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^{1}H NMR, ^{13}C NMR and mass spectral studies of some Schiff bases derived from 3-amino-1,2,4-triazole

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ABSTRACT

Heterocyclic Schiff bases derived from 3-amino-1,2,4-triazole and different substituted aromatic aldehydes are prepared and subjected to ^{1}H NMR, ^{13}C NMR and mass spectral analyses. ^{1}H NMR spectra in DMSO exhibit a sharp singlet within the 9.35–8.90 ppm region which corresponds to the azomethine proton. The position of this signal is largely dependent on the nature of the substituents on the benzal moiety. It is observed that the shape, position and the integration value of the signal of the aromatic proton of the triazole ring (^{5}C) are clearly affected by the rate of exchange, relaxation time, concentration of solution as well as the solvent used. ^{13}C NMR is taken as substantial support for the results reached from ^{1}H NMR studies. The mass spectral results are taken as a tool to confirm the structure of the investigated compounds. The base peak (100%), mostly the M-1 peak, indicates the facile loss of hydrogen radical. The fragmentation pattern of the unsubstituted Schiff base is taken as the general scheme. Differences in the other schemes result from the effect of the electronegativity of the substituents attached to the aromatic ring.

1. Introduction

3-Amino-1,2,4-triazole has been reported as being a carcinogenic reagent, but its ring has shown a well known anti-microbial effect. It has been proved that the incorporation of this molecule into the biologically active azomethine linkage (–CH=N–) produces compounds with high pharmacological activity [1]. Heterocyclic Schiff bases of 2-aminobenzothiazole, benzoxazol, thiazole and triazole were prepared and characterized by their melting points, elemental analysis, IR, UV and NMR spectra [2]. It has been proven that they all have a planar configuration and an extended conjugation. ^{1}H and ^{13}C NMR study and AMI calculations of some azobenzenes and N-benzylideneanilines have been studied [3]. A correlation between NMR chemical shifts and the Hammet σ-constants of substituents and the resonance mechanism of transferring the substituents were found to dominate. ^{13}C and ^{17}O NMR spectra were reported for three series of Schiff bases: 2-(aminomethylene)-cyclohexanone (1), salicydeneamine (2) and N-[(2-hydroxy-1-naphthalenyl) methylene] amine (3) [4]. The data showed that Schiff bases (1) exist in keto enamine form, (2) in enol imine form and (3) as an equilibrium mixture of both forms. The tautomeric equilibria were found to be shifted towards the enol imine form in non-polar solvents and with increase in temperature. Some new liquid crystalline 2,5-disubstituted 1,3,4-thiadiazole derivatives incorporating a central group (–CH=N–) have been synthesized [5]. Their structures have been characterized with elemental analysis, IR, super ^{1}H NMR and MS, and their properties were determined using DSC and texture. Recently, new Schiff base hydrazones bearing 3-(4-pyridine)-5-mercapto-1,2,4-triazole were prepared and subjected to biological and computational studies [6].

Microwave-assisted synthesis, characterization and theoretical calculations of the first example of free and metallophthalocyanines from salen type, Schiff base, derivative bearing thiophen and triazole rings were studied [7]. The newly prepared compounds have been characterized by elemental analyses, IR, ^{1}H NMR, MS and UV–vis spectroscopy.

A series of metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized with newly biologically active ligands prepared by the condensation of 4-amino-5-mercapto-3-methyl-S-triazole, 4-amino-3-ethyl-5-mercapto-S-triazole with 2-acetylpyridine. The structures of the complexes have been proposed by elemental analysis, spectroscopic data i.e. IR, ^{1}H NMR, electronic and magnetic measurements. Antibacterial activities are also reported [8]. Synthesis and spectral studies of 5-[(1,2,4-triazzolyl-azo]-2,4-dihydrxybenzaldehyde (TA) and its Schiff base with 1,3-diaminopropane (TAAP) and 1,6-diaminohexane (TAAH) were reported [9]. The authors discussed the analytical application of the prepared compounds for spectrophotometric microdetermination of cobalt (II). Some radiochemical studies were also presented.

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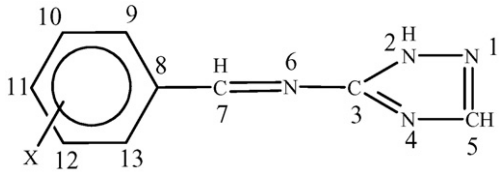
Table 1
Physical properties and elemental analysis of the investigated Schiff bases.

Compound	X	M.P. (°C)	Color	Analysis Calc. (Found)		
				%C	%H	%N
a	H	194	White	62.78 (62.50)	4.64 (4.40)	32.54 (32.11)
b	p-CH_3	190	White	64.43 (64.30)	5.36 (5.20)	30.07 (29.98)
c	p-OCH_3	195	Pale yellow	59.38 (59.40)	4.94 (5.20)	27.71 (28.03)
d	o-OH	178	Yellow	57.35 (56.70)	4.24 (4.20)	29.73 (27.00)
e	p-OH	193	Yellow	57.35 (57.50)	4.24 (4.50)	29.73 (29.52)
f	p-$N(CH_3)_2$	235	Bright yellow	61.38 (61.25)	6.09 (6.19)	32.53 (32.15)
g	p-NO_2	238	Orange yellow	49.77 (51.50)	3.22 (4.50)	32.26 (31.20)
h	p-Cl	205	Pale yellow	52.27 (53.00)	3.38 (3.70)	27.10 (27.51)

The present article deals with the synthesis and spectral characterization of some 1,2,4-triazole Schiff bases using ^{1}H NMR, ^{13}C NMR, EI-MS, CI-MS.

2. Experimental

All chemicals used were of the highest purity grade purchased from either Fluka (Germany) or Aldrich (USA). The heterocyclic Schiff Bases under study were prepared by the reflux of equimolar amounts of 3-amino-1,2,4-triazole and the appropriate aromatic aldehyde in 100 ml absolute ethanol for about 4 h. The products obtained were cooled, filtered off and crystallized from absolute ethanol. The prepared 3-amino-1,2,4-triazole Schiff bases have the following structural formulae:



where: x = H (a), p-CH_3 (b), p-OCH_3 (c), o-OH (d), p-OH (e), p-NMe_2 (f), p-NO_2 (g), and p-Cl (h).

