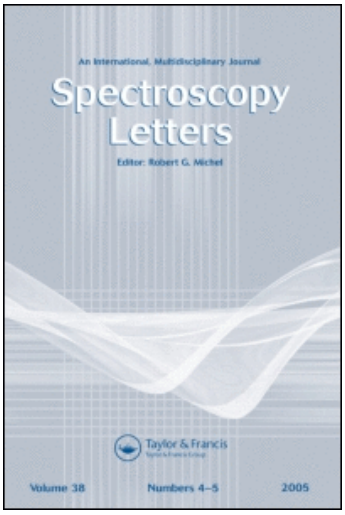

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Mass Spectral Study of Tauotomerism in Some Schiff Bases

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MASS SPECTRAL STUDY OF TAUOTOMERISM IN SOME SCHIFF BASES

Key Words
Keto-enol tautomerism, salicylidenaniline and naphthylidenaniline Schiff bases, FTIR spectroscopy, UV-Visible spectroscopy, NMR spectroscopy.

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Abstract .
Mass spectra of a series of substituted salicylaldehyde and 2-hydroxy-naphthaldehyde Schiff bases were used to investigate enol-keto tautomeric equiulibrium. Two model compounds, namely, salicylidinaniline and naphthylidinequinolineamine Schiff bases were used to represent the enol and keto forms, respectively. Mass spectral measurements reveal the fragmentation pattern in all compounds studied. Only naphthylidinequinoline amine Schiff base show a different fragmentation pattern compared to the other Schiff bases in the series which give an evidence for its suggested keto structure.

Introduction.

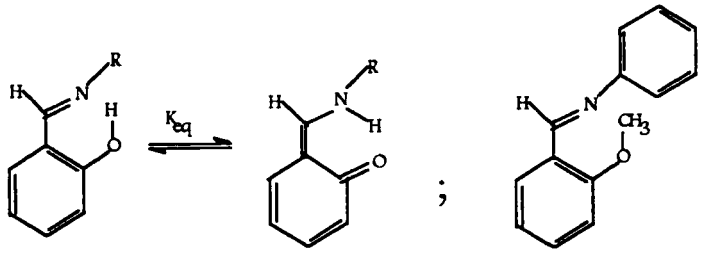
Compounds of the type Ar-CH=N-Ar, commonly, referred to as N-benzylidenaniline Schiff bases, have been the object of considerable interest. It has long been known that several of these compounds exhibit thermochromism and photochromism(1). This interest in photochromism and thermochromism of theses compounds, stimulated further spectroscopic studies for many years. It has been recognized that substituted salicylidenaniline (SA) Schiff bases when dissolved in polar hydrogen bonding solvents give rise to the appearance of a new electronic absorption band in the visible region. Different explanations for the source of this band has been proposed(2-7). It was suggested that this new band is due to the keto form in these compounds (Scheme 1b). Schiff bases derived from the condensation of 2-hydroxy-1-naphthaldehyde and aniline shows two bands in the visible region located above 400 nm. These two bands

were assigned to the keto form (Scheme 1 2b). Although, various spectroscopic methods were used to study the enol ↔keto equilibrium in Schiff bases and the factors affecting this equilibrium, to date no conclusive mass spectral data which support the existence of these equilibrium have been presented..In general, mass spectra of aromatic Schiff bases are scarce in the literature.Elias, et al.,(18) studied a series of substituted
N-benzylidenaniline and found that the molecular ion peak was the base peak in all cases except for ortho substituted compound. The aim of present work is to prepare compounds which exist either completely in the enol form (series 1) (Scheme 2), in enol-keto mixture (series 2) (Scheme 2) or in the keto form (series 3) (Scheme 2), and to use compound 1 from series 1 as a model compound for the enol form while compound 19 was used as a model compound for the keto form. The presence of two model compounds will enable us to use Mass spectroscopic technique to study equilibrium, substitution, and solvent effect on the keto-enol forms and to investigate the possibility of finding a pattern between Schiff base structure and their Mass spectroscopic properties.

