4-Chloro-3'-methylsulfinyl-5(6 or 8)-nitro-3,4'-diquinolinyl Sulfides

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This paper is dedicated in memory of Professor Raymond N. Castle

Reaction of 4-chloro-3'-methylthio-3,4'-diquinolinyl sulfides **3**, **9b**, **9c** with a nitrating mixture proceeds via the 3'-methylthio group monooxidation and yields 3'-methylsulfinyl diquinolinyl sulfides **4**, **5b**, **5c**, respectively. Further treatment of **4** with a nitrating mixture followed as C_5- and C_8-nitration and gives mixture of **5a** and **5c**. Treatment of 3'-methylsulfinyl quinolines **6** and **7** with hydrochloric acid / potassium iodide system causes reduction of the sulfoxide group in **6** and **7** to the sulfide group yielding **8**, in case of 4-methoxyquinolines **6**, hydrolysis of the 4-methoxyquinoline moiety to the 4-quinolinone moiety takes place simultaneously. The proton and carbon chemical shifts of **4** and **5a** were completely assigned following COSY, HETCOR and INEPT or COLOC studies.

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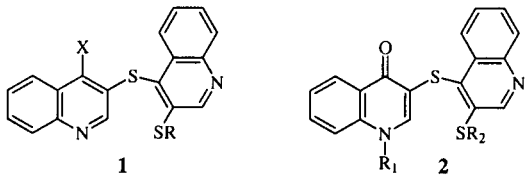
Introduction.

In previously published papers we presented transformations of 4-substituted 3'-methylthio-3,4'-diquinolinyl sulfides **1-2** caused by the action of a nitrating mixture (fuming nitric acid and concentrated sulfuric acid) [1-3].

Scheme 1



1

1a: X=OCH_3, R=CH_3
1b: X=SR, R=CH_3, C_2H_5, *n*-C_3H_7

2

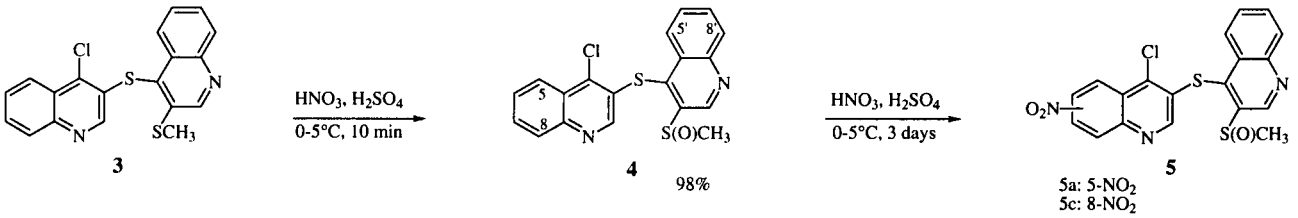
2a: R_1=H, R_2=CH_3
2b: R_1=R_2=CH_3

the production of 4-aminoquinoline drugs [4]. Taking this into consideration and to complete previously mentioned findings the present study deals with transformation of 4-chloro-3'-methylthio-3,4'-diquinolinyl sulfide **3** under the action of the nitrating mixture. As structures of final products **5a** and **5c** were difficult to analyze, the structure assignment was supported by independent syntheses of **5b** and **5c** from 4-oxo-1,4-dihydro-3'-methylsulfinyl-6(or 8)-nitro-3,4'-diquinolinyl sulfides **7b** and **7c**.

Results and Discussion.

Experimental conditions elaborated previously [1-3] were applied to the reaction of 4-chloro-3'-methylthio-3,4'-diquinolinyl sulfide **3** with the nitrating mixture. The reaction of **3** (dissolved in sulfuric acid) with the nitrating mixture (1 molar equivalent of nitric acid) at 0-5°C for 10 min gives 4-chloro-3'-methylsulfinyl derivative **4** with

Scheme 2



3

HNO_3, H_2SO_4
0-5°C, 10 min

4
98%

HNO_3, H_2SO_4
0-5°C, 3 days

5
5a: 5-NO_2
5c: 8-NO_2

4-Methoxy- and 4-oxo-1,4-dihydro-3'-alkylthio-3,4'-diquinolinyl sulfides **1a** and **2** first underwent the 3'-S-monooxidation followed by C_6- and C_8-nitration [1,2]. The reaction of 3',4-dialkylthio-3,4'-diquinolinyl sulfides **1b** with the nitrating mixture also proceeded as the 3'-S-monooxidation to give 3'-monosulfoxides which could then be oxidized at the 4-alkylthio group to give a mixture of 3',4-dialkylsulfinyl derivatives of **1b**. No nitration products were detected in this case [3].