The physical properties and the elemental analysis results of the prepared Schiff bases are given in Table 1. The ^{1}H NMR spectra were recorded on one of the following Bruker spectrometers: a WP-200 or an AC-200 (200 MHz for proton), an AM-300 (300 MHz

Table 2
^{1}H NMR chemical shift values (δ) of 3-amino-1,2,4-triazole Schiff bases (Ic-Ih) in different solvents.

Compound	Solvent	δ (ppm)							
		H^2	H^5	H^7	H^9	H^{13}	H^{10}	H^{12}	H^{11}
c	DMSO	13.9	8.49	9.13	7.97	7.93	7.11	7.06	3.84
	DMSO + D_2O	–	8.24	9.13	7.95	7.93	7.12	7.08	3.83
	CD_3CN	–	–	9.17	7.95	7.92	7.05	7.03	.85
	$CDCl_3$	–	–	9.24	7.95	7.91	7.03	6.99	3.87
	CD_3OD	–	8.17	9.08	7.96	7.93	7.08	7.04	3.87
	$(CD_3)CO$	–	And	5.29*	7.32*	7.29*	6.89*	6.86*	3.77*
		12.98	8.38	9.19	8.95	7.95	7.51	7.06	3.89
d	DMSO	14.11	.8.5	9.42	7.79	7.44	6.96	12.53	6.96
	DMSO + D_2O	–	.8.40	9.40	7.76	7.44	6.98	–	6.98
	CD_3OD	–	8.32	9.32	7.59	7.43	6.98	–	6.98
	$CDCl_3$	12.35	8.10	9.36	7.45	7.45	6.99	10.95	6.90
e	DMSO	13.95	8.47	9.07	7.84	7.81	6.90	6.88	10.43
		13.85							10.22
	DMSO + D_2O	–	8.43	9.07	7.85	7.83	6.91	6.88	–
	CD_3OD	–	8.17	9.05	7.88	7.83	6.93	6.88	–
			And	4.91*	7.33*	7.29*	6.82*	6.77*	–
f	DMSO	13.76	8.40	8.99	7.79	7.77	6.81	6.77	3.03
	CD_3OD	–	Broad	8.94	7.84	7.80	6.81	6.78	3.08
	$CDCl_3$	11.02	7.90	9.17	7.88	7.84	6.76	6.72	3.10
g	DMSO	14.18	8.58	9.35	8.27	8.23	8.38	8.34	–
	DMSO + D_2O	–	8.42	9.29	8.36	8.31	8.24	8.20	–
h	DMSO	14.04	8.53	9.21	8.04	7.99	7.63	7.58	–
	DMSO + D_2O	–	8.35	9.22	8.05	7.96	7.64	7.59	–
	CD_3OD	–	8.35	9.16	8.01	7.96	7.56	7.51	–
		–	And	5.82*	7.49*	7.48*	7.45*	7.34*	

X = p-OMe (c), o-OH (d), p-OH (e), p-NMe_2 (f), p-NO_2 (g), p-Cl (h).
* The signals of the hydrolysis product in presence of D_2O.

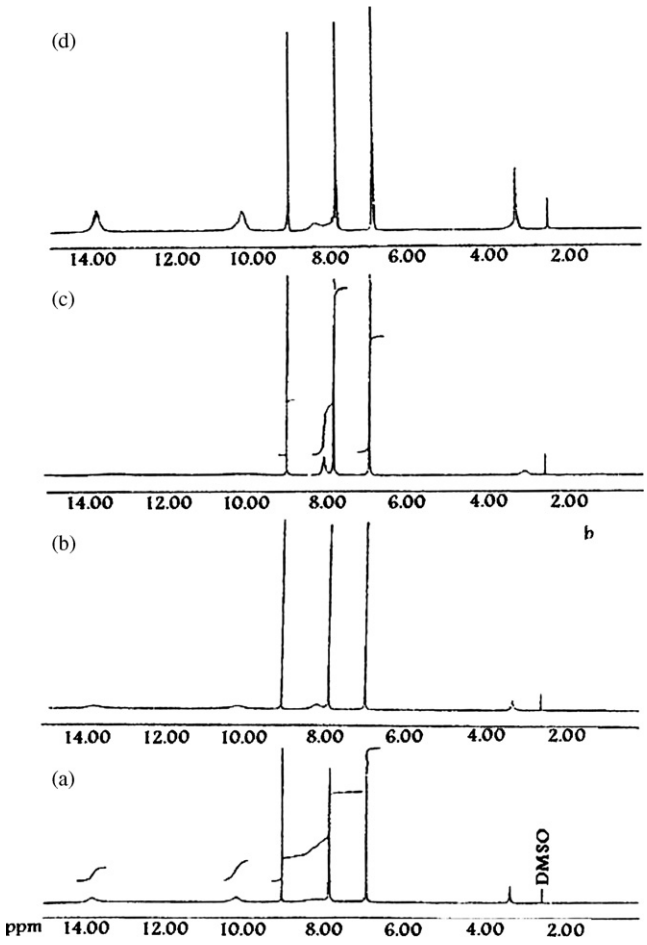


Fig. 1. ^{1}H NMR spectra of Ie in DMSO at different temperature 312 K (a), 315 K (b), 372 K (c) and 298 K (d).

