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The Effect of *o*-Substituents on Mass Spectra of Schiff Bases Synthesized from Salicylaldehyde

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Abstract: 21 Schiff bases were prepared from orto, meta and para substituted hydroxy, metoxy, floro, chloro, bromo, iodo anilines, benzyl amines, 2-hydroxy benzyl amines and salicylaldehyde. The Schiff bases were ionized with 20-140 eV electrons using Direct Inlet to determine their mass fragments. In the cases where the substituents are in meta or para position and in the range of 20 to 140 eV, the molecular peaks were observed as the base peaks. The base peak in the spectra of the substances, in which the substituent close to the aniline side is in ortho position, was found to be the M-X (m/z=196) peak. M+HX peaks were also observed in the spectrum of the bromine substituted compound which is probably due to that the formed HBr attacked the molecule and was added to it.

Key words: *o*-effect, Schiff bases, salicylaldimine, Direct Inlet, HX addition.

Salisilaldehitten Sentezlenen Schiff Bazlarının Kütle Spektrumlarında Orto Substituentlerin Etkisi

Özet: Orto, meta ve para substitue, hidroksi, metoksi, floro, kloro, bromo, iyodo anilinler, benzil amin, 2-hidroksi benzil amin ve salisilaldehit kullanılarak 21 tane Schiff bazı hazırlandı. Bu Schiff bazları 20-140 eV'luk elektronlarla direkt iyonlaştırıldı ve kütle fragmantleri belirlendi. Tüm Schiff bazlarında 20-140 eV'luk elektronlarla iyonlaşmada moleküler pik temel pik olarak gözlendi, 20-140 eV'luk elektronlarla iyonlaştırılmış Schiff bazlarında fragmentasyonun çok düşük olduğu spektrumda tek güçlü pikin moleküler pik olduğu görüldü. Anilin tarafında orto pozisyonunda substituent bulunması durumunda, temel pik M-X (m/z=196) olarak gözlendi. Brom içeren bileşiklerde gözlenen M+HX piklerinin, oluşan HBr'nin moleküle katılması sonucunda ortaya çıktığı sonucuna varıldı.

Anahtar kelimeler: *o*-etkisi, Schiff bazı, salisilaldimin, Direk Inlet, HX katılması.

1. Introduction

Schiff bases are ligands frequently used in coordination chemistry. Although they have been used for a long time, characterization of Schiff bases by mass spectrometry (MS) are less than expected in the literature. In some studies, mass spectrums of Schiff bases and complexes were performed with Fast Atom Bombardment (FAB) and Electrospray ionization (ESI) methods that indicate the molecular ion peak, at recent times. In these studies, characterization of metal complexes of Schiff bases were reported [1-7]. A number of studies about Schiff bases and method were reported in between 1970 and 1991 [8-12]. There is not so much interpretation of investigation of Schiff bases and mass fragmentation with electron ionization mass spectrometry.

In this study, 21 analogous Schiff bases were synthesized and ionized by 20,40,60,70, 100 and 140 eV electrons using Direct Inlet. The obtained m/z values were evaluated. Molecular structures of prepared Schiff bases can be seen in Fig 1.

