

## **Elucidation of Molecular Structure of New Schiff Bases Derived from Benzopyran-4-one Using Spectroscopic Techniques**

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**Summary.** New Schiff bases were prepared by condensation of (a) ethylenediamine and (b) trimethylenediamine with 6-formyl-7-hydroxy-5-methoxy-2-methyl-benzopyran-4-one (Schiff bases Ia and Ib) and with 5,7-dihydroxy-6-formyl-2-methyl-benzopyran-4-one (Schiff bases IIa and IIb). The four prepared Schiff bases were characterized by elemental analysis, UV/Vis, IR, <sup>1</sup>H-NMR and mass spectra. Moreover, the ionization constants of the hydroxyl (OH) groups present in the Schiff bases molecules were determined spectrophotometrically in ethanol-water medium. All the results were discussed in relation to the molecular structure of the four prepared Schiff bases. For Schiff bases IIa and IIb, simultaneous ionization occurs for the two hydroxyl groups in position five of the two benzopyrone moieties and only two pK<sub>a</sub> values were obtained.

### **Introduction**

The condensation of primary amines with aldehydes and ketones gives products known as imines which contain a C=N double bond. These compounds rapidly decompose or polymerize unless there is at least an aryl group bonded to the nitrogen or to the carbon atom. The latter imines are called Schiff bases, since their synthesis was first reported by Schiff.<sup>(1)</sup>

Metal complexes of Schiff bases have contributed widely to the inorganic chemistry of chelate system. The extreme sensitivity of physical and chemical properties of Schiff base compounds to small changes in the substitution and in the environment, together with their ready availability justify their extraordinary wide spread applications.<sup>(2-9)</sup>

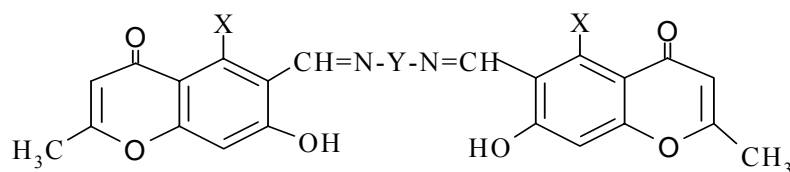
### **Experimental**

### Preparation of benzopyran-4-one derivatives<sup>(10)</sup>

6-Formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one(I) and 6-Formyl-7-hydroxy-5-methoxy-2-methylbenzopyran-4-one(II) were prepared as previously described.<sup>(10)</sup>

### Preparation of Schiff bases

The target Schiff bases were prepared by addition of ethylenediamine (0.005 Mol) or trimethylenediamine in 20 ml ethanol drop wise with continuous stirring to a solution of (I) or to a solution of (II) (0.01 Mol) for preparation of the target Schiff bases (Ia, b and IIa, b). The mixtures were stirred at room temperature for at least 30 min and the solids obtained were filtered off, washed with ethanol and recrystallized from ethanol [Schiff bases Ia and Ib] and from DMF [Schiff bases IIa and IIb]. All the prepared Schiff bases were subjected to elemental analysis in the microanalytical center, Cairo University, Cairo, Egypt.



Where

No.	X	Y
Ia	OCH <sub>3</sub>	(CH <sub>2</sub> ) <sub>2</sub>
Ib	OCH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub>
IIa	OH	(CH <sub>2</sub> ) <sub>2</sub>
IIb	OH	(CH <sub>2</sub> ) <sub>3</sub>

### Determination of dissociation constant spectrophotometrically

The dissociation constants of Schiff bases (Ia, b and IIa, b) were determined spectrophotometrically at ionic strength 0.1 and 25 °C. Stock solutions of Schiff bases were prepared in 60% (by volume) ethanol-water mixture. Fresh solutions ( $5 \times 10^{-5}$  M) of these Schiff bases were prepared by diluting known volumes of their stock solutions in the requisite percentages of solvent in 100 ml volumetric flasks. In all cases the solutions were made 0.2 M in HCl. The solutions were then partially neutralized with

freshly prepared carbonate-free concentrated sodium hydroxide solution made up from the same solvent. The pH of the solution was measured by using Jenway 3010 pH-Meter, and the spectra of the solutions at different pH values were recorded using the same solvent as a blank. Since the total volume of the base added did not exceed 1% of the total volume of the test solution, dilution correction was unnecessary. Each run was repeated twice or more. The spectrophotometric methods applied for the determination of the  $pK_a$  values are the half-wave height and the limiting absorbance methods.<sup>(11)</sup>

### Results And Discussion

These Schiff bases were subjected to C, H and N elemental analyses. The obtained results of the elemental analyses of Schiff bases are in good agreement with the theoretical values. The physical properties and elemental analysis values of such Schiff bases are given in Table (1).