4-Chloroquinolines are important intermediates for functionalizing quinoline and find industrial application in

98% yield. Further treatment of **4** with an excess of the nitrating mixture (up to 2.6 molar equivalent of nitric acid) leads to a mixture of two isomeric 4-chloro-3'-methylsulfinyl-5(or 8)-nitro-3,4'-diquinolinyl sulfides **5a** and **5c**, as judged from ^{1}H nmr, ir and mass spectral data as well as from elemental analysis.

The same products **5a** and **5c** were obtained directly from sulfide **3** by treating with 3.6 molar equivalent of nitric acid.

Separation or isolation of individual nitrosulfoxides **5a** and **5c** by crystallization as well as by column

Table 1

Summary of INEPT Long-range Proton-carbon and HETCOR Single-bond Correlations of 4-Chloro-3'-methylsulfinyl-3,4'-diquinolinyl Sulfide (**4**)

Proton δ_H [ppm]	Carbon single bond coupling δ_C [ppm]		Carbon three bond coupling δ_C [ppm]		Carbon two bond coupling δ_C[ppm]	
H-2	C-2	147.9	C-4	139.6	C-3	127.1
8.02			C-8a	147.0		
H-5	C-5	123.7	C-4	139.6		
8.23			C-7	130.5		
			C-8a	147.0		
H-6	C-6	128.8	C-4a	126.2		
7.69			C-8	130.0		
H-7	C-7	130.5	C-5	123.7		
7.74			C-8a	147.0		
H-8	C-8	130.0	C-4a	126.2		
7.99			C-6	128.8		
H-2'	C-2'	145.6	C-4'	136.0	C-3'	143.2
9.53			C-8'a	149.9		
H-5'	C-5'	125.1	C-4'	136.0		
8.26			C-7'	131.8		
			C-8'a	149.9		
H-6'	C-6'	129.3	C-4'a	127.8		
7.62			C-8'	131.0		
H-7'	C-7'	131.8	C-5'	125.1		
7.85			C-8'a	149.9		
H-8'	C-8'	131.0	C-4'a	127.8		
8.28			C-6'	129.3		
$CH_3S(0)$	$CH_3S(0)$	43.1	C-3'	143.2		
2.94						

chromatography was ineffective. Analytical samples of **5a** and **5c** were obtained by TLC separations.

As starting point for the spectral analysis of **5a** and **5c**, the ^1H and ^{13}C nmr data for sulfoxide **4** were totally solved first with the use of 2D COSY, HETCOR and SPT INEPT nmr techniques, as described previously [5] (see Table 1).

Preliminary data in the ^1H nmr assignment of **5a** and **5c** were obtained from the ^1H-^1H COSY spectra (at 300 MHz). They allow segregating seven benzene ring protons into two groups. The first group is due to four protons of ABMX system. The signals of the second group confirm the presence of three protons of the ABX system with the nitro group in the quinolinyl type positions 5 or 8. This means that four isomeric (5- or 5'-, 8- or 8'-) nitroderivatives of **4** could be considered as the nitration products. Compound **5c**, i.e. isomer of **5** with the nitro group in position 8, could be prepared by an independent synthesis from 8-nitro-4-methoxy-3'-methylsulfinyl-3,4'-diquinolinyl sulfide **6c** or 8-nitro-1,4-dihydro-3'-methylsulfinyl-3,4'-diquinolinyl sulfide **7c**. It induced the three step transformation of **6b-c** and **7b-c** as presented in Scheme 3.

