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Total Assignment of NMR Spectral Lines of Schiff Base Derivatives with Pyridine Core

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Abstract: Identification was made on a series of synthesized pyridine derivatives with various length of alkanoyloxy chain (C_{n-1} H_{2n-1} COO-, where n = 12, 14, 16, 18). The complete assignments of ^{1}H and ^{13}C NMR spectral lines were achieved by careful analysis of their homo- and heteronuclear two-dimensional NMR spectra.

Key words: Schiff bases · Pyridine · 1D and 2D NMR · Spectral assignments

INTRODUCTION

Compounds consisting of $C_6H_5CH=NC_6H_5$ as the core system are commonly referred to as *N*-benzylideneaniline Schiff bases. This system has received a considerable attention from many researchers owing to its importance in exhibiting thermochromism and photochromism [1]. A series of studies on photochromic compounds have been undertaken with an attempt to explore the applications of these photochromic materials in various fields such as the control and measurement of radiation intensity, optical computers and display systems. In view of the importance and usefulness of these compounds, chemists are prompted to generate the derivatives by introducing different substituents into the existing skeleton of the molecule. The presence of a long alkyl chain at the *para* position of the aldehyde and aniline fragments of Schiff bases has been regarded as one of the important elements which favours the existence of liquid crystal phases [2-5].

Subsequent to the concerted effort in studying Schiff bases, an attempt to study Schiff base esters consisting of a pyridine moiety was carried out (Fig. 1). Single crystal x-ray diffraction is a well established tool for crystal structure elucidation of new compounds in solid state. However, not all crystals are suitable for x-ray diffraction studies. Furthermore, the conformation of organic molecules in solution state may differ from its crystal structure. For instance, the crystal structure of cholesteryl *p-n*-hexyloxybenzoate was different compared

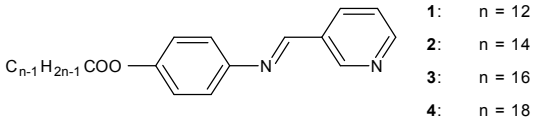

Fig. 1: Structure of compounds studied, pyridine 1-4

to the conformation deduced from the detailed NMR studies carried out in solution state [6-7]. Therefore, high resolution NMR techniques were adopted in this study to reveal the homonuclear (^{1}H-^{1}H) and heteronuclear (^{1}H-^{13}C) interactions and to investigate the probable conformation of the title compounds in $CDCl_3$.

MATERIALS AND METHODS

Techniques: All NMR experiments were recorded at 298 K on a Bruker Avance 400 MHz NMR Spectrometer operated at 400.132 and 100.622 MHz for ^{1}H and ^{13}C, respectively and equipped with an inverse-detection 5 mm probe (BBI probe, ^{1}H 90° pulse width = 8.3 μs, ^{13}C 90° pulse width = 20.0 μs). Deuterated chloroform was used as solvent and tetramethylsilane as internal standard. Standard Bruker pulse programs were used throughout the entire experiment [8]. For ^{1}H NMR experiments, the spectral width: 20 ppm; number of data points: 66 K; acquisition time: 4.0 s; relaxation delay: 1.0 s; number of transients: 18. In the ^{13}C NMR experiments, the spectral width: 250 ppm; number of data points: 65 K with the zero filling to 130 K; acquisition

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time: 1.3 s; relaxation delay: 2.0 s; number of transients: 1879. The decoupled experiments were performed using Waltz decoupling during acquisition.

The 2D COSY spectra were obtained by acquiring 16 transients each for 256 values of the evolution period. The spectral width used was 18 ppm with 2048 time domain points in F_2 and 256 points in F_1. The acquisition time and relaxation time were 0.3 s and 2.0 s, respectively. Before Fourier transformation, the data were multiplied with a sine-bell function and zero filling in F_1 dimension. The HMQC experiments were performed with relaxation delay 1.0 s, acquisition time 0.09 s and number of transients 20. In the HMQC experiments, the spectral range were 20 ppm in F_2 (^{1}H axis) and 200 ppm in F_1 (^{13}C axis). The number of data points were 1024 and 512, respectively in F_2 and F_1 channels.