**Table (1):** Elemental analysis data for the prepared Schiff bases.

Comp.	Formula	m. p. °C	Color	C%	H%	N%
				Calc. (Found)	Calc. (Found)	Calc. (Found)
Ia	C <sub>26</sub> H <sub>24</sub> N <sub>2</sub> O <sub>8</sub>	260	Yellow	63.34 (63.14)	4.91 (4.91)	5.69 (5.59)
Ib	C <sub>27</sub> H <sub>26</sub> N <sub>2</sub> O <sub>8</sub>	200	Yellow	64.02 (63.92)	5.17 (5.10)	5.53 (5.19)
IIa	C <sub>24</sub> H <sub>20</sub> N <sub>2</sub> O <sub>8</sub>	Charring at 300	Reddish yellow	62.06 (61.34)	4.43 (4.55)	6.03 (6.08)
IIb	C <sub>25</sub> H <sub>22</sub> N <sub>2</sub> O <sub>8</sub>	Charring at 260	Reddish yellow	62.75 (61.89)	4.63 (4.84)	5.85 (5.49)

### Mass spectra of Schiff bases

A trial is made to correlate the observed signals with molecular structure and to evaluate a general scheme for fragmentation of the Schiff bases under investigation.

The parent benzopyran-4-one compound (m/e 146) exhibits an abundant molecular ion and the loss of a stable neutral molecule of carbon monoxide (CO) is a very important fragmentation process, resulting in the base peak at m/e 118<sup>(12)</sup>. The subsequent fragmentation of the M-CO ion (m/e 118) (M is the molecular weight) by a

loss of a second molecule of carbon monoxide followed by loss of a hydrogen atom to give ( $m/e$  89) is very similar to that of benzofuran itself and suggests that the M-CO ion may be formulated as the benzofuran radical ion.

The spectra of the prepared Schiff bases show molecular ion peaks at (M+1) (at  $m/e$  value representing the molecular weight +1) for Schiff base Ia ( $m/e$  493) and at M (at  $m/e$  values corresponding to the molecular weight) for Schiff bases Ib ( $m/e$  506), IIa ( $m/e$  464) and IIb ( $m/e$  478).

It is observed that the most abundant fragment of all the Schiff bases studied appears at  $m/e$  218. Such band represents the benzopyran-4-one ring attached to the azomethine group. This means that the fragmentation process occurs by breaking of the bond between nitrogen atom and  $CH_2$  group; according to this pattern of fragmentation a peak at ( $m/e$  246) is found in all Schiff bases (Ia, b and IIa, b). Such fragment ion loses  $CH_2$  group to give another fragment at  $m/e$  232 in the Schiff bases Ia, b and IIb, the spectra of the Schiff base IIa missed this band. The fragment ion of  $m/e$  218 undergoes further loss of  $CH_2$  group giving another fragment ion at  $m/e$  204 in Schiff bases IIa and IIb. Another fragment ion at  $m/e$  192 appears in the spectra of Schiff bases IIa and IIb due to the presence of 5,7-dihydroxy-2-methylbenzopyran-4-one ring.

Most of the fragmentation patterns of target Schiff bases (Ia, b and IIa, b) are ended with aliphatic products.<sup>(12)</sup>

