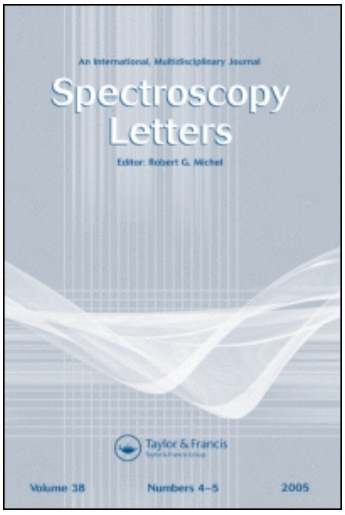

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Benzene Induced ^{1}H NMR Shifts of Chromeno-Compounds: An Aid to Differentiate Linear and Angular Chromenoflavones

A. Banerji[a]; D. L. Luthria[a]
[a] Chemical Ecology Section, Bio-Organic Division, Bhabha Atomic Research Centre, Bombay, India

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BENZENE INDUCED ^{1}H NMR SHIFTS OF CHROMENO-COMPOUNDS: AN AID TO DIFFERENTIATE LINEAR AND ANGULAR CHROMENOFLAVONES

Key Words: Benzene Induced Shifts, ^{1}H NMR, Chromeno-compounds, Differentiation of linear and angular chromenoflavones

A. Banerji and D. L. Luthria

Chemical Ecology Section, Bio-Organic Division,
Bhabha Atomic Research Centre, Trombay,
Bombay 400 085, India.

ABSTRACT: Benzene-induced shifts (BIS) in the ^{1}H NMR spectra of nine chromeno-compounds have been studied. It provides a simple non-destructive technique for distinguishing linear isomers of chromenoflavones from their angular counterparts. BIS also assists in the assignment of chromene proton signals in chromeno-compounds.

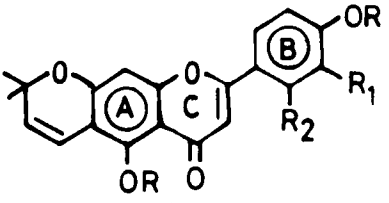
INTRODUCTION

Solvent induced ^1H NMR shift is one of the simple and non-destructive spectroscopic techniques which has been utilized extensively in solving structural, stereochemical and conformational problems [1]. Use of this technique for the structural analysis of simple flavonoids has been reported previously [2]. We have studied benzene induced shifts (BIS) $\{\Delta ppm = \delta(CDCl_3) - \delta(C_6D_6)\}$ to get an insight into the molecular architecture of structurally related chromenoflavones (1a-c, 2a-c). This technique not only provides a simple method for differentiation of angular and linear isomers, but is also useful in the assignment of signals due to chromene protons. The present paper reports the BIS studies of nine compounds containing chromene ring (FIG. 1).

RESULTS AND DISCUSSIONS

Recently, we have isolated two new chromenoflavones *viz.* atalantoflavone (2d) and racemoflavone (2e) from *Atalantia racemosa* [3]. Assignment of the position of chromene ring presents a major problem in the elucidation of structures of such compounds [4]. Color reactions such as Gibbs test have been used in determining the position of the fused chromene moiety [5,6], but this method has often proved to be inadequate in many instances [4,7,8], thereby upfield shift of chromene proton A are expected for linear isomers (1a-c), while in the case of angular

CHROMENOFLAVONES

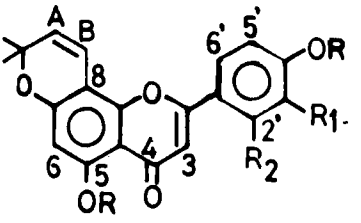


(1)

a) R = Me, R_1 = R_2 = H

b) R = Me, R_1 = OMe, R_2 = H

c) R = Me, R_1 = H, R_2 = OMe



(2)

a) R = Me, R_1 = R_2 = H

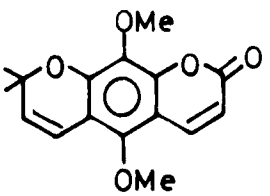
b) R = Me, R_1 = OMe, R_2 = H

c) R = Me, R_1 = H, R_2 = OMe

d) R = R_1 = R_2 = H

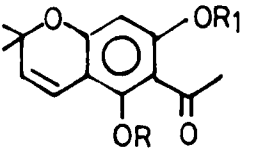
e) R = R_2 = H, R_1 = OMe

CHROMENOCOUMARIN



(3)

ACETYLCHROMENES



(4)

a) R = Me, R_1 = H

b) R = H, R_1 = Me

FIG. 1. Structure of Chromeno-compounds.

isomers (2a-c) both the chromene protons (A and B) are expected to show an upfield shift. Suresh *et al.* [11] have reported similar effects in dihydropyranoisoflavones. However, in the present study it was observed that irrespective of the position of the chromene ring in chromenoflavones, B proton always showed a downfield shift (≃-0.2) while an upfield shift (+ 0.02 to +0.14) was observed for A proton. Other compounds *viz.* racemosin (3), evodionol (4a) and isoevodionol (4b), having different disposition of carbonyl group relative to A and B protons of chromene ring also showed similar BIS. Thus, carbonyl functionality does not seem to influence shifts of chromene protons. These difference may be due to the diffused solute solvent interaction arising from the steric effect of gem dimethyl group. (Table 1).