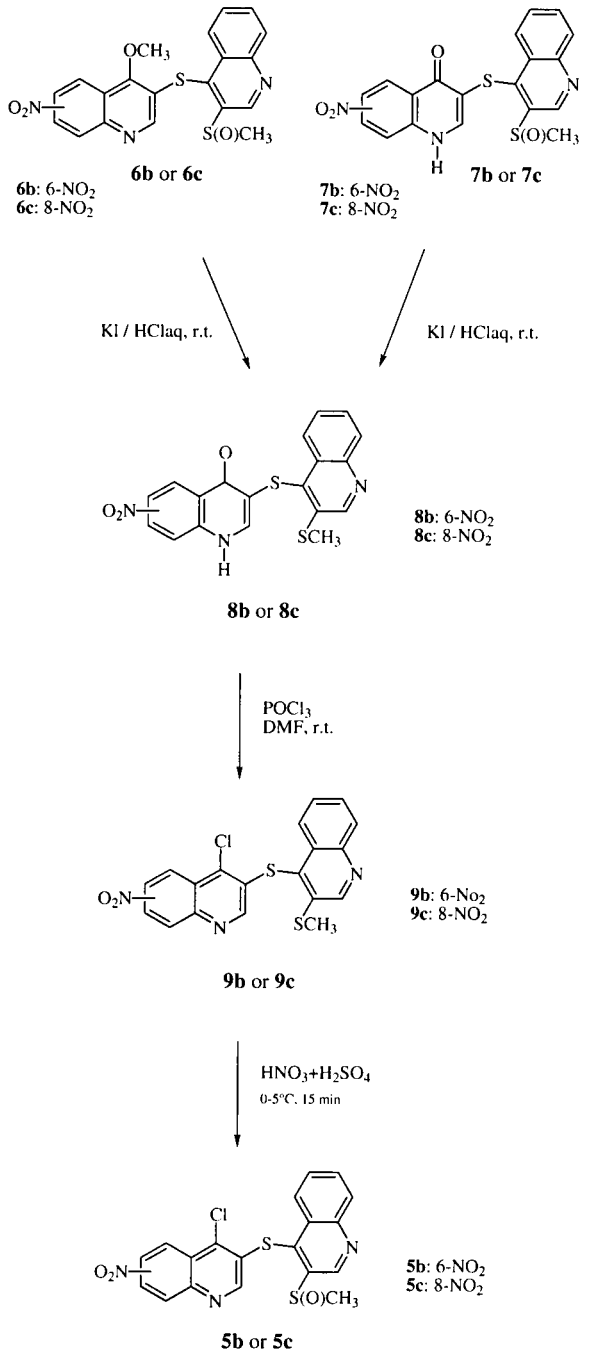
Even though demethoxy-chlorination of **1a** and deoxychlorination of **2a** with posphoryl chloride give **3** in high yield [6], the treatment of nitromethylsulfinyl-4-quinolinones **7b** and **7c** with phosphoryl chloride at room temperature leads to a multicomponent mixture. This may result from susceptibility of the methylsulfinyl group toward phosphoryl chloride. To remove the sulfoxide moiety reduction of **6** and **7** with aqueous hydrogen iodide (generated from potassium iodide and hydrochloric acid) was attempted for ten minutes at room temperature. The reducing system converts smoothly quinolinyl sulfoxides **6** and **7** into quinolinyl sulfides **8b** and **8c** (94-96%). However, the action of the reducing system toward methoxysulfoxides **6** causes simultaneously reduction of the sulfinyl group to the sulfide one and hydrolysis of the 4-methoxyquinoline part to the 4-quinolinone moiety yielding sulfides **8**.

The compounds **8** could then be converted in reaction with phosphoryl chloride to 4-chloroquinolines **9b** and **9c** (78-79%). Finally, the methylthio derivatives **9b** and **9c** were oxidized with the nitrating mixture to the methylsulfinyl derivatives **5b** and **5c**.

NMR Assignment of Nitrosulfide **5a**.

The ^1H nmr spectrum of **5a** at 500 MHz reveals a singlet of three protons of methylsulfinyl group, two singlets of α-quinolinyl protons and well-separated multiplets of seven benzene-ring protons. The latter could be easy divided into ABX and ABMX systems, due to multiplicity of proton signals. ABX group is composed of three double doublets, two with one *ortho* and one *meta* couplings (J_{ortho} = 8.4 Hz or 7.6 Hz and J_{meta} = 1.3 Hz, respectively) and one with two *ortho* couplings. It indicates that the nitro substituent is located at the 5- or 8-quinolinyl position.

Scheme 3



The main problem, however, was to find out correlations between α-quinolinyl protons H2 and H2' and benzene ring protons of ABX or ABMX systems. As shown earlier [5], in this approach the key part is played by long-range proton-carbon correlations between bridged quaternary carbon atoms of both aromatic rings and the respective protons. In the case of 3,4'-diquinolinyl sulfides it should be those of carbon C8a or C8'a (see Figure 1).