### **The infrared spectra of Schiff bases**

In the present study, the IR spectra of the compounds under investigation (Table 2) show a broad band at 3386, 3398, 3429 and 3433  $cm^{-1}$  for the Schiff bases Ia, b and IIa, b, respectively. Such broad band indicates that the OH groups of the investigated Schiff bases are involved in intramolecular hydrogen bonds.<sup>(13)</sup> These Schiff bases show the OH deformation bands by medium intensity at 1110  $cm^{-1}$  for Schiff bases (Ia, b and IIb) and 1133  $cm^{-1}$  for Schiff base (IIa) and show C-O stretching bands at 1218 for Schiff base (Ia) while for Schiff bases Ib, and IIa, b this band appears at 1222  $cm^{-1}$ . Strong C=O stretching band<sup>(14)</sup> appears at 1654, 1662, 1658 and 1651  $cm^{-1}$  in the IR spectra of Schiff bases Ia, b and IIa, b, respectively. The IR spectra of compounds Ia, b display a band at 1620  $cm^{-1}$  of weak intensity which can be

assigned to C=N stretching.<sup>(15)</sup> On the other hand, this band is not observed in the IR spectra of compounds IIa, b; the individuality of C=N absorption is completely lost. This is due to the conjugation with C=C band and the frequencies of the two are so close that, it is doubtful whether either can be regarded as retaining its individual character. These Schiff bases show weak C-N stretching band<sup>(16)</sup> at 1311 and 1315 cm<sup>-1</sup> for Schiff bases Ia, b and show weak doublet of this band at 1346 and 1357 cm<sup>-1</sup> for Schiff bases IIa, b, respectively.

**Table (2):** Assignment of IR bands of the Schiff bases Ia, Ib, IIa and IIb.

Ia	Ib	IIa	IIb	Band Assignment
3386 b	3398 b	3429 b	3433 b	$\nu$ OH
2927 m	2931 m	2927 m	2927 m	Asym. CH <sub>3</sub> def.
2850 m	2854 m	2850 m	2850 w	Sym. CH <sub>3</sub> def.
1654 s	1662 s	1658 s	1651 s	$\nu$ C=O chromone
1620 s	1620 s	1620 s	1612 s	$\nu$ C=N
1589 s	1589 s	1620 s	1612 s	$\nu$ C=C
1396 m	1396 m	13346 w	1346 w	$\nu$ C-N
1076 m	1076 m	1083 w	1083 w	Asym.C-O-C stre.
1168 w	1168 m	1164 w	1164 w	$\delta$ C-H in-plane def.
1110 m	1110 m	1133 m	1110 m	$\delta$ O-H def.
1218 m	1222 m	1222 m	1222 m	$\delta$ C-OH
840 m	840 m	848 w	813 w	$\gamma$ C-H out-of-plane def.

b: broad, s: strong, m: medium, and w: weak.

### Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra of the Schiff bases

The <sup>1</sup>H-NMR spectra of all Schiff bases exhibit singlet peak at 8.6–8.8 ppm due to the azomethine CH=N protons and the integration value in all Schiff bases under investigation is two. The chemical shifts of the OH protons<sup>(14)</sup> in position seven of the benzopyran-4-one moieties appear as singlet at 15.19 and 15.3 ppm for Ia and Ib respectively, with integration equivalent to two protons. For compounds IIa and IIb the OH groups in positions 5 and 7 of the benzopyran-4-one moieties appear at 14.4 ppm. The downfield shift of the OH protons may be due to that the OH groups are involved in hydrogen bonding. Thus for compounds Ia and Ib the OH protons in position seven are hydrogen bonded to the azomethine (CH=N) groups while for compounds IIa and IIb in addition to these hydrogen bonded groups another hydrogen bonding OH groups in position five with the carbonyl (C=O) groups in position four of the benzopyran-4-one ring. The presence of a sharp singlet in the spectra of these derivatives clearly

indicates that the magnetic environment is equivalent for all OH protons, suggesting the presence of a planar structure for the studied Schiff bases.<sup>(17)</sup> The disappearance of the signal of OH protons on deuteration confirms that they are ionizable protons.

**Table (3):** Proton NMR spectral data of the Schiff bases Ia, b and IIa, b.

Ia	Ib	IIa	IIb	Assignment
2.20	2.20	2.30	2.30	CH <sub>3</sub>
3.80	3.80	-	-	O-CH <sub>3</sub>
5.80	5.80	6.00	5.90	Arom. H (C <sub>3</sub> )
6.30	6.20	6.00	6.00	Arom. H (C <sub>8</sub> )
8.80	8.80	8.80	8.60	CH=N
-	-	14.30	14.40	C <sub>5</sub> -OH
15.19	15.30	14.30	14.40	C <sub>7</sub> -OH

