Competition Between *S*-Oxidation and Nitration in Reactions of Some β- and γ-Quinolinyl Sulfides with Nitrating Mixture

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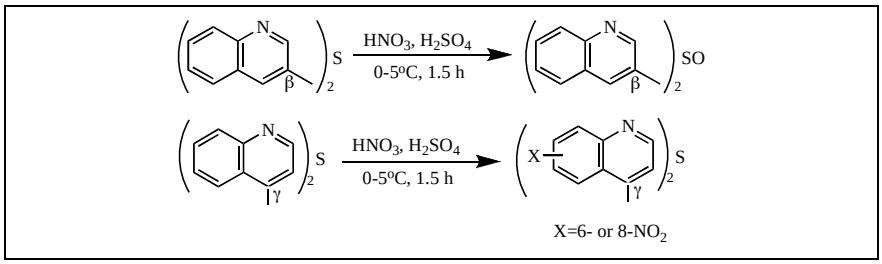

This study was performed in order to explain different orientation in the reaction of quinolinyl sulfides with nitrating mixture, which converted on one hand quinolinyl sulfides **1**, **3** and **5** to sulfoxides **2**, **4** and **8**, respectively, on the other hand, sulfides **6**, **7** to the respective nitroderivatives **9** and **10**. Competitive experiments showed following reactivity order: thianthrene **11** > thianthrene 5-oxide **12** > isothioquinanthrene **3** > thioquinanthrene **1** > 3,3'-diquinolinyl sulfide **5** > 3,4'-diquinolinyl sulfide **6** > 4,4'-diquinolinyl sulfide **7**. Considering that NO_2^+ (as reactive form of nitrating mixture) attacks the most electronodonating (sulfur or carbon) center the reactivity order well correlates with the results of HOMO as well as MEP calculations.

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INTRODUCTION

In the previously reported synthesis of 4-substituted 3-quinolinyl sulfides from quinoline the key-steps were sulfurization of quinoline with elemental sulfur yielding thioquinanthrene **1** (1,4-dithiino[2,3-*c*:5,6-*c*']diquinoline) and cleavage of the 1,4-dithiin ring of **1** with nucleophiles [1,2]. Reactions of thioquinanthrene with nucleophiles [2] proceeded with breaking of the γ-quinolinyl-sulfur bond as a displacement of 3'-quinolinethiolate fragment (as leaving group) by *O*-, *S*-, *N*- and *C*-nucleophiles.

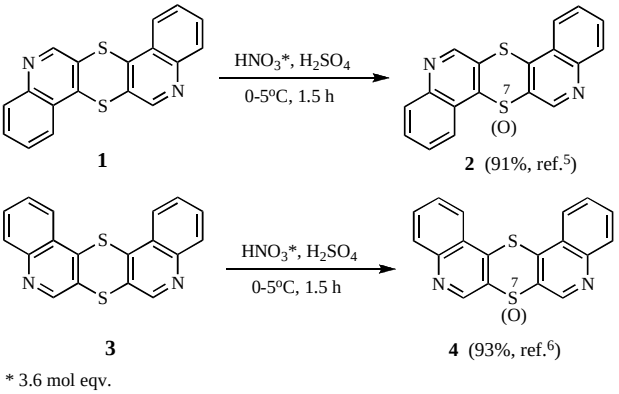
Organosulfinyl groups are better leaving groups than corresponding sulfide ones in reactions of *aza*-activated heteroaromatic systems [3]. Thus, *S*-oxidation of thioquinanthrene **1** to sulfoxide derivatives should involve activation of thioquinanthrene moiety towards nucleophilic displacement. In fact, although thioquinanthrene **1** did not react with phenoxide anion, thioquinanthrene *S*-oxide **2** was completely consumed even at – 20 °C [4].

The reaction of thioquinanthrene **1** with nitrating mixture is an effective source of thioquinanthrene *S*-oxide **2** [5] but the same reaction of 4,4'-diquinolinyl sulfide **7** leads to nitration products [6]. This study was performed to explain differences in the reactivity and regioselectivity of β- and γ-quinolinyl sulfides induced by action of nitrating mixture.

RESULTS AND DISCUSSION

Reactions with nitrating mixture. When thioquinanthrene **1** or isothioquinanthrene **3** were treated (in the form of respective quinolinium salts) with nitrating mixture, the reaction gave (after dilution and neutralization) high yields of thioquinanthrene 7-oxide **2** or isothioquinanthrene 7-oxide **4**, respectively [5,6]. To evaluate the reactivity of quinolinyl-sulfur bonds occurring in the molecules of cyclic β,γ-quinolinediyl bis-sulfides **1** or **3**, the behaviour of open-chain quinolinyl sulfides with β,β'-, β,γ'- and γ,γ'- bonds was studied. To complete the set of β,γ-diquinolinyl sulfides, 3,4'-diquinolinyl sulfide **6** was synthesized. Oxidation of sulfide sulfur atom was observed only in the case of β,β'-diquinolinyl sulfide **5** [6] but for β,γ'-, and γ,γ'- isomers **6** and **7** nitration products **9a**,**b** and **10a**,**b**,**c**, respectively [6], were isolated.