Experimental.
Preparation. Three series of aromatic Schiff bases were prepared. The first series (compounds 1-9, Scheme 2-1) include Schiff bases derived from the condensation of 2-hydroxybenzaldehyde (salicylaldehyde) or from the condensation of 2-methoxybenzaldehyde with several amine, namely, aniline, para substituted aniline and 2-naphthyl amine. The second series (compounds 10-18, Scheme 2-2) include Schiff bases derived from the condensation of 2-hydroxynaphthaldehyde with the same amines mentioned above plus cyclohexyl amine. The third series (compound 19, 20) (Scheme 2-3) contain Schiff bases prepared both from the condensation of 2-hydroxynaphthaldehyde and from the condensation of 2-methoxy derivatives with 8-aminoquinoline. All Schiff bases were synthesized by a standered procedure (9-13). The physical properties and elemenal analysis are given elsewere (15-17). The purity of these compounds were supported by ^{1}H-NMR, ^{13}C-NMR.

Mass spectral measurements. Mass spectra for all compounds were measured for a solid samples using Finnigan triple quadruple mass spectrometer model TSQ-70 quadruple operated in EI mode as an ionization technique and an inlet temperature (ion source temperature) of 250 °C and using Finnigan MAT mass spectrometer model 112 operating in the same ionization technique and inlet temperature.

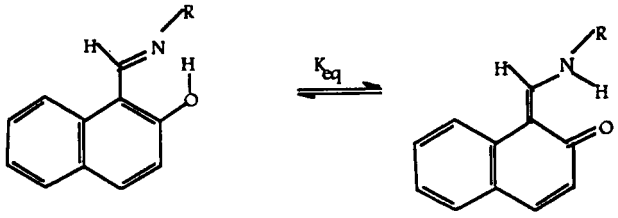
Results and Discussion .
The UV-Visible spectra of compounds 1-8 show no absorption above 400 nm in polar and non-polar solvents indicating that these compounds exists mainly in the enol form (14,17). Compound 19 show only the keto absorption above 400 nm in polar and nonpolar solvents indicating that this compound exist mainly in



enol (a) keto (b) (compound 8)

(compounds 1-7)

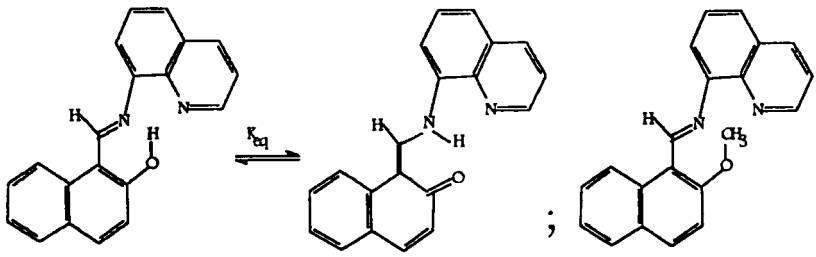
Series 1



enol (a) keto (b)

(compounds 10-18)

Series 2

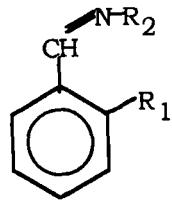


enol (a) keto (b) (compound 20)

(compound 19)

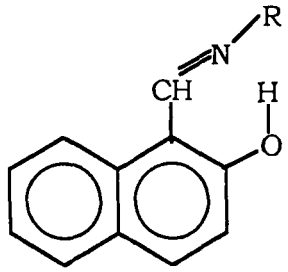
Series 3

Scheme 1



Comp. No.	R_1	R_2
1	OH	phenyl-
2	OH	p-toloyl-
3	OH	p-iodophenyl-
4	OH	p-bromophenyl-
5	OH	p-anisoyl-
6	OH	p-N,N-dimethylaniline
7	OH	p-nitrophenyl-
8	OCH_3	phenyl-
9	OCH_3	naphthyl-

