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The ^1H and ^{13}C nmr spectra of 4-methoxy-3'-methylsulfinyl-3,4'-diquinoliny sulfides **2**, **3** and **4** were totally assigned using a combination of nmr techniques. As compared to the spectral data of sulfoxide **2** typical values of nitro group substituents effects in nitroquinolines **3** and **4** were observed. The H-2' protons in sulfoxides **2**, **3** and **4** are strongly influenced by *ortho* methylsulfinyl group and deshielded by about 0.7 ppm. PM3 method calculations support the structural conclusion that sulfinyl group oxygen points in direction of the positions 2'.

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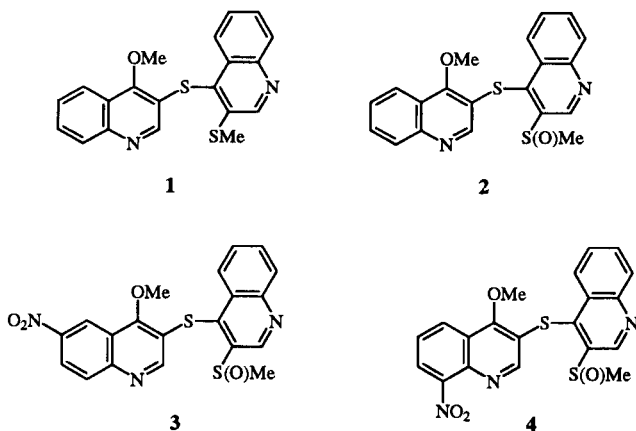
Introduction.

We have been interested in the functionalization of quinoline *via* 3,4-quinolinediyl bis-sulfides or 3,4'-diquinoliny sulfides both prepared from thioquinanthrene [1]. In the preceding paper we reported the synthesis of 6- and 8-nitro-4-methoxy-3'-methylsulfinyl-3,4'-diquinoliny sulfides **3** and **4** from 4-methoxy-3'-methylthio-3,4'-diquinoliny sulfide **1** [2]. As an extension of our spectroscopic studies concerning the structure of compounds **3** and **4**, we now present the complete assignment of the ^1H and ^{13}C nmr spectra of sulfides **3** and **4** as well as those of sulfide **2** taken as a reference compound.

Results and Discussion.

4-Methoxy-3'-methylsulfinyl-3,4'-diquinoliny sulfide **2** is a primary product of 4-methoxy-3'-methylthio-3,4'-diquinoliny sulfide **1** reaction with a nitrating mixture [2]. Further treatment of sulfoxide **2** with a nitrating mixture led to its 6- and 8-nitro derivatives **3** and **4** accompanied by some amounts of 6- and 8-nitro derivatives of 1,4-dihydro-4-oxo-3'-methylsulfinyl-3,4'-diquinoliny sulfide [2].