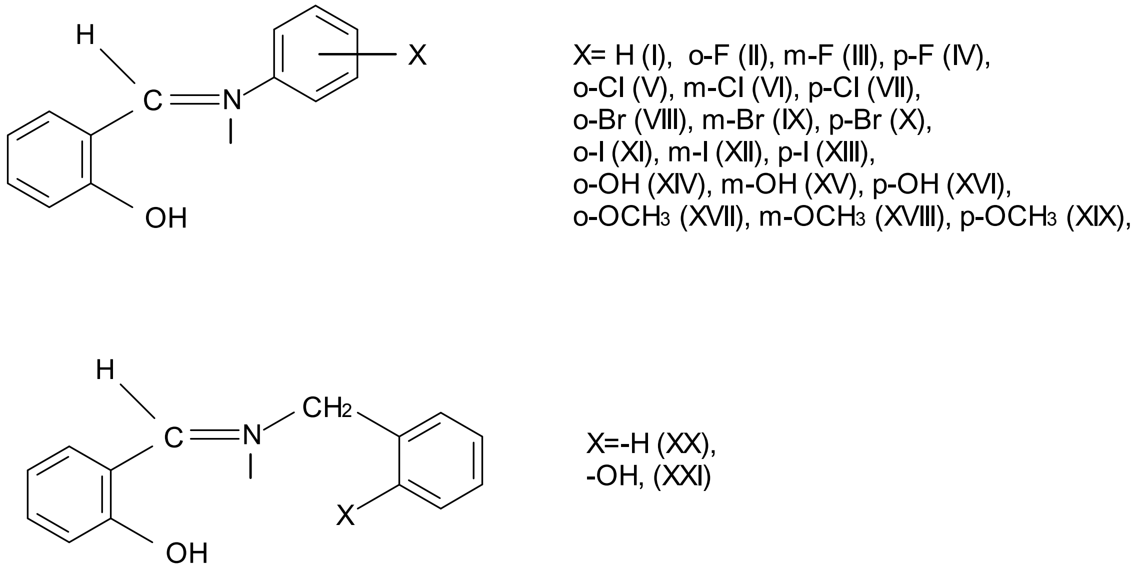

Figure 1. Molecular structure of prepared Schiff bases.

A study similar to this one carried out by A. Issa and coworkers can be found in the literature [13]. In that study, various Schiff bases were prepared from ortho, meta and para substituted benzaldehydes and amino-1,2,4-triazol. The fragments obtained by electron impact were determined [14]. In a study concerning the effect of *o*-substituents, reported in 1976, Schiff bases ranging between *o*-nitro benzaldehyde and ortho $-CH_3$, -Br, -OH and –COOH substituted anilines were used [15]. One study was performed on the ortho effect in fragmentation of some Schiff bases derived from amphetamine [16].

2. Materials and Methods

All Schiff bases were prepared according to literature with corresponding anilines and salicylaldehyde in EtOH medium [17-22]. 0.01 moles of aniline (or benzyl amine) was dissolved in 25 mL hot EtOH, to this solution, added was the 25 mL hot solution of salicylaldehyde. The final mixture was allowed to stand for 1-2 days. The precipitate was filtered and air dried. The Schiff bases were recrystallized in 25 mL MeOH and were characterized by IR and TG-DTA. In the study, IR spectra were recorded with Shimadzu Infinity ATR equipped with FTIR instrument and determined $\nu_{C=N}$ strechings. Melting points of Schiff bases were determined on the Schimadzu DTG-60H instrument. For the Mass spectra was employed Shimadzu 2010 Plus GCMS instrument. Schiff bases were injected to the instrument with Direct Inlet unit, GC column was not used.

3. Results and Discussion

Table 1. Obtained m/z values

Schiff Bases	Measured Melting Point Using DTA(°C)	Energy of ionization source (eV)	m/z
(I) o-HO-C_6H_4-CH=N-C_6H_4-H	51.74	20	197 (BP,MP), 180, 167,149,111,97,71
		70	197(BP,MP), 196 (M-1), 180,168, 120,77
		100	197(BP,MP), 196 (M-1), 180,168, 120,77, 51
		140	197(BP,MP), 196 (M-1), 180,168, 120,77, 51
(II) o-HO-C_6H_4-CH=N-C_6H_4-F (o)	68.55	20	215(BP,MP), 214(M-1),196, 120
		70	215(BP,MP), 214(M-1),196, 120
		100	215(BP,MP), 214(M-1),196, 120
		140	215(BP,MP), 214(M-1),196, 120
(III) o-HO-C_6H_4-CH=N-C_6H_4-F (m)	47.65	20	215(BP,MP), 214(M-1),198, 120
		70	215(BP,MP), 214(M-1),196, 120,95
		100	215(BP,MP), 214(M-1),196, 120,95
		140	215(BP,MP), 214(M-1),196, 120
(IV) o-HO-C_6H_4-CH=N-C_6H_4-F (p)	86.15	20	215(BP,MP), 214(M-1),198, 120,95
		70	215(BP,MP), 214(M-1),198, 120,95
		100	215(BP,MP), 214(M-1),198, 120,95
		140	215(BP,MP), 214(M-1),198, 120
(V) o-HO-C_6H_4-CH=N-C_6H_4-Cl (o)	83.96	20	231(MP), 214, 196 (BP),120,77
		70	231(MP), 214, 196 (BP),120,111,75
		100 ve 140	231(MP), 214, 196 (BP),120,111,77
(VI) o-HO-C_6H_4-CH=N-C_6H_4-Cl (m)	98.06	20	231(MP, BP), 214, 196 ,120,77
		70	231(MP, BP), 214, 196 ,167,120,75
		100	231(MP, BP), 214, 196 ,167,120,75
		140	231(MP, BP), 214, 196 ,167,120,75
(VII) o-HO-C_6H_4-CH=N-C_6H_4-Cl (p)	104.71	20	231(MP, BP), 196, 120, 77
		70	231(MP, BP),230(M-1) 196, 16, 120, 75
		100	231(MP, BP), 230(M-1) 196, 167, 120, 75
		140	231(MP, BP), 230(M-1) 196 , 167, 120, 75
(VIII) o-HO-C_6H_4-CH=N-C_6H_4-Br (o)	87.58	20	275(MP), 258, 196(BP), 167, 120,77
		70	355,275(MP), 258, 196(BP), 167, 120,77
		100	275(MP), 258, 196(BP), 167, 120,77
		140	275(MP), 258, 196 (BP), 167, 120,77
(IX) o-HO-C_6H_4-CH=N-C_6H_4-Br (m)	98.21	20	275(MP,BP), 258, 196 , 167, 120,77
		70	275(MP,BP), 258, 196 , 167, 120,77
		100	275(MP,BP), 258, 196 , 167, 120,77
		140	275(MP,BP), 258, 196 , 167, 120,77,51
(X) o-HO-C_6H_4-CH=N-C_6H_4-Br (p)	111.45	20	275(MP,BP), 258, 196 , 167, 120,77
		70	275(MP,BP), 258, 196 , 167, 120,76,75
		100	275(MP,BP), 258, 196 , 167, 120,77,75
		140	275(MP,BP), 258, 196 , 167, 120,77,75
(XI) o-HO-C_6H_4-CH=N-C_6H_4-I (o)	47.92	20	323(MP), 306, 196(BP),120,77
		70	323(MP), 306, 196(BP),120,167,77
		100	323(MP), 306, 196(BP),167,120,77
		140	323(MP), 306, 196(BP),120,167,77
(XII) o-HO-C_6H_4-CH=N-C_6H_4-I (m)	95.19	20	323(MP,BP), 306, 196, 120,77
		70	323(MP,BP), 306, 196,167, 120,76,51
		100	323(MP,BP), 306, 196,167, 120,76,75,51