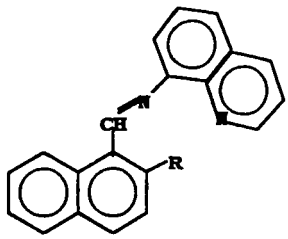
Scheme 2-1



Comp. No.	R
10	phenyl-
11	p-toloyl-
12	p-iodophenyl-
13	p-bromophenyl-
14	p-anisoyl-
15	p-N,N-dimethylaniline
16	p-nitrophenyl-
17	naphthyl-
18	cyclohexyl-

Scheme 2-2

Scheme 2



Compd. No.	R
19	OH
20	OCH_3

Scheme 2-3

Scheme 2. Continued

the keto form (15,16). Compound 10-18 show the bands above 400 nm in equilibrium with the enol form and that the intensity of the keto bands increased with increasing polarity. ^1H and ^{13}C NMR and IR data of these compounds supports the UV-Visible results and indicate the absence of a zwitter ion in compound 19 (15,16).

Mass spectra for the studied compounds were performed and the m/e ratio of the principal peaks are listed in Tables 1-3 . The following points can be presented under two general subtitles.

Mass spectra for ortho-hydroxy Schiff bases.

Either the molecular ion $(M)^{+\cdot}$ peak or $(M-1)^+$ peak was the base peak in all cases except compound 19 and compound 20. Table 1. We divided the main spectral peaks of the mass spectra for these Schiff bases according to the type of fragmentation pathways :(Scheme 3).

1. $M^{+\cdot}$: the molecular ion.
2. $(M-1)^+$: formed by loss of the azomethine proton.
3. **Fragment 1** : formed by loss of the OH radical group from the molecular ion peak.
4. **Fragment 2** : formed by the α-cleavage (19) of amine ring carbon-azomethine nitrogen bond.
5. **Fragment 3** : the processes of formation of this fragment are as follow : The keto form (B) of the molecular ion undergoes α-cleavage (20) to give fragment (C) which further fragments to give fragment 3 by the loss of the :C=O. Possibly it has rearranged itself to a tropylium ion-like structure in order to facilitate this step(20). The driving forces for the formation of this fragment is the loss of the elements of stable carbon monoxide and acetylene gaseous molecules.
6. **Fragment 4** : formed by the α-cleavage(19) of aldehyde ring carbon-azomethine carbon bond followed by the loss of CO molecule. Clearly a

Table 1. Principal peaks for mass spectra of the first series Schiff bases.

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.	211(100), 210(88), 196(13), 167(8), 120(13), 104(13), 91(45), 77(13), 65(24), 51(13).
3.	324(13), 323(100), 322(40), 203(8), 195(13), 120(8), 98(10), 83(10), 77(10), 76(23), 51(8).
4.	278(13), 277(95), 276(68), 275(100), 274(55), 196(13), 195(13), 167(13), 155(15), 120(18(, 98(15), 83(25), 76(23), 75(15), 51(15).
5.	227(100), 226(28), 212(68), 183(8), 154(8), 138(8), 114(8), 94(20), 93(10), 77(30), 65(8), 51(13).
6.	241(13), 240(100), 239(41), 223(13), 207(8), 136(8), 120(28), 119(18), 104(13), 91(8), 77(26), 51(8).
7.	243(18), 242(100), 241(33), 212(8), 195(45), 167(20), 151(8),121(8), 120(33), 94(8), 77(15), 76(33), 51(15).
8.	210(3), 195 (4), 179(5), 166(5), 119(30), 118(10), 104(8), 93(100), 91(30), 77(30), 51(20).
9.	261(22), 217(8), 144(10), 143(100), 127(28), 119(40), 91(35), 77(13), 51(8).

rearrangement of hydrogen away from the OH group must take place. Perhaps via keto-enol tautomerism(20). Again, the driving force for this kind of fragmentation is the apparent loss of CO molecule (stable gas).