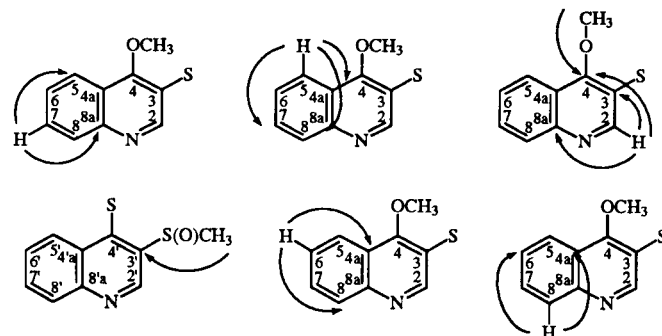
Scheme 1



In the structure assignment of **3** and **4**, sulfoxide **2** served as a reference compound. The molecule of **2** possesses two close 3,4-disubstituted quinoline moieties. They are distinguishable by the use of COSY spectra followed by nOe experiments with methoxy group protons [2]. We would like to confirm the previously established structure assignment of **2**, **3** and **4** by means of proton-carbon long range correlation. The starting problem was how to prove the correlation between α -quinoliny protons (H-2 and H-2') and benzene-ring protons (H-5, H-6, H-7 and H-8 or H-5', H-6', H-7' and H-8', respectively). It could be solved indirectly with the help of long-range proton-carbon correlations as presented in Scheme 2. As shown by Castle *et al.* [3] and our earlier attempts [4], the key parts in this methodology are played by the proton-carbon correlations between the bridged quaternary carbon being part of both aromatic rings and respective protons. From this point of view, in the case of 3,4'-diquinoliny sulfides studied, the key correlations are those of carbon C8a_{quinoliny} which should show long-range correlations with H-2_{quinoliny}, H-5_{quinoliny} and H-7_{quinoliny}. The position of second bridged carbon atom *i.e.* C4a_{quinoliny}, is for all sulfides studied: **2**, **3** and **4** difficult to reach (see Tables 1, 2 and

Scheme 2

Set of Long-range Correlations used in the NMR Assignments of Compounds **2**, **3** and **4**.



3). Therefore, the use of ^{13}C -nmr, ^{13}C - ^1H -two dimensional (HETCOR) spectrum and INEPT experiment were necessary to generate a total nmr assignment of compounds **2**, **3** and **4**.

In the case of sulfide **2**, on the basis of HETCOR spectrum, recorded are the single-bond proton-carbon correlations at positions 2, 5, 7, 8, 2', 5', 7' and 8' (see Table 1). However, due to very close chemical shift values of H-6 and H-6' ($\delta = 7.57$ ppm and $\delta = 7.58$ ppm, respectively) no distinction between the positions of carbon C-6 and C-6' signals could be afforded with the HETCOR spectrum.

As seen from the structure of compound **2**, H-7 ($\delta = 7.69$ ppm) should show correlations with carbon resonances corresponding to C8a and C5. The correlation at $\delta = 121.5$ ppm is assigned to C5 and the correlation at $\delta = 149.0$ ppm is assigned to C8a, because quaternary carbon C8a should have lower intensity in ^{13}C nmr. Long-range coupling with the methoxy group protons ($\delta = 4.14$ ppm) is observed in the INEPT experiment at $\delta = 161.2$ ppm. Therefore, this carbon is assigned as C4. Long-range couplings with H-2 ($\delta = 8.26$ ppm) are observed in the INEPT experiment at $\delta = 118.7$ ppm, $\delta = 149.0$ ppm and $\delta = 161.2$ ppm. According to the above deduction, the correlation at $\delta = 149.0$ ppm is assigned to C8a and the one at $\delta = 161.2$ ppm to C4. The correlation of quaternary carbon at $\delta = 118.7$ ppm is assigned to C3. Even though C-H two-bond couplings are usually small, the two-bond H2/C3 coupling $^2J_{\text{C-H}}$ is comparable with $^3J_{\text{C-H}}$ one. Similar effects were noted in the case of some polycyclic arenes [3,5,6] and six-membered azaheterenes [3,5,6], and also in the case of thienopyridines [6].

As seen from the structure of compound **2**, H-5 ($\delta = 8.04$ ppm) should show $^3J_{\text{C-H}}$ correlations with quaternary carbon resonances corresponding to C4 and C8a and with that of tertiary carbon C-7. In fact, long-range couplings with H5 are observed in the INEPT experiment at $\delta = 130.2$ ppm, $\delta = 149.0$ ppm and $\delta = 161.2$ ppm. According to the above deduction, the correlation at $\delta = 149.0$ ppm is assigned to C8a and the one at $\delta = 161.2$ ppm to C4. Tertiary carbon C7 is assigned to $\delta = 130.2$ ppm, because of its higher intensity. Long-range couplings with H-8 ($\delta = 7.99$ ppm) are observed in the INEPT experiment at $\delta = 123.3$ ppm and $\delta = 127.4$ ppm. The correlation at $\delta = 123.3$ ppm is assigned to C4a and the one $\delta = 127.4$ ppm to C6.