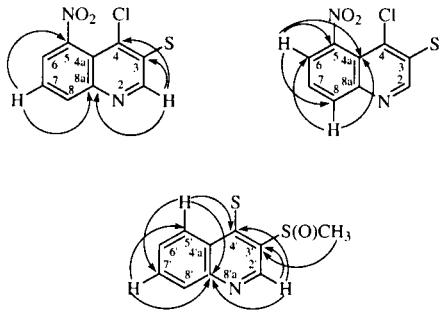


Figure 1. Set of Long-rang Correlations used in the NMR Assigments of Compounds **4** and **5a**.

The starting spectral position of the H2' proton (δ_H = 9.58 ppm) could be deduced both from *ortho* substituent effect of the methylsulfinyl group [2,5] ($\Delta\delta_H = \delta_{sulfoxide} - \delta_{sulfide}$ = 0.71 ppm) and from long-range correlations of the C3' carbon both with the H2' and methylsulfinyl group protons. The three-bond $^3J_{C-H}$ correlations between the H2' proton (δ_H = 9.58 ppm) and the C4' and C8'a carbons and those of the H5' proton (δ_H = 8.21 ppm) with the C4' and C8'a carbons confirm the connectivity link between the H2' and H5' protons, i.e. between the aromatic rings of the "right side part" of sulfide **5a**. As the H5' proton forms the part of four-proton ABMX system, the newly-introduced nitro group must be located in the "left-side part" of the quinoline moiety of sulfide **5a** in the way required by ABX system, i.e. in position 5 or 8.

Because the structure of the 8-nitro isomer **5c** was proved through an independent synthesis (discussed above), compound **5a** has to be the 5-nitro isomer. This conclusion is in full agreement with long-range proton-carbon correlations of H2/C3,C4,C8a; H6/C8,C4a,C5; H7/C5,C8a and H8/C6,C4a, (Table 2).

As in the case of other nitroquinolines [2,5,7], two-bond proton-carbon correlations H6/C5, H2/C3 and H2'/C3' were also observed.

Conclusions.

Even though the starting sulfide **3** represents a multifunctional structure, its reactions with the nitrating mixture proceeded in the manner observed for other 4-substituted 3'-alkylthio-3,4'-diquinolinyl sulfides [1,2]. Thus, the first functional group to react is the 3'-methylthio group of **3** which undergoes oxidation to the 3'-methylsulfinyl one in **4**. This primary product then undergoes nitration at position 5 or 8 of the benzene ring of the 4-chloro-3-quinolinyl sulfide moieties. The same orientation was observed for nitration of 4-chloroquinoline in strong acidic solution [8,9]. During this study no nitration products of the 3,4-quinolinediyl bis-sulfide moiety of **3** and **4** were detected.

Table 2

Summary of COLOC long-range proton-carbon and HETCOR single-bond correlations of 4-chloro-5-nitro-3'-methylsulfinyl-3,4'-diquinolinyl sulfide (**5a**)

Proton δ_H [ppm]	Carbon single bond coupling δ_C [ppm]		Carbon three bond coupling δ_C [ppm]		Carbon two bond coupling δ_C [ppm]	
H-2	C-2	148.3	C-4	134.3*	C-3	131.9*
7.94			C-8a	147.3		
H-6	C-6	124.5	C-4a	117.9	C-5	146.1
7.82			C-8	134.1		
H-7	C-7	128.5	C-5	146.1		
7.74			C-8a	147.3		
H-8	C-8	134.1	C-4a	117.9		
8.17			C-6	124.5		
H-2'	C-2'	145.8	C-4'	134.3	C-3'	143.8
9.57			C-8'a	150.1		
H-5'	C-5'	124.8	C-4'	134.3		
8.21			C-7'	132.1		
			C-8'a	150.1		
H-6'	C-6'	129.8	C-4'a	127.8		
7.68			C-8'	131.2		
H-7'	C-7'	132.1	C-5'	124.8		
7.90			C-8'a	150.1		
H-8'	C-8'	131.2	C-4'a	127.8		
8.33			C-6'	129.8		
$CH_3S(0)$	$CH_3S(0)$	43.3	C-3'	143.8		
2.98						

*assignments may be reversed

EXPERIMENTAL

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 deuteriochloroform or 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, HETCOR, INEPT, COLOC) were recorded with a Bruker AM 500 spectrometer (125.76 MHz carbon frequency, deuteriochloroform, internal tetramethylsilane). IR spectra were recorded with a Magma – IR 500 (Nicolet, USA) spectrophotometer in potassium bromide pellets. LSI mass spectra (Cs^+, 15 keV, nba) and EI mass 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 methanol - chloroform 1:9 (v/v) as developing system.