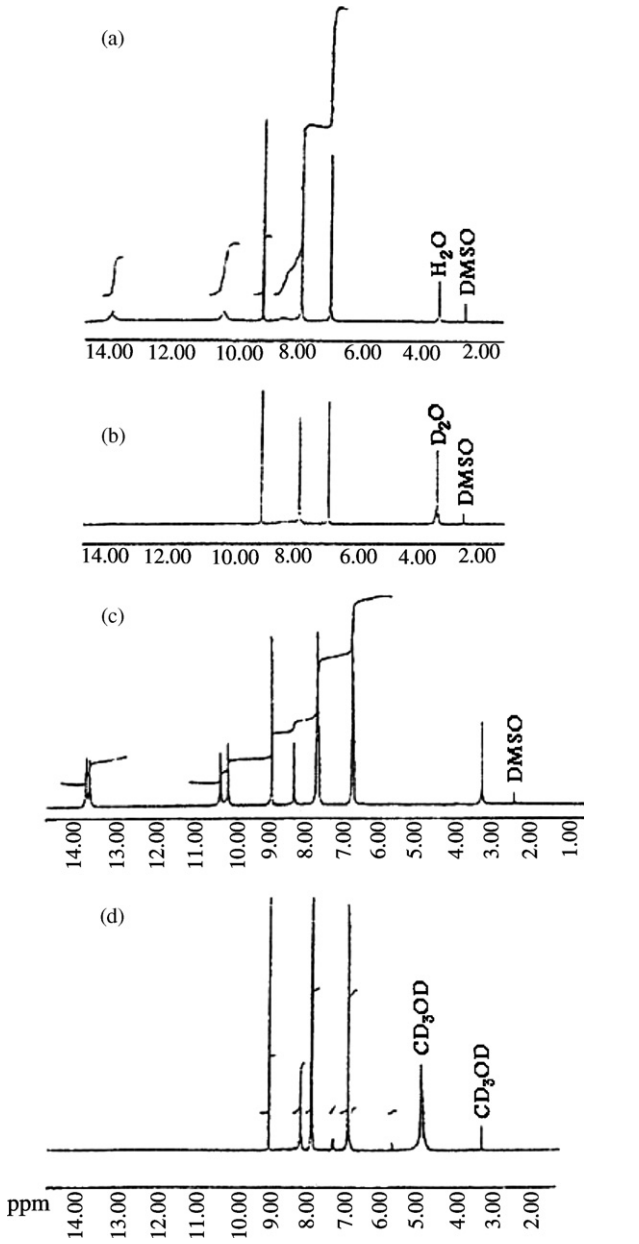


Fig. 2. ^{1}NMR spectra of Ie in DMSO (a), DMSO + H_2O (b), DMSO conc. (c), and CD_3OD (d).

for proton), or a WP-360 (360 MHz for proton). ^{13}C NMR spectra were obtained using a high-power broad-band proton decoupling. The probe was usually at ambient temperature. All low temperature experiments were recorded on the AM-300 instrument. All the spectra are reported in ppm with respect to tetramethylsilane (TMS, $\delta = 0.00$ ppm), and were referenced vs TMS or the appropriate solvent peak. All deuterated solvents (CD_3CN, DMSO, CD_3OD) were purchased from Aldrich in sealed ampoules that were opened immediately prior to the experiment.

Mass spectra were recorded with one of the following Kratos double-focusing instruments at the Penn State University (USA) mass spectrometry facility: a MS-950 mass spectrometer in the electron-impact mode (reported as EI-MS), and a MS-25 mass spectrometer for chemical ionization (reported as CI-MS).

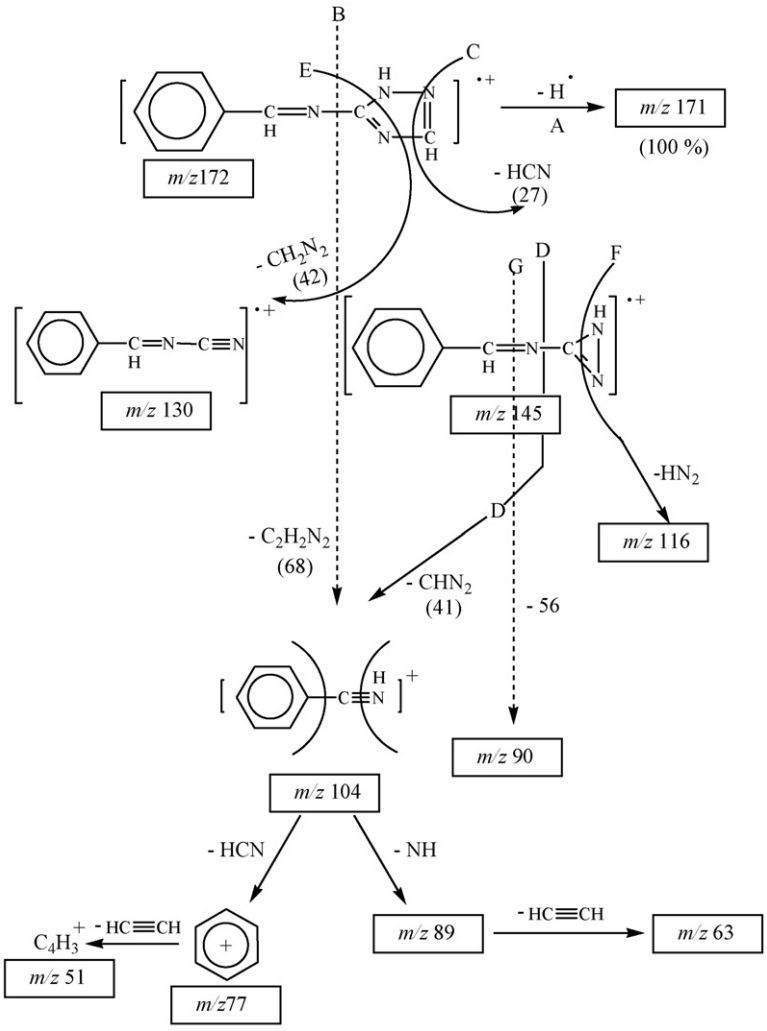
3. Results and discussion

3.1. ^{1}H NMR and ^{13}C NMR spectral studies

The ^{1}H NMR main signals-chemical shifts of the investigated heterocyclic Schiff bases (Ic-Ih) recorded in DMSO are given in Table 2. In each case, D_2O was then added to check for the hydrolysable protons. The chemical shifts of the different types of protons of the investigated Schiff bases in different solvents (whenever possible) are reported in Table 2.

A sharp singlet is observed within the 9.36–8.90 ppm region of spectrum, which corresponds to the azomethine proton. It is remarkable that the downfield chemical shift ($\delta = 9.35$ ppm) corresponds to the azomethine proton of the p-NO_2 derivative (Ig), which has the highest electron affinity; while the upperfield value ($\delta = 8.9$ ppm) is of the p-NMe_2 substituent (If) with the highest donating power. Thus, it can be concluded that the position of the azomethine proton is strongly affected by the electronegative character of the substituents on the benzal ring. As the electron-affinity of the substituent increases, the azomethine proton is shifted downfield due to increased deshielding effect.

The chemical shift of the aromatic proton of the triazole ring (C^5) is observed within the 8.59–8.17 ppm region of spectrum. The shape, the position, and the integration value of this signal are clearly affected by the rate of exchange; the relaxation time, the concentration of the solution, as well as the solvent used. In most cases (especially when using DMSO), the signal corresponding to this proton appears as a broad peak with ~half its integration value; while the other half integration value is revealed by a peak at ~7.92–7.80 ppm. In most cases, this latter peak can hardly be distinguished from the aromatic protons of the benzal ring (H^9



Scheme 1. Fragmentation pattern of unsubstituted 1,2,4-triazole Schiff base (a).