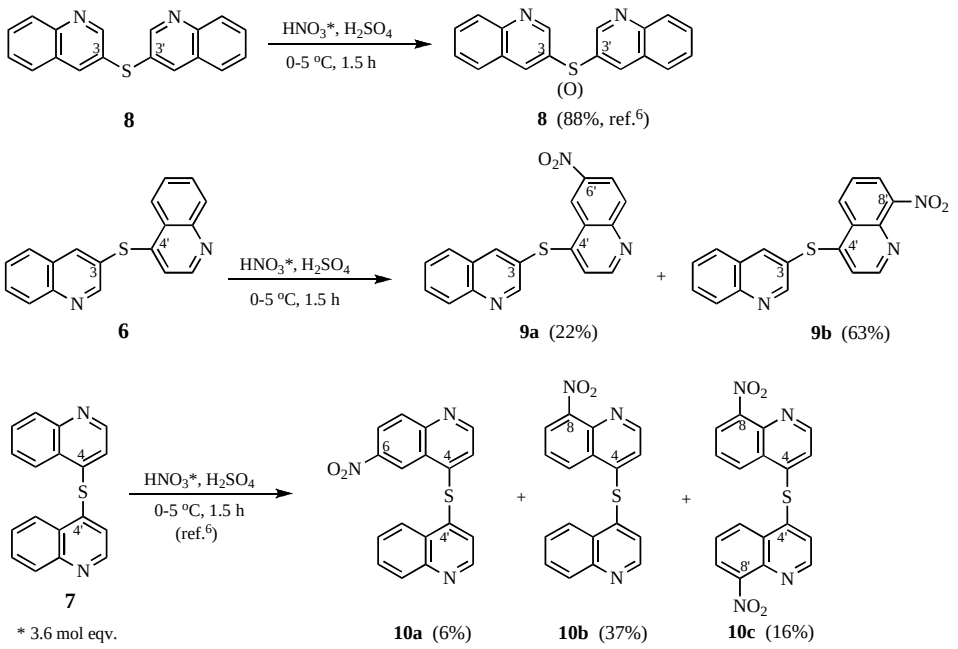
Scheme I



* 3.6 mol eqv.

Structure assignment of compounds 6, 9a and 9b. Total analysis of the ^1H and ^{13}C NMR spectra of 3,4-

Scheme II



diquinolinyl sulfide **6** was performed using 1D and 2D NMR spectrometry, including COSY, HSQC and HMBC techniques. The crucial data in the structure assignment of **6** result from long-range proton-carbon correlation deduced from HMBC spectra. The observed three-bond ^3J correlations H2/C4,C8a, H4/C2,C5,C8a, H5/C4,C7,C8a and H7/C5,C8a, as well as H2'/C4',C8'a, H5'/C4',C7',C8'a and H7'/C5',C8'a confirm the connectivity link between members of aromatic rings of quinoline moieties.

Elemental analysis, MS and IR spectral data have shown that compounds **9a** and **9b** were formed by introduction of one nitro group into a molecule of sulfide **6**. Their IR spectra have shown strong bands due to aromatic nitro groups at 1343 cm^{-1} and 1530 cm^{-1}.

The ^{1}H NMR chemical shift values for 3-substituted quinoline moiety of sulfides **6**, **9a** and **9b** are very close. Positioning of the nitro groups in the 4-substituted nitroquinoline moieties in **9a** and **9b** was based on the comparison of substituent effects caused by the nitro group in the benzene ring of nitroquinolines [7], furthermore, this assignment fits well with the respective data of the same quinoline type unit of sulfides **10a** or **10b**, respectively [6].

Competitive reaction with nitrating mixture. To obtain more accurate data concerning relationship between the nature of the quinolinyl-sulfur bond and the reactivity of sulfides **1**, **3**, **5**, **6** and **7** with nitrating mixture, several competitive reactions were performed. For this purpose the sulfides studied were grouped into two sets and nitrating mixture was dropped into a solution of equimolar mixture of sulfides **1**, **3** and **5** (set 1) or mixture of **5**, **6** and **7** (set 2) in conc. sulfuric (0°C) and then treated and analyzed as presented in the experimental part. The composition of the mixture consisting of substrates and products were deduced from the intensity of the selected proton signals in ^{1}H NMR spectra.

The first set of quinolinyl sulfides was composed of thioquinanthrene **1** (with β-quinolinyl- and γ-quinolinyl sulfide bonds), isothioquinanthrene **3** and 3,3'-diquinolinyl sulfide **5** (both with two β-quinolinyl sulfide bonds). Each sulfide of this set undergoes only oxidation to the respective β-sulfoxide. The data collected in Figure 1A show that the reactivities of compounds **1**, **3**, **5** decrease in the order: **3** >> **1** > **5**.