4-Chloro-3'-methylthio-3,4'-diquinolinyl sulfide (**3**) [6], 4-methoxy-3'-methylsulfinyl-6-nitro-3,4'-diquinolinyl sulfide (**6b**) [1], 4-methoxy-3'-methylsulfinyl-8-nitro-3,4'-diquinolinyl sulfide (**6c**) [1], 1,4-dihydro-4-oxo-3'-methylsulfinyl-6-nitro-3,4'-diquinolinyl sulfide (**7b**) [1] and 1,4-dihydro-4-oxo-3'-methylsulfinyl-8-nitro-3,4'-diquinolinyl sulfide (**7c**) [1] were prepared as described previously.

Oxidation of sulfides **3**, **9b** or **9c**.

Diquinolinyl sulfide (2.5 mmol) was dissolved with stirring in 96% sulfuric acid (7.5 ml) at 0°C. The nitrating mixture (fuming nitric acid, d = 1.50 g/ml, 0.1 ml, *ca* 2.5 mmol of nitric acid and 0.1 ml of conc. sulfuric acid) was then added dropwise at 0-5°C within ten minutes. The solution was then cautiously poured onto 125 g of ice and neutralized at 0°C with 25% aqueous ammonia. The solid was removed by filtration, washed twice with cold water, then with cold methanol, and air-dried to give a yellow-colored solid. The product was recrystallized from methanol to give pure sulfoxide **4, 5b** or **5c**.

4-Chloro-3'-methylsulfinyl-3,4'-diquinolinyl Sulfide (**4**).

This compound had mp 194-195.5 °C, yield 98%; LSIMS: $(M+1)^+$ = 385, $[M-O]^+$ = 369; ir: $\nu_{S=O}$ = 1033 cm^{-1}; ^{1}H nmr (500 MHz, deuteriochloroform) δ: 2.94 (s, 3H, 3'-S(O)CH_3), 7.62 (m, 1H, ^{3}J = 8.5, ^{3}J = 6.9, ^{4}J = 1.3 Hz, H-6'), 7.69 (m, 1H, ^{3}J = 8.3, ^{3}J = 6.9, ^{4}J = 1.4 Hz, H-6), 7.74 (m, 1H, ^{3}J = 8.4, ^{3}J = 6.9, ^{4}J = 1.5, H-7), 7.85 (m, 1H, ^{3}J = 8.5, ^{3}J = 6.9, ^{4}J = 1.3 Hz, H-7'), 7.99 (m, 1H, ^{3}J = 8.4, ^{4}J = 1.4, ^{5}J = 0.7 Hz, H-8), 8.02 (s, 1H, H-2), 8.23 (m, 1H, ^{3}J = 8.3, ^{4}J = 1.5, ^{5}J = 0.7 Hz, H-5), 8.26 (m, 1H, ^{3}J = 8.5, ^{4}J = 1.3, ^{5}J = 0.6 Hz, H-5'), 8.28 (m, 1H, ^{3}J = 8.5, ^{4}J = 1.3, ^{5}J = 0.6 Hz, H-8'), 9.53 (s, 1H, H-2').

Anal. Calcd. for $C_{19}H_{13}N_2S_2OCl$ (384.90): C, 59.30; H, 3.41; N, 7.29; S, 16.67; Cl, 9.22. Found C, 59.22; H, 3.29; N, 7.48; S, 16.52; Cl, 9.14.

4-Chloro-3'-methylsulfinyl-6-nitro-3,4'-diquinolinyl sulfide (**5b**).