7. **Fragment 5** : arise from fragment 3 by the loss of stable acetylene unit or from other cleavage typical of aromatic structure.

8. **Fragment 6** : arise from the same α-cleavage(19) that give rise to fragment 2 but with the formation of a phenyl cation at this time. Formation of the stable HCN molecule enhance this processes.

9. **Fragment 7** : peak typical of aromatic-type fragmentation which requir-es a great deal of energy, thus, observed with very low intensity in most cases.

In our attempts to utilize these spectral data to confirm the existence of the enol-keto toutomerism in question and to support the keto formation suggested, a quantitative comparison of the above fragments among the studied 2-hydroxy compounds which display this type of tautomerism is presented in Tables 4-6. The following conclusions can be readily made; First an exception from the

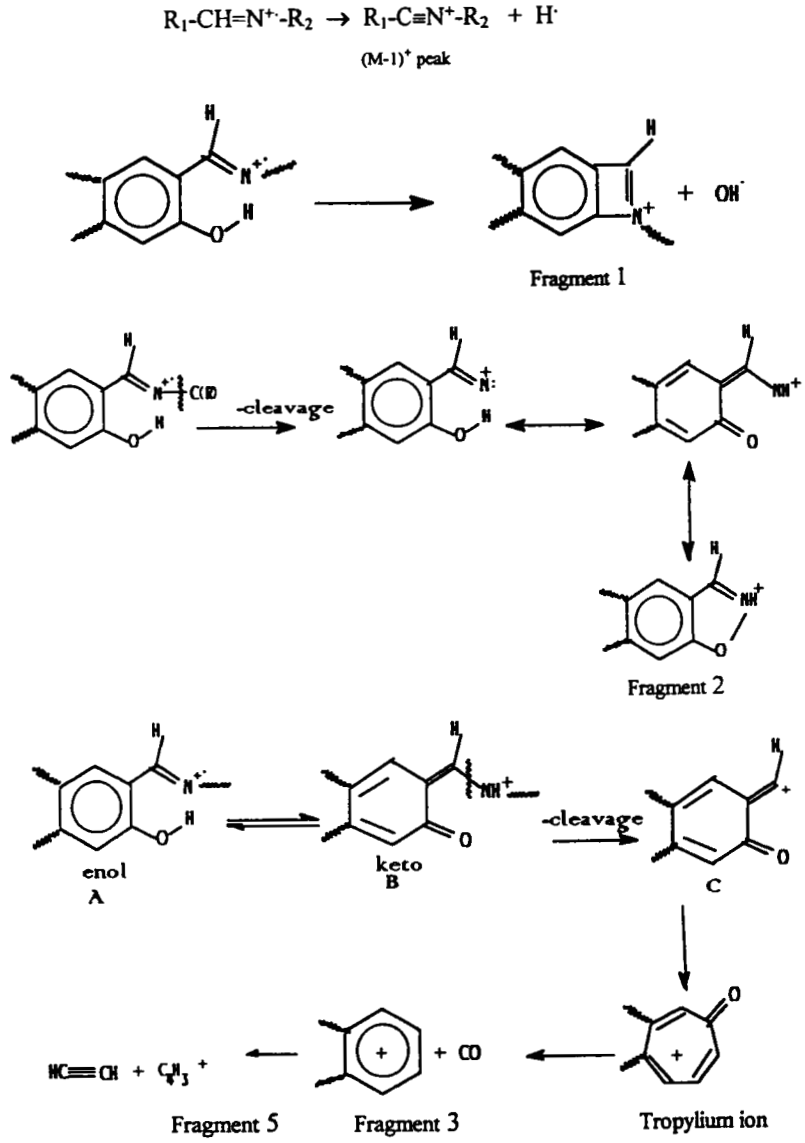
Table 2. Principal peaks for mass spectra of the second series Schiff bases.

