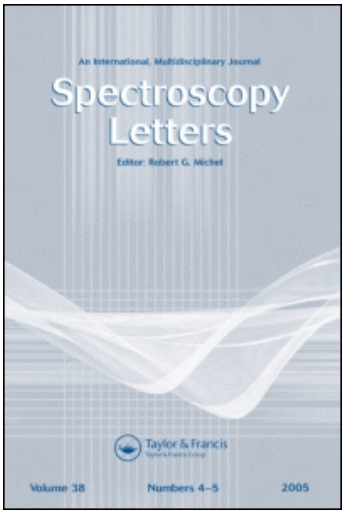

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MASS SPECTRAL STUDY OF TAUTOMERISM IN SOME 1-HYDROXY-2-NAPHTHALDEHYDE SCHIFF BASES

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ABSTRACT

Enol-Keto tautomerism in a new novel series of naphthylidineaniline Schiff bases were studied using their mass spectrum. Two model compounds, namely, salicylidineaniline (Model compound 1, series 1) and naphthylidinequinolinamine Schiff base (Model compound 2, series 4) were used to represent the enol and the keto forms. The mass spectra of the novel series (compounds 4–12) (series 3) are compared with compound 3 which is a representative compound of series 2. The mass spectral measurements reveal the fragmentation pattern in all the new series compounds. It was found that the fragmentation in the new series (series 3) resembles that of the series 2.

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Key Words: Mass spectrum; Naphthylidineaniline Schiff bases; Enol-keto tautomerism; Salicylidineaniline Schiff bases; Model compounds

INTRODUCTION

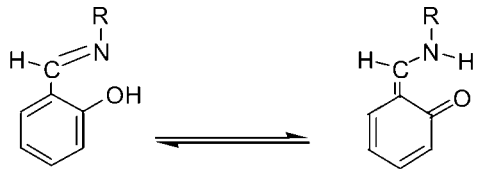
Schiff bases derived from the condensation of salicylaldehyde with aniline and naphthaldehyde with aniline exists as enol,[1–9] keto[10], or enol/keto mixtures[11–18] (Sch. 1). The UV-Visible spectrum of different Schiff bases which exists mainly as enol structure indicate the presence of a band at < 400 nm, while compounds of series 2, 3 and 4 exists either as keto or as mixture of enol-keto forms shaw a new band, especially in polar solvents at > 400 nm. Different techniques were used to show the presence of the enol and keto forms, among them is UV-Visible, IR and proton, carbon and nitrogen NMR spectroscopy. In a recent publication[18] the mass spectra of some naphthylidineaniline Schiff bases (series 2) were compared with two model compounds, to see if it is possible to use mass spectrum to determine the keto-enol equilibrium. The first compound, which is part of a series of Schiff bases (series 1), i.e., salicylidineaniline exists completely in the enol form in all solvents.[1–9] The second model compound 2, namely naphthylidinequinoline amine Schiff base (series 4) (Sch. 1) exists in the keto form in all solvents.[10] Series 2, which were prepared from the condensation of 2-hydroxy-1-naphthaldehyde with aniline and substituted aniline, exists as a mixture of enol and keto forms.[11–18]

The enol-keto equilibrium depends on the solvent used. Usually the keto ratio increase in polar solvents such as ethanol and DMSO.[13] A novel series (series 3) were prepared from the condensation of 1-hydroxy-2-naphthaldehyde with aniline and para-substituted aniline (Sch. 2). The UV-Visible spectrum of some compounds in this series indicates that the keto/enol ratio of series 3 is higher than that in series 2.[19]

The aim of this work is to study the mass spectral data and the fragmentation pattern of the new series and compare it with the mass spectral pattern of the model compounds 1, 2 and a representative compound 3 from series 2, to see if it is possible to find a correlation between the fragmentation trend and their chemical structure of compounds 4–12.

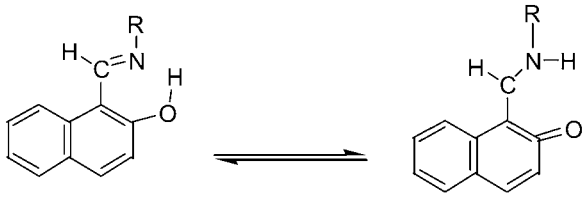
EXPERIMENTAL

Compound 1 (model compound 1) was prepared previously[5] from the condensation of 2-hydroxybenzaldehyde and aniline. Compound 2 (model