A general downfield shift for H-3 and A ring aromatic proton (H-6 or H-8) was observed in chromenoflavones (1a-c, 2a-c). This is in contrast with the observation made by Vyas *et al.* [12] for polyoxygenated flavones, wherein an uniform downfield shift (-0.01 to -0.15) for the H-3 proton and an upfield shift (+0.32 to +0.50) for A ring aromatic proton (H-8) were observed. In case of compounds with 4' methoxyl group (1a, 2a) a downfield shift (-0.25) resulting in the erroneous assignment of structures. Differences in the chemical shifts of unsubstituted A ring proton (H-6 or H-8) can also be utilized for the

TABLE 1

Chemical Shifts of Chromene Protons A and B in $CDCl_3$ and C_6D_6.

COMPOUND	PROTON	$CDCl_3$	C_6D_6	Δ
ANGULAR ISOMERS				
2a	A	5.60	5.55	+0.05
	B	6.83	7.06	-0.23
2b	A	5.60	5.54	+0.06
	B	6.81	7.08	-0.27
2c	A	5.56	5.53	+0.03
	B	6.79	7.11	-0.32
4b	A	5.45	5.36	+0.09
	B	6.65	7.24	-0.59
LINEAR ISOMERS				
1a	A	5.69	5.55	+0.14
	B	6.74	7.00	-0.26
1b	A	5.69	5.56	+0.13
	B	6.74	7.01	-0.27
1c	A	5.67	5.55	+0.12
	B	6.74	7.01	-0.27
3	A	5.74	5.49	+0.25
	B	6.58	6.65	-0.07
4a	A	5.60	5.44	+0.16
	B	6.49	6.58	-0.09

differentiation of isomers. This too has limitation, due to occasional overlapping of signals of H-3, H-6 and H-8 protons [4]. This prompted us to explore the possibility of utilizing BIS for the characterization of chromenoflavones. Therefore, BIS of nine chromeno-compounds of known structures were studied.

In the present study on chromenoflavones the downfield shifts ($\lesssim$ -0.3) were observed for the signals of C-5 methoxyl protons of all the linear isomers (1a-c). The observed downfield shifts were due to their close proximity to the negative end of the carbonyl dipole. However, in the case of angular isomers (2a-c), the downfield shift due to the carbonyl group is offset by a marked upfield ($\lesssim$ +0.3) shift because of the presence of free ortho proton (H-6). Thus, the shifts of C-5 methoxyl protons are of diagnostic value for the differentiation of angular and linear isomers. Methoxyl protons of the B ring showed expected upfield shifts (FIG. 2). These BIS for the methoxyl protons are in agreement with the observations made by Wilson *et al.* [9]

BIS studies of the chromene protons (A and B) of compounds (1a-c, 2a-c, 3a,b and 4) revealed some interesting features. According to carbonyl plane rule [10] a downfield shift of chromene proton B and an for H-3 proton was observed. Addition of methoxyl group at positions 3' (compounds 2a, 2b) and 2' (compounds 3a, 3b) resulted in increase in the magnitude of downfield shifts (-0.35 and -0.50