		140	323(MP,BP), 306, 196,167, 120,76,75,51
(XIII) o-HO-C_6H_4-CH=N-C_6H_4-I (p)	132.40	20	323(MP,BP), 306, 196,167, 120,77
		70	449, 323(MP,BP), 306, 196,167, 120,76,51
		100	449, 323(MP,BP), 306, 196,167, 120,76
		140	449, 323(MP,BP), 306, 196,167, 120,76,51
(XIV) o-HO-C_6H_4-CH=N-C_6H_4-OH (o)	189.82	20	213(BP, MP),120,93
		70	213(BP, MP), 212(M-1)120,93
		100	213(MP), 212 (M-1),196, 120 (BP), 93,77,65
		140	213(MP), 212 (M-1),196, 120 (BP), 93
(XV) o-HO-C_6H_4-CH=N-C_6H_4-OH (m)	132.02	20	213(BP,MP), 196, 120
		70	213(BP,MP), 212 (M-1), 196,120
		100	213(BP,MP), 212 (M-1), 196,120
		140	213(BP,MP), 212 (M-1), 196,120
(XVI) o-HO-C_6H_4-CH=N-C_6H_4-OH (p)	141.78	20	213(BP,MP), 212 (M-1), 196
		70	213(BP,MP), 212 (M-1), 196,120, 93,77
		100	213(BP,MP), 212 (M-1), 196,120,93,65
		140	213(BP,MP), 212 (M-1), 196,120, 93,65
(XVII) o-HO-C_6H_4-CH=N-C_6H_4-OCH_3 (o)	59.95	20	227(BP,MP), 209, 196, 120,108
		70	227(BP,MP), 209, 196,180, 120,108,77,65,51
		100	227(BP,MP), 209, 196, 120,108,77,65,51
		140	227(BP,MP), 209, 196, 120,108
(XVIII) o-HO-C_6H_4-CH=N-C_6H_4-OCH_3 (m)	61.31	20	227(BP,MP), 211,196
		70	227(BP,MP), 211,196,120,77,64,51
		100	227(BP,MP), 211,196,120,77,64,51
		140	227(BP,MP), 211,196,120,77,64,51
(XIX)o-HO-C_6H_4-CH=N-C_6H_4-OCH_3 (p)	85.42	20	227(BP,MP), 212
		70	227(BP,MP), 212,120, 94,77,63,51
		100	227(BP,MP), 212,77,63,51
		140	227(BP,MP), 212
(XX) o-HO-C_6H_4-CH=N-$CH_2C_6H_5$	36.76	20	302, 211 (BP,MP),194,120,91
		70	302, 211 (MP),194,120,91 (BP),65
		100	302, 211 (MP),194,120,91 (BP),65
		140	302, 211 (MP),194,120,91 (BP),65
(XXI)o-HO-C_6H_4-CH=N-$CH_2C_6H_5$-OH (o)	179.91	20	227(BP,MP), 121, 107
		70	227(MP), 121(BP), 107, 93,77
		100	227(MP), 121(BP), 107, 93,77
		140	227(MP), 121(BP), 107, 93,77