The 2D HMBC spectra, which correlate the ^{1}H with ^{13}C resonances via long-range couplings, were obtained with the inverse technique and processed in the magnitude mode [9]. The evolution period for the long-range couplings was set at 3.1 ms, equivalent to ^nJ(C,H) = 8 Hz. The HMBC experiments were carried out with relaxation delay 1.0s, acquisition time 0.4s and number of transients 18. The spectral width used was 20 ppm in ^{1}H axis (F_2) and 200 ppm in ^{13}C axis (F_1). The number of data points were 4096 and 512, respectively in F_2 and F_1 channels. The data in both domains (F_1 and F_2) were zero-filled and multiplied by sine-bell function before Fourier Transformation.

RESULTS AND DISCUSSION

One- and Two-Dimensional NMR Studies: The complete ^{1}H and ^{13}C NMR assignments, ^{1}H-^{1}H COSY and ^{13}C-^{1}H HMQC and HMBC correlations of pyridine 1-4 are tabulated in Tables 1-4, respectively. The structure of pyridine 4 along with the atom-numbering scheme is shown in Fig. 2 as a representative illustration. The representative COSY and HMBC spectra of pyridine 4 are shown in Fig. 3 and 4a, respectively.

The ^{1}H NMR spectrum (Table 4) of pyridine 4 exhibited an azomethine proton as a singlet at chemical shift of 8.50 ppm (H13) and this value conforms with the earlier reported analogues [2-5]. The double of doublets at 8.71 ppm (J = 4.8 and 1.7 Hz), attributed to H7 of the pyridine fragment indicated a *meta*-substituted pyridine compound [10]. Whilst the doublet at 9.01 ppm (J = 1.9 Hz) was attributed to H9, the signal corresponding to H11 appeared at 8.29 ppm (dt, J = 8.0, 1.9 and 1.7 Hz). H12 was assigned to the doublet of doublet at 7.41 ppm (J = 8.0 and 4.8 Hz) based on its correlation with H11 as inferred from the COSY spectrum (Fig. 3). This further supports the *meta*-substituted pyridine system. The resonance at 7.26 ppm (dt, J = 8.9 and 2.2 Hz, H2 or H6) and 7.14 ppm (dt, J = 8.8 and 2.2 Hz, H3 or H5) originated from the *para*-substituted aromatic ring in pyridine 4.

The triplets at 0.90 ppm (J = 7.0 and 6.7 Hz) and 2.58 ppm (J = 7.6 and 7.4 Hz) were unambiguously assigned to H31 and H15 respectively. Based on

Table 1: ^{1}H and ^{13}C chemical shifts, characteristic coupling constants, ^{1}H-^{1}H and ^{13}C-^{1}H correlations of pyridine 1[a]

