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# Synthesis, spectroscopic and molecular structures investigations of some carboxylated schiff bases

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#### Abstract

A series of nine carboxylated Schiff bases (five of them are newly prepared viz. compounds **5–9**), are prepared and characterized by various physico-chemical techniques. The molecular structures of synthesized Schiff bases are investigated by IR, UV–Visible, molar conductivities at different concentrations in two different solvents and by their pH values in ethanolic solutions.

The IR spectra show absorptions due to = NH- stretching and -N-H bending vibrations, the UV-Visible spectra indicates absorptions are due to protonated species. The molar conductivities,  $0.1-0.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , prove that these compounds are weak electrolytes and are even weaker than tyrosine and phenylalanine,  $2.5-13 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . The melting points and pH values of Schiff bases are compared with those of some  $\alpha$ -aminoacids and some related Schiff bases that have no COOH group in their structures. On the bases of these data, it was concluded that carboxylated Schiff bases exist in two forms, the ionized and the free base where the later is predominant. The ionized form is similar to the zwitterion of the  $\alpha$ -aminoacid, in which a proton is transferred from COOH to the azomethine (-CH=N-) group.

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## 1. Introduction

Previously, it is well known that *p-N,N*-dimethylaminobenzylidene-anilines (Scheme 1) give red colour in glacial acetic acid or in aqueous sulphuric or hydrochloric acids [1-4]. These Schiff bases form monoacid salts, these salts were isolated as red to orange solids from their aqueous sulphuric acid solutions, they have high melting points, above 200 °C [2-4]. Upon neutralization with dilute sodium hydroxide, the free Schiff base was recovered in every case. In some cases, the rate of a chemical reaction can be conveniently followed by monitoring the conductance of the solution as a function of time and as the conductance depends on the number of ions or ionic species in the solution and therefore on the degree of ionization of the electrolyte and hence on the molecular structure.

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Recently very few studies are found to study and investigate the behaviour of some carboxylic acids by conductometric techniques like tartaric acid in which ion-solvation behaviour was investigated by molar conductance at different solvents mixtures [5]. Thermodynamics parameters related to association and solvation have also been determined.

A clear understanding of the molecular structures of carboxy Schiff bases is required, since they are the precursor of many pharmaceutical products [6] and its important as the carboxylic group increases the stability of the aldimine Schiff base structure [7,8].

To achieve useful results a systematic study of synthesis, characterization and molecular structural is investigated. In the present work, structural studies of nine carboxylayed Schiff bases are attempted by following their melting points, IR and UV–Visible spectra, pH values of their ethanolic solutions, and their conductivities in ethanol and dimethylsulphoxide (DMSO).

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Scheme 2.

## 2. Experimental

Compounds 1–4 (Scheme 2) are well-known compounds and were prepared according to standard literature procedure as discussed elsewhere [9-11]. The new carboxylated Schiff bases viz. compounds 5-9 were prepared by refluxing for 90 min, equimolar amounts of *p*-amino benzoic acid and the corresponding aldehyde in ethanol. On cooling, a solid product in every case was collected and recrystallized from ethanol. Ethanol and DMSO were of 'Fluka' spectrosil grade, glacial acetic acid was of 'Analar' grade BDH (99.6%), and they were used directly without further purifications. The elemental C, H and N analyses were performed on Perkin Elmer 240B elemental analyzer. The IR and UV-Visible spectra were measured on Pye Unican SP3-300 IR spectrometer and Shimadzu UV-160 UV-Visible spectrometer, respectively. IR spectra were measured as KBr disks. The pH values were measured by Metrohm G32 pH-meter in ethanol solutions  $(10^{-3} \text{ mol dm}^{-3})$  at 298 K. The molar conductivities were measured at 298.15 K (cell constant =  $0.1796082 \text{ cm}^{-1}$ ) on a conductivity bridge Wyne Kerr Auto Balance precision Bridge, type B 331 MK II, connected to a frequency

and voltage stabilized power supply supplied from WTEC, Ltd. The minimization method of Fouss and Hisa [12] was used for the analysis of the conductivity data.