Next, we turned to the assignment of the "right side part" of methoxymethylsulfinyldiquinoliny sulfide **2**. As seen from the structure of compound **2**, H-7' ($\delta = 7.80$ ppm) should show correlations with carbon resonance corresponding C8'a and C5'. The correlation at $\delta = 125.1$ ppm is assigned to C5' and the correlation at $\delta = 149.6$ ppm is assigned to C8'a, because quaternary carbon C8'a should have lower intensity in ^{13}C nmr. Long-range coupling with methylsulfinyl group protons ($\delta = 2.89$ ppm) is observed in the INEPT experiment at $\delta = 142.5$ ppm.

Therefore this carbon is assigned as C3'. Long-range couplings with H-2' ($\delta = 9.48$ ppm) are observed in the INEPT experiment at $\delta = 137.4$ ppm, $\delta = 142.5$ ppm and $\delta = 149.6$ ppm. According to the above deduction, the correlation at $\delta = 149.6$ ppm is assigned to C8'a and the one at $\delta = 142.5$ ppm to C3'. The correlation of quaternary carbon at $\delta = 137.4$ ppm is assigned to C4'. Again, as in the case of the "left side part", the two-bond H2'/C3' coupling $^2J_{\text{C-H}}$ is comparable with $^3J_{\text{C-H}}$ one. Long-range couplings with H5' are observed in the INEPT experiment at $\delta = 131.4$ ppm, $\delta = 137.4$ ppm and $\delta = 149.6$ ppm. According to the above deduction, the correlation at $\delta = 149.6$ ppm is assigned to C8'a and the one at $\delta = 137.4$ ppm to C4'. Tertiary carbon C7' is assigned to $\delta = 131.4$ ppm, because of its higher intensity. Long-range couplings with H-8' ($\delta = 8.23$ ppm) are observed in INEPT experiment at $\delta = 127.7$ ppm and $\delta = 128.9$ ppm. The correlation at $\delta = 127.7$ ppm is assigned to C4'a and $\delta = 128.9$ ppm to C6'. The nmr assignments of sulfide **2** are summarized in Table 1.

The assignment of C2, C3, C4, C5 and C8a carbon atoms of sulfide **3** was performed in the same steps as for sulfide **2**.

As seen from the structure of compound **3**, H-5 ($\delta = 9.01$ ppm) should show $^3J_{\text{C-H}}$ correlations with quaternary carbon resonances corresponding to C4 and C8a and with that of tertiary carbon C-7. However, long-range couplings with H5 are observed in the INEPT experiment at $\delta = 123.5$ ppm, $\delta = 146.3$ ppm, $\delta = 150.6$ ppm and $\delta = 161.9$ ppm. According to the above deduction, the correlation at $\delta = 150.6$ ppm is assigned to C8a and the one at $\delta = 161.9$ ppm to C4. Tertiary carbon C7 is assigned to $\delta = 123.5$ ppm, because of its higher intensity. The remaining quaternary carbon ($\delta_{\text{C}} = 146.3$ ppm) is assigned to C-6, because it is deshielded by about 19 ppm, as compared with the C6 carbon atom signal of compound **2**. It fits well with the nitro group effect on the position of $\text{C}_{\text{arom-NO}_2}$ carbon atom signal [7] - see Table 4. Also, in this case the two-bond H5/C6 coupling $^2J_{\text{C-H}}$ is comparable with $^3J_{\text{C-H}}$ one. Long-range couplings with H-8 ($\delta = 8.12$ ppm) are observed in the INEPT experiment at $\delta = 122.8$ ppm and $\delta = 146.3$ ppm. The correlation at $\delta = 122.8$ ppm is assigned to C4a and the one at $\delta = 146.3$ ppm to C6.