Compd. No.	m/e with relative intensity in parentheses.
10.	248(15), 247(75), 246(100), 230(10), 170(8), 122(8), 115(10), 109(8), 77(20), 51(10).
11.	262(13), 261(75), 260(100), 244(15), 217(7), 130(21), 115(23), 91(18), 89(7), 65(13), 63(7).
12.	374(19), 373(100), 372(75), 356(3), 245(19), 127(8), 123(13), 115(8), 109(8), 76(19), 73(20).
13.	328(13), 327(80), 326(100), 325(90), 324(95), 310(8), 308(13), 244(23), 217(13), 189(13), 170(18), 140(8), 127(13), 123(50), 115(61), 104(35), 94(13), 76(18), 75(23), 63(13), 50(8).
14.	274(18), 277(100), 276(95), 262(13), 260(11), 204(8), 169(8), 144(8), 139(13), 127(11), 115(18), 92(8), 77(13), 63(8).
15.	291(21), 290(100), 289(70), 273(26), 246(8), 170(8), 145(13), 144(26), 120(13), 104(8), 77(13), 42(8).
16.	293(18), 292(100), 291(95), 275(18), 245(31), 244(10), 189(8), 169(18), 140(8), 127(13), 115(29), 114(10), 75(13), 77(8), 50(8).
17.	297(100),296(80),281(15),267(10),154(18),148(15),128 (16),127(30), 115(15),101(5), 77(15).
18.	254(15), 253(90),252(15), 236(15), 210(18), 196(15), 182(15), 171(20), 170(100), 157(21),128(18),127(20), 115(30), 97(80), 82(15), 55(20), 41(35).

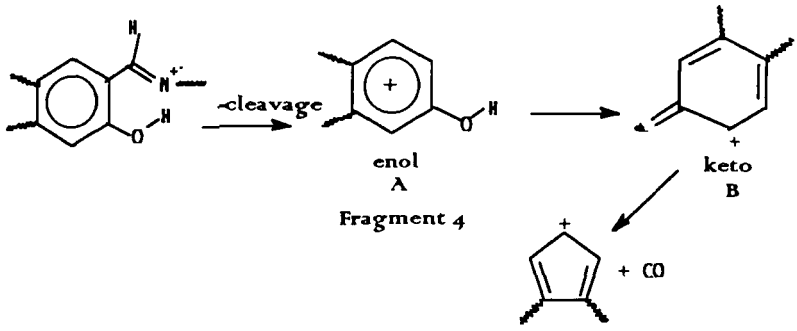
Table 3. Principal peaks for mass spectra of the third series Schiff bases.

Compd .No.	m/e with relative intensity in parentheses
19.	297(60), 296(50), 144(50), 130(50), 129(100), 76(50).
20.	145(20), 144(100), 143(20), 118(20), 117(90), 116(30), 90(40), 89(40), 83(21), 59(22), 52(18), 51(18), 50(18).

above general type of fragmentation pattern was shown by compound 19, where all the fragments are not shown by this compound. This indicates that compound 19 must posses a different structure from the other Schiff bases which may be the suggested keto structure. Second, the base peak for compound 19 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 as shown in Scheme 3. The first step in the sequence of this mechanism provides by itself a clear evidence for the keto structure shown above. However, no other alternative pathway seems to be possible. Third, for compound 18 the base peak was fragment 2 not the M^+.

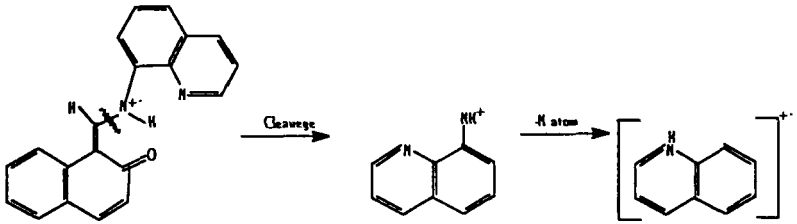


Scheme 3



$$R—CH=N^{+\cdot}—C(R) \xrightarrow{\text{HCN}} R—CH=N^{+\cdot} + {}^{+}C(R) \longrightarrow R^{\cdot} +$$

α-cleavage Fragment 6



Fragment 7

Scheme 3. Continued

Table 4. Main fragments and Relative intensity in the mass spectra of the first series Schiff bases.

