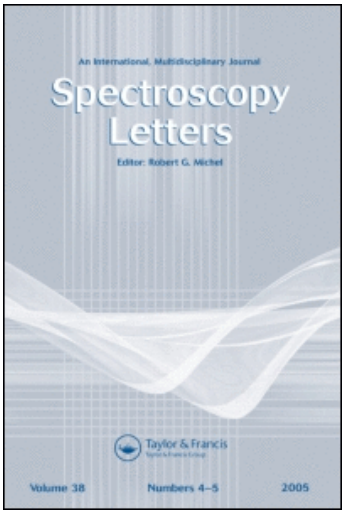

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Magnetic Anisotropic Effect as Demonstrated by High Resolution PMR in Some Benzoxazinones, Quinazolinones and Their Thiono Analogues

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Magnetic Anisotropic Effect As Demonstrated by High Resolution PMR in Some Benzoxazinones , Quinazolinones and Their Thiono Analogues

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Abstract

A number of 3,1-benzoxazin-4-ones and 4(3H)-quinazolinones and their thiono analogues were recorded with high resolution ^{1}H NMR 400 MHz spectrometer. The magnetic anisotropic effect of (C=O) and (C=S) groups was also discussed. The study of ^{1}H NMR chemical shift correlated to 2-D PMR allowed the complete assignment of such structure. The introduction of sulphur atom has influenced remarkably the chemical shift of H^5 of the benzeniod moiety as well as the chemical shift of the two ortho protons of the phenyl group.

Key words: 3,1-benzoxazin-4-one, 4(3H)-quinazolinones , 3,1-benzothiazin-4-thione , 4(3H)-quinazolinethiones

In the literature we have only found scattered and unsystematic information on the nuclear magnetic resonance of 3,1-benzoxazin-4-ones, 4(3H)-quinazolinones and their thiono analogues[1-7]. We wish to report the ^{1}H NMR data of elevem derivatives of 1,3-benzoxazin-4-one and 4(3H)-quinazolinone as well as their thiono analogues with various substitutent gruops on the 2- and 3-positions of the heterocyclic nucleus.

6-Bromo-2-phenyl-3,1-benzoxazin-4-one 1a was obtained from the reaction of 5-bromoanthranlic acid and benzoyl chloride in pyridine as a reaction medium[8]. The corresponding 6-bromo-

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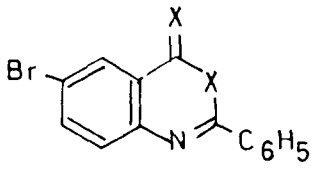
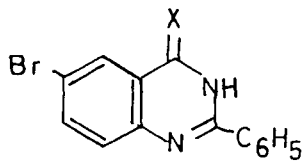
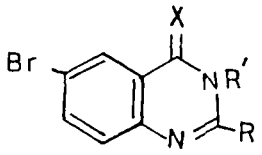
2-phenyl-4(3H)-quinazolinone 2a was prepared by the action of formamide on 1a[9]. The thiono analogues, 6-bromo-2-phenyl-3,1-benzothaizin-4-thione 1b and 6-bromo-2-phenyl-4(3H)-quinazolinone-4-thione 2b were obtained by the reaction of 1a or 2a with phosphorus pentasulphide solubilized in triethylamine in the presence of acetonitrile[10]. 3-Substituted 2-phenyl-4(3H)-quinazolinones 3a, 3c and 3e were obtained by the reaction of 1a with hydrazine hydrate, phehyl hydrazine and aniline, respectively. Whereas, the corresponding thiones 3b, 3d and 3f were formed by the reaction of 3a, 3c and 3e with triethylamine solubilised phosphorus pentasulphide[10]. 6-Bromo-2-phenyl-3(p-chlorophenylidene)-4(3H)-quinazolinone 3g was obtained from the reaction of 3a with p-chlorobenzaldehyde[11].





a ; X = O b ; X = S



	X	R	R'
3a	O	C_6H_5	NH_2
3b	S	C_6H_5	NH_2
3c	O	C_6H_5	NHC_6H_5
3d	S	C_6H_5	NHC_6H_5
3e	O	CH_3	C_6H_5
3f	S	CH_3	C_6H_5
3g	O	C_6H_5	$N{=}CH\text{-}C_6H_4\text{.Cl-p}$

High resolution proton magnetic resonance (400 Hz) data of these compounds are collected in Table 1. Table 1 represents a complete assignment of the total protons of the compound under investigation.