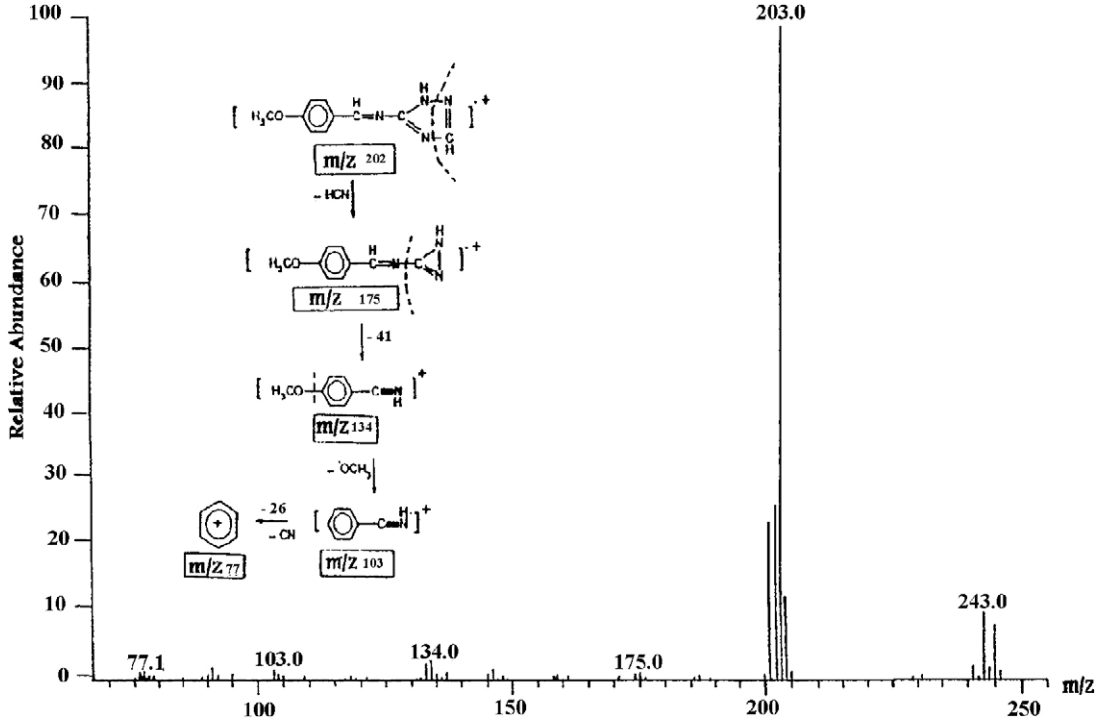
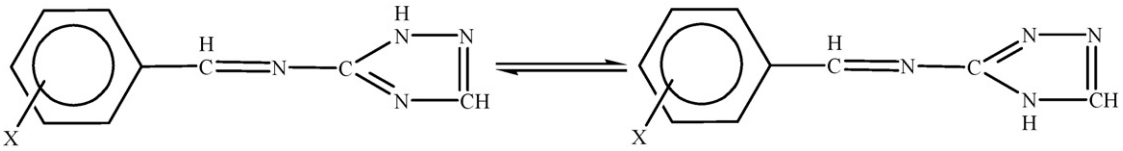


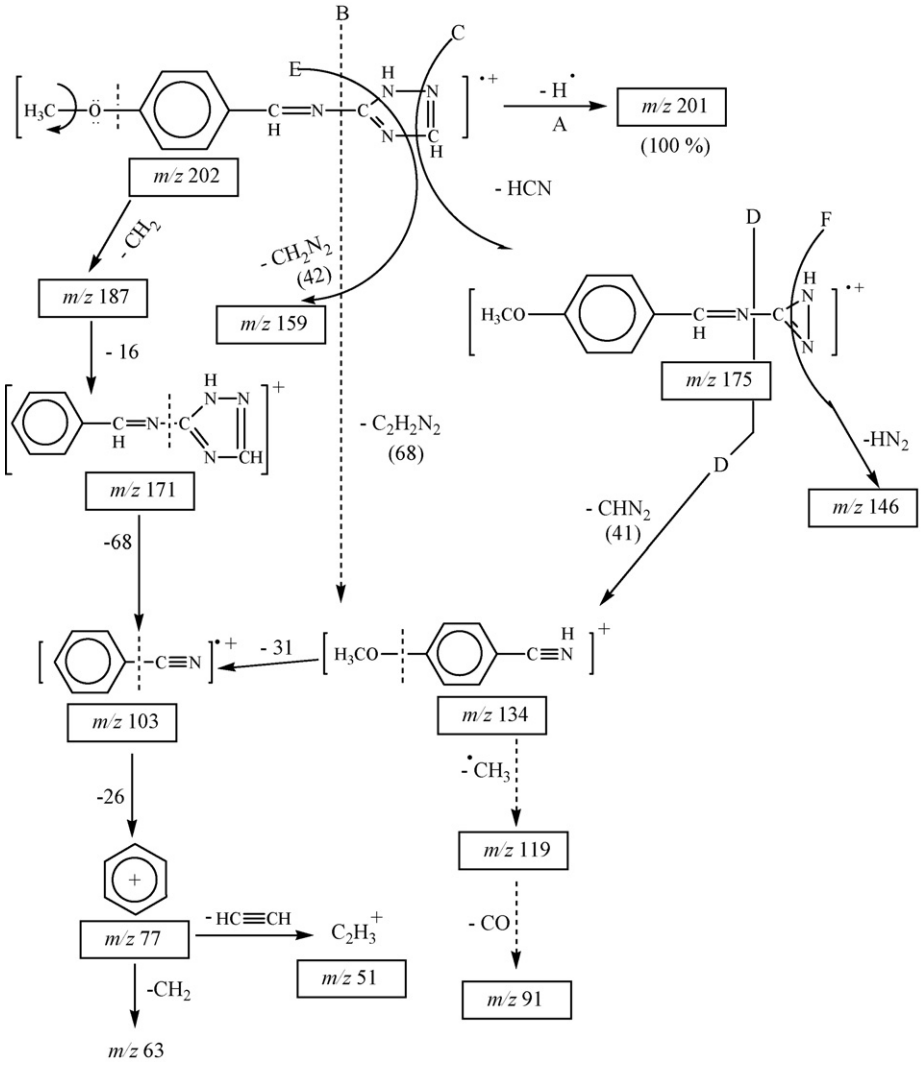
Fig. 3. CI-MS of Ic.