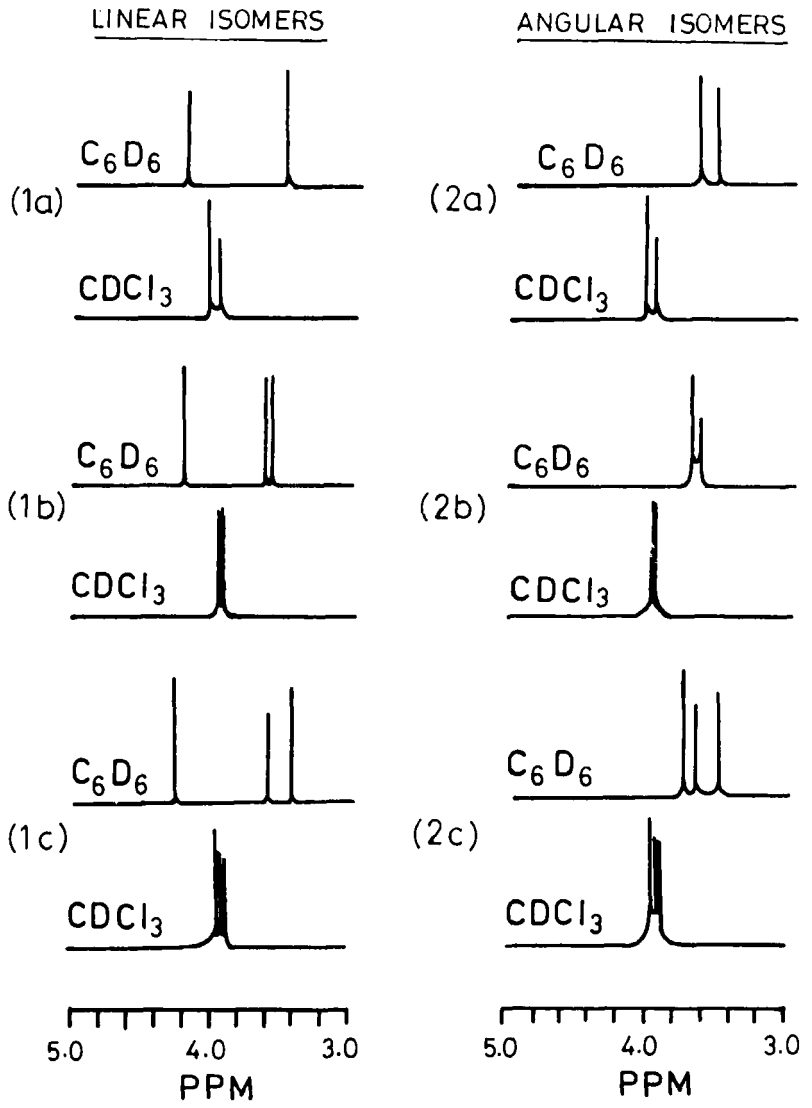


FIG. 2. Chemical Shifts of the Methoxyl Protons in $CDCl_3$ and C_6D_6 of Chromenoflavones.

Table 2

Chemical Shifts of Protons of A,B and C Rings of Chromenoflavones.

COMPOUND	H_3	H_6	H_8	$H_{2'}$	$H_{6'}$	$H_{3'}$	$H_{5'}$	C_5-OMe
1a	6.52 6.78 (-0.26)	-	6.72 6.88 (-0.16)	7.78 7.70 (+0.08)		6.99 6.89 (+0.10)		3.92 4.22 (-0.30)
1b	6.53 6.86 (-0.33)	-	6.69 6.91 (-0.22)	7.33 7.35 (-0.02)	7.46 7.47 (-0.01)	-	6.96 6.75 (+0.21)	3.93 4.23 (-0.30)
1c	6.85 7.35 (-0.50)	-	6.63 6.90 (-0.27)	-	7.76 7.89 (-0.13)	6.54 6.50 (+0.04)	6.60 6.58 (+0.02)	3.93 4.22 (-0.29)
2a	6.54 6.79 (-0.25)	6.31 6.45 (-0.14)	-	7.79 7.71 (+0.08)		6.99 6.90 (+0.09)		3.93 3.66 (+0.27)
2b	6.55 6.87 (-0.32)	6.32 6.46 (-0.14)	-	7.32 7.35 (-0.03)	7.47 7.48 (-0.01)	-	6.97 6.76 (+0.21)	3.94 3.63 +0.31)
2c	6.85 7.35 (-0.50)	6.29 6.45 (-0.16)	-	-	7.76 7.89 (-0.13)	6.55 6.52 (+0.03)	6.61 6.58 (+0.03)	3.93 3.66 (+0.27)

1) Normal values are obtained with $CDCl_3$ as solvent while underlined values correspond to C_6D_6.
2) values in the parenthesis indicate BIS $\{\Delta = \delta(CDCl_3) - \delta(C_6D_6)\}$.

respectively). Thus the magnitude of downfield shifts depends on the proximity of the methoxyl groups to H-3. The shifts for the other aromatic protons were of no diagnostic value (Table 2).

Thus,it can be concluded that BIS study is a simple complementary technique which provides useful information for structural elucidation of chromenoflavones.

EXPERIMENTAL

The physical and the spectral data of the compounds (1a,c; 2a,b; 3 and 4a,b) were in perfect agreement with those reported in the literature [3,6,13,14]. Compounds (1b and 2c) were synthesized and their structures were established by physical and spectral analyses (mp, microanalysis, ^{1}H NMR, UV, IR, MS) [15].

The ^{1}H NMR spectra were recorded on a Bruker AM-500 MHz FT-NMR spectrometer. The spectra of compounds (3, 4a and 4b) were recorded at room temperature. However, owing to the poor solubility of compounds (1a-c, 2a-c) in C_6D_6 their spectra were recorded at 65°C both in $CDCl_3$ and C_6D_6. The concentrations of the compounds (3, 4a and 4b) were 10mg/0.3ml, while for compounds (1a-c, 2a-c) were 2mg/0.3ml. Accuracies of chemical shifts are within $\pm$ 0.02.

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