### Spectra in aqueous ethanol solution of varying pH-values

The absorption spectra of all Schiff bases at low pH values are characterized by a broad strong band absorbing maximally at the wavelength of 330 nm this band is due to the absorption of the acid form containing the hydroxyl groups liable to exist in such solutions and may be assigned to  $\pi-\pi^*$  transition within the azomethine groups<sup>(18)</sup> influenced by the charge transfer within the whole molecule. On increasing the pH value up to  $\sim 6$  the absorbance of this band increases mean while, a new band appears in all compounds where its intensity increases by increasing pH of the medium. This can be ascribed to the ionization of hydroxyl groups attached to the benzopyran-4-one moieties. Such ionization reflects itself in a high electron delocalization within the molecule and consequently facilitates the CT interaction.<sup>(11)</sup>

### Determination of acid dissociation constant

The spectrophotometric methods applied for the determination of the acid dissociation constant values (pKa) are the half-wave height and the limiting absorbance methods.<sup>(11)</sup>

The pKa values obtained are depicted in Table (4). The data obtained in this table reveal the following facts

1- The constructed absorbance-pH relations at the selected wavelength for compounds Ia and Ib are typical S shaped curves, each comprising a clear inflection, indicating typical dissociation. Thus this behavior can be considered as an evidence for the

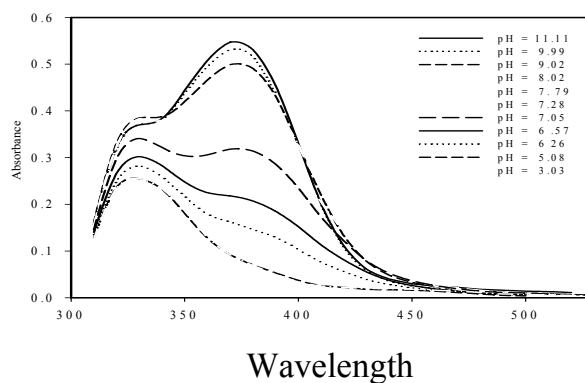
simultaneous ionization of the hydroxyl groups C<sub>7</sub>-OH of the two benzopyran-4-one moieties.

2- The constructed absorbance-pH curves at the selected wavelength for compounds IIa and IIb displayed two inflections pointing out to the existence of two dissociation steps for these compounds. The first dissociation step can be assigned to the simultaneous dissociation of the C<sub>7</sub>-OH groups, meanwhile the second dissociation can be assigned to the C<sub>5</sub>-OH groups.

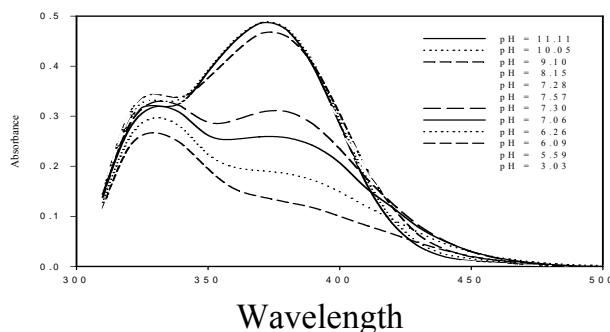
3- The pK<sub>a2</sub> values for compounds IIa and IIb are higher than that of pK<sub>a1</sub> this may be due to the interaction between C<sub>5</sub>-OH and benzopyran-4-one carbonyl in position 4 through intramolecular hydrogen bonding (as indicated by IR and <sup>1</sup>H-NMR). This, in turn, results in a difficult liberation of the C<sub>5</sub>-OH proton that is released at high pH value.

**Table (4):** pK<sub>a</sub> values of the Schiff bases Ia, b and IIa, b.

Compound no.	Method 1		Method 2	
	pK <sub>a1</sub>	pK <sub>a2</sub>	pK <sub>a1</sub>	pK <sub>a2</sub>
Ia	7.08	-	7.42	-
Ib	7.09	-	6.91	-
IIa	7.80	11.40	7.50	11.30
IIb	8.00	11.00	8.00	11.07



**Fig. (1)** Absorption spectra of Schiff base Ia in ethanol-water mixtures of varying pH values.



**Fig. (2)** Absorption spectra of Schiff base Ib in ethanol-water mixtures of varying pH values.

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