and H[13]). Accordingly, when this signal is merged into the doublet corresponding to those two protons, its integration is added to the value equal to the two aromatic protons. This phenomenon may be attributed to the presence of a rapid tautomeric equilibrium between the following two structures:



In CD_3OD or DMSO + H_2O, the latter peak is shifted upfield and appears as a sharp singlet with an integration of one proton at $\delta \sim 8.42$–8.17 ppm. This can be explained on the basis that, when the rate of exchange is low; the probe can see both tautomers and the observed peak is an average between both forms. However, when the rate of exchange is rapid (e.g. in presence of H_2O), only one tautomeric form prevails and can be detected. It can also be revealed from Table 2 that this signal is shifted to lower field values by strong electron-withdrawing substituents (p-NO_2, and p-Cl); and is shifted to higher fields with electron-donating substituents (p-NMe_2, p-OCH_3, and p-OH). Such observations indicate that the electronic effects of the substituents on the benzal ring are transferred to the heterocyclic ring through the azomethine linkage. It is worthwhile mentioning that, the mesomeric effects can only be transferred to the heterocyclic ring in planar molecules. This confirms the planarity of the investigated Schiff bases.

The NH peak of the triazole ring appears as a broad signal strongly shifted downfield ($\delta \sim 14.18$–11.02 ppm), indicating the possibility of its involvement in either an intramolecular or an intermolecular hydrogen bonding with the solvent. This is attributed to the fact that hydrogen bonding decreases the electron density around the proton, and thus moves the proton absorption to lower field [10]. The position of this signal is solvent dependent. The upfield shift ($\delta \sim 12.3$ ppm) observed in deuterated $CDCl_3$ (non-polar solvent) is in accordance with the presence of intermolecular hydrogen bonding. The appearance of the NH signal as a doublet in some spectra and as a singlet in others; is in agreement with the presence of a rapid tautomeric equilibrium which is dependent on the rate of exchange, as well as, the concentration of the solution. The disappearance of the NH signal from the ^1H NMR spectra recorded in D_2O or in CD_3OD confirms its ionizable



Scheme 2. Fragmentation pattern of p-methoxy 1,2,4-triazole Schiff base (c).

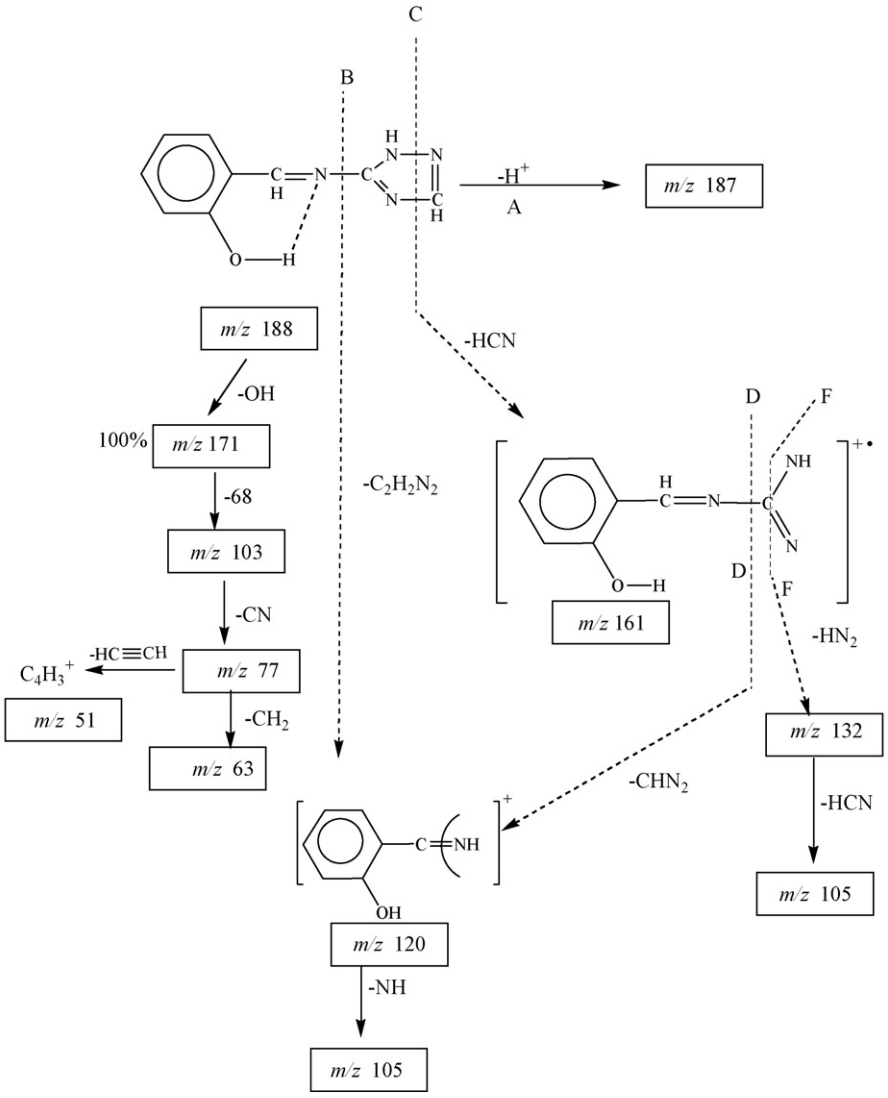
character. The relation between the chemical shift of this signal and the substituents on the benzal ring is the same as in the case of the azomethine proton (H^7) and the aromatic proton of the triazole ring (H^5). This fact further confirms the direct effect of the substituents of the benzal ring on the proton of the heterocyclic ring, giving a proof of the planarity of the molecule.

The four aromatic protons of the investigated Schiff bases appear as two doublets each with an integration value corresponding to two protons. These doublets appear at chemical shift values of 8.28–7.79 ppm corresponding to H^9 and H^{13}, and 8.38–6.77 ppm for H^{10} and H^{12}. It has to be mentioned that, when there is a large chemical shift difference between the two protons of each set, the peaks appear as clear distinct doublets with a quite wide separation, as in the case p-NMe_2 (Id). In the case where the four protons are nearly in the same chemical environment, there is only a small chemical shift difference and the peaks appear as almost a quartet as in the case of the p-NO_2 (Ie).

