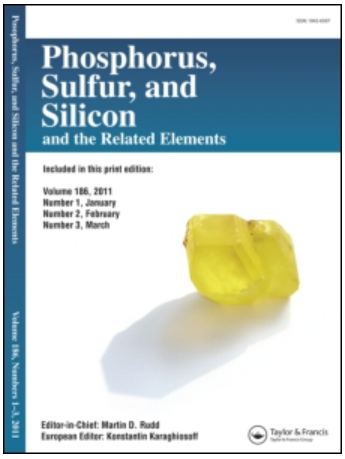

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STRUCTURE OF 4-SUBSTITUTED 3,4'-DIQUINOLINYL SULFIDES STUDIED BY ^{1}H AND ^{13}C NMR AND X-RAY ANALYSIS

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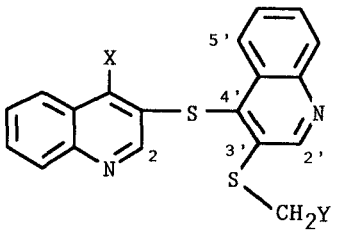
Abstract NMR and X-ray data show that 4-substituted 3,4'-diquinolinyl sulfides exist both in a solution and in solid state in a *skew* conformation at the main sulfide bridge and that non-typical position of H-2 proton may be attributed to its shielding by aromatic rings of a second quinoline fragment.

3,4'-diquinolinyl sulfides are of interest for us as intermediates in the functionalization of quinoline via thioquinathrene [1]. However, NMR spectral data of these diquinolinyl sulfides do not correspond to typical features of 3,4'-disubstituted quinolines. Non-typical spectroscopic properties of 4-substituted 3,4'-diquinolinyl 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-quinolinyl 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 A 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, derivatives **4**,**5** and **6** were synthesized. Small differences in ^{1}H 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)	Δδ	Δδ	Δδ
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 OCH_3 signal			
	3%	3%	2%	

The NOE enhancements observed between 4-OCH_3 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 apeared 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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