Tautomerism in 1-hydroxy-2-naphthaldehyde Schiff bases: Calculation of tautomeric isomers using carbon-13 NMR

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Abstract. Tautomeric equilibria in intramolecularly hydrogen bonded Schiff bases is studied on the basis of solution ¹³C NMR chemical shifts. NMR spectroscopic data and comparison with two anils model compound, namely, salicylideneaniline (1A) and naphthalylidenequinoline (2A) were used to represent the enol (A) and the keto (H) forms. The ¹³C NMR chemical shifts data of the novel series 4A (compounds, 4-12) were used together with the values ¹³C chemical shifts data of compounds 1A and 2A to calculate the % keto form. The calculated % keto form of 3A was compared to that calculated for series 4A compounds.

Keywords: Carbon-13 chemical shift, keto–enol equilibrium, UV-Vis spectroscopy, 1-hydroxy-2-naphthaldehyde Schiff bases, percentage of the keto form

1. Introduction

Tautomerism in Schiff bases derived from the condensation of salicylaldehyde and other aromatic aldehydes with anilines were the subject of a number of studies using different spectroscopic techniques.

It was found that some of these Schiff bases exist as enol form A [1–9], keto form H [10], or enol $\rightleftharpoons$ keto mixtures $A \rightleftharpoons H$ [11–18] (Scheme 1). UV-visible spectrum of Schiff bases which exists mainly as enol structure indicate the presence of a band at <400 nm, while compounds which exists either as keto or as mixture of enol–keto forms show a new band, especially in polar solvents at >400 nm. Different techniques were used to indicate the presence of the enol and keto equilibria $A \rightleftharpoons H$, among them is UV-visible, IR, ¹H, ¹³C and ¹⁵N-NMR spectroscopy.

It was suggested that Schiff bases derived from the condensation of salicylaldehyde and anilines 1A are exists mainly in the enol-form in all solvents [5–7].

The % keto form in Schiff bases derived from the condensation of 2-hydroxy-1-naphthaldehyde with anilines 3A increase in polar solvent and that substitution in the aniline ring effects significantly the enol–keto equilibrium [16].

Carbon-13 chemical shifts study of the 2-hydroxy Schiff bases series 3A [11,16] suggested that the percentage of the keto form in DMSO change from 38% when R = Ph to 16% when R = naphthyl. The UV-visible data of this series was suggested that the band, which appears above 400 nm is due to the keto form [16].

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Scheme 1.

In this work a novel 1-hydroxy Schiff bases series 4A were prepared by the condensation of 1-hydroxy-2-naphthaldehyde with anilines (compounds, 4-12).

The aim of this work, ¹³C chemical shift of series 3A was used to calculate the relative ratio between the enol and the keto form using the ¹³C chemical shift of the two model compounds 1A and 2A. The calculated % keto form for series 4A is compared with that of Schiff bases derived from 2-hydroxy-1-naphthaldehyde (series 3A).

2. Experimental

All solvents (Fluka) were of spectroscopic grade and used as such. Anil 1A was prepared previously [5] from the condensation of salicylaldehyde and aniline. Compound 2A was prepared from the condensation of 2-hydroxy-1-naphthaldehyde with 8-aminoquinoline [10]. Compound 3A was prepared from the condensation of 2-hydroxy-1-naphthaldehyde with aniline [11–17]. All Schiff bases were synthesized by a standard procedure [5–18] and were recrystallized (twice) from ethanol until show a sharp

melting points, also a satisfactory microanalysis was obtained: C $\pm$ 0.4%, H $\pm$ 0.2% and N $\pm$ 0.3%. The structure elucidation for all compounds of series 3A and 4A were confirmed by a satisfactory ^1H -NMR, ^{13}C -NMR and mass spectra. UV-visible spectra were recorded using Perkin Elmer EZ 210. The ^{13}C spectra of solutions of series 3A in CDCl_3 were measured on Bruker 400 MHz spectrometer operating at 100.573 MHz, and at 303 K. Typical spectral parameters were as follows: spectral width, 25000 Hz; acquisition time 1.99 s; 1000 transient; delay time 1.0 s; pulse width 10 μsec ; line broadening 1 Hz. The UV-visible were run for a solution of optimal concentration of 5×10^{-5} M using a quartz cell of 1.0 cm path length.