The ^{1}H NMR spectra of Ib (o-OH) and Ie (p-OH) in DMSO showed the hydroxyl proton as a broad signal at δ 12.53 ppm and δ 10.43 ppm, respectively; with an integration value corresponding to one proton in each case. In CD_3OD and D_2O, the peak corresponding to this proton disappears. The strong downfield shift of the hydroxyl proton signal in the case of the o-OH derivative, confirms its participation in intramolecular hydrogen bonding where it becomes more deshielded than in the case of the p-OH derivative. In the nonpolar deuterated chloroform ($CDCl_3$) solvent, the signal corresponding to the o-OH proton is shifted upfield (δ 10.95 ppm).

On raising the temperature of the DMSO solution of Ie (p-OH), from 312 K up to 372 K, the peaks at 13.90 ppm and 10.43 ppm; corresponding to the NH and OH protons, are slightly shifted upfield and started to broaden until they nearly disappeared and could not be picked (Fig. 1). Also, it is remarkable that the peak corresponding to the CH proton of the triazole ring (H^5) started to sharpen with increasing the temperature giving the correct integration of one proton; indicating the prevalence of one tautomer at high temperatures. On lowering the temperature, the disappeared peaks started to sharpen again, while the one corresponding to H^5 appeared broad again.

The ^{13}C NMR of the heterocyclic Schiff bases Ic-Ih in DMSO and CD_3OD are used as complementary technique for confirming the structure of the prepared Schiff bases. The ^{13}C NMR spectra of Ic is characterized by very sharp peaks at 114.48 and 131.16 ppm, corresponding to C^{10} and C^{12}, and C^9 and C^{13} of the aromatic ring, respectively. The downfield peaks at 163.39 and 162.71 ppm are attributed to C^7 and C^{11}, respectively. The downfield shift of these signals is due to the descreening effect of the electronega-



Scheme 3. Fragmentation pattern of unsubstituted 1,2,4-triazole Schiff base (a).

tive nitrogen and oxygen atoms, respectively. The signal observed at δ 127.99 ppm corresponds to C^8. The upfield peak at 55.46 ppm is attributed to the ^{13}C of the CH_3 group of the p-OCH_3 substituent. In the case of Ie, the spectrum showed the same sharp peaks with a close chemical shift values as those in the case of Ic.

The ^{13}C NMR spectrum of Id (o-OH), is also characterized by a number of sharp peaks which are in good agreement with the expected chemical shift values. The upfield peaks at 116.69, 119.48, and 119.18 ppm correspond to the aromatic carbon atoms C^{12}, C^{10}, and C^{11}, respectively. The downfield peaks at 164.85 and 134.16 ppm are assigned to C^9 and C^8. The peaks corresponding to C^3 and C^5 are broad and may or may not be easily picked.

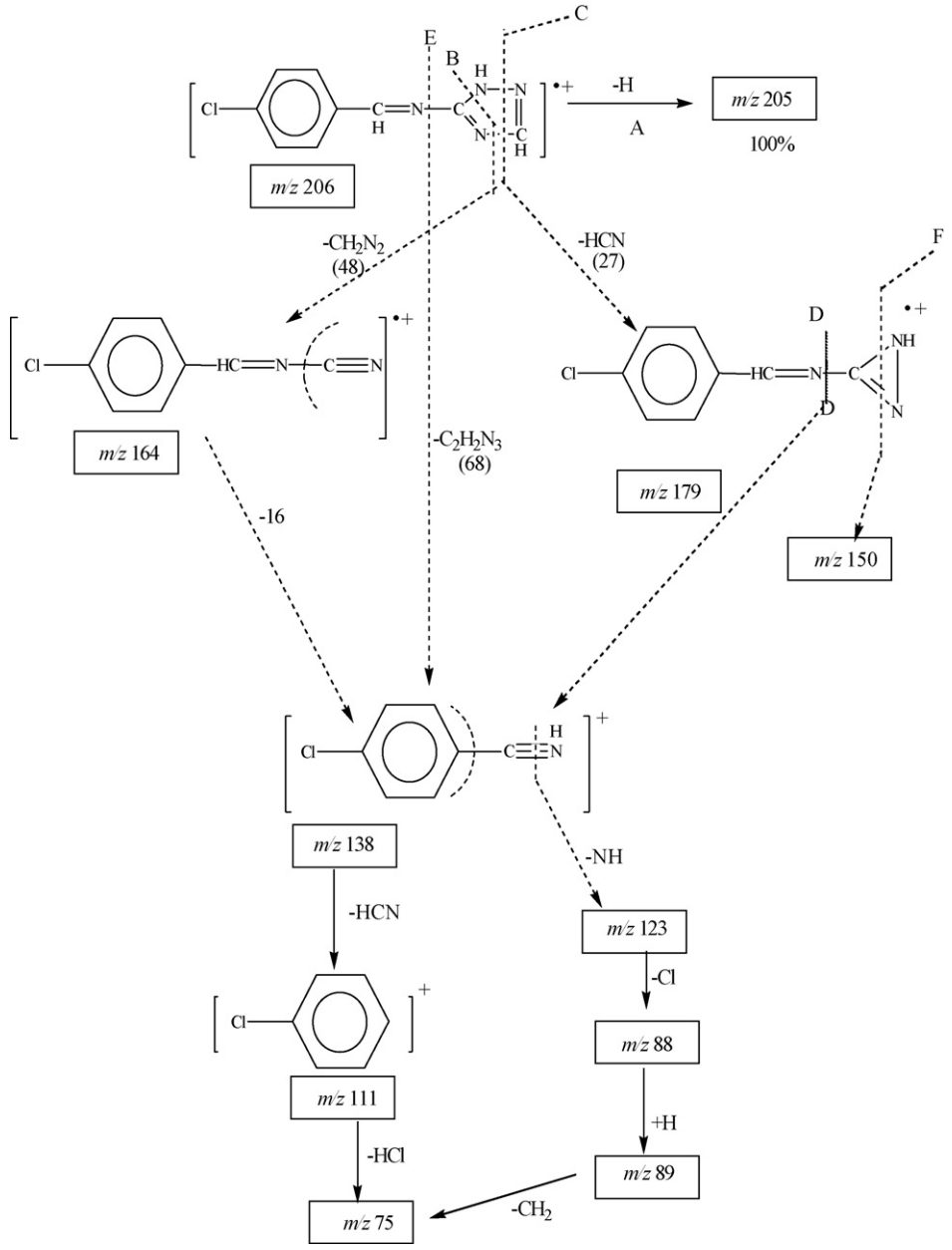
In the case of p-NMe_2, Schiff base derivative (If), the peaks at 39.62 and 111.48 ppm are the only observed sharp peaks in the spectrum. These peaks correspond to the methyl groups of the NMe_2 and to the aromatic carbon C^{10} and C^{12}, respectively. The rest of the signals appeared broad, but at the expected chemical shift values. The ^{13}C chemical shifts corresponding to the aromatic carbons C^{10} and C^{12} are significantly shifted downfield (δ 124.04 ppm). This is the new signal of the diminishing peak at 123.66 ppm, indicating the presence of two tautomeric forms of the compound in solution. The peak at 130.12 ppm is assigned to C^9 and C^{13}. The peaks at 128.50, 140.85, 144.78, 149.27 and 161.97 ppm correspond to C^8, C^3, C^5, C^{11}, and C^7, respectively.

