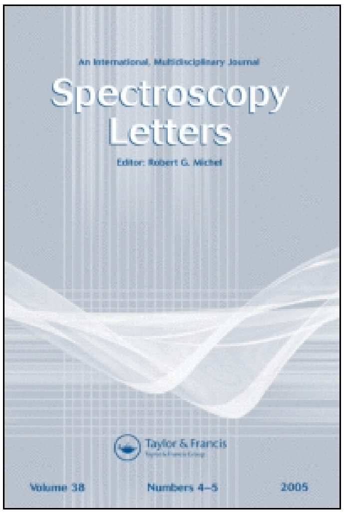

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Infra-Red Study of Tautomerism in Some Schiff Bases.

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To cite this Article Salman, Salman R. and Saleh, Na'il A. I.(1997) 'Infra-Red Study of Tautomerism in Some Schiff Bases.', Spectroscopy Letters, 30: 7, 1289 — 1300

To link to this Article: DOI: 10.1080/00387019708006724

URL: http://dx.doi.org/10.1080/00387019708006724

SPECTROSCOPY LETTERS, 30(7), 1289-1300 (1997)

Infra-Red Study of Tautomerism in Some Schiff Bases.

Key Words: Keto-enol tautomerism, Schiff bases, FTIR spectroscopy, UV-Visible spectroscopy, NMR spectroscopy.

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Abstract:

Infra-Red spectra of a series of substituted salicylaldehyde and 2-hydroxynaphthaldehyde Schiff bases were used to investigate enol-keto tautomeric equilibrium. Two model compounds, namely, salicylidinaniline and naphthylidinequinolineamine Schiff bases were used to represent the enol and keto forms, respectively. From the IR spectra of the model compounds it was possible to assign the IR absorption for the C=O and the C=N groups in both the keto and the enol form. It was also possible to assign other absorptions which were either specific to the keto or the enol forms. Specific pattern were observed for all the studied compounds.

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Introduction:

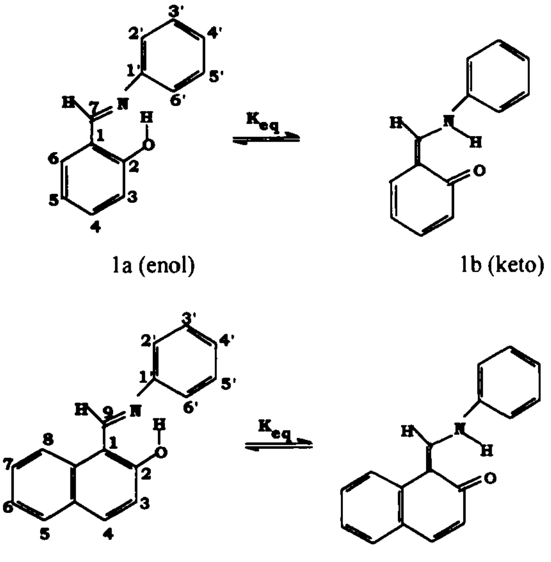
Compounds of the type Ar-CH=N-Ar, commonly, referred to as N-benzylidenaniline Schiff bases have been the subject of considerable interest. It has been recognized (1-3) that substituted ortho-hydroxy-substituted salicylidine aniline (SA) when dissolved in polar hydrogen bonding solvents give rise to a new band in the visible region located between 400 and 450 nm. Different explanations for the source of this band has been proposed(1-18). 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).

Clougherty, et al.,(19) examined the Infra-Red of seventeen anils in KBr pellets and found a frequency range of 1631-1613 cm^{-1} which was assigned to C=N stretching frequency. Chemical evidence was obtained for the band assignment, since the absorption disappeared when selected compounds were reduced to the corresponding N-benzylanilines with sodium borohydride. Minkin, et al.,(15) discussed the tautomerism phenomena in N-salicyliden-aniline Schiff bases and argued strongly for the benzenoid structure (enol-form) on the basis of the UV and IR spectral behavior, they showed that salicylidenaniline hydrochloride has a band displaced to 1652 cm^{-1} a result which should not be observed if the tautomer has the quinoid structure. Recently, Olivieri, et al.,(13) studied the IR spectra for (SA) and the corresponding anils derived from 2-hydroxynaphthaldehyde (NA) and 10-hydro-xyphenantheren-9-carbaldehyde (PA). The three compounds show bands in the region expected for C=O or C=N stretching vibration. For example, (SA) shows band at 1615 cm^{-1} which was ascribed to the C=N stretching vibration whereas (PA) anil shows a similarly intense band at 1625 cm^{-1} corresponding to the C=O stretching. It was not possible before to assign the carbonyl absorption in a pure keto compound in the present series due to the fact that no schiff bases of this group was prepared before which exist in the keto form. In this work we report the FTIR results of some schiff bases based on the assignment of a model Schiff base which exists mainly in the keto form and another model compound which exist in the enol form. The aim of the present communication is to give a complete assignment of the IR absorption for the enol and keto form by using two model compounds. Scheme 2 show the compounds which were studied in this work.