This compound had mp 205-206.5 °C, yield 71%; LSIMS: $(M+1)^+$ = 430; ir: $\nu_{S=O}$ = 1068 cm^{-1}, ν_{NO2} = 1517 cm^{-1}; ^{1}H nmr (300 MHz, deuteriochloroform) δ: 3.00 (s, 3H, 3'-S(O)CH_3), 7.68 (m, 1H, ^{3}J = 8.3, ^{3}J = 7.2, ^{4}J = 1.1 Hz, H-6'), 7.91 (m, 1H, ^{3}J = 8.2, ^{3}J = 7.2, ^{4}J = 1.4 Hz, H-7'), 8.08 (s, 1H, H-2), 8.15 (d, 1H, ^{3}J = 9.2 Hz, H-8), 8.23 - 8.26 (m, 1H, H-5'), 8.32 - 8.35 (m, 1H, H-8'), 8.48 (dd, 1H, ^{3}J = 9.2, ^{4}J = 2.4 Hz, H-7), 9.18 (d, 1H, ^{4}J = 2.4 Hz, H-5), 9.57 (s, 1H, H-2').

Anal. Calcd. for $C_{19}H_{12}N_3S_2O_3Cl$ (429.90): C, 53.08; H, 2.81; N, 9.78; S, 14.92; Cl, 8.25. Found: C, 52.91; H, 2.94; N, 9.86; S, 14.68; Cl, 8.12.

4-Chloro-3'-methylsulfinyl-8-nitro-3,4'-diquinolinyl sulfide (**5c**).

This compound had mp 234-235 °C, yield 80%; LSIMS: $(M.+1)^+ = 430$; ir: $\nu_{S=O} = 1040$ cm^{-1}, $\nu_{NO2} = 1532$ cm^{-1}; ^{1}H nmr (500 MHz, deuteriochloroform) δ: 2.97 (s, 3H, 3'-S(O)CH_3), 7.67 (m, 1H, $^3J = 8.4$, $^3J = 6.9$, $^4J = 1.2$ Hz, H-6'), 7.79 (m, 1H, $^3J = 8.6$, $^3J = 7.5$ Hz, H-6), 7.90 (m, 1H, $^3J = 8.4$, $^3J = 6.9$, $^4J = 1.3$ Hz, H-7'), 8.03 (dd, 1H, $^3J = 7.5$, $^4J = 1.3$ Hz, H-5'), 8.04 (s, 1H, H-2), 8.24 (m, 1H, $^3J = 8.4$, $^4J = 1.3$, $^5J = 0.5$ Hz, H-5'), 8.32 (m, 1H, $^3J = 8.4$, $^4J = 1.2$ Hz, $^5J = 0.5$ Hz, H-8'), 8.47 (dd, 1H, $^3J = 8.6$, $^4J = 1.3$ Hz, H-8), 9.55 (s, 1H, H-2').

Anal. Calcd. for $C_{19}H_{12}N_3S_2O_3Cl$ (429.90): C, 53.08; H, 2.81; N, 9.78; S, 14.92; Cl, 8.25. Found: C, 52.81; H, 3.02; N, 9.81; S, 14.81; Cl, 8.07.

Nitration of 4-Chloro-3'-methylsulfinyl-3,4'-diquinolinyl Sulfide (**4**).

Diquinolinyl sulfide **4** (369 mg, 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, 0.16 ml, *ca.*, 3.6 mmol of nitric acid and 0.16 ml of conc. sulfuric acid) was then added dropwise at 0-5°C, the mixture was maintained at 0°C for 1.5 hour, and 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 (435 mg) containing the 8-nitro and 5-nitro isomers **5a** and **5c** in 2 : 1 ratio (as judged from the ^{1}H nmr spectrum). Analytical samples of **5a** and **5c** were obtained by TLC separations, as mentioned above.

4-Chloro-3'-methylsulfinyl-5-nitro-3,4'-diquinolinyl Sulfide (**5a**).

