The ^{1}H and ^{13}C NMR analysis of amide derivatives of 3,4-quinolinediyl bis-sulfides by means of the spectroscopy.

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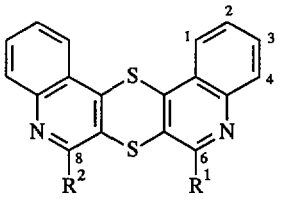
The reaction of protonated azine with DMF / hydroxylamine-O-sulfonic acid / Fe++ ion system led to α- and or γ-substituted azines with N,N-dimethylcarbamoyl and (or) N-methyl-N-formylaminomethyl substituents [1, 2, 3, 4].
In the previous articles [5, 6] we presented the products of the reaction of thioquinanthrene with radicals formed from DMF and X-ray and spectral analysis of 6-(N,N-dimethylcarbamoyl)thioquinanthrene. In the case of isothioquinanthrene **1** both type of products, i.e. 6-(N,N-dimethylcarboamoyl)isothioquinanthrene **2**, 6,8-bis-(N,N-dimethylcarboamoyl)-isothioquinathrene **3**, 6-(N-methyl-N-formylaminomethyl)isothioquinanthrene **4** and bis-6,8-(N-methyl-N-formyl-aminomethyl)isothioquinanthrene **5** were obtained (scheme 1).

Scheme 1

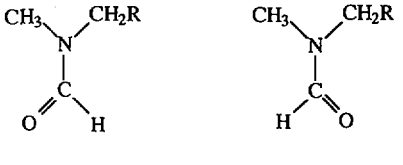


1 $R^1=R^2=H$
2 $R^1=CON(CH_3)_2$, $R^2=H$
3 $R^1=CH_2N(CH_3)CHO$, $R^2=H$
4 $R^1=R^2=CON(CH_3)_2$
5 $R^1=R^2=CH_2N(CH_3)CHO$

In order to complete the NMR assignment for the new compounds several NMR experiments have been made (COSY, HMQC, HMBC, NOESY).
The ^{1}H and ^{13}C NMR spectra of **2**, **3**, **4** were completely assigned with a combination of 1D and 2D NMR techniques. The key-part in this methodology were long-range proton carbon correlation and NOESY experiments with N-methyl-N-formylaminomethyl substituent and the correlation of the benzene protons (ABMX spin system) with the amide substituent and α-quinolinyl protons H-8.

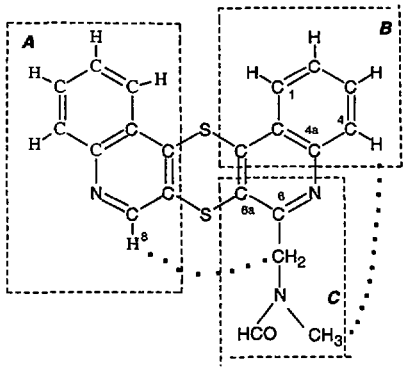
The N-methyl-N-formylaminomethyl derivatives exist in solution as a mixture of E and Z conformers (scheme 2a). The ^{1}H and ^{13}C nmr spectra of 6-(N-methyl-N-formylaminomethyl)isothioquinanthrene **3** show the lines of the same functional groups of two species with very close intensities and shapes. It has been also observed the transmission of the restricted rotation effect through the 1,4-dithiin ring and the condensed aromatic rings. Due to the folded shape of **3a** and **3b** rotamers, distances between some protons of alkyl substituents and benzene rings protons of **3** are within the limit required for the occurrence of NOESY. Thus, connectivity link between areas A, B and C (scheme 2b) for both rotamers could be deduced from NOESY experiments indicating the interaction of methylene group protons with H-8 proton and methyl group protons with H-4 proton.

Scheme2



3a (E) **3b (Z)**

R = 6-isothioquinanthrenyl



a./ b./

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