The second set was composed of diquinolinyl sulfides **5**, **6** and **7**. However, after treatment with nitrating mixture they react in different ways, because β,β'-diquinolinyl sulfide **5** undergoes *S*-oxidation to sulfoxide **8** but β,γ'- and γ,γ'-diquinolinyl sulfides **6** and **7** undergo nitration in the γ-quinolinylthio unit to form 6- and 8-nitroderivatives **9** and **10**, respectively. As could be deduced from Figure 1B, the most reactive appeared to be 3,3'-diquinolinyl sulfide **5**, then 3,4'-diquinolinyl sulfide **6** and 4,4'-diquinolinyl sulfide **7**.

In search for explanation of the reactivity mode of 1,4-dithiinodiquinolines **1**, **3**, a literature review was performed. It revealed that thianthrene **11** after treatment with nitrating mixture or nitric acid may undergo *S*-mono- and *S*,*S*'-dioxidation [8]. To compare its behavior to those of 1,4-dithiinodiquinolines **1**, **3**, it was subjected to reactions with nitrating mixtures under the conditions applied for quinolinyl sulfides **1**, **3**. The results presented in scheme III suggest that thianthrene **11**, oxidized at both *S*-atoms, is more reactive than quinolinyl sulfides **1**, **3**.

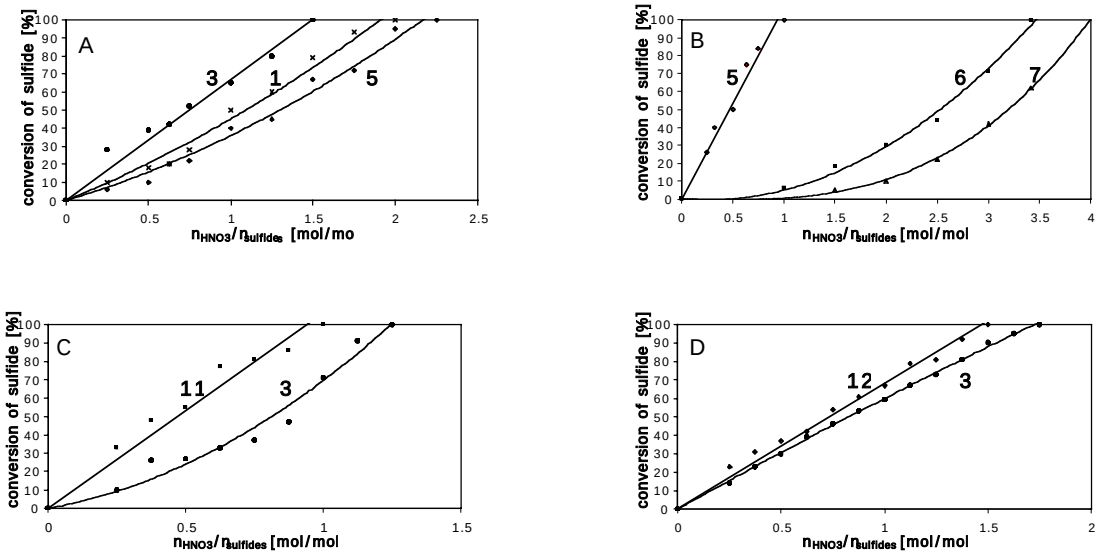
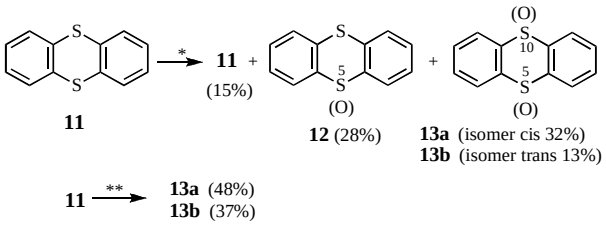


Figure 1. Correlations between conversion of sulfide and quantity of applied HNO_3, determined for competitive experiments between the mixtures of sulfides (sets A, B, C and D) and nitrating mixture (solid lines are quides to the eye)
A: mixture of thioquinanthrene **1** (**x**), isothioquinanthrene **3** (●) and 3,3'-diquinolinyl sulfide **5** (♦) in the ratio 1:1:1, total sulfides amount 1 molar eqv.
B: mixture of 3,3'-diquinolinyl sulfide **5** (♦), 3,4'-diquinolinyl sulfide **6** (■) and 4,4'-diquinolinyl sulfide **7** (▲) in the ratio 1:1:1, total sulfides amount 1 molar eqv.
C: mixture of isothioquinanthrene **3** (●) and thianthrene **11** (■) in the ratio 1:1, total sulfides amount 1 molar eqv.
D: mixture of isothioquinanthrene **3** (■) and thianthrene 5-oxide **12** (♦) in the ratio 1:1, total sulfides amount 1 molar eqv.

Scheme III

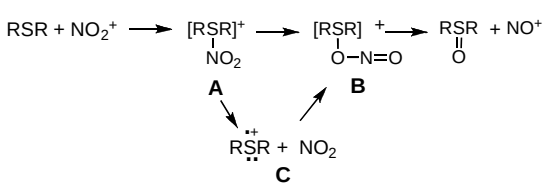


* HNO_3 (1.5 mol eqv.), H_2SO_4, 0-5 °C, 15 min.
** HNO_3 (3.6 mol eqv.), H_2SO_4, 0-5 °C, 1.5 h

This conclusion was than confirmed by the competition experiments with the mixture of thianthrene **11** and isothioquinanthrene **3** as well as thianthrene *S*-oxide **12** and isothioquinanthrene **3**, which demonstrated the reactivity order: thianthrene **11** > thianthrene oxide **12** > isothioquinanthrene **3** (see Figure 1C and 1D).