This compound had mp 224-225°C; LSIMS: $(M+1)^+ = 430$; ir: $\nu_{S=O} = 1067$ cm^{-1}, $\nu_{NO2} = 1528$ cm^{-1}; ^{1}H nmr (500 MHz, deuteriochloroform) δ: 2.98(s, 3H, 3'-S(O)CH_3), 7.68 (m, 1H, $^3J = 8.3$, $^3J = 6.9$, $^4J = 1.2$ Hz, H-6'), 7.74 (m, 1H, $^3J = 8.4$, $^3J = 7.6$ Hz, H-7), 7.82 (m, 1H, $^3J = 7.6$, $^4J = 1.3$ Hz, H-6), 7.90 (m, 1H, $^3J = 8.4$, $^3J = 6.9$, $^4J = 1.3$ Hz, H-7'), 7.94 (s, 1H, H-2), 8.17 (dd, 1H, $^3J = 8.4$, $^4J = 1.3$ Hz, H-8), 8.21 (m, 1H, $^3J = 8.3$, $^4J = 1.3$, $^5J = 0.5$ Hz, H-5'), 8.33 (m, 1H, $^3J = 8.4$, $^4J = 1.2$, $^5J = 0.5$ Hz, H-8'), 9.57 (s, 1H, H-2').

Anal. Calcd. for $C_{19}H_{12}N_3S_2O_3Cl$ (429.90): C, 53.08; H, 2.81; N, 9.78; S, 14.92; Cl, 8.25. Found: C, 52.85; H, 3.03; N, 9.66; S, 14.78; Cl, 8.11.

Reduction of Sulfoxides **6** and **7** to Sulfides **8**

A mixture of sulfoxide **6** or **7** (1 mmol), 3.5 ml of conc. hydrochloric acid and 0.4 g of potassium iodide was stirred at room temperature for twenty minutes. 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. The solid was air-dried and recrystallized from N,N-dimethylformamide. For analytical purposes, sulfides **8** were purified by column chromatography (neutral aluminium oxide, chloroform and a mixture of chloroform / 95% ethanol, 19 : 1, v/v)

4-Oxo-1,4-dihydro-3'-methylthio-6-nitro-3,4'-diquinolinyl sulfide (**8b**).

This compound had mp 289-290°C, yield 94 %; EIMS: M^+ = 395 (78 %), $[M\text{-}SCH_3]^+ = 348$ (100%); ir: $\nu_{NO2} = 1506$ cm^{-1}; ^{1}H nmr (500 MHz, hexadeuteriodimethyl sulfoxide) δ: 2.68 (s, 3H, 3'-SCH_3), 7.63 (m, 1H, $^3J = 8.3$, $^3J = 6.9$, $^4J = 1.3$ Hz, H-6'), 7.70 (m, 1H, $^3J = 8.3$, $^3J = 6.9$, $^4J = 1.4$ Hz, H-7'), 7.73 (d, 1H, ^3J = 9.0 Hz, H-8), 7.74 (s, 1H, H-2), 8.03 (m, 1H, $^3J = 8.3$, $^4J = 1.3$, $^5J = 0.5$ Hz, H-8'), 8.39 (dd, 1H, $^3J = 9.2$, $^4J = 2.7$ Hz, H-7), 8.42 (m, 1H, $^3J = 8.3$, $^4J = 1.4$, $^5J = 0.5$ Hz, H-5'), 8.81 (d, 1H, $^4J = 2.7$ Hz, H-5), 8.88 (s, 1H, H-2'), 12.43 - 12.46 (broad, 1H, N-H).

Anal. Calcd. for $C_{19}H_{13}N_3S_2O_3$ (395.45): C, 57.71; H, 3.31; N, 10.63; S, 16.21. Found: C, 57.48; H, 3.53; N, 10.48; S, 16.08.

4-Oxo-1,4-dihydro-3'-methylthio-8-nitro-3,4'-diquinolinyl Sulfide (**8c**).

This compound had mp 267-268°C, yield 96 %; EIMS: M^+ = 395 (16 %), $[M\text{-}SCH_3]^+ = 348$ (100%); ir: $\nu_{NO2} = 1498$ cm^{-1}; ^{1}H nmr (500 MHz, hexadeuteriodimethyl sulfoxide) δ: 2.69 (s, 3H, 3'-SCH_3), 7.39 (s, 1H, H-2), 7.54 (t, 1H, $^3J = 8.0$ Hz, H-6), 7.66 (m, 1H, $^3J = 8.2$, $^3J = 7.0$, $^4J = 1.1$ Hz, H-6'), 7.73 (m, 1H, $^3J = 8.2$, $^3J = 7.0$, $^4J = 1.2$ Hz, H-7'), 8.06 - 8.08 (m, 1H, H-8'), 8.36 - 8.38 (m, 1H, H-5'), 8.58 (dd, 1H, $^3J = 8.0$, $^4J = 1.4$ Hz, H-5), 8.64 (dd, 1H, $^3J = 8.0$, $^4J = 1.4$ Hz, H-7), 8.95 (s, 1H, H-2'), 11.87 - 11.95 (broad, 1H, N-H).

