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## Conformations of Monosubstituted and Disubstituted 3,4'-,3,3'- and 4,4'-Diquinolinyl Sulfides Studied by NMR Spectroscopy

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# CONFORMATIONS OF MONOSUBSTITUTED AND DISUBSTITUTED 3,4'-, 3,3'- AND 4,4'-DIQUINOLINYL SULFIDES STUDIED BY NMR SPECTROSCOPY

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- 3',4-Disubstituted 3,4'-diquinolinyl sulfides 1 exibit nontypical and unexpected spectral properties manifested mainly in proton NMR spectroscopy being results of different conformations at a central sulfide bridge¹. To complete studies on steric structure-spectral properties relationship in diquinolinyl sulfides several 4,4'-disubstituted-3,3'-diquinolinyl sulfides 2 and 3-mono- and 3,3'-disubstituted 4,4'-diquinolinyl sulfides 3 were synthesized and investigated by proton and carbon NMR spectroscopy.

To verify our conclusion that the spectral properties of 3',4-disubstituted 3,4'-diquinolinyl sulfides 1 are the final results of strong attractive interaction of both pairs of heteroatoms (as above), we started our study with proton and carbon NMR spectra of selected 4,4'-disubstituted 3,3'-diquinolinyl sulfides 2a-c. In the case of unsymetrical derivatives 2b(X = OMe) and 2c (X = Cl) significant differences in the chemical shift values of the H-2 and H-2' protons up to 0.55 ppm were observed. The unusual upfield shifts of the  $\alpha$ -quinolinyl proton in sulfides 2b-c were found for the H-2' proton located in methylthioquinoline moiety what is contrary to the results obtained for sulfides  $1^2$ . The H-2' hydrogen is located in aromatic shielding cone of the pyridine ring of methoxy- and chloroquinoline moieties. The differences in the chemical shifts of the C-2 and C-2' carbons (up to 8.1 ppm) seem to be more affected by the influence of the 4-heteroatom than by the conformation of the whole molecule. Whereas the H-5 proton signal is shifted downfield (the through-space interactions with the 4-heteroatom) the C-5 carbon signal is found upfield (cf quinoline). The X-ray study confirmed a twist conformation for sulfide 2a and a skew conformation for sulfide 2b<sup>2,3</sup>.

Although there was one conformer of dimethylthiocompounds  $1a^4$  and  $2a^3$  (X = SMe) in solid state, we observed two conformers for sulfide 3f (X = H' = SMe)<sup>5</sup>. In proton and carbon spectra in CDCl<sub>3</sub> solution only one single structure was observed. For unsymmetrical sulfides 3b-c (X = Cl, SMe, X' = H resp.) we observed the significant differences of the H-2 and H-2' proton signals (up to 0.61 ppm) and shielding of the H-3' proton signal (0.74 ppm).

The correlation peaks measured between the H-3' and H-5 protons in NOESY spectra and negative NOE enhancements in 1D ROESY spectra indicate the spatial proximity between the H-5 and H-3' protons in compounds **3a-b**.

To find out if there are structural preferences for any conformation in vacuo, extensive calculations were done using HyperChem v.3.0 package<sup>6</sup>. For compounds **3a-b** short distances between the H-5 and H-3' atoms were obtained, 3.56 Å and 3.34 Å. On the other hand, for compounds **3c** and **3f** these distances were longer than 5 Å, but short distances between the H-5 and H-5' atoms were found (2.83 Å and 2.61 Å resp.).

The obtained calculation results indicate the conformer A to be energetically favoured in vacuo for compounds **3a-b** and the conformer B for compounds **3c** and **3f**. These results are in accordance with NMR results for CDCl<sub>3</sub> solution.

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