Olah and co-workers [9] studied the reaction of dialkyl, arylalkyl and diaryl sulfides with nitronium hexafluorophosphate or tetrafluoroborate and proposed the following mechanism:

Scheme IV



An initially formed *S*-nitrosulphonium ion A rearranges into the *S*-nitritosulphonium ion B, which is then stabilized by loss of NO^+ ion to give the corresponding sulfoxide.

On the other hand, during the oxidation of sulfides the presence of cation-radicals was observed. In the case of thianthrene **11** and thianthrene *S*-oxide **12** the respective cation-radical was formed even by dissolution of **11**, as well as **12**, in conc. sulfuric acid. However, in the case of thioquinanthrene **1** and isothioquinanthrene **3** the formation of cation-radical species with g values 2.0087 for **1** or 2.0078 for **3** was observed only after addition of nitrating mixture. Furthermore, the *S*-radicals disappeared after consumption of 1 mol. equiv. of nitric acid. No presence of radicals was observed after treatment of solution of thioquinanthrene 7-oxide **2** or isothioquinanthrene 7-oxide **4** with nitrating mixture [10]. This suggested that the formation of thioquinanthrene S-oxide **2** and isothioquinanthrene S-oxide **4**, as well as thianthrene oxide **12**, should proceed *via* formation of sulfur cation radical C and nitrogen dioxide, which recombine to form nitritosulfonium species B, being finally decomposed to *S*-oxide and NO^+.

ESR spectral study showed formation of cation-radical species during oxidation of thioquinanthrene **1** and isothioquinanthrene **3** as well as of thianthrene **11** and thianthrene S-oxide **12**. Values of ionization energy calculated for thianthrene **11** and protonated forms of compounds **1, 3** and **12** fall in order: thianthrene **11** (6.05

eV) < thianthrene *S*-oxide **12** (11.30 eV) < isothioquinanthrene **3** (11.94 eV) ≤ thioquinanthrene **1** (11.99 eV) and are in agreements with observed relative reactivity in competitive experiments.

Computational study. The calculations were carried out with use of the Gaussian 98 program [11]. The full geometry optimization of the investigated compounds was performed in the 6-31G* basis set. The electrostatic potentials and molecular orbitals were calculated in the 6-311+(2d) basis set. The Molecular Electrostatic Potential Maps and molecular orbitals contours were plotted with the gOpenMol program [12].

The geometrical structures of compounds **1**, **3**, **5-7**, **11**, **12** and their protonated forms were calculated. Bond distances and bond angles for thioquinanthrenediinium ion and thianthrene **11** are in good agreement with the respective values deduced from X-ray measurements [13,14].

The value of C-S-C bond angles calculated for compounds **5** and **7** are close to those obtained from X-ray analysis of derivatives of 3,3'- and 4,4'-diquinolinyl sulfides [15].

Highest occupied molecular orbitals (HOMOs). The contours of HOMOs of thianthrene **11** and protonated forms of compounds **1**, **3**, **5-7**, **12** are presented in Figure 2. In the case of electrophilic attack, the reaction usually takes place at atoms with the largest coefficients in HOMO [16]. From an inspection to the frontier Molecular Orbitals, it can be deduced that for compounds **1**, **3**, **5**, **11** and **12**, which undergo oxidation to *S*-oxides when treated with nitrating mixture, the highest HOMO is localized on sulfur atoms (Figure 2). In the case of compounds **6** and **7** which undergo nitration(at 6- or 8-quinolinyl positions), the highest HOMO is localized on the benzene ring carbon atoms.

In the case of 3,4'-diquinolinyl sulfide **6** the HOMO is localized only at the carbon atoms of 4-quinolinyl moiety – mainly on C8' and C5' atoms, to a less extent on C6' atom. It correlates very well with the orientation in the reaction of sulfide **6** with a nitrating mixture, *i.e.* leading to the formation of 8'-nitro and 6'-nitro isomers **9a** and **9b**. An analogical correlation for 4,4'-diquinolinyl sulfide **7** was found.

Molecular electrostatic potential maps (MEPs). The electrostatic potential maps can be used to predict sites and relative reactivities towards electrophilic attack [16]. In the majority of the maps, regions of negative values of electrostatic potential, V(r), correspond to local minima and are site candidates of electrophilic attack.

Only in the case of thianthrene **11** the MEPs plotted onto essentially the van der Waals surface of the molecule show the negative potential at the sulfur atoms. Since compounds **1**, **3**, **5**, **6** and **7** are present as salts protonated at nitrogen atoms, the respective MEPs show only positive values (Figure 3, Table 1).

However, the V(r) values calculated on sulfur atoms for compound **1**, **3** and **5** are far less positive compared to those of sulfides **6** and **7**, still indicating an affinity for electrophiles. The "border value" seems to be 0.203 au. Sulfur atoms of compounds **1**, **3** and **5** with lower value of V(r) undergo oxidation in reaction with nitrating mixture (as donator of electrophile), but compounds **6** and **7** with higher V(r) value undergo nitration in benzene ring.

