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NMR STUDIES ON 4-SUBSTITUTED-3-(3-ALKYLTHIO-4-QUINOLINYLTHTIO)-QUINOLINES

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NMR STUDIES ON 4-SUBSTITUTED-3-(3-ALKYLTHIO-4-QUINOLINYLTIO)-QUINOLINES

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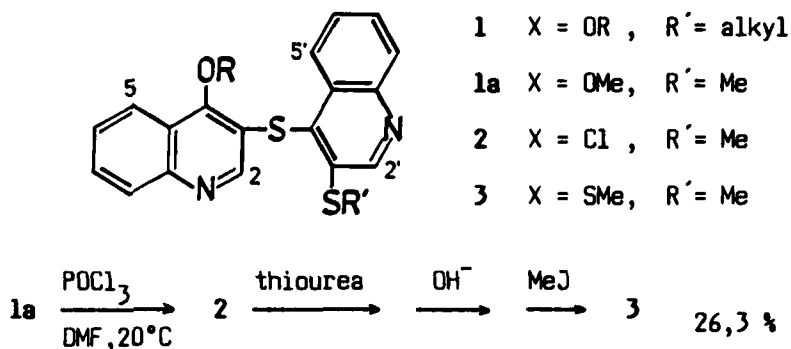
Abstract 4-Substituted-3-(3'-alkylthio-4-quinolinythio)-quinolines (X = OMe, Cl, SMe) were synthesized and studied by means of 2D NMR techniques. Downfield shifts of protons 5 and 5' due to the "peri" effect of 4-heterosubstituent (up to 0.87 ppm for X = SMe) were observed. Strong upfield shifts of proton 2 (up to -1.05 ppm for X = SMe) were found and interpreted in terms of proton 2 shielding caused by electron lone pairs of 3'-sulfide atom.

INTRODUCTION

In the course of our studies on reactions of thioquinanthrene with alkoxides, 4-alkoxy-3-(3-alkylthio-4-quinolinythio)quinolines **1** (X=OR) were prepared ¹. Unusual effects observed in the ¹H NMR spectra of compounds of type **1** were supported by X-ray examination of 4-methoxy derivative **1a** crystal ². It inspired us to more detailed evaluation of the steric and stereoelectronic interactions occurring in the molecule of **1a** by means of modern NMR techniques.

RESULTS AND DISCUSSION

In order to recognize the magnitude of the stereoelectronic effects existing in molecules of **1**, their 4-modified derivatives **2** (X=Cl, R'=Me) and **3** (X=SMe, R'=Me) were synthesized as presented below.



During the preparation of 4-methylthio derivative **3** from **2** and thiourea, a very low reactivity of 4-chlorine-substituent was noted.

We report here the total assignment of the proton and carbon NMR spectra of compounds **1a**, **2** and **3**, which illustrates the concerted application of two-dimensional techniques.

For compound **1a** we would like to present the NMR assignment strategy (Table I). NOE difference spectra and reversed heteronuclear shift correlation (one-bond and long-range) gave the proton chemical shifts. Additionally double-quantum filtered COSY was used. In order to assign the carbon spectra a selective INEPT pulse sequence was run for several protons. A long-range RHSC experiment accomplished the assignment of quarternary carbons. The results from the NOE experiment (specially the enhancement of H-5' proton when OCH₃ group was irradiated as well as the enhancement of H-2' proton when SCH₃ group was irradiated) suggest that compound **1a** has the same conformation both in a solid state and in solution.

The DQCOSY spectrum was quite useful in assignment of two overlapping ABCD system of both benzene ring protons. Taking into account strong cross-peaks from ortho-coupling and weak cross-peaks from meta-coupling. This assignment was accomplished by the LAOCOON-3 simulation.

TABLE I ¹H and ¹³C assignment of compound 1a.

δ	¹³ C			¹ H, δ		
	mult. ^a	RHSC ^b	DQCOSY ^c	RHSC, 1r. ^d	sel.INEPT	Assig.
160.5	s			8.12	8.12, 4.19	4
150.5	d	8.12				2
148.5	s			8.07, 7.64	8.12	8a
146.3	d	8.83				2'
146.0				8.40, 7.65	8.83, 8.40	8a'
					7.65	
139.3	s			8.83	8.83, 2.60	3'
133.8	s			8.83, 8.40	8.83, 8.40	4'
130.2	d	8.10	7.65, 7.55	7.55	8.40, 7.55	8'
129.8	s			8.10	8.10, 7.55	4a'
129.6	d	7.96	7.64 7.55	7.55	7.64, 7.55	8
129.4	d	7.64	7.96, 8.07 , 7.55	8.07	8.07	7
128.8	d	7.65	8.40 , 8.10, 7.55	8.40	8.40	7'
128.5	d	7.55	7.65, 8.10 , 8.40	8.10	8.10	6'
127.0	d	7.55	7.64 7.96	7.96	7.96	6
124.6	d	8.40	7.65 , 7.55, 8.07	7.65	7.65	5'
123.5	s			7.55, 7.96	8.07, 7.96	4a
					7.55	
121.4	d	8.07	7.64 , 7.55	7.64	7.64	5
119.6	s			8.12	8.12	3
61.9	q	(4.19)		n.d.	n.d.	CH ₃ O
15.8	q	(2.60)		n.d.	n.d.	CH ₃ S

^aMultiplicity from APT experiment. ^bReversed heteronuclear shift correlation, one-bond experiment. ^cIn brackets: weak cross-peak from meta-coupling. ^dLong-range experiment.