The assignment of the "right side part" of nitrodiquinoliny sulfide **3** was performed in the same manner as that of sulfoxide **2**. In spite of the same chemical shift values of H-5' and H-8' protons ($\delta = 8.28$ ppm), the complete assignment of benzene-ring protons and carbons could be deduced from the INEPT experiments with H-6' and H-7' protons as well as from the one-bond proton-carbon correlations (see Table 2).

The spectral data of sulfide **4** exhibited much more complexity. Thus, in the total ^1H and ^{13}C nmr assignment

concerted use of the COSY, ^1H - ^1H nOe, decoupled ^{13}C nmr spectrum, HETCOR and selective INEPT experiments must be engaged. The COSY spectrum (at 500 MHz) permits segregation of the seven benzene-ring protons into two groups with three protons of AMX system and four protons of ABMX one, both of quinoliny type. The position of H-5 ($\delta = 8.29$ ppm) proton was established by means of nOe experiments with 4-methoxy group protons ($\delta = 4.23$ ppm). It proves for the positions of H-6 and H-7 protons. The most deshielded singlet ($\delta = 9.51$ ppm) is assigned to H-2' due to the deshielding effect of methylsulfinyl group ($\Delta\delta = 0.69$) [8]. The nOe experiment with 3'-methylsulfinyl group protons ($\delta = 2.93$ ppm) causes enhancement of both α -quinoliny singlets, *i.e.* that of H-2' protons ($\delta = 9.51$ ppm) and the second one of H-2 proton ($\delta = 8.26$ ppm). Unfortunately, due to identical or very close chemical shifts values of H-2 and H-5' protons ($\delta = 8.26$ ppm) as well as those of H-5 and H-8' protons ($\delta = 8.29$ and 8.28 ppm respectively), the HETCOR experiment permits direct assignment of methoxy, methylsulfinyl, C-2, C-6, C-7, C-6' and C-7' carbons only. However, the complete assignment of the "right" quinoliny part of sulfide **4** could be reached in the same steps as for sulfides **2** and **3**, using the INEPT experiments with H-2', H-6', H-7' and methylsulfinyl protons. Taking into account the positions C-5' and C-8' carbons ($\delta = 124.9$ and 131.0 ppm) one would assign the positions of C-2 and C-5 carbons on the basis

of HETCOR experiment data mentioned above. The INEPT experiments with CH_3O , H-6 and H-7 protons indicate and confirm at least the positions of C-4, C4a, C-5, C8 and C-8a carbons.

The remaining quaternary carbon atom signal at $\delta_{\text{C}} = 121.3$ ppm must be that of C3. Considering that for diquinoliny sulfides **2** and **3** studied the $\text{H}_{\alpha\text{-quinoliny}} - \text{C}_{\beta\text{-quinoliny}}$ coupling $^2J_{\text{C-H}}$ is comparable with $^3J_{\text{C-H}}$ one, we tried to confirm the assignment of C3 with the help of INEPT experiment with H-2 proton. Because H-2 and H-5' protons signals were of identical chemical shift values ($\delta = 8.26$ ppm) we expected to observe proton ($\delta = 8.26$ ppm)-carbon correlations with six carbons *i.e.* three carbons: C3 ($\delta = 121.3$ ppm), C8a ($\delta = 139.8$ ppm) and C4 ($\delta = 160.4$ ppm) from the correlation with H-2 and the next three ones: C7' ($\delta = 131.8$ ppm), C4' ($\delta = 135.5$ ppm) and C8'a ($\delta = 149.8$ ppm) from the correlation with H-5'. However, two further correlations at C6' ($\delta = 129.3$ ppm) and C4'a ($\delta = 127.7$ ppm), both derived from H-8' ($\delta = 8.28$ ppm), were also observed. The collected nmr assignments of sulfide **4** are summarized in Table 3.

Conclusions.