						^{13}C-^{1}H HMQC	^{13}C-^{1}H HMBC			
Atom no.	δ (^{1}H)[c] (ppm)	$J_{(H,H)}$ (Hz)	^{1}H-^{1}H COSY	δ (^{13}C) (ppm)	Atom H	$^1J_{(C,H)}$	$^2J_{(C,H)}$	$^3J_{(C,H)}$	$^4J_{(C,H)}$	$^b J_{(C,H)}$
1	-	-	-	149.27	-	-	-	-	-	-
2 or 6[c]	7.27 (dt)	8.8, 2.2	3 or 5, 12	122.19	2 or 6[c]	C2 or C6	C1, C3 or C5	C4	-	-
3 or 5[d]	7.14 (dt)	8.8, 2.0	2, 6	122.74	3 or 5[d]	C3 or C5	C2 or C6, C4	C1	-	-
4	-	-	-	149.76	-	-	-	-	-	-
7	8.72 (dd)	4.7, 1.5	9, 11, 12, 13	152.47	7	C7	C12	C9	C10	C13
9	9.02 (d)	1.9	7, 11, 13	151.35	9	C9	C10	C11, C13	C12	-
10	-	-	-	132.14	10	C10	-	-	-	-
11	8.30 (dt)	7.9, 1.9, 1.5	7, 9, 12, 13	135.32	11	C11	C10, C12	C7, C9, C13	-	-
12	7.43 (dd)	7.8, 4.8	2 or 6, 7, 11	124.22	12	C12	C7, C11	C10	-	C2 or C6
13	8.51 (s)	-	7, 9, 11	157.63	13	C13	C10	C1, C9, C11	C2 or C6	-
14	-	-	-	172.78	-	-	-	-	-	-
15	2.58 (t)	7.5	16	34.81	15[g]	C15	C14, C16	-	-	-
16	1.77 (qt)	7.3, 7.5, 7.6	15, 17-25	25.34	16[g]	C16	C15	C14	-	-
17-22	1.29-1.44 (m)	-	16, 25	P[f]	17-22	C17-C22	-	-	-	-
23				32.30	23	C23	-	-	-	-
24				23.07	24	C24	-	-	-	-
25	0.90 (t)	6.3, 7.0	17-25	14.51	25	C25	C24	C23		

[a] Solvent = $CDCl_3$, TMS used as internal standard

[b] Intramolecular interaction

[c] C2 and C6 are equivalent; H2 and H6 are equivalent

[d] C3 and C5 are equivalent; H3 and H5 are equivalent

[e] Multiplicity of the signals shown in parentheses: s = singlet, d= doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, qt= quintet, m = multiplet

[f] P = 26.02, 29.51, 29.65, 29.73, 29.85, 30.00 ppm

[g] Correlates with C17-C22

Table 2: ^{1}H and ^{13}C chemical shifts, characteristic coupling constants, ^{1}H-^{1}H and ^{13}C-^{1}H correlations of pyridine 2[a]

						^{13}C-^{1}H HMQC	^{13}C-^{1}H HMBC			
Atom no.	δ (^{1}H)[c] (ppm)	$J_{(H,H)}$ (Hz)	^{1}H-^{1}H COSY	δ (^{13}C) (ppm)	Atom H	$^{1}J_{(C,H)}$	$^{2}J_{(C,H)}$	$^{3}J_{(C,H)}$	$^{4}J_{(C,H)}$	$^{b}J_{(C,H)}$
1	-	-	-	149.26	-	-	-	-	-	-
2 or 6[c]	7.27 (dt)	8.7, 2.0	3 or 5, 12	122.19	2 or 6[c]	C2 or C6	C1, C3 or C5	C4	-	-
3 or 5[d]	7.14 (dt)	8.7, 1.9	2 or 6, 12	122.74	3 or 5[d]	C3 or C5	C2 or C6, C4	C1	-	-
4	-	-	-	149.76	-	-	-	-	-	-
7	8.71 (dd)	4.6, 1.4	9, 11, 12, 13	152.45	7	C7	C12	C9	C10	C13
9	9.01 (d)	1.9	7, 11, 13	151.35	9	C9	C10	C11, C13	-	-
10	-	-	-	132.14	-	-	-	-	-	-
11	8.29 (dt)	7.9, 1.9, 1.5	7, 9, 12, 13	135.30	11	C11	C10, C12	C7, C9, C13	-	-
12	7.42 (dd)	7.8, 4.7	2 or 6, 3 or 5, 7, 11	124.21	12	C12	C7, C11	C10	-	C2 or C6
13	8.50 (s)	-	9, 7, 11	157.62	13	C13	C10	C9, C11	C2 or C6	-
14	-	-	-	172.77	-	-	-	-	-	-
15	2.58 (t)	7.5	16	34.80	15[g]	C15	C14, C16	-	-	-
16	1.78 (qt)	7.3, 7.4, 7.5	15, 17-26	25.34	16[g]	C16	C15	C14	-	-
17-24	1.28-1.43 (m)	-	16, 27	P[f]	17-24	C17-C24	-	-	-	-
25				32.31	25	C25	-	-	-	-
26				23.08	26	C26	-	-	-	-
27	0.90 (t)	6.2, 7.0	17-26	14.52	27	C27	C26	C25	-	-