MP: Molecular Peak BP: Base Peak

Obtained m/z values are given in Table 1. There is a powerful hydrogen bond between the OH group in the aldehyde side and the iminic nitrogen [23-26]. This hydrogen bond becomes more powerful, when there is ortho substituted in the aniline side [26]. Therefore this OH and the phenyl ring of aldehyde component must be approximately on the same plane [22]. There is possibility of free rotating between iminic group and aniline ring so; there is the collision possibility with substituents in the aniline side with OH group of salicylaldehyde. Formation of common peaks of aniline derivatives of Schiff Bases and unexpected peaks can be seen in Fig 2a. When *o*-substituents are OH,·F,·Cl,·Br and·I, the collision possibility with OH group of salicylaldehyde is higher. So these *o*-substituents are broken easier than meta or para substituents. Consequently, at *o*-substituents, the base peaks belonged to the M-X fragmentation and at meta or para substituents the base peaks were the molecular ones. Even then, in the cases where the substituents are OH or O-CH_3, molecular peaks again arise to be the base peaks. The presence of ortho OH and O-CH_3 substituents contribute to elimination of H_2O and CH_3OH but the base peaks did not belong to the corresponding molecules, (M-H_2O) and (M-CH_3-OH). It is very probable that these species are formed significantly harder than their halogen acid counterparts. The reason is that the OH or OCH_3 groups in the aniline side participated in the strong hydrogen bonding between (phenolic) O-H….N (iminic) in the aldehyde side [22-26]. A similar situation was observed in the study of Ref. 15. However the effect was not clearly seen since the aldehyde component used was ortho nitro benzaldehyde. In Schiff Base number XXI there is a –CH_2– bridge between the iminic nitrogen and the phenyl ring which forces the *o*-substituent OH to not participate in the hydrogen bonding. Besides, –CH_2– bridge prevents the collision of two OH groups decreasing the possibility of H_2O formation. Indeed, there was no M-H_2O peak in the mass spectra of this compound or if there was any, it was of insignificant relative intensity. Base peaks belonging to the Schiff bases number XX and XXI were at 121 and 91 because the group connected to the iminic nitrogen, tended to form benzyl carbenium. And because of the stability of benzyl radical or benzyl carbenium, these groups can add to the imine bond. This situation can be observed as a weak $[M+91]^+$ peak (m/z=302) in the mass spectrum of Schiff base XX (Fig 2b).