## 3. Results and discussion

The elemental analysis of the synthesized carboxy Schiff bases revealed their empirical formula. Table 1 shows the analytical data, melting points, colour and yield for these new compounds.

#### 3.1. IR spectra

Table 2 shows the major IR bands in the spectra of carboxylated Schiff bases 1-9, the characteristic features of these spectra are: (i) The appearance of very broad strong bands in the region of  $3300-2300 \text{ cm}^{-1}$ , (ii) the appearance of strong absorption in the region of  $1690-1670 \text{ cm}^{-1}$  and (iii) the appearance of medium absorption in region of  $550-530 \text{ cm}^{-1}$ . These absorptions are generally not observed in the IR spectra of any kind of Schiff bases not containing NH or NH<sub>2</sub> group in their structures [13–19]. The absorption at  $3300-2300 \text{ cm}^{-1}$  is characteristic of the quaternary ammonium salts [20] and accordingly, this absorption is assigned to the stretching vibration of =NH- in the IR spectra of our Schiff bases. Bending vibration of N-H and its torsinol oscillation are located at  $1690-1670 \text{ and } 550-530 \text{ cm}^{-1}$ , respectively, [20]. The only way, which leads to such absorptions in our Schiff bases, is proton transfer from COOH group to the azomethine group (-N=CH-) forming a di-polar ion structure similar to that occurs in the  $\alpha$ -amino acid (zwitterion ion), Scheme 3 (I). Since some spectra of our Schiff bases show stretching vibrations of O-H bond (Table 2), therefore it can be suggested that the proton transfer is limited.

The iminium-phenolato zwitterions were also proved by the IR and NMR spectra of phenolic Schiff bases and iminium-phenolato tautomerizes to imine-phenol upon reaction with carboxylates [21].

Table 1

Numerals, names, melting points, yield and analytical data of synthesized Schiff bases

Compd no.	Name of compound/Stiochiometric	m.p.°C (d)	Yield %	Colour	Calcd (Found)		
					%C	%H	%N
5	C <sub>11</sub> H <sub>13</sub> NO <sub>2</sub> <i>n</i> -Butylidene- <i>p</i> -aminobenzoic acid	131	88	Yellow powder	69.11 (68.98)	6.81(6.77)	7.33(7.62)
6	C <sub>14</sub> H <sub>10</sub> NO <sub>2</sub> Cl <i>N</i> -( <i>p</i> -Chlorobenzylidene)- <i>p</i> -aminobenzoic acid	269	76	Yellow solid	64.74(64.41)	3.84(3.82)	5.41(5.40)
7	$C_{14}H_{10}N_2O_4$ <i>N</i> -( <i>p</i> -Nitrobenzylidene)- <i>p</i> -aminobenzoic acid	267	69	Yellow needles	62.22(62.01)	3.70(3.68)	10.37(10.41)
8	C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> <i>N</i> -( <i>p</i> - <i>N</i> , <i>N</i> -Dimethylbenzylidene)- <i>p</i> -amino- benzoic acid	293	82	Yellow powder	71.64(71.42)	5.97(5.81)	10.45(10.32)
9	C <sub>14</sub> H <sub>11</sub> NO <sub>2</sub> Benzylidene-p-aminobenzoic acid	185	92	Colourless powder	74.70(74.50)	4.90(5.10)	6.20(6.10)

d, decomposition.