TABLE II The proton and carbon chemical shifts of compounds 2 and 3.

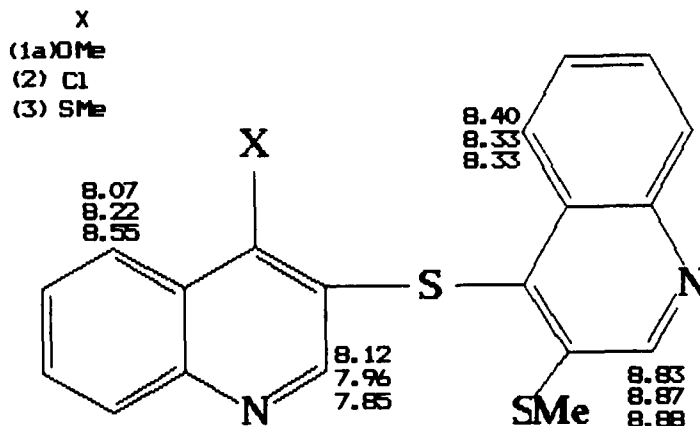
^1H , δ		^{13}C , δ		Assignment
2	3	2	3	
7.96	7.85	148.8	146.8	2
		146.7	146.3	8a
8.87	8.88	146.3	146.2	2'
		146.1	146.1	8a'
		140.0	140.0	3'
		139.1	139.8	4
		132.8	133.4	4'
8.13	8.14	130.3	130.3	8'
7.96	7.95	129.74	130.1	8
7.68	7.65	129.67	128.9	7
		129.6	129.8	4a'
7.68	7.68	129.0	129.0	7'
7.56	7.55	128.8	128.7	6'
7.64	7.65	128.3	128.1	6
		128.0	135.9	3
		126.4	129.7	4a
8.33	8.33	124.5	124.6	5'
8.22	8.55	123.5	125.0	5
2.63	2.62	15.7	15.6	CH S-3'
	2.65		18.6	CH ₃ S-4

Spectra were run on a Varian XL-300 at 300 MHz (^1H) and 75.4 MHz (^{13}C) in CDCl_3 solutions at room temperature.

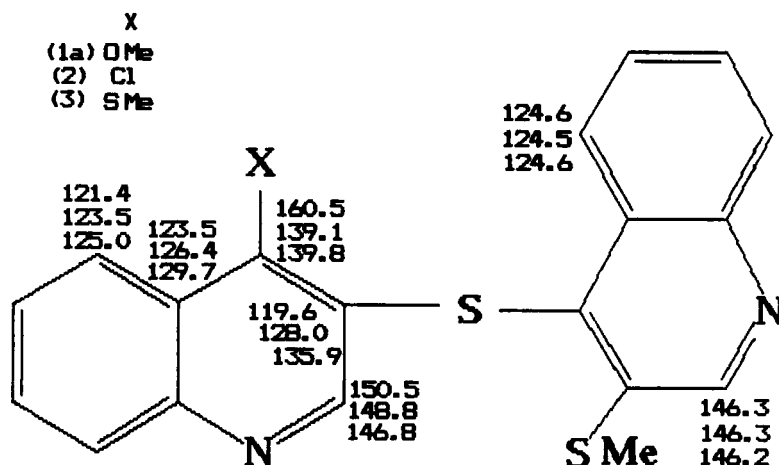
Proton and carbon chemical shifts of compounds 2 and 3 are collected in the Table II.

Obtained results of both proton and carbon chemical shifts allow for some generalization:

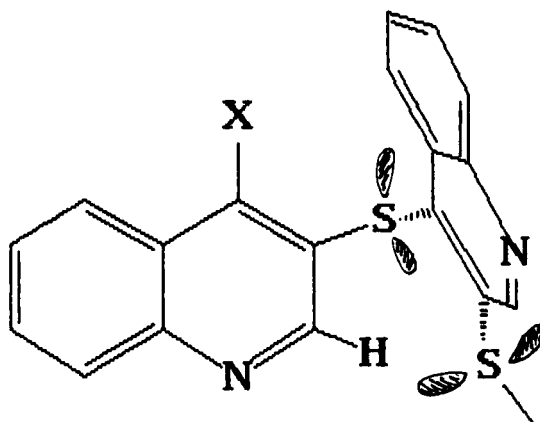
- signals of protons 5 and 5' are shifted downfield due to "peri" effect of 4-hetero- or 4'-thio-substituents. Because 4'-substituent is the same in all compounds, the chemical shifts of proton 5' are almost constant. This effect is a result of through space interaction caused by lone pairs of 4- or 4'-substituent. The largest "peri" effect, $\Delta\delta = 0.87$, comes from sulfide substituent.



- the carbon chemical shifts of 3-methylthio-bis sulfide parts of all three compounds are almost constant. Also the chemical shifts of proton 2' do not change and are similar to this in quinoline. But the strong upfield shift of proton 2 was observed in all compounds. On the other hand carbon chemical shifts of both 2 and 2' atoms are very similar. These results could be interpreted in terms of stereoelectronic interactions between three (X,S,S) heteroatoms. In X-ray structures of other 3,4-quinolinediyl bis-sulfides we found that there is a short contact between both sulfur atoms, shorter by about 0.7 Å than a sum of van der Waals radii ^{2,3,4}.



In the conclusion, we suggest that unusual upfield shift of proton 2 of compounds **1a**, **2** and **3** is a result of its shielding caused by electron lone pairs of 3'-sulfide atom.



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