[a] Solvent = $CDCl_3$, TMS used as internal standard

[b] Intramolecular interaction

[c] C2 and C6 are equivalent; H2 and H6 are equivalent

[d] C3 and C5 are equivalent; H3 and H5 are equivalent

[e] Multiplicity of the signals shown in parentheses: s = singlet, d= doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, qt= quintet, m = multiplet

[f] P = 25.34, 29.51, 29.66, 29.75, 29.86, 30.00, 30.04, 30.07 ppm

[g] Correlates with C17-C24

Table 3: ^{1}H and ^{13}C chemical shifts, characteristic coupling constants, ^{1}H-^{1}H and ^{13}C-^{1}H correlations of pyridine 3[a]

						^{13}C-^{1}H HMQC	^{13}C-^{1}H HMBC			
Atom no.	δ (^{1}H)[c] (ppm	$J_{(H,H)}$ (Hz)	^{1}H-^{1}H COSY	δ (^{13}C) (ppm)	Atom H	$^{1}J_{(C,H)}$	$^{2}J_{(C,H)}$	$^{3}J_{(C,H)}$	$^{4}J_{(C,H)}$	$^{b}J_{(C,H)}$
1	-	-	-	149.27	-	-	-	-	-	-
2 or 6[c]	7.26 (dt)	8.7, 1.9	3 or 5, 12	122.19	2 or 6[c]	C2 or C6	C1, C3 or C5	C4	-	-
3 or 5[d]	7.14 (dt)	8.7, 1.8	2 or 6	122.74	3 or 5[d]	C3 or C5	C2 or C6, C4	C1	-	-
4	-	-	-	149.76	-	-	-	-	-	-
7	8.72 (dd)	4.7, 1.4	9, 12, 13	152.46	7	C7	C12	C11, C9	-	C13
9	9.02 (d)	1.8	7, 11, 13	151.36	9	C9	C10	C7, C11, C13	-	-
10	-	-	-	132.14	-	-	-	-	-	-
11	8.30 (dt)	7.9, 1.8, 1.4	9, 12, 13	135.30	11	C11	C10, C12	C7, C9, C13	-	-
12	7.41 (dd)	7.8, 4.8	2 or 6, 7, 11	124.20	12	C12	C7	C10	-	C2 or C6
13	8.51 (s)	-	7, 9, 11	157.61	13	C13	C10	C1, C9, C11	C2 or C6	-
14	-	-	-	172.76	-	-	-	-	-	-
15	2.58 (t)	7.5	16	34.80	15[g]	C15	C14, C16	-		
16	1.78 (qt)	7.3, 7.4, 7.5	15, 17-28	25.34	16[g]	C16	C15	C14	-	-
17-26	1.23-1.45 (m)	-	16, 29	P[f]	17-26	C17-C26	-	-	-	-
27				32.32	27	C27	-	-	-	-
28				23.08	28	C28	-	-	-	-
29	0.90 (t)	6.4, 7.0	17-28	14.51	29	C29	C28	C27	-	-

[a] Solvent = $CDCl_3$, TMS used as internal standard

[b] Intramolecular interaction

[c] C2 and C6 are equivalent; H2 and H6 are equivalent

[d] C3 and C5 are equivalent; H3 and H5 are equivalent

[e] Multiplicity of the signals shown in parentheses: s = singlet, d= doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, qt= quintet, m = multiplet