As presented in Scheme 2, the long-range (mainly three-bonds) proton-carbon correlations recorded with the help of INEPT experiment proved very useful [9] for the total ^1H and ^{13}C nmr assignment of fused bicyclic systems with two very close moieties. However, for sulfides **2**, **3** and **4**, INEPT experiment can only be selective when $\Delta\delta_{\text{H}}$ (at 500

Table 1

Summary of INEPT Long-range Proton-carbon and HETCOR Single-bond Correlations of 4-Methoxy-3'-methylsulfinyl-3,4'-diquinoliny Sulphide **2**

Proton δ [ppm]	Carbon single bond coupling δ [ppm]	Carbon three bond coupling δ [ppm]	Carbon two bond coupling δ [ppm]
H-2 (8.26)	C-2 (150.5)	C-8a (149.0) C-4 (161.2)	C-3 (118.7)
H-5 (8.04)	C-5 (121.5)	C-4 (161.2) C-8a (149.0) C-7 (130.2)	
H-6 (7.57)	C-6 (127.4)	no determined [a]	
H-7 (7.69)	C-7 (130.2)	C-5 (121.5) C-8a (149.0) C-6 (127.4)	
H-8 (7.99)	C-8 (129.6)	C-4a (123.3)	
H-2' (9.48)	C-2' (145.3)	C-8'a (149.6) C-4' (137.4)	C-3' (142.5)
H-5' (8.31)	C-5' (125.1)	C-4' (137.4) C-8'a (149.6) C-7' (131.4)	
H-6' (7.58)	C-6' (128.9)	no determined [a]	
H-7' (7.80)	C-7' (131.4)	C-5' (125.1) C-8'a (149.6) C-6' (128.9)	
H-8' (8.23)	C-8' (130.7)	C-4'a (127.7)	
$\text{CH}_3\text{S}(0)$ (2.89)	$\text{CH}_3\text{S}(0)$ (42.9)	C-3' (142.5)	
CH_3O (4.14)	CH_3O (62.4)	C-4 (161.2)	

[a] INEPT experiment was not performed due to very small differences between chemical shifts values of H-6 and H-6' protons ($\Delta\delta = 0.01$ ppm).

Table 2

Summary of INEPT Long-range Proton-carbon and HETCOR Single-bond Correlations of 4-Methoxy-3'-methylsulfinyl-6-nitro-3,4'-diquinoliny Sulfide (3)

Proton δ [ppm]	Carbon single bond coupling δ [ppm]	Carbon three bond coupling δ [ppm]	Carbon two bond coupling δ [ppm]
H-2 (8.31)	C-2 (153.8)	C-8a (150.6) C-4 (161.9)	C-3 (120.8)
H-5 (9.01)	C-5 (118.9)	C-4 (161.9) C-8a (150.6) C-7 (123.5)	C-6 (146.3)
H-7 (8.43)	C-7 (123.5)	C-5 (118.9) C-8a (150.6)	
H-8 (8.12)	C-8 (131.7)	C-6 (146.3) C-4a (122.8)	
H-2' (9.51)	C-2' (145.6)	C-8'a (149.9) C-4' (136.0)	C-3' (143.0)
H-5' (8.28)	C-5' (124.9)	no determined [a]	
H-6' (7.63)	C-6' (129.3)	C-4'a (127.7) C-8' (131.1)	
H-7' (7.86)	C-7' (131.8)	C-5' (124.9) C-8'a (149.9)	
H-8' (8.28)	C-8' (131.1)	no determined [a]	
CH ₃ S(0) (2.95)	CH ₃ S(0) (43.2)	C-3' (143.0)	
CH ₃ O (4.31)	CH ₃ O (63.2)	C-4 (161.9)	

[a] INEPT experiment was not performed due to the same chemical shifts values of H5' and H8' protons ($\delta = 8.28$ ppm).