Table 2 The major IR bands in the spectra of compounds **1–9** measured as KBr disks

Compd no.	$\delta$ , $\nu$ /cm <sup>-1</sup>							
	ν/O–H	$\nu = \stackrel{\oplus}{\mathrm{N}} \mathrm{H}$	δ/N–H	$\nu/C = N$	Asym. C(–O) <sub>2</sub>	Sym. C(–O) <sub>2</sub>	Torsinol oscillation N–H	
1	_	3200–2400,m;br	1670,s	1620,m	1585,s	1415,s	545,m	
2	3600 <sup>a</sup> ,m;br	3100-2300,s;br	1670,s;br	_b	1595,s	1405,s	545,m	
3	3320,s	3200-2400,s;br	1690,s	1660,s	1590,s	1410,s	540,m	
4	_	3100-2500,s;br	1670,s	1620,m	1585,s	1415,s	545,m	
5	3390,s 3320,m	3300-2400, vs;vbr	1680,s	1615,m	1600,s	1415,s	545,m	
6	_	3100-2400,s;br	1675,s	1620,m	1595,s	1420,s	530,m	
7	_	3100-2500,s;br	1670,s	1615,m	1585,s	1410,s	535,m	
8	_	3100-2500,s;br	1675,s	1620,m	1590,s	1420,s	535,m	
9	3360,w 3460,w	3200-2500,s;br	1670,s	1620,m	1590,s	1420,s	550,m	

m, medium; br, broad; s, strong; vs, very strong; vbr, very broad; w, weak.

<sup>a</sup> Overlapped with pyrrole N–H.

<sup>b</sup> Overlapped with the absorption at  $1670 \text{ cm}^{-1}$ .

#### 3.2. The electronic spectra

Table 3 shows the longer wavelength absorption bands in the electronic spectra of compounds 1-9 in ethanol and glacial acetic acid. n-Butylidene-p-aminobenzoic acid, compound 5 has only one absorption band in its electronic spectrum, at 286 nm. This transition is certainly originates from the lonely aromatic ring in its structure, since aliphatic structures do not absorb light in this region. The absorption at 286 nm is observed in the spectra of all compounds at the same position and almost with close intensity. Owing to these facts, the same moiety in every Schiff base molecule must be responsible for this transition, namely moiety (I) of Scheme 3. The longer wavelength absorption band at 358-319 nm is not observed in the spectrum of compound 5. Since all compounds except compound 5 contain either benzaldehyde, substituted benzaldehyde or five-membered heterocyclic ring in their structures, therefore the absorptions at 358-319 nm (Table 2) may represent the local excitations of these moieties. These transitions are affected by the nature of substituent. In glacial acetic acid, these absorptions are blue-shifted, whereas the absorptions at 270-288 nm are red-shifted to 286-294 nm. Structure (II) of Scheme 3 may be responsible for the transitions at 286-294 nm in glacial acetic acid. The UV/visible absorption spectra of some polymeric Schiff bases dissolved in concentrated sulphuric acid showed a band near 300 nm indicating the presence of iminium ion [22].



#### 3.3. Conductivity measurements

Owing to the fast hydrolysis of Schiff bases in aqueous solutions [10,14,16,23], we used ethanol and DMSO as a media for measuring the molar conductivities. Fig. 1 represents the variation of molar conductivities with molar concentrations of tyrosine and phenylalanine as a standard. The figure shows that molar conductivities increase rapidly with increasing dilution, and their molar conductivies lie in the range 2.5–13  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> at concentrations of 0.001–0.00002 mol dm<sup>-3</sup>. On comparing, the conductivities of the carboxylated Schiff bases with that of strong electrolytes such as HCl and NaOH, it is clearly indicated that these compounds have very much smaller molar conductivity and even much smaller than that of weak electrolytes such as acetic acid [24]. According to these information, we can conclude that the carboxylated Schiff bases are weak electrolytes as tyrosine and phenylalanine.

Figs. 2–4 represents the variation of molar conductivities with molar concentrations of compounds 1, 2, 6, 8 and 7 in ethanol and DMSO solutions, the data of these figures

Table 3

The longer wavelength absorption bands in the electronic spectra of compounds **1–9** in ethanol and glacial acetic acid

Compd no.	In ethanol $\lambda_{\max}/nm$ ( $\in/m^2 \text{ mol}^{-1}$ )	In glacial acetic acid $\lambda_{max}/nm$ ( $\in/m^2 \text{ mol}^{-1}$ )			
1	Sh. 325(490), 283(2130)	Sh. 302(1420), 290(1920)			
2	334(1500), 285(1500)	Sh. 314(970), 292(3270)			
3	327(2000), 288(2200)	_			
4	Sh. 319(850), 282(1800)	_			
5	286(1100)	288(1630)			
6	Sh. 324(870), 284(1950)	Sh. 298(1670), 288(2070)			
7	358(1350), 270(1780)	346(2300), 294(2000)			
8	Sh. 330(830), 285(3600)	Sh. 295(1870), 286(2180)			
9	Sh. 328(330), 285(2050)	Sh. 298(1200), 289(2100)			

Sh. Shoulder.