[f] P = 25.34, 29.52, 29.66, 29.76, 29.86, 30.00, 30.05, 30.09 ppm

[g] Correlates with C17-C26

Table 4: ^{1}H and ^{13}C chemical shifts, characteristic coupling constants, ^{1}H-^{1}H and ^{13}C-^{1}H correlations of pyridine 4[a]

						^{13}C-^{1}H HMQC	^{13}C-^{1}H HMBC			
Atom no.	ä (^{1}H)[c] (ppm)	$J_{(H,H)}$ (Hz)	^{1}H-^{1}H COSY	ä (^{13}C) (ppm)	Atom H	$^{1}J_{(C,H)}$	$^{2}J_{(C,H)}$	$^{3}J_{(C,H)}$	$^{4}J_{(C,H)}$	$^{b}J_{(C,H)}$
1	-	-	-	149.27	-	-	-	-	-	-
2 or 6[c]	7.26 (dt)	8.9, 2.2	3 or 5, 12	122.18	2 or 6[c]	C2 or C6	C1, C3 or C5	C4	-	-
3 or 5[d]	7.14 (dt)	8.8, 2.2	2 or 6, 12	122.72	3 or 5[d]	C3 or C5	C2 or C6, C4	C1	-	-
4	-	-	-	149.79	-	-	-	-	-	-
7	8.71 (dd)	4.8, 1.7	9, 13	152.47	7	C7	C12	C9, C11	-	C13
9	9.02 (d)	1.9	7, 13	151.38	9	C9	C10	C7, C11, C13	-	-
10	-	-	-	132.15	-	-	-	-	-	-
11	8.29 (dt)	8.0, 1.9, 1.7	12, 13	135.26	11	C11	-	C7, C9, C13	-	-
12	7.41 (dd)	8.0, 4.8	2 or 6, 3 or 5, 11	124.17	12	C12	C7	C10	-	C2 or C6
13	8.50 (s)	-	7, 9, 11	157.57	13	C13	C10	C1, C9, C11	C2 or C6	-
14	-	-	-	172.69	-	-	-	-	-	-
15	2.58 (t)	7.4, 7.6	16	34.79	15[g]	C15	C14, C16	-	-	-
16	1.77 (qt)	7.3, 7.4, 7.5, 7.6	15, 17-30	25.34	16[g]	C16	C15	C14	-	-
17-28	1.23-1.45 (m)	-	16, 31	P[f]	17-28	C17-C28	-	-	-	-
29				32.32	29	C29	-	-	-	-
30				23.08	30	C30	-	-	-	-
31	0.90 (t)	6.7, 7.0	17-30	14.51	31	C31	C30	C29	-	-

[a] Solvent = $CDCl_3$, TMS used as internal standard

[b] Intramolecular interaction

[c] C2 and C6 are equivalent; H2 and H6 are equivalent

[d] C3 and C5 are equivalent; H3 and H5 are equivalent

[e] Multiplicity of the signals shown in parentheses: s = singlet, d= doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, qt= quintet, m = multiplet