MHz) is over the value of 0.02 ppm. When $\Delta\delta_{\text{H}}$ is 0.02 ppm or less, the concerted use of other nmr techniques must be engaged to obtain the complete ¹H and ¹³C nmr assignment.

The molecules of compounds 1 and 2-4 are constituted of 4-methoxyquinoline part (the "left" part) and 3,4-

quinolinediyl bis-sulfide or sulfide-sulfoxide part (the "right" part). Selected substituted chemical shift values $\Delta\delta_{\text{H}}$ and $\Delta\delta_{\text{C}}$, where $\Delta\delta = \delta_{\text{sulfoxide}} - \delta_{\text{sulfide}}$ are presented in Scheme 3. As previously presented for $\Delta\delta_{\text{H}}$ [2] and outlined in Scheme 3 as well as in Table 4, $\Delta\delta_{\text{H}}$ and $\Delta\delta_{\text{C}}$

Table 3

Summary of INEPT Long-range Proton-carbon and HETCOR Single-bond Correlations of 4-Methoxy-3'-methylsulfinyl-8-nitro-3,4'-diquinoliny Sulfide 4

Proton δ [ppm]	Carbon single bond coupling δ [ppm]	Carbon three bond coupling δ [ppm]	Carbon two bond coupling δ [ppm]
H-2 (8.26)	C-2 (152.1)	C-8a (139.8) [a] C-4 (160.4) [a]	C-3 (121.3) [a]
H-5 (8.29)	C-5 (125.8)	no determined	
H-6 (7.67)	C-6 (126.3)	C-4a (124.6) C-8 (148.4)	
H-7 (8.01)	C-7 (124.3)	C-5 (125.8) C-8a (139.8)	
H-2' (9.51)	C-2' (145.5)	C-8'a (149.8) C-4' (135.5)	C-3' (143.2)
H-5' (8.26)	C-5' (124.9)	C-4' (135.5) [a] C-8'a (149.8) [a] C-7' (131.8) [a]	
H-6' (7.64)	C-6' (129.4)	C-4'a (127.8) C-8' (131.0)	
H-7' (7.86)	C-7' (131.8)	C-5' (124.9) C-8'a (149.8)	
H-8' (8.28)	C-8' (131.0)	C-6' (129.4) [a] C-4'a (127.8) [a]	
CH ₃ S(0) (2.93)	CH ₃ S(0) (43.2)	C-3' (143.2)	
CH ₃ O (4.23)	CH ₃ O (62.8)	C-4 (160.4)	

[a] INEPT experiment with H-2 and H-5' protons ($\delta_{\text{H}} = 8.26$ ppm) showed long-range correlations with the carbons marked.

of benzene ring members in the "left" parts of compounds 2-4 are typical for the introduction of nitro group in positions 6- or 8- of quinoline molecule [10,8,11].

The ^1H and ^{13}C chemical shift values of sulfoxides 2-4 "right" parts are very close. Relative to the starting sulfide 1 the most influenced are the H-2' protons deshielded by about 0.66-0.69 ppm, while typical sulfinyl group effect in diphenyl sulfoxides reaches 0.31 ppm

required for the occurrence of nOe [14]. It should also be noted that signals of H-5' protons are shifted upfield ($\Delta\delta_{\text{H}} = 0.09\text{-}0.14$ ppm).

As compared to the sulfinyl group effect in phenylsulfinyl- and methylsulfinylbenzenes [11,18], some changes in $\Delta\delta_{\text{C}}$ (relative to sulfide 1) were observed in near environment of methylsulfinyl group in sulfoxides 2-4. The $\text{C}_{\text{arom}}\text{-S(O)}$ (*i.e.* C3') carbon atoms are less