The chemical shift of the four aromatic carbon atoms in case of Ih is very close indicating a very similar chemical environment.

The spectra of all investigated Schiff bases in CD_3OD revealed the same peaks as in the case of DMSO with a slight downfield shift.

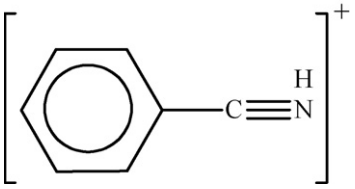
3.2. Mass spectral studies

The fragmentation pattern of the unsubstituted Schiff base (Ia) is taken as a general scheme showing the main fragmentation paths involved (Scheme 1). Differences of fragmentations patterns of Schiff bases Ib-Ih is attributed to the effect of the electronegativity of the substituents attached to the aromatic ring. The mass



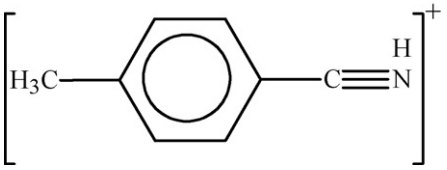
Scheme 4. Fragmentation pattern of p-chloro 1,2,4-triazole Schiff base (c).

spectral pattern of Ia (Fig. 2) shows a strong molecular ion peak (*m/z* 172, 22.5%) which loses a hydrogen radical (path (A)) to give the base peak at M-1 (*m/z* 171, 100%). The loss of a neutral molecule of HCN (path (C), Scheme 1) through break of ^{4}N–^{5}C and ^{1}N–^{2}N bonds is a general feature of the prepared Schiff bases. This step gives the characteristic peak at *m/z* 145 (4%) and is usually followed by loss of HN_2 (path (F)) or CHN_2 (path (D)); giving the peaks at *m/z* 116 (6%) and 104 (11%), respectively. It is evident from Scheme 1 that cleavage at ^{6}N–^{3}C bond (path (B)) gives the predominant peak at *m/z* 104 through the loss of $C_2H_2N_3$ (*m/z* 68). This peak corresponds to the stable ion:



This ion then looses either NH or HCN giving the characteristic peaks at *m/z* 89 (9%) and *m/z* 77 (9%), respectively. These latter fragments are responsible of the prominent peaks at *m/z* 63 (6.5%) and 51 (6%), respectively; through loss of an acetylene molecule.

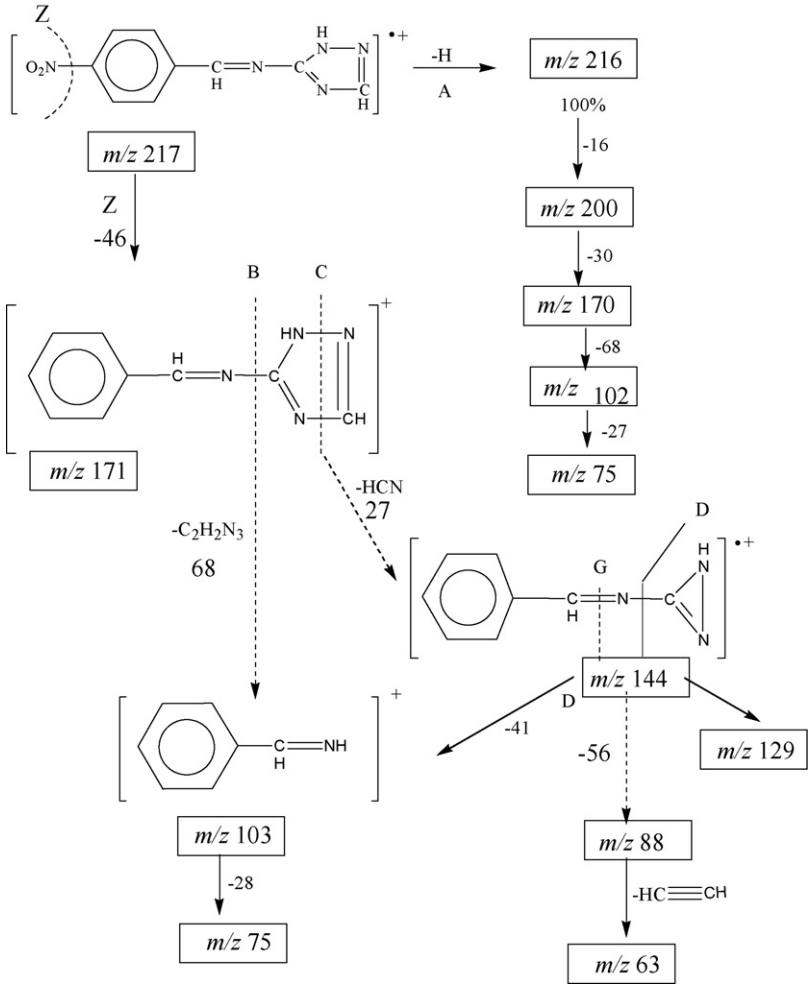
The EI-MS of Ib (p-CH_3) and Ic (p-OCH_3) show all the expected prominent peaks following the same previously proposed fragmentation paths, with but few exceptions related to the presence of CH_3 and OCH_3 attached to the benzal ring, respectively. In cases of Ib, the base peak is the M-1 (*m/z* 185, 100%) and the parent peak at M-68 (*m/z* 118, 12%) corresponds to the stable ion:



This ion gives the characteristic peaks at *m/z* 91 (9.7%) and 103 (6.5%) through loss HCN molecule or CH_3 radical, respectively. The peak at *m/z* 91 $(C_6H_5CH_2)^+$ is a tropylium rather than a benzylic cation (Scheme 2). The observed peak at *m/z* 65 (6%), results from the elimination of a neutral acetylene molecule from the tropylium cation. The loss of the CH_3 radical from the ionic fragment at *m/z* 118 (*m/z* 103, 6.5%) is more favorable than from the molecular ion at *m/z* 186 (*m/z* 171, 2.6%).