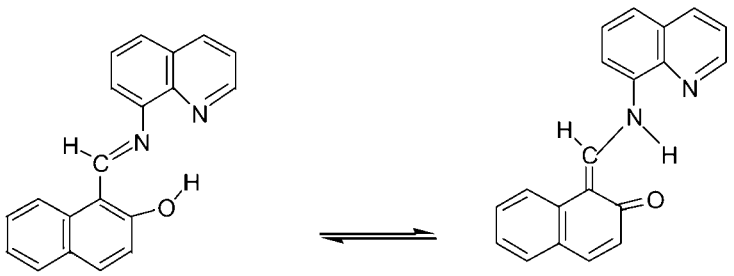
enol Keto

Series 1 (compound 1; R= phenyl)



enol Keto

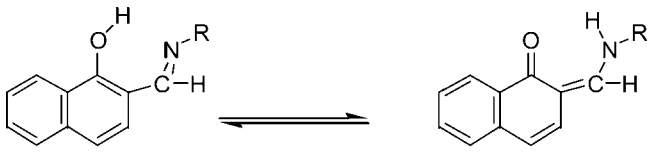
Series 2 (Compound 3; p =phenyl)



enol Keto

series 4 (compound 2)

Scheme 1.



Scheme 2. Compound 4, R = phenyl, compound 5, R = P-toloyl, compound 6, R = p-lodophenyl, compound 7, R = p-bromo phenyl, compound 8, R = p-anisoyl, compound 9, R = p-N, N-dimethylaniline, compound 10, R = p-nitrophenyl, compound 11, R = p-chloro phenyl compound 12, R = p-cyano phanyl.

compound 2) was prepared from the condensation of 2-hydroxy-1-naphthaldehyde with 8-aminoquinoline.[10] Compound 3 was prepared from the condensation of 2-hydroxynaphthaldehyde with aniline.[11–17] All Schiff bases were synthesized by a standard procedure.[5–18] All compounds were recrystallized (twice) from ethanol and show sharp melting points, also a satisfactory microanalysis was obtained: C 0.4, H 0.2, N 0.3%. The purity of these compounds were checked by ^{1}H-NMR and ^{13}C-NMR. The mass spectra EI (70 eV) were obtained using a TMS HX/HX 110 mass spectrometer.

RESULTS AND DISCUSSION

The UV-Visible of compound 1 show no absorption above 400 nm in polar and non-polar solvents indicating that this compound exists completely in the enol form, while the UV-Visible spectrum of compound 2 show only the keto absorption above 400 nm in polar and non polar solvents indicating that this compound exists mainly as a keto form in all solvents.

In general mass spectra of aromatic Schiff bases are scarce in the literature. Elias and Gillis[20] studied a series of substituted N-benzylidineaniline and found that the molecular ion peak was the base peak in all cases except for ortho substituted compound. Mass spectra for compounds 1–3 is studied before and shown in Table 1. The mass spectra for series 3 compounds are given in Table 2. The main fragments and relative intensity in the mass spectra of the present series Schiff bases are given in Table 3.

Table 1. Principal Peaks for Mass Spectra of the Model Compound 1, 2, and 3

Compd. No.	m/e with Relative Intensity in Parentheses
1	197(100), 196(80), 180(8), 167(8), 120(10), 104(8), 77(51), 65(8), 51(30), 39(8), 28(60)
2	248(15), 247(75), 246(100), 230(10), 170(8), 122(8), 115(10), 109(8), 77(20), 51(10)
3	297(60), 296(50), 144(50), 130(50), 129(100), 76(50)

Table 2. Principle Peaks for Mass Spectra of Series 3 Compounds

Compd. No.	m/e with Relative Intensity in Parentheses
4	248(19), 247(100), 246(27), 230(7), 170(4), 124(4), 115(5), 109(8), 77(77), 51(2)
5	262(21), 261(100), 260(24), 244(7), 217(1), 131(4), 115(5), 91(6), 89(1), 65(3)
6	374(19), 373(100), 372(10), 356(2), 245(5), 127(2), 123(5), 115(4), 109(5), 76(3)
7	327(98), 326(35), 325(100), 324(17), 310(10), 308(4), 246(6), 217(4), 189(2), 170(6), 140(3), 127(3), 123(10), 115(11), 109(9), 77(3), 76(4)
8	278(20), 277(100), 276(6), 262(23), 260(2), 169(2), 144(1), 139(5), 127(3), 115(3), 92(1), 77(2), 64(1)
9	291(23), 290(100), 289(8), 273(4), 246(1), 145(10), 144(3), 120(2), 104(1), 77(2)
10	293(32), 292(100), 291(5), 246(15), 245(22), 244(3), 189(3), 169(5), 146(4), 140(2), 127(5), 115(6), 114(3), 77(3), 76(3)
11	283(56), 282(44), 281(100), 280(36), 264(10), 246(6), 245(4), 189(3), 170(9), 169(6), 144(3), 140(6), 127(4), 115(16), 114(6), 111(8), 109(9), 77(4), 75(6)
12	273(59), 272(100), 271(63), 255(20), 242(8), 170(17), 169(9), 144(4), 140(5), 136(13), 127(8), 115(22), 114(7), 109(5), 102(11), 77(4), 75(4)

Mass Spectra for Hydroxy-Schiff Bases

Either the molecular ion $(M)^+$. Peak or $(M-1)^+$ peak was the base peak in all cases except compound 2. Table 1. The main spectral peaks of the mass spectra for these Schiff bases were divided according to the type of the fragmentation pathway[18] and Table 3.