It is noteworthy to mention that, H^5 of the 4(3H)-quinazolinones or 4(3H)-quinazolinethiones appears at δ = 8.21-8.86 ppm. The chemical shift of H^5 is highly influenced by the magnetic anisotopic effect of the carbonyl or thiocarbonyl groups. Thus, the H^5 chemical shifts of the quinazolinethione derivatives 1b 2b, 3b, 3d and 3f resonate at relatively lower magnetic field thane those of the corresponding quinazolinone derivatives 1a, 2a, 3a, 3c, 3e and 3g due to the highly relative electronegativity of the suphur atom. On the other hand, H^7 and H^8 chemical shift appear at δ = 7.82-7.92 ppm and δ = 7.68-7.76 ppm, respectively and show a slight effect in introducing the sulphur atom.

Generally, the two ortho protons of the phenyl ring attached to the 2-position resonate at lower magnetic field (δ = 7.60-7.70 ppm) than the remaining three protons (δ = 7.41-7.50 ppm). The chemical shift of these two protons is also affected by the anisotropic magnetic effect of the sulphur atom particularly in the case of 2-phenyl-1,3-benzothiazin-4-thione 1b.

Fig. 1 represent one dimension ^1H NMR spectrum of 2-phenyl-3-(p-chlorophenylidene)-4(3H)-quinazolinone 3g. The spectrum comprises of a singlet located at δ = 9.06 ppm assigned as (=CH) proton. The 5-position proton of the quinazolinone nucleus resonates as a doublet at δ = 8.45 ppm. The remaining two protons attached to the 7- and 8-positions of the benzeniod ring in the quinazolinone moiety resonate at δ = 7.86 ppm and δ = 7.68 ppm, respectively. A typical A_2X_2 system of parasubstituted benzene is also observed by two doublets with approximately equal intensities resonate at δ = 7.60 ppm and δ = 7.39 ppm (J_{AX} = 9.4 Hz).The two ortho protons of the phenyl group attached to the 2-position of the quinazolinone nucleus resonate as multiplet at δ = 7.63 ppm, whilst the remaining three protons of the same group appear as multiplet at δ = 7.45 ppm.

Further additional proof for these findings is gathered by a COSY experiment of ^1H shift correlated to the two dimension PMR. Figure 2 shows the correlation of H^5-H^7 and H^7-H^8 of the quinazolinone nucleus. The correlation of the phenyl protons attached to the 2-position as well as the four protons of the parasubstituted benzene has also been observed (cf. Fig. 2).

Table 1: High Resolution (400 MHz) ^{1}H NMR data for compounds 1a,b , 2a,b and 3a-g

Compd	^{1}H NMR assignment (chemical Shifts in (ppm)*				
	H^5	H^7	H^8	2Ho	Remarks
1a	8,35	7.86	7.72	7.63	7.23 - 7.35 (m,3H,ArH)
1b	8.82	7.90	7.78	7.70	7,28 - 7.40 (m,3H,ArH)
2a	8.35	7.86	7.76	7.64	7,25 - 7.38 (m,3H,ArH)
2b	8.83	7.88	7.78	7.68	7.28 - 7.42 (m,3H,ArH)
3a	8.29	7.82	7.73	7.62	7.25 - 7.38 (m,3H,ArH) & 5.74(s,2H,NH_2)
3b	8.85	7.90	7.76	7.68	7.35 - 7.46 (m,3H,ArH) & 5.88(s,2H,NH_2)
3c	8.21	7.80	7.72	7.62	7.22 - 7.38 (m,8H,ArH) & 9.12(s, 1H,NH)
3d	8.86	7.92	7.74	7.66	7.30 - 7.52 (m,8H,ArH) & 9.32(s,1H,NH)
3e	8.33	7.83	7.71	7.65	2,19(s,3H,CH_3) & 7.35 - 7.45 (m,3H,ArH)
3f	8.83	7.92	7.74	7.72	2.20(s,3H,CH_3) & 7.38 - 7.58 (m,3H,ArH)
3g	8.45	7.86	7.68	7.63	7.38 - 7.62 (m,7H,ArH) & 9.06(s,1H,=CH)

* Chemical shifts are accurate within ± 0.01 ppm
Coupling constant are accurate within ± 0.1 Hz
$J_{7,8}$ = 8.3 Hz , $J_{5,7}$ = 2,6 Hz and $J_{5,8}$ = 1.1 Hz