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Comparison of the reactivity of sulfides 1, 3, 5, 11 and 12. The data collected in Table 1 show that reactivites of compounds **1**, **3, 5, 11** and **12** towards oxidization on sulfur atom by treatment with nitrating mixture should decrease in the sequence: **11** > **12** > **3** ≥ **5** > **1**. The competitive experiments demonstrated the relative reactivity order: **11** > **12** > **3** > **1** > **5**. Reactivity of

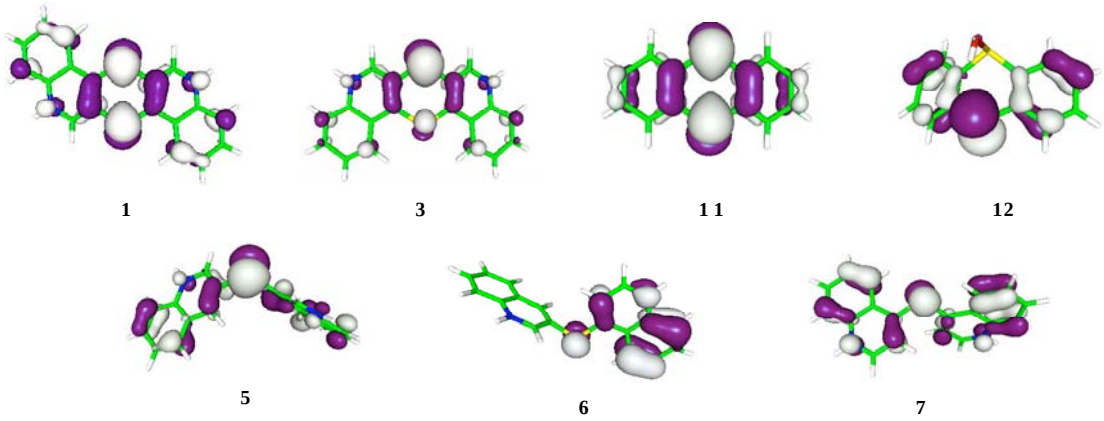

Figure 2. Plots of HOMO orbitals for protonated form of sulfides **1**, **3** , **5**, **6**, **7**, **12** and thianthrene **11**

sulfide **5**, lower then expected from theoretical calculations probably results from the flexibility around the C-S bond. Such possibility does not appear in more fixed molecules of dithiines **1** and **3**.

The greater ability towards nitrating reaction of 3,4'-diquinolinyl sulfide **6** comparatively to 4,4'-diquinolinyl sulfide **7** is also in full agreement with conclusions deduced from the analysis of HOMO and MEP effects.

Quinolinyl sulfides **1**, **3**, **5**-**7** were subjected to reaction with nitrating mixture in the form of quinolinium salts, which reduced electronodonating properties of endocyclic nitrogen atoms towards electrophiles, therefore NO_2^+ ion may attack either sulfur substituent or benzene ring atoms.

The reactivity and regioselectivity (on sulfur or carbon atom) of sulfides **1**, **3**, **5**-**7** towards nitrating mixture (as a source of NO_2^+ ion) seems to depend on the nature of

Table 1

Selected electronic properties of sulfides **1**, **3**, **5**, **6**, **7**, **11**, **12**

Compound	**1**	**3**	**5**	**6**	**7**	**11**	**12**
HOMO eigenvalue [eV]	-12.98	-12.92	-12.92	-13.06	-13.14	-5.93	-10.34
The lowest potential [au]	0.1937 (C3)	0.1935 (S7)	0.1908 (C6)	0.1868 (C6')	0.1933 (C6)	-0.037 (S5)	0.1135 (S10)
Potential by S atom [au]	0.2021 (S7) 0.2021 (S14)	0.1935 (S7) 0.2070 (S14)	0.1937	0.2042	0.2170	-0.037 (S5) -0.037 (S10)	0.1505 (S5) 0.1135 (S10)

CONCLUSIONS

Nitrating mixture generates powerfull electrophilic NO_2^+ ion. It may react with electronodonating carbon or heteroatom (*e.g.* nitrogen or sulfur) centers of aromatic or heterocyclic compounds [17].

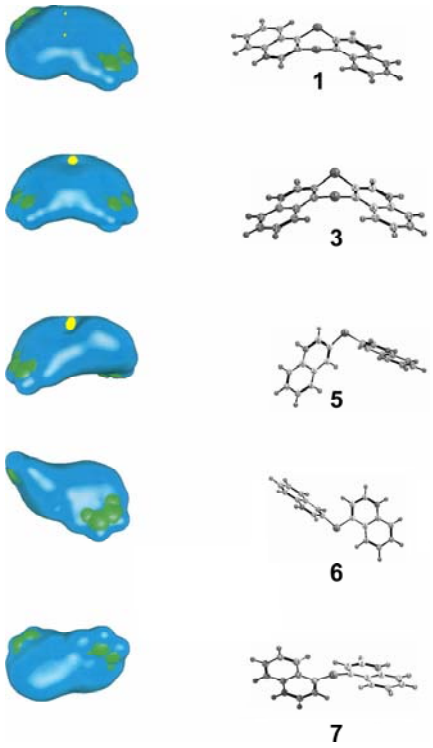

Figure 3. Three-dimensional isopotential contours of MEP at 0.203 a.u. for protonated form of sulfides **1**, **3** , **5**, **6**, **7**