Experimental:

Various aromatic Schiff bases were prepared. The prepared compounds can be divided into three series. The first series (compounds 1-9, Scheme 2-1) include Schiff bases derived from the condensation of equi molar quantities of 2-hydroxybenzaldehyde (salicylaldehyde) or from the condensation of 2-methoxybenzaldehyde with several amine, namely, aniline, para substituted aniline and 2-naphthylamine. The second series (compounds 10-18, Scheme 2-2) include Schiff bases derived from the condensation of 2-hydroxynaphthaldehyde with the same amines mention 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 o-methoxy derivatives with 8-aminoquinoline. The physical properties and elemental analysis is give elsewhere (18). For compound 20 the structure was supported by NMR data.



1a (enol) 1b (keto)

2a (enol) 2b (keto)

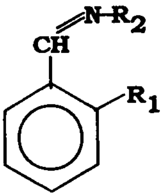
(Scheme 1)

FT-Infrared spectra were recorded on a Nicolet impact FT IR-400 spectrophotometer. A thin transparent disk of each sample was obtained by mixing 2-3 mg of it with ½-1 g of dry KBr, grinding well using a mortar and pestle and hydraulically pressed at 12 ton/m^2.

Results and Discussion:

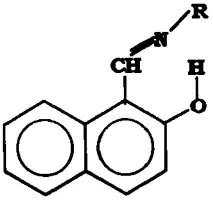
The UV-Visible spectra of compounds 1-8 show no absorption above 400 nm in polar and non-polar solvents indicating that these compounds exists mainly in the enol form (7,8). Compound 19 show only the keto absorption above 400 nm in polar and nonpolar solvents indicating that this compound exist mainly in the keto form (17,18). 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. ^{1}H and ^{13}C NMR data of these compounds supports the UV-Visible results and indicate the absence of a zwitter ion in compound 19 (18).

The observed vibrational bands in the 1800-1200 cm^{-1} in all Schiff bases studied are listed in Tables 1, 2-1, 2-2 and 2-3 and can be classified into five categories. This classification permits a thorough comparison of these bands among all the compounds studied.



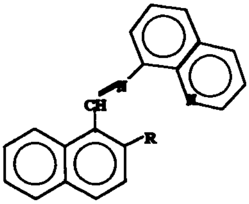
1	OH	phenyl-
2	OH	p-toloyl-
3	OH	p-iodophenyl-
4	OH	p-bromophenyl-
5	OH	p-anisoyl-
6	OH	p-N,N-dimethylaniline
7	OH	p-nitrophenyl-
8	OCH_3	phenyl-
9	OCH_3	naphthyl-

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



Compd. no.	R
19	OH
20	OCH_3

Scheme 2-3

Table 1: Vibrational assignments of some selected Infrared regions for all the presented compounds.

Regions (cm^{-1})	Assignment
1624-1633	$\nu_{C=O}$
1614 -1623	$\nu_{C=N}$
1581 -1612	ν_{ph}
1565 - 1587	$\nu_{ph} + \nu_{C=N}$
1540 -1546	$\nu_{C=C}$
1213 - 1217	ν_{C-N}

(1) 1624-1633 cm^{-1} region :

While compound 19 shows a strong sharp band at 1626 cm^{-1} in this region, compound 1 did not show this band. Therefore, it can be assigned to the C=O (carbonyl) stretching frequency of the keto tautomer.

This band is not shown by substituted (SA) which prove that these compounds exist in the enol form.

On the other hand, some of the 2nd series Schiff bases (compounds 10, 12, 14, 16 & 18) display this peak as a shoulder but of strong intensity, compounds 11, 13, 15 & 17 show it overlapped with the neighboring band located near 1618 cm^{-1} region which indicates that the keto tautomer of these compounds exist in an appreciable amount compared to the enol form. The latter observation can be explained by the fact that on IR time scale the proton transfer is rapid, therefore, overlapped bands for both tautomer were detected. The assignment of this band was also ascribed by Olivieri, et al.,(13) to the stretching motion of C=O of 10-hydroxyphenanthrene-9-carbaldehyde Schiff base (PA).

The assumption that this new peak being due to $C=NH^+$ stretching motion of a zwitterionic structure is not accepted since, as pointed out by Aton(20), it seems reasonable to expect that the $C=NH^+$ stretching to occur at lower frequency than that of C=N (i.e, protonation should lower the C=N force constant and increase the effective mass of the nitrogen and both of these effects tend to lower the stretching frequency).