The EI-MS of the p-OCH_3 Schiff base derivative (Ic) shows all the expected prominent peaks following the same previously proposed fragmentation paths for Ia. As the case of Ib the loss of a CH_3 radical from the OCH_3 group is confirmed by the fragment at M-15 (*m/z* 187, 4.3%). The OCH_3 group either cleaves from the $M^{+\bullet}$ or from the prominent ion at *m/z* 134 giving the ions at *m/z* 171 (5%) or 103 (13%), respectively.

The CI-MS of Ic (Fig. 3) confirms its molecular formula, as well as, the proposed major fragmentation mechanism. In chemical ionization spectra, since the ions that are chemically produced do not have the high excess of energy associated with the ionization by EI,



Scheme 5. Fragmentation pattern of p-nitro 1,2,4-triazole Schiff base (g).

they undergo less fragmentation. Fig. 3 shows the quasi-molecular ion MH^+ (*m*/*z* 203, 100%) as the base peak and confirms the ease loss of the H^+ by the intense peaks at *m*/*z* 202 and 201. The peaks at *m*/*z* 243 and 245 correspond to M^++$C_3H_5^+$ (M+41) and M^++$C_3H_7^+$ (M+43), respectively. The radicals C_3H_5 and C_3H_7 belong to the isobutane gas used in the CI-MS. The other peaks corresponding to *m*/*z* 75, 134, 103 and 77 are of just low intensities.

In the case of the p-OH Schiff base derivative, Ie, the loss of the OH group is not a favorable step (*m*/*z* 171, 1.63%). Thus it follows the general fragmentation patter as for the unsubstituted Schiff base. On the contrary to the p-OH Schiff base; the o-OH compound (Id), is very easily cleaved from the ring giving the most stable ion at *m*/*z* 171, 100%. This step is followed by several available cleavages at *m*/*z* 104 (5%), 77 (18%), 63 (25%) and 51 (15%); as in the case of Ia. The peaks at *m*/*z* 120 (8%), 161 (1.4%) and 132 (5%) confirm the proposed fragmentation paths (B, C, and C, F), Scheme 3.

It is apparent from the spectral presentation of the p-Cl Schiff base derivative (Ih), that there is one chlorine atom in the molecule, as the intensity of the M+2 peak (*m*/*z* 208, 8.4%) is almost 1/3 the intensity of the parent peak (*m*/*z* 206, 26.4%). This is also confirmed by the relative abundance of the base peak (*m*/*z* 205, 100%) which corresponds to M-1 and the peak at *m*/*z* 207, 35% (noting that part of this ratio belongs to the ^{13}C isotope contribution of the parent peak). The intensity of the fragment peak at *m*/*z* 181 (2%) is about 1/3 the intensity of the fragment formed through loss of HCN molecule (path (C), Scheme 4) at *m*/*z* 179 (6%). These peaks correspond to fragments containing one chlorine atom each. This fact is also confirmed for the ions producing the peaks at M-68 (4.3%) and 125 (1.9%); and at *m*/*z* 111 (4.5%) and 113 (1.9%). The fragment at M-Cl (*m*/*z* 171, 2.2%) has no M+2 peak, confirming the absence of chlorine. Also, the fragments at *m*/*z* 89 (5.7%) and *m*/*z* 75 (5.8%) has no M+2 (Scheme 4).

In the case of the p-NO_2 Schiff base derivative, Ig, the major step in the fragmentation pattern is the loss of the NO_2 radical from the molecular ion (M-46). This step may take place through loss of an oxygen radical from the M-1 ion (*m*/*z* 200, 6.6%), followed by loss of a neutral NO molecule giving the prominent peak at *m*/*z* 170, 41%. The diagnostic peak at *m*/*z* 30 (13%), confirms the loss of the NO^+ ion which is a characteristic feature of the nitro compounds [10]. Also, the peak at *m*/*z* 46 (4%) corresponds to NO_2^+. The observed additional peaks resemble those resulting from the molecular ion of the unsubstituted Schiff base. The presence of the fragments bearing NO_2 is less favored because of its electron-withdrawal effect which destabilizes the positively charged fragments (Scheme 5).

On the contrary to the p-NO_2 and the o-OH Schiff bases, the p-NMe_2 group is very difficulty cleaved from the benzene ring. In fact the most stable fragments are those bearing the NMe_2 group; because of its high electron-donating power which stabilizes the positively charged ionic fragments. It is clear that the most stable fragment is the one at *m*/*z* 146 (54%), which corresponds to (Mp-1)—68.

4. Conclusion

^1H NMR spectra of the heterocyclic Schiff bases in DMSO show a sharp singlet within the 9.35–8.90 ppm region of the spectrum which corresponds to the azomethine proton. The position of this signal is found to be largely dependent on the electronegative character of the substituent on the benzal ring. As the electron-affinity of the substituent increases, the azomethine proton is shifted downfield due to increased deshielding effect. The shape, the position and the integration value of the signal of the aromatic proton of the triazole ring (C^5) ion appears to be affected by the rate of exchange, the relaxation time, the concentration of the solution, as well as the solvent used. The signal appears as a broad peak with ~half its integration value; while the other half integration value is revealed by a peak at ~7.92–7.80 ppm. This phenomenon is attributed to the presence of a rapid tautomeric equilibrium between two structures. The ^{13}C NMR measurements are used as complementary tool for confirming the structure of the prepared Schiff bases.

The mass spectral studies are used to give more insight on the structure of the investigated Schiff bases. A general fragmentation pattern is proposed from which it is evident that primary cleavages occur at the hetero-carbon bond. The major cleavage pathways may take place through loss of a neutral HCN molecule, followed by elimination of either HN_2 or CHN_2, or through of $C_2H_2N_2$. It is also evident from the spectra that the base peak (100%) is, mostly, the M-1 peak, indicating the facile loss of hydrogen radical. The base peak for the o-OH Schiff base derivative is that corresponding to the M-OH.

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