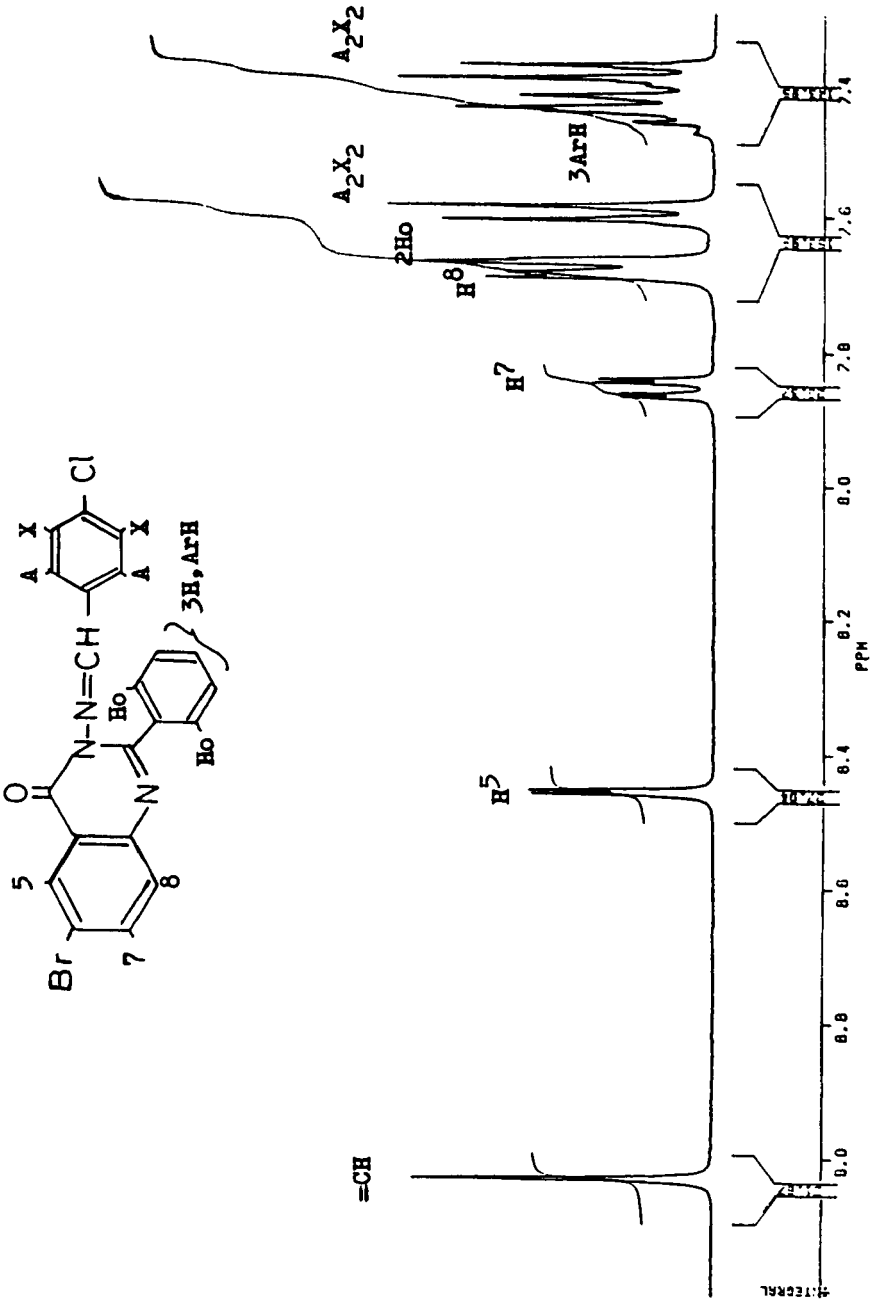


Fig.1: High resolution 400 MHz ^{1}H NMR spectrum of compound 3g

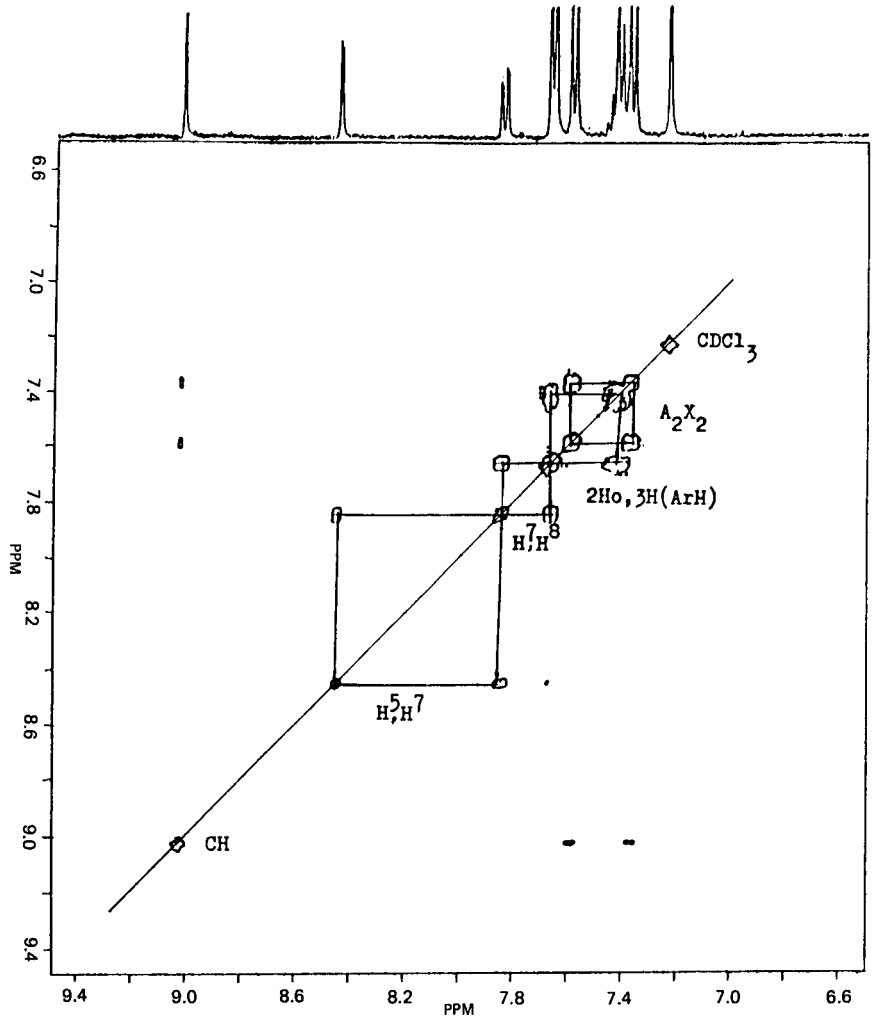


Fig. 2 : 400 MHz ^{1}H shift-correlated 2-D (WM-400) for 0.1 M (3g) in ($CDCl_3$) at 303° K. A COSY experiment with P-type selection. Parameters: x_1 = 512 , x_2 = 1K N_5 = 16 , N_1 = 1K , N_2 = 2K ; W_1 = ± 500 Hz , W_2 = 1KHz , recycle delay 3 sec. , t_1 = 1 msec. Acquisition ca 8 hours , transform ca 90 min. with sine bell in t_2 , squared sine-bell (pseudo-echo) in t_1 .

Experimental

6-Bromo-2-phenyl-3,1-benzoxazin-4-one 1a was prepared according to the method described by Bain and Smally[8].

6-Bromo-2-phenyl-4(3H)-quinazolinone 2a was prepared following the Patel and Patel method[9].

6-Bromo-2-phenyl-3,1-benzothaizine-4-thione 1b, 6-bromo-2-phenyl-4(3H)-quinazoline-4-thione and 6-bromo-3-substituted-4(3H)-quinazoline-4-thione 3b, 3d and 3f were prepared according to the method reported by Dash et al[10].

6-Bromo-2-phenyl-3-substituted-4(3H)-quinazolinones 3a, 3c and 3e and 6-bromo-2-phenyl-3-(p-chlorophenylidene)-4(3H)-quinazolinone 3g were prepared according to the method described by Teniou[11].

Thaited Benzoxazinone and Quinazolinones Derivatives with Triethylamine Solublized Phosphorus pentasulphide (P_4S_{10}): General Procedure

The appropriate benzoxazinone or quinazolinone (1 equiv.) in acetonitrile (generally 10 % solution) was first treated with P_4S_{10} (1 equiv.) and to this stirred suspension triethylamine (4 equiv.) was added in three portions while cooling the mixture in ice-water to moderate the exithermic reaction. The resulting solution was left stirred at room temperature for 24 hours and then poured onto an ice-cold water. The products was filtered and recrystallized from ethanol to give the desired benzothiazin-4-thione or quinazoline-4-thione derivatives.

The ^1H NMR spectra were recorded with a Brüker (400 MHz) Spectrometer Model (WM-400) in $CDCl_3$ (5-10 mg/0.4 ml) and tetramethylsilane as internal reference.

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