Fig. 1. The variation of molar conductivities with molar concentrations of tyrosine and phenylalanine in ethanol at 298 K.

shows that: (i) The molar conductivities of these compounds,  $0.1-0.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  at concentrations of  $(0.78-13.8) \times 10^{-4}$  mol dm<sup>-3</sup>, are smaller by about 23 times than that of tyrosine and phenylalanine, (ii) the molar conductivities increase rapidly with increasing dilution and (iii) the dielectric constant of the solvent has no effect on the results (Fig. 4). Due to (i) and (ii) we can consider that compounds 1, 2, 6, 7 and 8 are weak electrolytes and weaker than tyrosine and phenylalanine. The variation of molar conductivities with molar concentrations in ethanol and DMSO of compound 5 (Fig. 5) seems to be unusual since the molar conductivities increase slightly with increasing concentration, however the values  $0.25-0.45 \ \Omega^{-1} \ \mathrm{cm}^2 \ \mathrm{mol}^{-1}$ are still much smaller than those of tyrosine and phenylalanine. Based on these results, it can be concluded that our Schiff bases are less ionized than aminoacids. They may be existed in two forms, the ionized species I of Scheme 3 (zwitterion) in an appreciable amount and, predominately existed in the free (unionized) form.

This study is in agreement with the X-ray data, FTIR and CPMAS spectroscopy of Schiff base derived of 2,2'-dihydroxybiphenyl-3-carbaldehyde with *n*-butylamine (which contains less acidic group than carboxylic group, i.e. phenolic OH) in which they obtained two symmetry-independent zwitterions in unit cell [25]. Also the NMR spectra of



Fig. 2. The variation of molar conductivities with molar concentrations of compounds **1**, **2** and **6** in ethanol at 298 K.



Fig. 3. The variation of molar conductivities with molar concentrations of compound **8** in DMSO at 298 K.

equimolar mixtures of some Schiff bases and substituted acetic acids were studied in relation to the nature of the state of protonation indicate that, in low polarity solvents, weak acids can only partially protonate the Schiff base, while in a more polar medium the protonation percentages are higher [26].

## 3.4. Melting points and pH values

According to the IR, UV–Visible and molar conductivities data on our carboxylated Schiff bases, we have decided to compare the followings: (i) the melting points of



Fig. 4. The variation of molar conductivities with molar concentrations of compound **7** in ethanol and DMSO at 298 K.



Fig. 5. The variation of molar conductivities with molar concentrations of compound **5** in ethanol and DMSO at 298 K.

Table 4

Our Compd no.	m.p./°C decomp.	pH <sup>a</sup> Value	Related Schiff base no.	m.p. <sup>b</sup> /°C	α-amino-acid name	m.p/°C <sup>c</sup> decomp.	pH <sup>a</sup> value
1	197	$5.80 \pm 0.05$	10	Liquid	Glycine	232	
2	163	$5.72 \pm 0.02$	11	86	Alanine	297	
3	197	$5.72 \pm 0.11$	12	Liquid	Histidine	277	
4	187	$5.78 \pm 0.04$	13	Liquid	Arginine	238	
5	131	$5.92 \pm 0.01$	14	Liquid	Cystein	260	
6	269	$5.99 \pm 0.05$	15	161	Tryosine	318	$6.57 \pm 0.02$
7	267	$6.22 \pm 0.08$	16	91	Phenyl-alanine	320	$6.57 \pm 0.02$
8	293	$5.98 \pm 0.04$	17	79			
9	185	$5.96 \pm 0.11$	18	51			