3. Results and discussion

Using the absorbency of the keto form A_{keto} and the enol form A_{enol} obtained from the UV-visible spectrum of each compound it was possible to calculate the approximate % of each form. Table 1 shows the approximate percentage of the keto forms in 3A and 4A based on the approximate calculations that the $A_{\text{enol}} + A_{\text{keto}} = 100\%$. Table 1 show that in series 4A the keto form 4H is higher than 3H for 3A series in all solvents. The keto form in 4H is the dominant structure in all solvents except cyclohexane. In series 3A and even in polar solvents the enol form is the dominant structure.

From previous studies it was found that compound 1A exists mainly in the enol form while compound 2A exists in the keto form 2H, therefore ^{13}C chemical shift of the carbon atom attached to the hydroxyl group in series 1A (163.7 ppm) and 2A (181.8 ppm) will be used as model compounds from which we can calculate the % keto form in series 4A (compounds 4-12). The appearance of one set of ^{13}C signals for each tautomer for the studied compounds support the fact of a fast proton transfer between the two tautomeric forms and allows us to use the equation below

$$\delta_{\text{ob}} = \delta_{\text{K}}P_{\text{K}} + \delta_{\text{E}}P_{\text{E}}. \quad (1)$$

The ratio of the keto forms for series 4A can be calculated from the ^{13}C chemical shifts of the model compounds 1A and 2A, where δ_{K} represent the ^{13}C chemical shift values for the model compound 2A and δ_{E} for the model compound 1A.

Equation (1) can be used to calculate the keto and the enol percentage in compounds of series 4A (Table 2) using the ^{13}C chemical shifts of the carbons under study when it is in the enol (series 4A), in the keto form (4H), together with the observed carbon chemical shift of compounds 4-12 which represent a mixture of both of them and taking into account that

$$P_{\text{K}} + P_{\text{E}} = 1. \quad (2)$$

The keto form can be calculated by using ^{13}C chemical shifts of C-H, C=O, and C-N_{Ar} (Table 3). In this work the most reasonable % keto values was obtained when using the ^{13}C chemical shift of the carbonyl group.

$$K_{\text{eq}} = \frac{\delta_{\text{ob}} - \delta_{\text{E}}}{\delta_{\text{K}} - \delta_{\text{ob}}}, \quad (3)$$

$$\Delta G = -RT \ln K_{\text{eq}}. \quad (4)$$

Table 1
Approximate keto and enol percentage in different solvents

Solvent	4A, %keto	3A, %keto
Cyclohexane	35.1	14.6
Ethanol	69.0	38.8
DMSO	70.0	51.1
CHCl ₃	70.9	50.6

Table 2
¹³C chemical shift for compounds 4-12 in CDCl₃

	H	CH ₃	OCH ₃	Cl	Br	I	CN	NO ₂	N(CH ₃) ₂
1	172.33	172.41	169.98	169.09	169.30	169.76	169.77	170.17	170.88
2	110.77	110.66	110.87	111.18	111.21	111.16	109.12	111.70	110.73
3	124.86	124.85	124.56	124.56	124.62	124.64	124.75	124.84	124.62
4	116.93	116.68	116.80	117.64	127.32	117.64	118.43	118.72	116.20
5	127.48	127.49	127.35	127.26	117.68	127.36	127.43	127.49	127.42
6	130.11	130.17	129.61	129.91	129.98	130.03	130.47	130.65	129.45
7	127.29	127.28	127.27	127.22	127.26	127.23	127.11	127.10	127.23
8	125.38	125.31	125.25	125.53	125.57	125.55	125.83	125.48	125.08
9	128.22	128.34	127.75	127.35	127.37	127.40	127.43	130.49	128.19
10	136.94	136.92	136.70	136.66	136.70	136.73	136.88	136.97	136.59
11	155.84	155.41	155.92	157.65	157.53	157.18	158.06	158.05	153.89
13	142.84	140.19	136.60	142.93	143.35	143.83	148.23	150.00	129.45
14	119.22	119.07	120.72	120.91	121.26	121.47	120.16	119.85	120.44
15	129.59	130.17	114.77	129.62	132.60	138.54	133.63	125.58	113.05
16	126.11	136.14	158.19	131.68	119.46	90.20	111.49	145.20	148.00
CH ₃	—	20.88	55.42	—	—	—	—	—	40.59