[f] P = 29.51, 29.66, 29.76, 29.86, 30.00, 30.05, 30.10 ppm

[g] Correlates with C17-C28

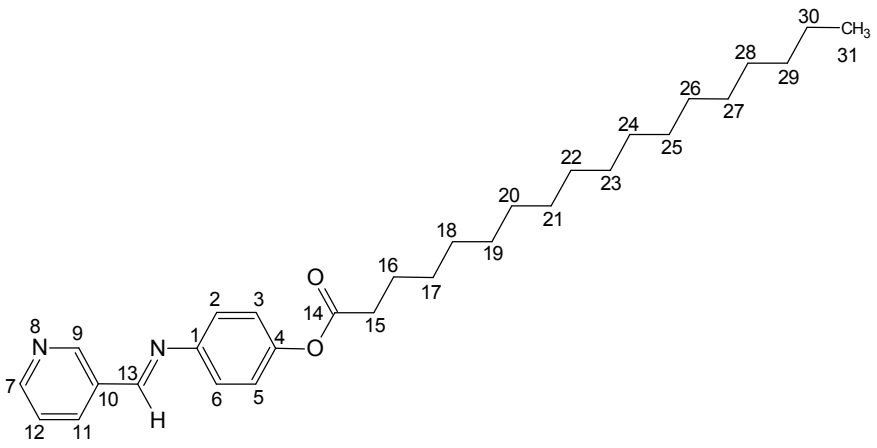

Fig. 2: Atom numbering of pyridine 4

the HMBC experiment (Fig. 4a, Table 4), the cross peaks between C14 (δ = 172.69 ppm) and the signal at 2.58 ppm confirmed the assignment of H15 due to the close proximity of H15 with C14 rather than with H31. The correlations between H15 and the signal at chemical shift of 1.77 ppm as observed in the COSY spectrum enabled the assignment of H16. Hence, the multiplet between 1.23-1.45 ppm was attributed to the protons (H17 -H28) of the alkyl chain in the fatty acid fragment.

The ^{13}C NMR spectrum (Table 4) was assigned with the aid of the HMQC and HMBC experiments. The long range correlations between H2 (or H6) with C1 (δ = 149.27 ppm), H3 (or H5) with C4 (δ = 149.79 ppm) as inferred from the HMBC spectrum firmly establish the positions of these quaternary carbons in pyridine 4. The signal owing to C10 (δ = 132.15 ppm) was assigned based on its correlation with its nearest neighbours, H9 and H13 as revealed in the HMBC spectrum.

Following the similar discussion above, the ^{1}H and ^{13}C NMR spectra of pyridine 1, 2 and 3 were assigned (Tables 1-3).

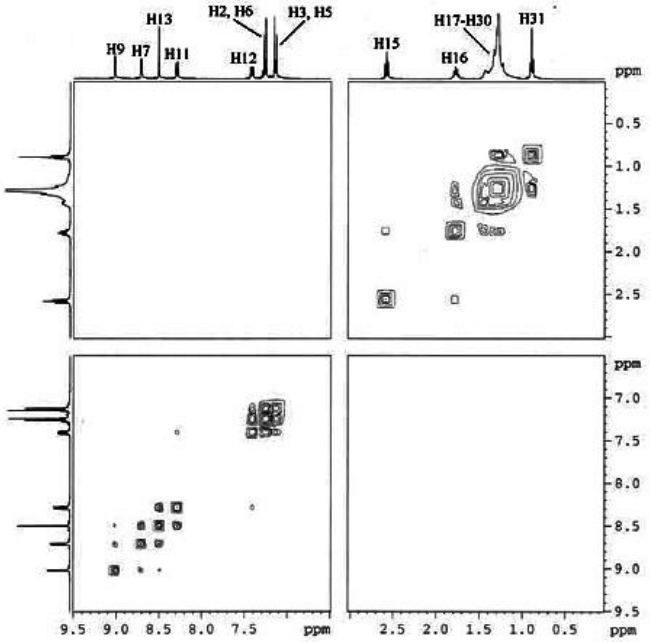

Fig. 3: ^{1}H-^{1}H COSY spectrum of pyridine 4.