sulfur bridge. Electron donating properties of sulfur atoms in sulfides **1**, **3**, **5**-**7** expressed by the HOMOs and MEPs data, showed that oxidation ability of $\beta_{quinolinyl}$ – sulfur atoms in compounds **1**, **3** and **5** are greater than for $\gamma_{quinolinyl}$ – sulfur ones (for compounds **6** and **7**), and furthermore, that electron donating properties of $\gamma_{quinolinyl}$ – sulfide sulfur are ever weaker than those of benzene ring carbons in sulfides **6**, **7**. Calculation results supported experimental observations.

The compounds with only $\beta_{quinolinyl}$–S–$\beta_{quinolinyl}$ bonds (isothioquinanthrene **3** and 3,3'-diquinolinyl sulfide **5**) undergo *S*-oxidation when treated with nitrating mixture (for reactions mechanism see scheme IV). However, 4,4'-diquinolinyl sulfide **7** with $\gamma_{quinolinyl}$–S–$\gamma_{quinolinyl}$ bonds undergoes nitration in the benzene ring. From two compounds containing $\beta_{quinolinyl}$–S–$\gamma_{quinolinyl}$ bonds thioquinanthrene **1** undergoes *S*-oxidation, but only at one sulfide bridge, while 3,4'-diquinolinyl sulfide **6** undergoes nitration.

Thianthrene **11** and even thianthrene S-oxide **12** are more reactive towards nitrating mixture then each of quinolinyl sulfide **1**, **3**, **5**. This shows that electron-withdrawing effects induced by protonated *endo*-cyclic nitrogen reduced the electron-donating properties both at sulfide atom and at benzene ring atoms in the molecules of quinolinyl sulfides.

EXPERIMENTAL

Melting points were taken on Boetius Apparatus. IR spectra were recorded with a Spectrum One (Perkin Elmer) spectrophotometer in KBr pellets. EIMS (70 eV) were determined with an AMD-604 mass spectrometer. ^1H, ^{13}C and correlation NMR spectra were recorded using TMS as internal

standard for $CDCl_3$ solutions with a Bruker AM 500 (500.13 MHz proton frequency and 125.76 MHz carbon frequency) and Bruker 400 Avance (400.13 MHz proton frequency) spectrometers.

Compounds **1-5**, **7**, **8**, **10-13** were prepared as described previously [5,6,18-20]. For analytical purposes presented below ^{1}H NMR spectra (500 MHz, $CDCl_3$) of thianthrene **11**, thianthrene 5-oxide **12**, *cis* and *trans* isomer of thianthrene 5,10-dioxide **13a** and **13b** are recorded [δ_H, ppm]: for thianthrene **11**: 7.23 (dd, 4H, J = 5.8, J = 3.4 Hz, H-2, H3, H7, H8), 7.47 (dd, 4H, J = 5.8, J = 3.4 Hz, H-1, H-4, H-6, H-9); for thianthrene 5-oxide **12**: 7.43 (ddd, 2H, J = 7.6, J = 7.6, J = 1.4 Hz, H-2, H-8), 7.56 ppm (ddd, 2H, J = 7.6, J = 7.6, J = 1.1 Hz, H-3, H-7), 7.64 (dd, 2H, J = 7.6, J = 1.1 Hz, H-1, H-9), 7.93 (dd, 2H, J = 7.6, J =1.4 Hz, H-4, H-6); for *cis* - thianthrene 5,10-dioxide **13a**: 7.72 (dd, 4H, J = 5.6, J = 3.2 Hz, H-2, H-3, H-7, H-8), 8.07 (dd, 4H, J = 5.6, J = 3.2 Hz, H-1, H-4, H-6, H-9); for *trans* - thianthrene 5,10-dioxide **13b**: 7.66 (dd, 4H, J = 5.6, J = 3.3 Hz, H-2, H-3, H-7, H-8), 8.11 (dd, 4H, J = 5.6, J = 3.3 Hz, H-1, H-4, H-6, H-9).

