MAGNETIC RESONANCE IN CHEMISTRY, VOL. 36, 73–75 (1998)

Note

Complete Assignment of the ^{1}H and ^{13}C NMR Spectra of Thioquinanthrene and Isothioquinanthrene†

Andrzej Maślankiewicz,[1]* Krystian Pluta,[1] Mirosław Wyszomirski,[1] Adolf Gogoll[2] and Maria J. Maślankiewicz[3]

[1] Department of Organic Chemistry, Silesian School of Medicine, Jagiellońska 4, 41-200 Sosnowiec, Poland
[2] Department of Organic Chemistry, University of Uppsala, S-751 21 Uppsala, Sweden
[3] Institute of Chemistry, Silesian University, Szkolna 9, 40-004 Katowice, Poland

Received 6 January 1997; revised 10 July 1997; accepted 9 August 1997

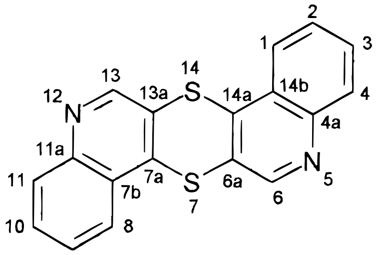
ABSTRACT: The proton and carbon chemical shifts and the coupling constants ^{n}J(H,H) and ^{n}J(C,H) of thioquinanthrene and isothioquinanthrene were completely assigned from COSY, HETCOR and INEPT studies. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; 1,4-dithiinodiquinolines; 3- and 4-quinolinyl sulfides

INTRODUCTION

Although thioquinanthrene (**1**) has been known for about 100 years, the determination of its structure caused problems from the beginning.[1] Additional objections arose when its isomer, isothioquinanthrene (**2**) was isolated from the reaction mixture.[2,3] Only in the 1980s was **1** assigned as 1,4-dithiino[2,3-*c*;5,6-*c*′]diquinoline and **2** as 1,4-dithiino[2,3-*c*;6,5-*c*′]diquinoline.[4]

The simple ^{1}H NMR spectra of 60 MHz of both dithiins **1** and **2** as quinoline derivatives showed two types of signals: a singlet signal of the α-quinolinyl proton (the H-6/H-13 in **1** and the H-6/H-8 in **2**), and a multiplet assigned to the remaining protons.[4] Both spectra proved dithiins **1** and **2** to be 3,4-disubstituted quinolines. Nevertheless, some doubts still remained.[5] The structure of dithiin **1** was definitely confirmed by x-ray determination (using thioquinanthrene dihydrochloride)[6] and that of isomer **2** using the 1,4-dithiin ring-opening reactions with nucleophiles.[7]



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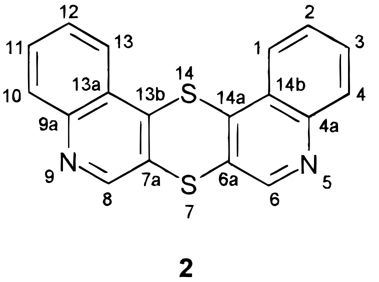

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The present study deals with the complete ^{1}H and ^{13}C NMR assignments and the distinction of the two dithiins on the basis of ^{1}H and ^{13}C NMR spectra.

RESULTS AND DISCUSSION

The simple ^{1}H NMR spectra at 500 MHz of dithiins **1** and **2** showed one singlet of H-6 and four well separated multiplets of four benzene ring protons [H-1, H-2, H-3 and H-4 (both ^{1}H and ^{13}C NMR spectra indicated the symmetry of both dithiins because the number of proton and carbon signals was half the number of these nuclei; to simplify the discussion, only the right part of both molecules, possessing the same numeration, was used in the discussion; Table 1 contains the complete assignment)]. The ^{13}C NMR spectra (125 MHz) of **1** and **2** showed five tertiary carbon signals (C-1, C-2, C-3, C-4 and C-6) and four quaternary carbon signals (C-4a, C-6a, C-14a and C-14b).

In order to assign unquestionably all of these signals we used 2D NMR techniques: COSY, HETCOR and INEPT. The HETCOR spectrum permitted the assignment of the tertiary carbon signals and the proton signals via the one-bond proton–carbon correlation. The INEPT spectrum made possible the assignment of the quaternary carbon signals via the three-bond proton–carbon correlation.

The COSY spectrum made it possible to segregate the benzene proton signals as two multiplets with two *ortho* couplings (H-2 and H-3) and two other multiplets with one *ortho* coupling (H-1 and H-4). The distinction between H-1 and H-4 was previously assigned at 80

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* *Correspondence to*: A. Maślankiewicz, Department of Organic Chemistry, Silesian School of Medicine, Jagiellonśka 4, 41-200 Sosnowiec, Poland.