Cpd. No.	$M^{+\cdot}$	$(M-1)^{+}$	Fragment 1.	Fragment 2.	Fragment 3.	Fragment 4.	Fragment 5.	Fragment 6.
1	197(100)	196(80)	180(8)	120(10)	77(51)	65(8)	51(30)	77(51)
2	211(100)	210(88)	194(8)	120(13)	77(13)	65(24)	51(13)	91(45)
3	323(100)	322(40)	306(4)	120(8)	77(10)	65(4)	51(8)	203(8)
4	275(100)	274(55)	258(6)	120(18)	77(15)	65(13)	51(15)	155(12)
4	277(95)	276(68)	260(6)	-	-	-	-	157(12)
5	227(100)	226(28)	-	-	77(30)	65(8)	51(13)	-
6	240(100)	239(41)	223(13)	120(28)	77(20)	65(4)	51(8)	120(28)
7	242(100)	241(33)	225(8)	120(33)	77(15)	65(13)	51(15)	120(33)

Table 5. Main fragments and Relative intensity in the mass spectra of the second series Schiff bases.

Cpd. No.	$M^{+\cdot}$	$(M-1)^{+}$	Fragment 1.	Fragment 2.	Fragme nt 3.	Fragme nt 4.	Fragme nt 6.	Fragme nt 7.
10	247(75)	246(100)	230(10)	170(8)	127(3)	115(10)	77(20)	77(20)
11	261(75)	260(100)	244(13)	170(8)	127(4)	115(23)	91(18)	77(8)
12	273(100)	272(75)	356(13)	170(4)	127(8)	115(8)	76(19)	77(5)
13	325(90)	324(95)	310(13)	170(18)	127(13)	115(61)	76(18)	77(6)
13	327(80)	326(100)	308(8)	-	-	-	-	
14	277(100)	276(95)	260(11)	170(6)	127(11)	115(18)	108(13)	77(13)
15	290(100)	289(70)	273(26)	170(13)	-	115(12)	120(13)	77(13)
16	292(100)	291(95)	229(13)	170(8)	127(13)	115(29)	122(8)	77(8)
17	297(100)	296(80)	-	170(3)	127(30)	115(15)	127(30)	77(15)
18	253(90)	252(15)	236(15)	170(100)	127(20)	115(30)	82(15)	77(8)

Table 6. Main fragments and Relative intensity in the mass spectra of the third series Schiff bases.

Cpd. No.	M+.	(M-1)+	Fragment 1.	Fragment 2.	Fragme nt 3.	Fragme nt 4.	Fragme nt 6.	Fragme nt 7.
19	-	297(60)	-	-	-	-	-	76(50)

because, the cleavage of amine ring carbon-azomethine nitrogen bond was easily accomplished and give rise to stable acetylene and ethylene molecules plus other metastable fragment. This is an expected result in view of the fact that in compound 18 the percentage keto is greatly enhanced, therefore, this type of cleavage will be further enhanced. Fourth, the Relative intensity of the fragment can't provides us with the useful information regarding toutomerism because, the same fragment can be arise from more than one pathways and from different sources. All the above fragmentation requires a large deal of energy, therefore, the fragments posses low intensity which, also play a role in their useless information regarding tautomerism. Fifth, cleavage was more easily occurred at the amine ring-nitrogen bond than at the aldehydic ring-carbon bond since the number of fragments forming from the former are greater (i.e., fragment 2 and fragment 6 in the former vs. fragment 4 in the latter).

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