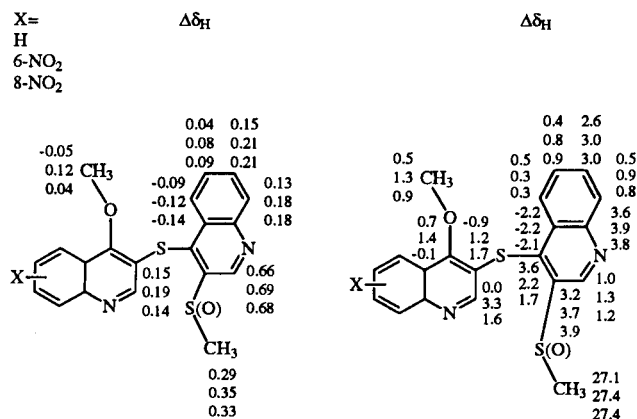
Table 4

^{13}C NMR Substituents Effects Caused by the Nitro group in the 6 or 8-Nitroquinolines ($x\text{-O}_2\text{N-Q}$) Relative to Quinoline (Q), ref [11], versus Those Measured for Nitro-3,4'-diquinolyl Sulfides 3, and 4 Relative to 4-Methoxy-3'-methylsulfinyl-3,4'-diquinolyl Sulfide 2

	$\Delta\delta = \delta(\text{Nitroquinoline}) - \delta(\text{Parent Quinoline})$			$\Delta\delta(\text{C-7})$	$\Delta\delta(\text{C-8})$	$\Delta\delta(\text{C-8a})$	$\Delta\delta(\text{C-NO}_2)$
	$\Delta\delta(\text{C-4a})$	$\Delta\delta(\text{C-5})$	$\Delta\delta(\text{C-6})$				
6-nitroisomers							
6-O ₂ N-Q/Q	-1.3	-3.1		-6.6	1.9	1.9	19.0
3/2	-0.5	-2.6		-6.7	2.1	1.6	18.8
8-nitroisomers							
8-O ₂ N-Q/Q	0.7	4.4	-1.2	5.8		-9.0	18.8
4/2	1.3	4.3	-1.1	-5.9		-9.2	18.8

Scheme 3

Selected Substituted Chemical Shift Values $\Delta\delta_{\text{H}}$ and $\Delta\delta_{\text{C}}$ of 3'-Methylsulfinyl-3,4'-diquinolyl Sulfides 2-4 as Related to Sulfide 1, when $\Delta\delta = \delta_{\text{sulfoxide}} - \delta_{\text{sulfide 1}}$



[12]. The next important information concerning the spatial structure of sulfoxides 2-4 came from $^1\text{H}\text{-}^1\text{H}$ nOe experiments with *S*-methyl group protons. In the case of sulfide 1 irradiation of 3'-methylthio group protons causes only the enhancement of H-2' proton signal [13], whereas the signal of H-2 proton remains unaffected. It indicates spatial proximity of H-2' and S-CH₃ group protons, *i.e.* the 3'-methylthio group should be pointing towards position 2'. This conclusion was fully confirmed by an X-ray examination of sulfide 1 [13]. In case of sulfoxides 2-4 irradiation of *S*-methyl group protons causes not only the enhancement of H-2' signals but even that of the H-2 ones. Considering the steric requirement for the occurrence of nOe, the distance between 3'-*S*-methyl group protons and H-2 proton should be within the limit

deshielded by about of 3.7-6.0 ppm. The *ortho* carbon atoms are influenced non-equivalently, the C-4' carbon atoms are more deshielded up to 10 ppm, while the C-2' carbon atoms are more deshielded by 5-7.6 ppm only.