† Part XLV in the series Azinyl Sulfides.

CCC 0749-1581/98/010073–03 $17.50

Table 1. Complete proton and carbon chemical shifts and summary of HETCOR single-bond and INEPT long-range correlations of dithiins **1** and **2**

Dithiin	Proton	Carbon single-bond coupling	Carbon two-bond coupling	Carbon three-bond coupling
1	H-1/H-8 (8.37)	C-1/C-8 (123.7)		C-3/C-10 (130.3) C-4a/C-11a (147.2) C-7a/C-14a (144.2)
	H-2/H-9 (7.69)	C-2/C-9 (128.0)		C-4/C-11 (130.0) C-7b/C-14b (126.8)
	H-3/H-10 (7.77)	C-3/C-10 (130.3)		C-1/C-8 (123.7) C-4a/C-11a (147.2)
	H-4/H-11 (8.13)	C-4/C-11 (130.0)		C-2/C-9 (128.0) C-7b/C-14b (126.8)
	H-6/H-13 (8.89)	C-6/C-13 (148.0)	C-6a/C-13a (126.7)	C-4a/C-11a (147.2) C-7a/C-14a (144.2)
2	H-1/H-13 (8.44)	C-1/C-13 (123.5)		C-3/C-11 (130.0) C-4a/C-9a (147.1) C-13b/C-14a (141.6)
	H-2/H-12 (7.66)	C-2/C-12 (127.9)		C-4/C-10 (130.1) C-13a/C-14b (126.9)
	H-3/H-11 (7.74)	C-3/C-11 (130.0)		C-1/C-13 (123.5) C-4a/C-9a (147.1)
	H-4/H-10 (8.10)	C-4/C-10 (130.1)		C-2/C-12 (127.9) C-13a/C-14b (126.9)
	H-6/H-8 (8.86)	C-6/C-8 (148.1)	C-6a/C-7a (128.9)	C-4a/C-9a (147.1) C-13b/C-14a (141.6)

MHz with the help of 2,4,9,11-tetradeuterothioquinanthrene (**1a**).[8] It could also be more conveniently performed by means of a three-bond proton–carbon ^3J(C,H) correlation, as the H-1 proton correlates with three carbons, C-3, C-4a and C-14a, but the H-4 proton correlates with only two carbons, C-2 and C-14b. The identification of the H-1 proton permits complete assignment of benzene ring protons. The long-range correlations H-1/C-14a and H-1, H-3 and H-6/bridged quaternary C-4a and also H-2 and H-4/C-14b confirm a connecting link between the pyridine and benzene parts of **1** and **2**, as outlined in Table 1.

The H-6 proton shows ^3J(C,H) correlations with quaternary carbon resonances corresponding to C-4a and C-14a (at 147.2 and 144.2 ppm, respectively) and ^2J(C,H) correlation corresponding to C-6a (126.7 ppm). Even though the two-bond C–H couplings ^2J(C,H) are usually small, the two-bond H-6/C-6a coupling in **1** and **2** (8.3 Hz) is comparable to ^3J(C,H). Similar effects have been noted with some polycyclic arenes,[9–11] six-membered aza-hetarenes[9–11] and thienopyridines.[10]

The assignment of proton and carbon atoms in dithiin **2** was made analogously to dithiin **1**.

One would expect to observe changes in the positions of protons and carbons in the NMR spectra of dithiins **1** and **2** being in the environment of the 3- and 4-sulfide substituents compared with quinoline. However, the H-6 proton signal in both dithiins was almost unaffected ($\delta_{\text{quinoline}} = 8.92$ ppm[12]), but the C-6 carbon signals were shifted upfield by $\Delta\delta = 2.6$–2.7 ppm in comparison with the signal in quinoline (150.7 ppm[13]) Downfield shifts of the signals of C-6a and C-14a (i.e. 3- and 4-quinolinyl) for **1** (126.7 and 144.2 ppm, respectively) and for **2** (128.9 and 141.6 ppm, respectively) were observed. The differences in magnitude of the deshielding effects are attributable, in our opinion to the differences in the boat conformations of the 1,4-dithiin ring.

The most influenced protons are 5-quinolinyl, i.e. H-1, being shifted downfield in thioquinanthrene (**1**) by $\Delta\delta = 0.59$ ppm and in isothioquinanthrene (**2**) by $\Delta\delta = 0.66$ ppm (in comparison with quinoline, 7.78 ppm[12]). In our opinion, the greater deshielding effect in **2** than in **1** is caused not only by the steric interaction between the S-14···H-1 and S-14···H-13 atoms (the *peri* effect) but also by additional steric interaction between the H-1···H-13 atoms. The same interactions have been observed for other heterocyclodiquinolines.[11] The different deshielding effects appear fundamental for the distinction of the two dithiins. It is worth nothing that other known pairs of isomeric pentacyclic 1,4-dithiinodiazines with a linear fused ring system, 1,4-dithiinodiquinolines (2,3-disubstituted quinolines)[14] and 1,4-dithiinodipteridines,[15] showed identical ^{1}H NMR spectra. Whereas the *peri*-influenced H-1 atoms were deshielded, the carbon atoms connected with them were shielded ($\Delta\delta = 4.7$ ppm for **1** and $\Delta\delta = 4.9$ ppm for **2**) in comparison with the appropriate signals in quinoline.

