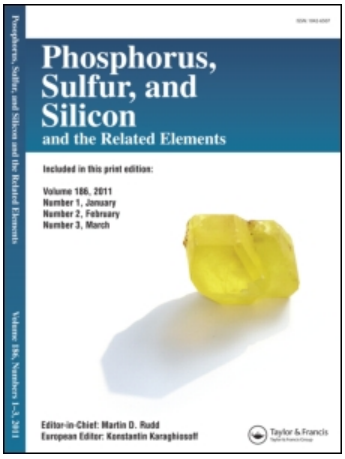

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3,3'-Diquinolinyl Sulfides. The Conformations and ^{1}H and ^{13}C NMR Spectroscopic Effects

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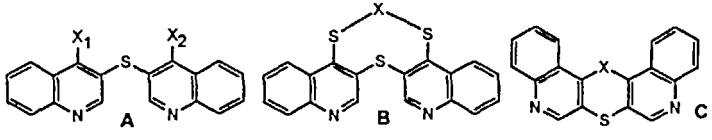
Non-typical NMR effects in 3,3'-diquinolinyl sulfides and the chemical shift – conformation dependences are discussed.

Keywords: diquinolinyl sulfides; conformations; ^{1}H and ^{13}C NMR

We have studied NMR effects (ortho, meta and peri) in disubstituted 3,3'-diquinolinyl sulfides **A**, **B** and **C**, where a rotation around the central C-S-C bridge is permitted, restricted or hindered.



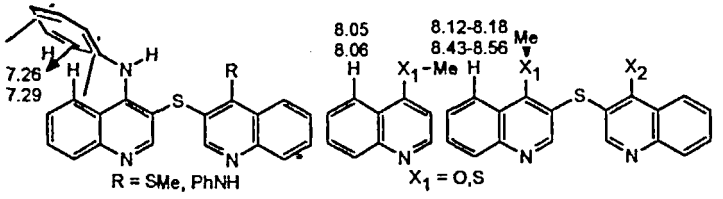
The peri effects calculated in relation to unsubstituted 3,3'-diquinolinyl sulfide ($\delta_{H\text{-}5}$ = 7.70 ppm) are as follows:

StBu > SEt > SAllyl > SMe > SCH_2Ph > $SeCH_2Ph$ > SPh > Cl >PhCHCN, OMe

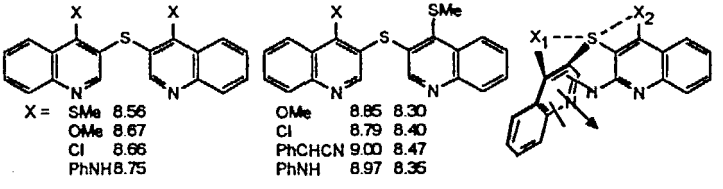
+0.98 0.89 0.86 0.73-0.86 0.76 0.73 0.72 0.52-0.55 0.47 0.42-0.48

The peri effect of the phenylamino group (-0.41-0.44 ppm) is unexpectedly contrary to the rest of the substituents and is a result of the ring current effect of the phenyl group. The peri effect of the methoxy and methylthio groups is different than in monosubstituted quinolines and is attributed to

a rotation around the C_4-X bond. The perpendicular orientations of these groups were confirmed by X-ray analyses[1-3].



The crucial element determining the H-2 and H-2' proton shifts is a rotation of the sulfide bridge. The X-ray analyses showed the H-2' atom to be under an influence of the ring current of the left quinoline ring[1-3].



Whereas the H-5 protons are deshielded, the carbons connected with them are shielded in opposite way up to 10 ppm.

As well as the C-4a, C-5 and methyl carbon signals in methylthio- and methoxydiquinolinyl sulfides depend on conformations of the methylthio and methoxy groups. These carbons are deshielded up to 6 ppm in comparison with the carbons found in 3-unsubstituted quinolines.

X-ray examinations showed the same conformations in the solid state as in $CDCl_3$ and revealed the donor-acceptor interactions of the heteroatoms.

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