Table 3
Calculated % keto of compounds 4-12 in CDCl₃ using ¹³C chemical shift data

Compound	%keto $\delta_{C=O}$	%keto δ_{CH}	K_{eq} from C=O	ΔG (kJ/mol)
H	48.8(38.0)	44.2(50.0)	0.95	+0.118
CH ₃	49.2(39.0)	48.4(53.0)	0.97	+0.083
OCH ₃	36.1(31.0)	20.9(57.0)	0.36	-2.532
Cl	31.3	26.2	0.45	-1.957
Br	32.4(30.0)	27.4(38.0)	0.48	-1.818
I	34.9(31.0)	30.9(42.0)	0.54	-1.540
CN	35.0	22.2	0.54	-1.537
NO ₃	37.5	22.3	0.60	-1.270
N(CH ₃) ₂	41.0(24.0)	63.5(82.0)	0.41	-2.216

() % keto for 3A series.

Taking into account that $\delta_E = 163.7$ ppm and $\delta_K = 181.8$ ppm, the calculated values for the studied compounds are given in Table 3.

The ¹³C chemical shift of the carbon atom attached to the hydroxyl group in the model compound 3A is equal 181.8 ppm, very similar to the carbonyl carbon in typical aromatic keto compounds, suggesting

that this carbon exists as a keto carbon. This suggests a complete transfer of the proton from the oxygen atom to the nitrogen atom. Therefore as the ^{13}C chemical shift of the carbon atom at position 1 in this series approach the model value of 181.8 ppm the keto percentage increase. It was reported [16] that increasing conjugation decreases the percentage keto form. This is also observed in this series therefore the keto percentage decrease in going from compound 1 to compound 8 and 9. Close examination of the results indicates that conjugation is not the sole factor determining the percentage of the keto form.

The data in Table 3 suggested that for compounds 4 and 5 the keto and the enol forms are nearly at equilibrium in CDCl_3 solution, while the K_{eq} and ΔG° values for other compounds suggest that the equilibrium be shifted to the enol form.

The chemical shifts data reported in Table 2 for compounds of series 4A (4-12) are all indicative that appreciable amounts of both tautomers exist at equilibrium in this case, based on the assignment of ^{13}C NMR chemical shifts data of previous reports [10,11,16] and using additivity rules with reported substitution effects in naphthalene derivatives [19,20]. In the compounds presently studied, where R substituents affect the chemical shifts of the aromatic carbons C-13, C-14 and C-16, the carbon of choice to study changes in equilibrium compositions is the C-O, carbon C-1. A qualitative information in this regards can also be drawn from carbons C-2, C-4, and C-13. According to this assignment, the carbon C-1 for series 4A appears deshielded at about 174.4 ppm, while that of C-2 shielded at about 110.0 ppm. The chemical shift observed for C-1 throughout the 4A series is rather high for an aromatic quaternary carbon, but may be explained as the result of a significant contribution of the keto form 4H. In general, no appreciable changes in the equilibrium chemical shifts are observed upon changing the substituent R, with the exception of C-11, where chemical shifts of 155.41, 158.05 and 153.89 ppm observed for CH_3 , NO_2 and NMe_2 substituents, respectively. As expected, C-1, C-11 and C-13 chemical shifts are considerably effected by the nature of the substituents R (Table 2).

On the other hand, calculated % keto values in different solvents reported in Table 1 for Schiff bases of 1-hydroxy-2-naphthaldehyde (4A series) and 2-hydroxy-1-naphthaldehyde (3A series) indicates that the keto tautomer is dominating for series 4A relative to series 3A and this possibly can be explained in term of the peri-proton (H-8) which may cause stabilization of the keto group via pseudo H-bond [21].

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