (%): 363 (100) [M^+], 317 (28) [M-NO_2]$^+$. IR ν: 1349 and 1526 cm^{-1} (NO_2). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.82 (m, 1H, ^3J = 8.4, ^3J = 7.0, ^4J = 1.1 Hz, H-9), 7.89 (m, 1H, ^3J = 8.3, ^3J = 7.0, ^4J = 1.3 Hz, H-10), 7.97 (dd, 1H, ^3J = 8.4, ^3J = 7.7 Hz, H-3), 8.08-8.11 (m, 1H, H-11), 8.34 (dd, 1H, ^3J = 7.7, ^4J = 1.1 Hz, H-2), 8.39 (m, 1H, ^3J = 8.4, ^4J = 1.3, ^5J = 0.6 Hz, H-8), 8.40 (dd, 1H, ^3J = 8.4, ^4J = 1.1 Hz, H-4), 8.86 (s, 1H, H-13), 9.20 (s, 1H, H-6). *Anal.* Calcd for $C_{18}H_9N_3O_2S_2$: C 59.49; H 2.50; N 11.56; S 17.64. Found C 59.32; H 2.47; N 11.47; S 17.49.

4-Nitrothioquinanthrene (**4b**): Yield 86 %. mp 248-250 ^{o}C. EI MS (70 eV), m/z (%): 363 (100) [M^+], 317 (27) [M-NO_2]$^+$. IR ν: 1384, 1525 cm^{-1} (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.81-7.86 (m, 1H, H-9), 7.88-7.93 (m, 1H, H-10), 7.95 (dd, 1H, ^3J = 8.1, ^3J = 7.9, H-2), 8.11-8.15 (m, 1H, H-11), 8.35-8.41 (m, 2H, H-8, H-3), 8.63 (dd, 1H, ^3J = 8.1, ^4J = 1.2 Hz, H-1), 9.01 (s, 1H, H-13), 9.11 (s, 1H, H-6).

1-Nitroisothioquinanthrene (**8a**): mp >225 ^{o}C (decomp). EI MS (70 eV), m/z (%): 363 (10) [M^+], 317 (6) [M-NO_2]$^+$. IR ν: 1384, 1526 cm^{-1} (NO_2). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.79-7.94 (m, 2H, H-11, H12), 7.91-7.97 (m, 1H, H-3), 8.04-8.09 (m, 1H, H-10), 8.10-8.15 (m, 1H, H-13), 8.25-8.29 (m, 1H, H-1), 8.37-8.41 (m, 1H, H-4), 8.79 (s, 1H, H-8), 9.0 (s, 1H, H-6).

4-Nitroisothioquinanthrene (**8b**): mp 238-240 ^{o}C. EI MS (70 eV), m/z (%): 363 (100) [M^+], 317 (33) [M-NO_2]$^+$. IR ν: 1025, 1534 cm^{-1} (NO_2). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.82 (m, 1H, ^3J = 8.0, ^3J = 6.9, ^4J = 1.2 Hz, H-12), 7.90 (m, 1H, ^3J = 8.5, ^3J = 6.9, ^4J = 1.2 Hz, H-11), 7.93 (dd, 1H, ^3J = 8.6, ^3J = 7.5 Hz, H-2), 8.08-8.12 (m, 1H, H-10), 8.34 (dd, 1H, ^3J = 7.5, ^4J = 1.2 Hz, H-3), 8.52-8.56 (m, 1H, H-13), 8.83 (dd, 1H, ^3J = 8.6, ^4J = 1.2 Hz, H-1), 8.99 (s, 1H, H-8), 9.09 (s, 1H, H-6). *Anal.* Calcd for $C_{18}H_9N_3O_2S_2$: C 59.49; H 2.50; N 11.56; S 17.64. Found C 59.38; H 2.48; N 11.51; S 17.46.

X-Ray Diffraction Analysis of **3a**

Crystals of **5a** were grown at room temperature by slow evaporation of a chloroform solution.

Crystal data: Empirical formula $C_{18}H_9N_3O_3S_2$, formula weight 379.40, monoclinic, space group P2(1)/c, a = 7.267(2), b = 16.338(4), c = 13.547(3) Å, β = 91.32(3)^0, V = 1608.0(8) Å^3, Z = 4, D_c = 1.567 Mg/m^3, F(000) = 776.

Data Collection and Processing: Kuma KM4 diffractometer, radiation Cu-K_α (λ = 1.54180 Å), T = 293(2) K, crystal size 0.15 x 0.20 x 0.20 mm, collection range 4.24 ≤ θ ≤ 80.23^0, index ranges –9 ≤ h ≤ 9, 0 ≤ k ≤ 20, -17 ≤ l ≤ 17, reflections collected 6339, independent reflections 3400 [R_{int} = 0.02691].

Structure Analysis and Refinement: The structure was solved by direct methods (SHELXS 97)[19] and refined by full-matrix least-squares analysis on all F^2 (SHELXL 97).[20] Non-hydrogen atoms were refine with anisotropic thermal parameters. Hydrogen atoms were located on difference Fourier map and refined with isotropic thermal parameters. Final agreement factors were $R_1 = 0.0450$ [$I<2\sigma(I)$], $wR_2 = 0.1126$ (all data) and GOF = 1.083 for 2845 data and 272 parameters. Largest diffraction peak an hole were 0.501 an –0.400 eÅ^{-3}.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (depository number CCDC-176 601). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK {Fax; (internat.) +44 (0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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