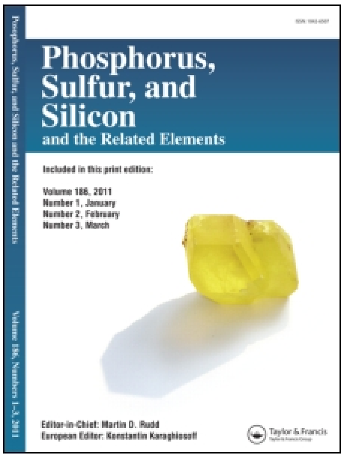


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

Mirosław Wyszomirski[a]; Andrzej Maślankiewicz[a]; Krystian Pluta[a]; Adolf Gogoll[b]; Tadeusz Głowiak[c]
[a] Department of Organic Chemistry, Silesian School of Medicine, Sosnowiec, Poland [b] Department of Organic Chemistry, University of Uppsala, Uppsala, Sweden [c] Institute of Chemistry, University of Wrocław, Wrocław, Poland

To cite this Article Wyszomirski, Mirosław , Maślankiewicz, Andrzej , Pluta, Krystian , Gogoll, Adolf and Głowiak, Tadeusz(1994) 'Conformations of Monosubstituted and Disubstituted 3,4'-,3,3'- and 4,4'-Diquinolinyl Sulfides Studied by NMR Spectroscopy', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 415 — 416

To link to this Article: DOI: 10.1080/10426509408034257

URL: http://dx.doi.org/10.1080/10426509408034257

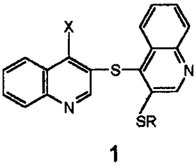
Phosphorus, Sulfur, and Silicon, 1994, Vol. 95-96, pp. 415-416
Reprints available directly from the publisher
Photocopying permitted by license only

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

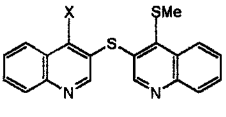
MIROSŁAW WYSZOMIRSKI[a], ANDRZEJ MAŚLANKIEWICZ[a], KRYSTIAN PLUTA[a], ADOLF GOGOLL[b] AND TADEUSZ GŁOWIAK[c]

[a] Department of Organic Chemistry, Silesian School of Medicine, Sosnowiec, Poland,
[b] Department of Organic Chemistry, University of Uppsala, Uppsala, Sweden ,
[c] Institute of Chemistry, University of Wrocław, Wrocław, Poland

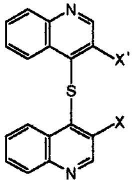
3',4-Disubstituted 3,4'-diquinolinyl sulfides **1** exibit nontypical and unexpected spectral properties manifested mainly in proton NMR spectroscopy being results of different conformations at a central sulfide bridge[1]. To complete studies on steric structure-spectral properties relationship in diquinolinyl 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 .



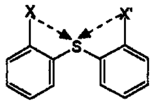
1



2



3

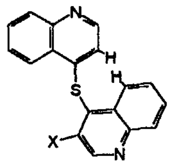


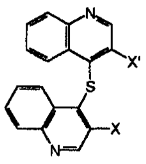
To verify our conclusion that the spectral properties of 3',4-disubstituted 3,4'-diquinolinyl sulfides **1** are the final results of strong attractive interaction of both pairs of heteroatoms (as above), we started our study with proton and carbon NMR spectra of selected 4,4'-disubstituted 3,3'-diquinolinyl 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 α-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**[2,3].

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)[5]. In proton and carbon spectra in $CDCl_3$ 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**.

conformer A





conformer B

To find out if there are structural preferences for any conformation in vacuo, extensive calculations were done using HyperChem v.3.0 package[6]. 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 $CDCl_3$ solution.

REFERENCES

1. A.Maślankiewicz, M.Wyszomirski, S.Boryczka, A.Gogoll and T.Głowiak, Phosphorus, Sulfur and Silicon, 74, 429,(1993).
2. K. Pluta and T. Głowiak, J. Chem. Cryst., (in press).
3. K. Pluta, A. Maślankiewicz and T. Głowiak, J. Cryst. Spectr. Res., 21, 153 (1991).
4. A. Maślankiewicz, K. Pluta, S. Boryczka and T. Głowiak, J. Cryst. Spectr. Res., 21, 729 (1991).
5. K. Pluta, A. Maślankiewicz and T. Głowiak, J. Cryst. Spectr. Res., 287, (1993).
6. HyperChem v. 3.0, Autodesk, Inc., Sausalito, CA94965, USA