Synthesis of 3,4'-diquinolinyl sulfide (6). A solution of 4-chloroquinoline (410 mg, 2.5 mmol), 3-mercaptoquinoline (400 mg, 2.5 mmol) in 20 mL of chloroform was refluxed for 15 h in nitrogen atmosphere. It was then cooled down to room temperature, washed with 5 mL of 2% aqueous sodium hydroxide and next with water. The chloroform solution was dried with anhydrous sodium sulfate and the solvent was distilled off. The residue was subjected to column chromatography (neutral Al_2O_3, CCl_4 - acetone 9:1 v/v) and was finally recrystallized from methanol to yield 446 mg (62%) of sulfide **6**, mp 103.5-104.5 °C; NMR (500 MHz, $CDCl_3$) δ_H [δ_C for carbons from single bond / long range proton-carbon correlations]: 6.81 (d, 1H, J = 4.7 Hz, H-3') [118.7 (C-3')/149.5 (C-2'), 146.9 (C-4), 126.1 (C-4'a)]; 7.62 (ddd, 1H, J = 8.4, J = 7.1, J = 1.2 Hz, H-6') [126.9 (C-6')/126.1 (C-4'a), 130.1 (C-8')]; 7.63 (ddd, 1H, J = 8.1, J = 7.1, J = 1.0 Hz, H-6); [127.7 (C-6)/128.3 (C-4a), 129.6 (C-8a)]; 7.77 (ddd, 1H, J = 8.3, J = 7.1, J = 1.2 Hz, H-7') [130.1 (C-7')/123.5 (C-5'), 147.8 (C-8'a)]; 7.82 (ddd, 1H, J = 8.3, J = 7.1, J = 1.2 Hz, H-7) [130.9 (C-7)/127.7 (C-5), 147.7 (C-8a)]; 7.83 (dd, 1H, J = 8.1, J = 1.2 Hz, H-5) [127.7 (C-5)/130.9 (C-7), 142.4 (C-4), 147.7 (C-8a)]; 8.12 (dd, 1H, J = 8.3, J = 1.2 Hz, H-8') [130.1 (C-8')/126.1 (C-4'a), 126.9 (C-6')]; 8.18 (dd, 1H, J = 8.3, J = 1.0 Hz, H-8) [129.6 (C-8)/127.7 (C-6), 128.3 (C-4a)]; 8.27 (dd, 1H, J = 8.4, J = 1.2 Hz, H-5') [123.5 (C-5')/130.1 (C-7'), 146.9 (C-4'a), 147.8 (C-8'a)]; 8.41 (d, 1H, J = 2.1 Hz, H-4) [142.4 (C-4)/124.1 (C-3), 127.7 (C-5), 147.7 (C-8a), 154.2 (C-2)]; 8.59 (d, 1H, J = 4.7 Hz, H-2') [149.5 (C-2')/118.7 (C-3'), 146.9 (C-4'), 147.8 (C-8'a)]; 8.96 (d, 1H, J = 2.1 Hz, H-2) [154.2 (C-2)/124.1 (C-3), 142.4 (C-4), 147.7 (C-8a)]; EIMS (70 eV) m/z: $(M)^+$ = 288 (100%). *Anal.* Calcd. for $C_{18}H_{12}N_2S$ (288.07): C, 74.97; H, 4.19; N, 9.71; S, 11.12. Found: C, 75.11; H, 4.04; N, 9.53; S, 10.94.

Nitration of 3,4'-diquinolinyl sulfide (6). 3,4'-Diquinolinyl sulfide (**6**) (144 mg, 0.5 mmole) was dissolved with stirring in 96% sulfuric acid (1.5 mL) at 0 ºC. The nitrating mixture (fumning nitric acid, d=1.52 g/mL, 0.008 mL, c.a. 1.8 mmoles of HNO_3 and 0.16 mL of conc. sulfuric acid) was then added dropwise at 0-5 ºC, the mixture was maintained at 0 ºC for 1.5 h, and then cautiously poured on 20 g of ice, and neutralized at 0 ºC with conc. aqueous ammonia. The solid was filtered off, washed twice with cold water and air-dried to give yellow products (140 mg) containing 8-nitro and 6-nitro isomers **9a** and **9b** in ratio 3:1 (as judged from ^{1}H NMR spectra). Analytical samples of **9a** and **9b** were obtained by TLC separations (Merck's silica gel 60 F_{254} plates with methanol - chloroform 1:30 (v/v) as developing system).

6'-Nitro-3,4'-diquinolinyl sulfide (9a). Mp 176.5-177.5 °C (methanol); IR: ν_{NO2} = 1341, 1578 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.86 (d, 1H, J = 4.8 Hz, H-3'), 7.67-7.72 (m, 1H, H-6), 7.86-7.92 (m, 2H, H-5, H-7), 8.21-8.23 (m, 1H, H-8), 8.24-8.26 (m, 1H, H-8'), 8.52-8.56 (m, 2H, H-4, H-7'), 8.70 (d, 1H, J = 4.8 Hz, H-2'), 8.98 (d, 1H, J = 2.1 Hz, H-2), 9.27 (d, 1H, J = 2.4 Hz, H-5'); EIMS (70 eV) m/z: $(M)^+$ = 333 (100%), $(M-NO_2)^+$ = 287 (22%). *Anal.* Calcd. for $C_{18}H_{11}N_3O_2S$ (333.06): C, 64.85; H, 3.33; N, 12.60; S, 9.62. Found C, 64.63; H, 3.30; N, 12.51; S, 9.45.