Anal. Calcd. for $C_{19}H_{13}N_3S_2O_3$ (395.45): C, 57.71; H, 3.31; N, 10.63; S, 16.21. Found: C, 57.51; H, 3.58; N, 10.62; S, 16.01.

4-Chloro-3'-methylthio-6(or 8)-nitro-3,4'-diquinolinyl sulfides (**9b**) and (**9c**).

A mixture of 1,4-dihydro-4-oxo-3'-methylsulfinyl-6(or 8)-nitro-3,4'-diquinolinyl sulfides (**8b** or **8c**) (424 mg, 1 mmol), *N,N*-dimethylformamide (10 ml) and phosphoryl chloride (0.55 ml) was stirred at room temperature for 10 minutes (in the case of **8c**) or 45 minutes (in the case of **8b**), then cautiously poured onto 50 g of ice, and neutralized at 0°C with conc. aqueous ammonia. The solid was filtered off, washed twice with cold water and air-dried to give yellow products containing 6-nitro- or 8-nitrosulfides **9b** or **9c**. The crude products were then recrystallized from methanol.

4-Chloro-3'-methylthio-6-nitro-3,4'-diquinolinyl Sulfide (**9b**).

This compound had mp 203-204 °C, yield 78 %; EIMS: M^+ = 413 (44%), $[M\text{-}Cl]^+ = 378$ (100%);ir: $\nu_{NO2} = 1522$ cm^{-1}; ^{1}H nmr (300 MHz, deuteriochloroform) δ: 2.66 (s, 3H, 3'-S(O)CH_3), 7.59 - 7.64 (m, 1H, H-6'), 7.72 - 7.75 (m, 1H, H-7'), 8.05 (s, 1H, H-2), 8.12 (d, 1H, $^3J = 9.0$ Hz, H-8), 8.16 - 8.19 (m, 1H, H-5'), 8.31 - 8.33 (m, 1H, H-8'), 8.43 (dd, 1H, $^3J = 9.0$, $^4J = 2.4$ Hz, H-7), 8.90 (s, 1H, H-2), 9.17 (d, 1H, $^4J = 2.4$ Hz, H-5).

Anal. Calcd. for $C_{19}H_{13}N_3S_2O_2Cl$ (414.01): C, 55.07; H, 3.16; N, 10.15; S, 15.44; Cl, 8.57. Found: C, 54.89; H, 3.42; N, 9.96; S, 15.21; Cl 8.36.

4-Chloro-3'-methylthio-8-nitro-3,4'-diquinolinyl sulfide (**9c**).

This compound had mp 232.5-233.5 °C, yield 79 %; EIMS: $M^+ = 413$ (69%), $[M\text{-}Cl]^+ = 378$ (100%); ir: $\nu_{NO2} = 1537$ cm^{-1}; ^{1}H nmr (300 MHz, deuteriochloroform) δ: 2.65 (s, 3H, 3'-S(O)CH_3), 7.60 (m, 1H, $^3J = 8.3$, $^3J = 7.2$, $^4J = 1.3$ Hz, H-6'), 7.71 (m, 1H, $^3J = 8.3$, $^3J = 7.2$, $^4J = 1.5$ Hz, H-7'), 7.73 (dd, 1H, $^3J = 8.6$, $^3J = 7.4$ Hz, H-6), 7.98 (dd, 1H, $^3J = 7.4$, $^4J = 1.2$ Hz, H-7), 8.00 (s, 1H, H-2), 8.13 - 8.18 (m., 1H, H-8') 8.30 (m, 1H, $^3J = 8.3$, $^3J = 7.2$, $^5J = 0.7$ Hz, H-5'), 8.46 (dd, 1H, $^3J = 8.6$, $^4J = 1.3$ Hz, H-5), 8.88 (s, 1H, H-2').

Anal. Calcd. for $C_{19}H_{13}N_3S_2O_2Cl$ (414.01): C, 55.07; H, 3.16; N, 10.15; S, 15.44; Cl, 8.57. Found: C, 54.87; H, 3.34; N, 9.93; S, 15.19; Cl 8.40.

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