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Structure of 4-Substituted 3,4'-Diquinoliny Sulfides Studied by ^1H and ^{13}C NMR and X-Ray Analysis

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STRUCTURE OF 4-SUBSTITUTED 3,4'-DIQUINOLINYL SULFIDES STUDIED BY ^1H AND ^{13}C NMR AND X-RAY ANALYSIS

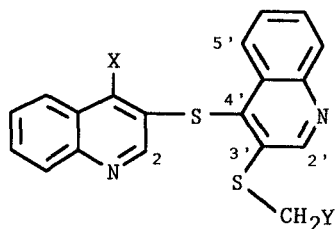
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Abstract NMR and X-ray data show that 4-substituted 3,4'-di-
quinolinyll sulfides exist both in a solution and in solid state in a
skew conformation at the main sulfide bridge and that non-typical
position of H-2 proton may be attributed to its shielding by
aromatic rings of a second quinoline fragment.

3,4'-diquinolinyll sulfides are of interest for us as intermediates in
the functionalization of quinoline via thioquinathrene ¹. However, NMR
spectral data of these diquinolinyll sulfides do not correspond to typical
features of 3,4'-disubstituted quinolines. Non-typical spectroscopic
properties of 4-substituted 3,4'-diquinolinyll sulfides **1-3** were manifested
mainly in deshielding of H-5 and H-5' protons ($\Delta\delta$ up to 0.87 ppm) by
peri heteroatom and in big shielding of α -quinolinyll H-2 proton signals
as compared to those of H-2' proton ($\Delta\delta$ ca 1 ppm) ². That latter effect
appears to be the consequence of the fact that molecules of sulfides **1-3**
exist in a skew conformation with respect to the main sulfide bridge,
as it can be seen from the X-ray analysis done recently. Additionally,
there are short contacts between pairs of *ortho*-situated heteroatoms,
shorter by 0.19-0.60 Å than sum of their van der Waals radii.

In order to find out if a conformation of sulfides **1-3** is controlled by
stereoelectronic effects between *ortho*-situated heteroatoms, derivati-
ves **4,5** and **6** were synthesized. Small differences in ^1H and ^{13}C
spectral parameters of compounds **4** and **5** were observed.



1 X=OMe, Y=H 4 X=Y=OMe

2 X=SMe, Y=H 5 X=OMe, Y=SMe

3 X=Cl, Y=H 6 X=Y=H

	1	4	5	6
	δ (ppm)	$\Delta\delta$	$\Delta\delta$	$\Delta\delta$
H-2	8.12	+0.04	+0.03	+0.59
H-2'	8.83	+0.33	+0.14	+0.04

NOE enhancements of H-5' proton signal
when irradiating OCH₃ signal

3%

3%

2%

The NOE enhancements observed between 4-OCH₃ and H-5' protons and X-ray data of compound **4**³ show that sulfides **4** and **5** also exist in a skew conformation and that anomeric effects in side chains of methylthio- homolog **4** and methoxy-homolog **5** do not change interactions between heteroatoms.

In the case of 4-deshetero (X=H) derivative **6** both H-2 and H-2' protons appeared at a typical α -quinolinyl region, contrary to sulfides **1-5**. That led us to the conclusion that stereoelectronic interactions of donor-acceptor type between pairs of *ortho*-situated heteroatoms are a substantial factor controlling a conformation of sulfides **1-5**.

Obtained data were also compared with the results of charge density calculations using the AM1 method.

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