8'-Nitro-3,4'-diquinolinyl sulfide (9b). Mp 156 - 158 °C (methanol); IR: ν_{NO2} = 1363, 1531 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.86 (d, 1H, J = 4.8 Hz, H-3'), 7.65-7.74 (m, 2H, H-6, H-6'), 7.84-7.90 (m, 2H, H-5, H-7), 8.07 (dd, 1H, J = 7.5, J = 1.3 Hz, H-7'), 8.20-8.22 (m, 1H, H-8), 8.48-8.51 (m, 2H, H-4, H-5'), 8.69 (d, 1H, J = 4.8 Hz, H-2'), 8.97 (d, 1H, J = 2.2 Hz, H-2); EIMS (70 eV) (m/z): $(M)^+$ = 333 (100%), $(M-NO_2)^+$ = 287 (31%). *Anal.* Calcd. for $C_{18}H_{11}N_3O_2S$ (333.06): C, 64.85; H, 3.33; N, 12.60; S, 9.62. Found C, 64.60; H, 3.26; N, 12.48; S, 9.39.

Oxidation of thianthrene (11) with a nitrating mixture. Reactions of thianthrene (**11**) (108 mg, 0.5 mmol) with a nitrating mixture (0.5 mmol or 1.8 mmol) were performed in the same manner as it was described for sulfide **6** (reactions time 15 min or 1.5 h) to give white solids (105 mg or 109 mg). The compositions of products were deduced from ^{1}H NMR spectra. In the reaction with one molar equivalent of HNO_3 the mixture of thianthrene (**11**), thianthrene 5-oxide (**12**), *cis* and *trans* isomers of thianthrene 5,10-dioxides (**13a**) and (**13b**) in ratio 1:1.9:2.1:0.9 was obtained. In the reaction with 3.6 molar equivalent of HNO_3 the product consisted only from isomers **13a** and **13b** in ratio 1.3:1.

Methodology of competitive experiments. Nitrating mixture with HNO_3 concentration of 0.5 mol·L^{-1} was prepared from 0.21 mL fuming nitric acid (d = 1.52 g·mL^{-1}) with addition of conc. sulfuric acid to the final volume of 10 mL.

Samples of sulfide mixture with each concentration of 0.05 mol·L^{-1} (composed of three or two sulfides) were prepared by addition of 1.25 mmol of each sulfide to 25 mL volumetric flask and the flask and supplemented with conc. sulfuric acid up to the final value of 25 mL.

1 mL of appropriate sulfide mixture, appropriate volume of nitrating mixture and conc. sulfuric acid up to final volume of 2 mL was shaken at 0 °C for 45 min. It was then poured onto 10 g of ice, neutralized with conc. aqueous ammonia and organic compounds were extracted with chloroform (3 x 2.5 mL). The combined extracts were washed with water and dried over anhydrous sodium sulfate. The drying agent was filtered off, the filtrate was evaporated to dryness. The residue was dissolved in $CDCl_3$ and subjected to ^{1}H NMR analysis.

The competitive experiments were performed with the following volumes of nitrating mixture: 0.075, 0.150, 0.225, 0.300, 0.375, 0.450, 0.525, 0.600 and 0.675 mL for mixture of sulfides **1**, **3** and **5**; 0.075, 0.150, 0.225, 0.300, 0.450, 0.600, 0.750, 0.900 and 1.000 mL for mixture of sulfides **5**, **6** and **7**; 0.050, 0.075, 0.100, 0.125, 0.150, 0.200 and 0.250 mL for mixture of sulfides **3** and **11**; 0.050, 0.075, 0.100, 0.125, 0.150, 0.175, 0.200, 0.275, 0.300, 0.325 and 0.350 mL for mixture of sulfides **3** and **12**.

Each experimental point was repeated three times and for each type of sulfide mixture a blind test was performed.

Conversion of each sulfide was determined by intensity ratio of signals listed below in relation sulfide - sulfoxide or sulfide - nitrosulfide or by intensity ratio of selected sulfide signal to summarized intensity of all signals presented in the spectrum. Both methods gave similar results.

The following signals [δ_H, ppm] were received as analytical: for thioquinanthrene (**1**): 8.37 (H-1, H-8); for thioquinanthrene 7-oxide (**2**): 9.30 (H-13); for isothioquinanthrene (**3**): 8.50 (H-1, H-13); for isothioquinanthrene 7-oxide (**4**): 8.54 (H-1, H-13); for sulfide **5**: 7.56 (H-6) and 8.87 (H-2); for sulfoxide **8**: 8.68 (H-4) and 8.97 (H-2); for sulfide **6**: 6.81 (H-3') and 8.96 (H-2); for nitroquinolinyl sulfides **9a** and **9b**: 6.86 (H-3'); for sulfide **7**: 7.16 (H-3); for nitroquinolinyl sulfides **10a**, **10b** and **10c**: 6.94 (H-3'), 7.06 (H-3') and 7.28 (H-3), resp.; for thianthrene (**11**): 7.47 (H-1, H-4, H-6, H-9); for thianthrene 5-oxide (**12**): 7.56 (H-3, H-7) and 7.64 (H-1, H-9); for *cis*-thianthrene 5,10-dioxide (**13a**): 8.07 (H-1, H-4, H-6, H-9); for *trans*- thianthrene 5,10-dioxide (**13b**): 8.11 (H-1, H-4, H-6, H-9).

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