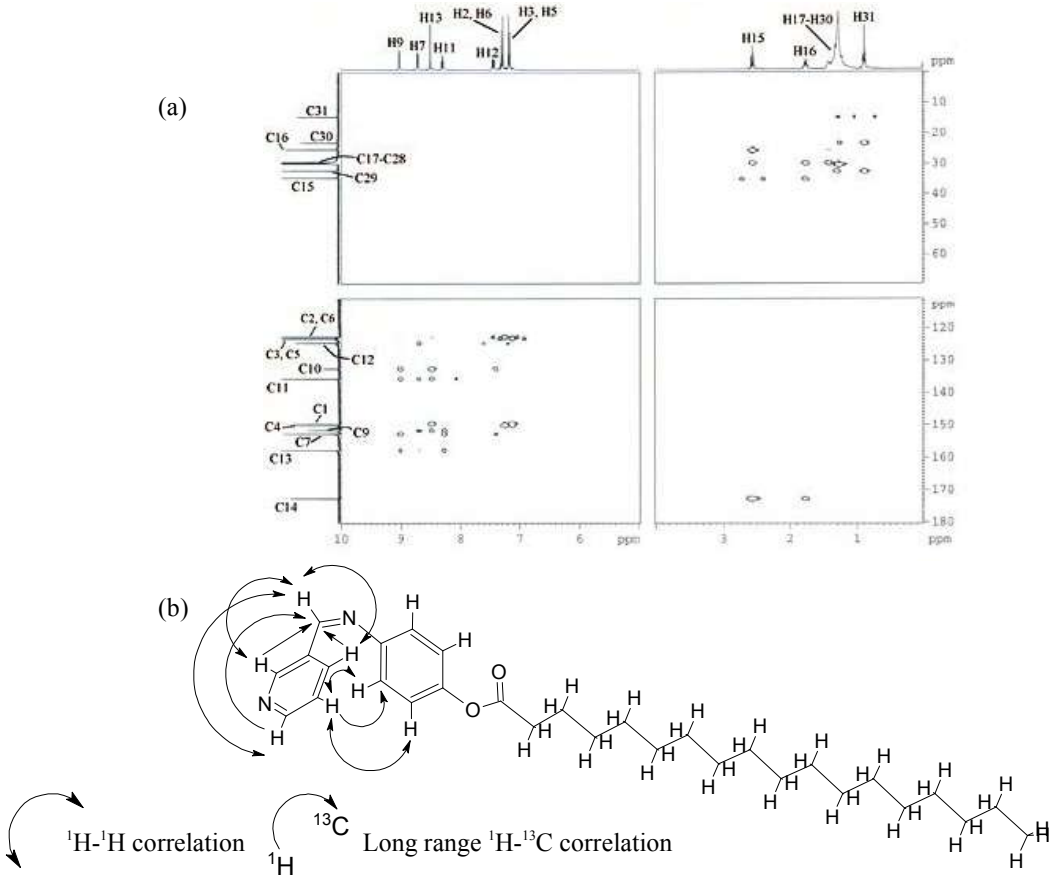

Fig. 4: (a) ^{13}C-^{1}H HMBC spectrum of pyridine 4 and (b) ^{13}C-^{1}H long range correlations as inferred from the HMBC spectrum of pyridine 4.

The investigation of the ^{1}H-^{1}H and long-range ^{13}C-^{1}H interactions in solution of pyridine 4 can be summarized as follows:

- From the COSY experiment, H13 was found to correlate with H7, H9 and H11 (Fig. 3, Table 4).
- From the HMBC experiment, C13 was found to correlate with H7, H9 and H11 (Fig. 4a).
- No correlations were observed between H12 and H13 in the COSY spectrum.
- No correlations were observed between C12 and H13 in the HMBC spectrum.
- H12 was found to correlate with H5 and H6 although these atoms are situated far from each other.
- H12 was found to correlate with C6 although these atoms are situated far from each other.

Based on (a)-(d), we propose that the azomethine proton (H13) is located on the same side with N8 (Fig. 4b) wherein H13 is closer to H7, H9 and H11 and further away from H12. The findings (e & f) further suggested that the position of the aniline and aldehyde fragments in pyridine 4 lie in close proximity which entails the interaction between H12 with H5, H6 and C6. Therefore, one of the possible conformations for pyridine 4 in $CDCl_3$ is depicted in Fig. 4b. Similar features were also inferred from the spectroscopic data of pyridine 2-4.

CONCLUSION

Complete ^{1}H and ^{13}C NMR spectral assignments of 4-[(pyridin-3-ylmethylene)amino]phenylalkanoates were determined by homo- and heteronuclear two-dimensional NMR spectra.

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