When a carbonyl is hydrogen bonded and resonance can occur which puts a negative charge on the carbonyl oxygen and a positive charge on the carbon atom which carries the bonding proton, the partial transfer of the proton enhance resonance and lowers the C=O stretching frequency(21). This can explain the lowering of the carbonyl stretching frequency to 1624-1633 cm^{-1} in the keto form.

(2) 1614-1623 cm^{-1} region :

A band in this region has been previously assigned by many authors to the C=N stretching frequency(16,21-25). This is in agreement with the results obtained in this study. Hence, all of the compounds studied (except compound 19) exhibit this band. The displacement of the 1626 cm^{-1} peak in the IR spectra of compound 19 by the 1618 cm^{-1} band in the IR spectra of compound 20, provides again a clear evidence for the claimed keto structure of 19.

Table 2-1. Infared absorption bands for the first series Schiff bases.

				Wavenumbers(cm^{-1})			
Compd. No.	1624-1633	1614-1623	1581-1612	1565-1587	1540-1546	1213-1217	other bands
1.	-	1618(s)	1591(m-s)	1570(m-s)	-	-	1486(s),1452(s),1395(m), 1361(m),1273(s).
2.	-	1619(s)	1597(m)	1571(s)	-	-	1510(s),1490(s),1450(w), 1417(w),1372(m),1320(w), 1285(s).
3.	-	1618(s)	1581(m)	1569(m)	-	-	1500(m),1482(s),1455(m), 1417(w), 1361(w),1285(s).
4.	-	1618(s)	1584(w)	1569(m-s)	-	-	1500(w),1482(s),1452(m), 1419(w),1360(m),1285(s).

5.	-	1623 (s)	1604(m-s)	1571(m-s)	1542(vw)	-	1561(w),1512(s),1493(s), 1459(m),1400(w),1368(w), 1281(s),1247(s).
6.	-	1614(s)	1593(m-s)	1567(w)	-	-	1561(w),1519(s),1459(m), 1368(s),1315(w),1289(s), 1232(w).
7.	-	1617(m)	1587(w-m)	1569(s)	1542(w)	1213(vw)	1601(ms),1561(s,sh), 1508(m),1480(m), 1451(m), 1379(w), 1338(w)1273(w).
8.	-	1618(s)	1601(s)	1587(s)	-	-	1522(s),1490(s),1466(s), 1350(m),1300(m),1275(s), 1250(s).

s = strong sh=shoulder m = medium v = very w = weak b = broad

Table 2-2. Infrared absorption bands for the second series Schiff bases.

				Wavenumbers (cm^{-1})			
Compd No.	1624-1633	1614-1623	1581-1612	1565-1587	1540-1546	1213-1217	other bands
10.	1626(s,sh)	1618(s,sh)	1595(m)	1571(w)	1546(m)	1217(w)	1578(w),1561(w),1521 (w), 1500(w), 1490(m), 1460(w), 1420(w), 1350(m),1320(m), 1315(m).
11.	-	1618(s,b)	1612(m-s,sh)	1571(w)	1544(w)	1217(w)	1579(w),1560(w),1512(m), 1490(w), 1460(w), 1350(m),1327(m),1317(m).
12.	1624(m-s,sh)	1618(s,b)	1611(m-s,sh)	1571(w)	1543(w-m)	1217(vw)	1604(m,sh),1578 (w-m), 1561(m), 1536 w),1500 (w-m),1496(w), 1460(w), 1350(w), 1323(w), 1315(w).
13.	-	1618(s,b)	1612(m-s,sh)	1572(w)	1545(w)	1217(w)	1579(w-m), 1561(m), 1536(w), 1496(m-s), 1460(w),1350(w), 1323(w),1315(w).

14.	1625(s,sh)	1618(s,b)	1612(m-s,sh)	1572(w)	1542(w)	1217(w)	1579(w),1561(w),1568((s), 1490(m),1460(m),1420(m), 1320(w),1300(m),1247(s).
15.	-	1618(s,sh)	1610(v s,b)	1572(w)	1544(w)	1217(w,sh)	1578(w),1561(w), 1524(m), 1490(w), 1460(w),1440(m), 1360(s),1228(w).
16.	1624(s,sh)-	1618(s,b)	1610(m,sh)	1572(w)	1546(s)	1213(w)	1579(w),,1561(w),1535(w), 1508(w),1460(w),1338(vs), 1289(s).
17.	-	1618(s)	1611(m-s,sh)	1570(m)	1543(w)	1213(w)	1563(w-m), 1536(w), 1530(w), 1450(w), 1398(w),1348(w), 1312(w-m).
18.	1633(vs)	1618(s)	1601(m,sh)	1570(vw)	1546(s)	1217(w-m)	1521(w-m),1498(w), (w), 1419(w), 1390(w), 1356(m), 1319(m), 1260(w),1248(w).

s=strong m = medium w = weak b = broad sh=shoulder v = very

Table 2-3. Infrared absorption bands for the third series Schiff bases.