Comparison between melting points and pH values of compounds 1–9 and of some  $\alpha$ -aminoacids and related Schiff bases. (pH in ethanol at fixed concentrations 0.001 mol dm<sup>-3</sup>)

Compounds **10**, **11**, **12** and **13** are thiophene-2-, pyrrole-2-, furan-2- and thiophene-3-carboxylideneaniline, respectively. Compound **14** is *n*-butylidene-aniline. Compound **15** is *p*-chlorobenzylidene-*p*-*N*,*N*-dimethyl-aminoaniline. Compound **16** and **17** are *p*-nitrobenzylidene and *p*-*N*,*N*-dimethylamino-benzylideneaniline, respectively. Compound **18** is benzylideneaniline.

<sup>a</sup> Each value is the average of at least two readings.

<sup>b</sup> Values taken from Refs. [9,10,23].

<sup>c</sup> Values taken from Ref. [27].

our Schiff bases with those analog which have not containing COOH group in their structures, (ii) to compare their melting points with the melting points of some  $\alpha$ -aminoacids and, (iii) their pH values in ethanolic solutions with the pH values of two aminoacids in the same solvent and concentration  $(0.001 \text{ mol dm}^{-3})$ . Table 4 represents these data, three important arguments can be observed firstly, the melting points of compounds 1–9 are much higher than those of their analogs, which contain no COOH group in their structures, and this means that the chemical structures between them are entirely different. Secondly, the melting points of compounds 1–9 are comparable with those of *p*-*N*,*N*-dimethylaminobenzylideneanilines mono-acid salts [1-4] to some extent with the melting points of  $\alpha$ -aminoacids, all are high and decompose without melting (Table 4) which means that compounds 1-9 may have structures of an ionic character similar to that of  $\alpha$ -aminoacids (Scheme 3). Thirdly, the pH values of their ethanolic solutions are close to the pH values of the ethanolic solutions of phenylalanine and tyrosine (Table 4) but they are slightly acidic, this is probably because the proton transfer from COOH to the azomethine group is not complete. The melting points and pH data represent a further support to our suggestion from being compounds 1–9 as a mixture of free and ionized forms, where the former is predominant.

### 4. Conclusion

The main purpose of this study is concerns to investigate the molecular structure and to allege the prototropic equilibrium between some *N*-aryl imines possessing a carboxyl substitutent and their zwitterionic iminium tautomers. The postulate is based on the assignment of IR, UV–Visible spectral absorptions and molar conductivities that provides a good evidence for the interpretations of postulated tautomeric equilibrium. The strong absorption band in IR spectra at  $1670-1690 \text{ cm}^{-1}$  are assigned to NH bend in the iminium tatuomer which is not obtained in any Schiff bases not containing NH or NH<sub>2</sub> group in their structures. In addition to other two absorption bands in the region of  $550-530 \text{ cm}^{-1}$  for torsinol oscillation N–H and  $3300-2300 \text{ cm}^{-1}$ , which is characteristic of the quaternary ammonium salts.

The absorption band at 270–288 nm in the electronic spectra of all compounds with nearly same intensity suggested the formation of the same moiety. Thus, this transition is due to the iminium tatuomer of the carboxylated anion, which is red-shifted to 286–294 nm in the presences of glacial acetic acid due to the protonation of the carboxylated anion.

Based on the conductivity measurements it is concluded that the carboxylated Schiff bases are less ionized than aminoacids and it may existed in two forms, the ionized form (zwitterion) and the free unionized form. The latter form is predominately existed. This is further consolidating our suggestion of the existence of both free and ionized forms. It is known that amino acids are zwitterionic compounds both in the solid and in solution. In solution, the zwitterion is in equilibrium with both its conjugated base and its conjugated acid and the position of equilibrium depends on the acidity of the medium. On comparing our carboxylated Schiff bases with amino\ acids we can further extended our support.

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