M^+: the molecular ion.

Table 3. Main Fragments* and Relative Intensity in the Mass Spectra of the Present Series Schiff Bases

Comp. No.	M^+	$(M-1)^+$	Fragt 1	Fragt 2	Fragt 3	Fragt 4	Fragt 6	Fragt 7
4	247(100)	246(27)	230(7)	170(4)	127(1)	115(5)	77(7)	77(7)
5	261(100)	260(24)	244(7)	170(3)	127(2)	115(5)	91(6)	77(1)
6	373(100)	272(10)	356(2)	170(2)	127(2)	115(4)	203(1)	77(1)
7	325(100)	324(17)	308(4)	170(4)	127(3)	115(10)	155(3)	77(3)
8	277(100)	326(7)	260(2)	–	127(3)	115(3)	–	77(2)
9	290(100)	276(8)	273(4)	–	–	115(2)	120(2)	77(2)
10	292(100)	289(5)	275(7)	170(3)	127(4)	115(6)	–	77(3)
11	281(100)	291(36)	264(10)	170(9)	127(4)	115(16)	111(9)	77(4)
12	272(100)	296(64)	255(20)	170(17)	127(8)	115(22)	102(12)	77(4)

*The key for the fragments pattern are shown in paper 18.

$(M-1)^+$: formed by loss of the azomethine proton.
Fragment 1: formed by the loss of OH radical group from the molecular ion peak.
Fragment 2: formed by the α-cleavage[21] of amine ring carbon-azomethane nitrogen bond.
Fragment 3: the process of formation of this fragment are as follow: The keto form (B) of the molecular ion undergoes α-cleavage[22] to give fragment (C)[18] with further fragments to give fragment 3 by the loss of :C=O. Possibly it has rearranged itself to a tropylium ion-like structure in order to facilitate this step[22]. The deriving forces for the formation of this fragment is the loss of stable carbon monoxide and acetylene gaseous molecules.
Fragment 4: formed by the α-cleavage[21] of aldehyde ring carbon-azomethane carbon bond followed by the loss of CO molecule. Clearly a rearrangement of hydrogen away from OH group must take place. Perhaps via keto-enol tautomerism.[21] Again, the deriving force for this kind of fragmentation is the apparent loss of CO molecule.
Fragment 5: arise from fragment 3 by the loss of stable acetylene unite or from other cleavage typical of aromatic structure.
Fragment 6: arise from the same α-cleavage[20] that give rise to fragment 2 but with the formation of a phenyl cation at this time. Formation of a stable HCN molecule enhances these processes.
Fragment 7: Peak typical of aromatic-type fragmentation, which requires a great deal of energy, thus, observed with very low intensity in most cases.

From Tables 1–3 one can draw the following conclusions:

1) It is assumed before[18] that for compound 1 which is used as a model compound for series 1 which exist mainly in the enol form and it will fragments to give the molecular ion with 100% intensity and it will show the presence of six fragments with proportion higher than 10%.
2) For compound 2, which exists exclusively in the keto form, no molecular peak was observed and $(M-1)^+$ peak with 60% and no fragmentation was observed except fragment 7.
3) The present series exists as a mixture of keto and enol tautomers. The percentage of each form depends on the polarity of the solvent. Our study for the UV-Visible of compound 3 (part of series 3) show that the percentage of the keto forms is appreciable even in non-polar solvent.
4) The fragmentation pattern of series 3 very similar to that of series 2 but the percentage of the fragments 2–7 in series 3 is very small compared to that of series 2. Comparing the fragmentation intensity of model compound 1 and model compound 2 with that of series 2 and 3 one can make the following assumption.
   a) The model compound 1 and its series are characterized with high intensity of the M^+ (100). Compounds of the series 2 and 3 have the same intensity for M^+ which is an indication of the presence of an appreciable quantity of the enol tautomer.
   b) The base peak for compound 2 was not the molecular ion peak which again give evidence that the structure of this compound is far from being an enol structure. The formation of the base peak might take the pathway where the first step in the sequence of this mechanism provides by itself a clear evidence for the keto structure,[18] no other alternative pathway seems to be possible.
   c) In observing the relative values of the intensity for compound 2 (and series 2)[18] and that for compound 4–12 it is observed that the keto percentage in series 3 compound is higher than that in series 2, while the fragmentation intensity in series 3 is less than in series 2, therefore one can conclude that the fragmentation pattern for the present series can be used to make the conclusion that for the present series the mass spectral pattern indicates qualitatively the increase trend in the four series toward increasing the percentage of the keto form in going from series 1–4.

Series 1 < series 2 < series 3 < series 4.

Also one can notice that in series 3 the intensity value for fragments 2–7 increase in the following order for compounds 5, 6 and 10.

Cl > Br > I.

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