The effects mentioned above seem to be due to the fact that the transformation of methylthio group in 1 into methylsulfinyl group in sulfoxides 2-4 leads to the pyramidal arrangement of the substituents linked to the sulfur atom in sulfoxides [15]. Furthermore, in the paper of Benassi *et al.* [16], the orientation of the sulfinyl oxygen was described as follows: "Situation near to coplanarity of the SO bond and aromatic ring is also found in *ortho*-substituted derivatives, and the sulfinyl oxygen points in the direction opposite to the substituent in the ring". From this point of view, the oxygen atom in sulfinyl groups of compounds 2-4 should point towards position 2' inducing an increase in the deshielding of H-2' up to $\Delta\delta_{\text{H}} = 0.66 - 0.69$ ppm). The position of sulfinyl oxygen causes further structural changes including the shift of the 3'-*S*-methyl group over the pyridine ring, more probably in the spatial proximity of the H-2 proton, as well as changes in the interaction of *ortho*-adjusted sulfur-sulfur substituents responsible for the magnitude of peri deshielding of H-5' protons.

To evaluate the conclusions drawn from nmr data some calculations concerning the structural features of sulfoxide 2 were performed. For optimized geometry (PM3 method) [17] the calculations gave the values of torsion angle C2'-C3'-S-O equal to -11.3 deg and that of C2'-C3'-S-C(CH₃) equal to 95.9 degrees. They indicate that sulfinyl group oxygen is pointing towards the positions 2' and that methyl part of sulfinyl group is located perpendicularly to the parent pyridine ring. Additionally, the distance

between the nearest proton of methylsulfinyl group and H-2 proton (3.02 A) or H-2' proton (3.41 A) are within the limit required for the occurrence of nOe [14].

EXPERIMENTAL

4-Methoxy-3'-methylsulfinyl-3,4'-diquinoliny sulfide **2**, 6- and 8-nitro-4-methoxy-3'-methylsulfinyl-3,4'-diquinoliny sulfides **3** and **4** were prepared by treatment of 4-methoxy-3'-methylthio-3,4'-diquinoliny sulfide **1** with a nitrating mixture as described previously [2].

Proton and carbon nmr spectra of compounds **2**, **3** and **4** were collected at 27° on a Bruker AM 500 spectrometer operating at proton frequency of 500.13 MHz and a carbon frequency of 125.76 MHz. Approximately 5 mg (for ¹H and ¹³C nmr) or 15 mg (for two-dimensional experiments) of each sample were dissolved in 0.5 ml of deuteriochloroform. The chemical shifts were referenced to tetramethylsilane. The proton spectra were obtained using a 8 μsec (60°) pulse and a 4 second acquisition time to ensure accurate integrals. 96 transients with 65 536 data points each were used. The ¹³C nmr spectra were obtained using a 3 μsec (45°) pulse and 1.1 second acquisition time to ensure accurate integrals. 272 transients with 65 536 data points each were used.

The homonuclear ¹H-¹H shift correlated two-dimensional diagrams were obtained using the COSY-90 pulse sequence [using program in the Bruker software]. The spectral widths were 1160 Hz. The spectra were collected as 512 x 256 blocks of data and were processed by sinusoidal multiplication in each dimension, followed by symmetrization of final data matrix. Other parameters were as follows: number of increments in t₁, 64; number of scans, 8; phase cycling, 8; and relaxation delay, 1.5 seconds.

Overhauser effect (nOe) experiments were measured on the same samples used to determine the ¹H nmr spectra as reported previously [2].

The HETCOR spectra were obtained using XHCORRD program in the Bruker software. The spectra were collected with 2K x 32 data points, a data acquisition of 8 scans x 32 in the t₁ domain. Spectral widths 0.5 and 5.0 kHz were employed in the F₂ (¹H) and F₁ (¹³C) dimensions, respectively. The relaxation delay D₁, was 1.5 seconds and D₂ was optimized as 3.6 mseconds.

The long-range heteronuclear CH correlation spectra [9] were obtained using the standard pulse sequence (SPT INEPT in the Bruker software). The spectral widths were 29 kHz and the

relaxation delay 1.5 seconds. The value of 8 Hz (or 10 Hz for H2-C8a and H2'-C8a' correlation) was used for the coupling.

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Part XLII in the series of Azinyl Sulfides.

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