	Wavenumbers(cm^{-1})					
Compd. No.	1624-1633	1614-1623	1581-1612	1565-1587	1540-1542	121
19.	1626(s)	-	1591(m)	1570(w)	1542(m-s)	121
20.	-	1618(w-m)	1595(m)	1575(m-s)	-	-

m = medium w = weak b = broad
sh=shoulder v = very

(3) 1581-1612 cm^{-1} and 1565-1587 cm^{-1} regions :

There is a general agreement(16,21-23) that the band in this regions may be attributed to the vibration of the aromatic skeleton which are said to be resolved in substituted benzene when the substituents are conjugated. The intensity of the bands in the region (1565-1587 cm^{-1}) decrease when the percentage of enol form decrease, which support the fact that this band has been found to be vibrationally coupled to $v_{C=N}$ band (24). Moreover, the exact position of these bands vary from one compound to another since the substituents on the aniline ring is varied.

(4) 1540-1546 cm^{-1} and 1213-1217 cm^{-1} regions :

These new bands occur only if there is a considerable amount of the keto tautomer. Hence, they didn't appear in the IR spectra of series 1 Schiff bases & compound 20. On the other hand, they appeared as a strong sharp bands at 1213 cm^{-1} (w-m) & 1542 cm^{-1} (m-s) in compound 19. Therefore, and in view of this experimental observation, the absorption in these regions must be related to a specific motion in the keto structure. For example, the band at the first region (1540-1545 cm^{-1}) is attributed to C=C (external double bond) stretching motion. This assignment was first pointed out by Cromwell(25) who found a band around 1540 cm^{-1} in acetylacetonimines in Nujol mulls and was assigned to either a "lowered" $\mathrm{C}\overset{--}{-}\mathrm{C}$ or an "enhanced" $\mathrm{C}\overset{--}{-}\mathrm{N}$ frequency. However, in our work we assigned the band near 1213-1217 cm^{-1} region to the C-N (single bond) stretching frequency since its appearance was accompanied by the C=O absorption at about 1626 cm^{-1} and it is the only band that appear in compound 19 while it is was absent in compound 20 in the expected C-N stretching region (i.e, approximately, 1200-1300 cm^{-1} region)(21). Series 2 of Schiff bases show these bands. Their relative intensity depends on the percentage of keto form in the mixture. For example, the strong intensity peaks in compound 18 indicates a large percentage of the keto tautomer.

(5) other bands :

Although these bands are not identical in compounds 1-20, they are classified in one category since they appear to be insensitive to the tautomerism and belongs to a specific motion in the molecule. Furthermore, this set of bands can be divided into three subgroups according to their source which are :

(I) bands arise from the interaction of the substituent with the aniline ring (e.g., there are some identical bands between the first & second series of Schiff bases which have the same substituent on the aniline ring).

(II) bands which appear to be due to coupling between other neighboring strong band (e.g., bands at 1578 cm^{-1} & 1561 cm^{-1} in most of the 2nd series of Schiff bases and at 1611-1614 cm^{-1} in the third series).

(III) The rest of the other bands are related to other vibration modes (i.e., bending, deformation......etc.) which occur at lower frequency regions.

The following general conclusions can be made :

In substituted (NA), as the electronic nature of the p-substituent R is changed from an electron-donating to electron-withdrawing one the % of keto form is decreased. This can be confirmed by observing the corresponding change in the intensity of the bands at 1540-1545 cm^{-1} and 1624-1626 cm^{-1} regions. By looking into the IR spectral characteristics of compound 18 and compound 17 we can conclude the following :

Increasing conjugation over the whole molecule will cause the equilibrium to shift to more enol form. This is shown in compound 7 which has no absorption at 1624-1626 cm^{-1} region and a weak absorption at 1543 cm^{-1}.
Increasing the basicity of nitrogen atom by substituting the cyclohexyl group instead of the phenyl group on the amine portion in compound 18 will shifts the equilibrium to the keto form. This is confirmed by the large shift of C=O band at 1633 cm^{-1} which is accompanied by an increase in the intensity of 1545 cm^{-1} & 1217 cm^{-1} bands and a decrease in the intensity of 1570 cm^{-1} band.

Acknowledgment: The Authors wish to thank university of Yarmouk for providing the grant 44/95.

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Date Received: February 2,1997
Date Accepted: April 21, 1997