The chemical shifts of the C-1, C-6, C-6a, C-14a and C-14b carbons in both dithiins calculated from the incremental effects of two quinolinylthio substituents, taken separately from the model compounds (3,3′-, 3,4′- and 4,4′-diquinolinyl sulfides), do not confirm the additivity law and suggest steric constraints in the 1,4-dithiin ring.

Whereas all the coupling constants ^nJ(H,H) were

Table 2. Coupling constants ^nJ(H,H) and ^nJ(C,H) (Hz) for dithiins **1** and **2**

^3J(H,H)			^1J(C,H)			^3J(C,H)		
H,H	**1**	**2**	C,H	**1**	**2**	C,H	**1**	**2**
1,2	8.3	8.3	1,1	162.0	161.8	1,3	7.7	7.6
2,3	6.9	6.9	2,2	162.3	162.1	2,4	8.5	8.5
3,4	8.4	8.4	3,3	161.7	161.9	3,1	8.9	8.8
^4J(H,H)			4,4	161.1	163.6	4,2	7.1	7.2
H,H	**1**	**2**	6,6	184.4	184.6	4a,1	6.0	6.2
1,3	1.4	1.4	^2J(C,H)			4a,3	9.7	9.3
2,4	1.3	1.3	C,H	**1**	**2**	4a,6	12.1	12.4
^5J(H,H)			6a,6	8.3	8.3	14a,1	4.9	5.0
H,H	**1**	**2**				14a,6	6.3	6.2
1,4	0.7	0.7				14b,2	8.8	8.7
						14b,4	5.2	5.3

identical for both dithiins, ^1J(C,H) and ^3J(C,H) were slightly different (Table 2).

EXPERIMENTAL

Materials

Compounds **1**^{16} and **2**^{7} were prepared as described previously.

Spectra

Proton and carbon NMR spectra of **1** and **2** were measured at 27 °C on a Bruker AM 500 spectrometer operating at a proton frequency of 500.13 MHz and a carbon frequency of 125.76 MHz. Approximately 5 mg (for ^{1}H and ^{13}C NMR) or 15 mg (for two-dimensional experiments) of each sample were dissolved in 0.5 ml of deuterochloroform. The chemical shifts were referenced to tetramethylsilane. The proton spectra were obtained using an 8 μs (60°) pulse and a 4 s acquisition time to ensure accurate integrals; 96 transients with 65 536 data points each were used. The ^{13}C NMR spectra were obtained using a 3 μs (45°) pulse and a 1.1 s acquisition time to ensure accurate integrals; 272 transients with 65 536 data points each were used.

The homonuclear ^{1}H–^{1}H two-dimensional correlated diagrams were obtained using the COSY-90 pulse sequence (using a program in the Bruker software). The spectral widths were 440 Hz. The spectra were collected as 25 × 32 blocks of data, three times zero-filled in the F_1 dimension to obtain the final matrix of 256 × 128 words. Other parameters were as follows: number of increments in t_1, 32; number of scans, 8; phase cycling, 8; and relaxation delay, 1.5 s.

The one-bond heteronuclear correlation (HETCOR) spectra were obtained using the XHCORRD program in the Bruker software. The spectra were collected using an acquisition time of 0.27 s, a pulse angle of 90°, a digital resolution of 3.7 Hz, an average ^1J(C,H) of 150 Hz, 32 increments with 8 transients and data processed as a 2048 × 128 matrix. In the F_1 dimension, the sweep was 350 Hz and the data point resolution was 5.5 Hz per point.

The long-range heteronuclear CH correlation spectra were obtained using the standard pulse sequence (SPT INEPT in the Bruker software). The spectral widths were 30 kHz, the acquisition time was 1.1 s and the relaxation delay was 1.5 s; 320 transients were used per pulsed proton multiplet. Delays for methine protons were adjusted for 8 Hz, giving $D_2 = 11$ ms and $D_3 = 21$ ms, with processing as for the ^{13}C NMR spectrum. The value of 8 Hz (or 10 Hz for H-6/C-4a correlation) was used for the coupling.

Selective heterodecoupling (SFDEC in the Bruker software) was used for the ^nJ(C, H) determination.

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