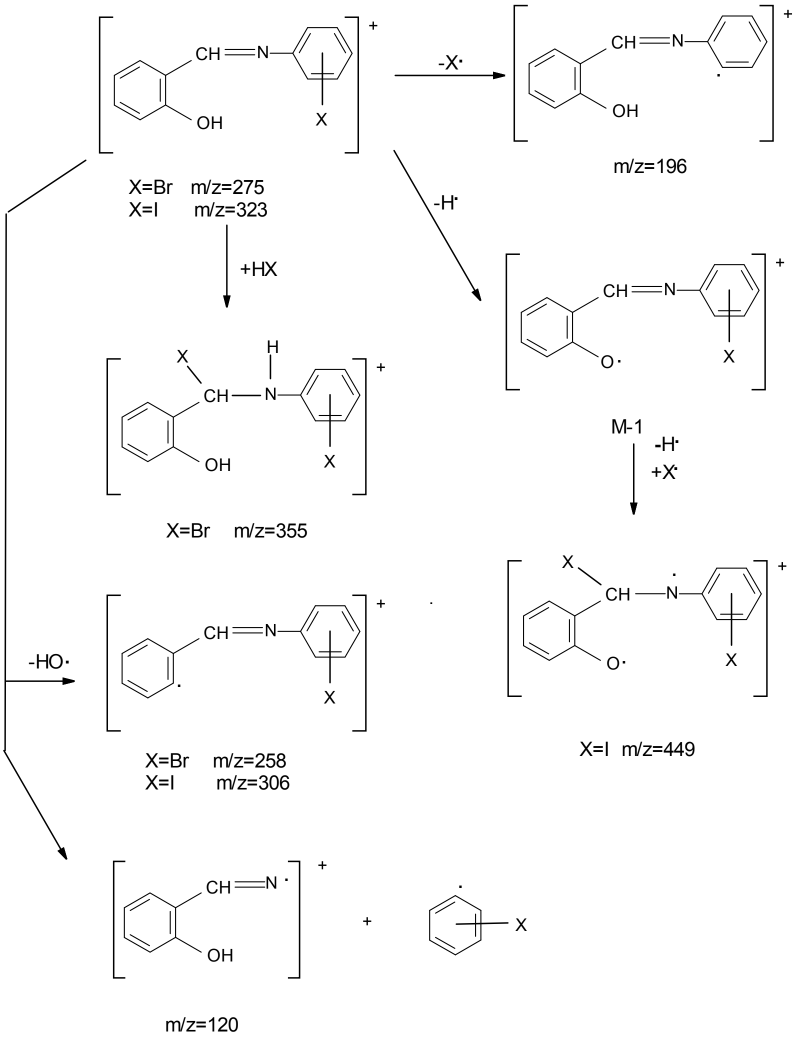

Figure 2a. Fragmentation scheme of compounds I-XIX.

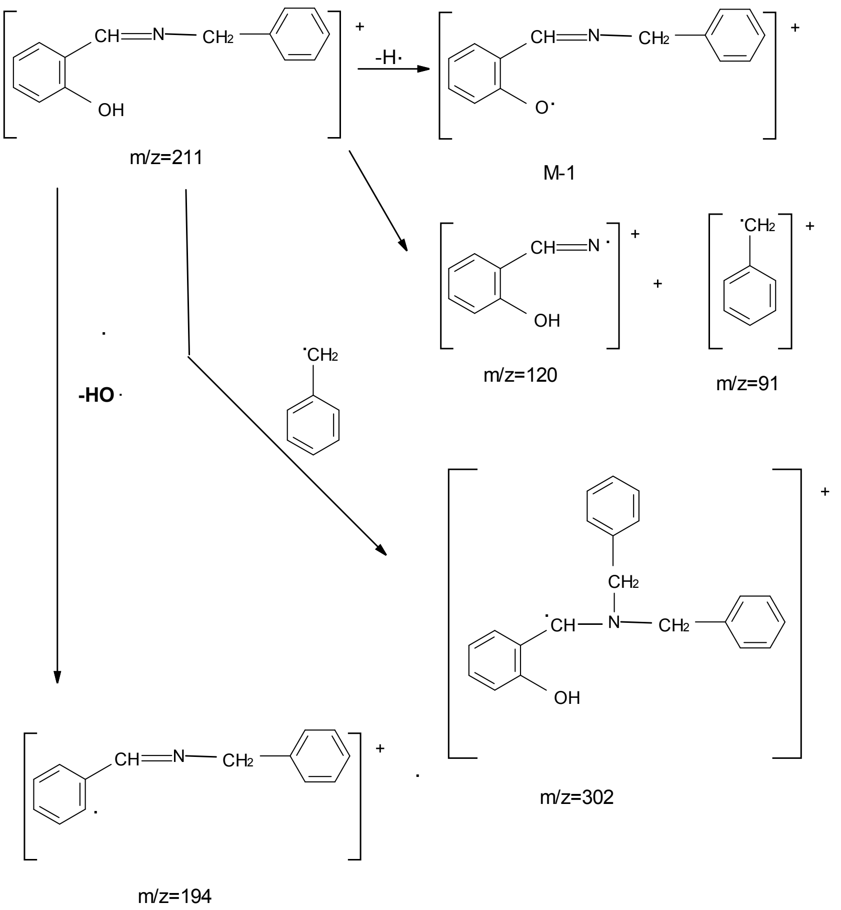

Figure 2b. Fragmentation scheme of compounds XX-XXI.

Another noteworthy fragment belonged to HBr and HI species adding to the molecule in the cases where bromine and iodine substituents were at ortho position. There is a small possibility that the formed acids protonated the nitrogen of the imine bond. However in such a case, the Schiff base molecule should be in ionic form. Therefore at this point, it is considerably more possible that the formed HBr and HI molecules add to the C=N imine bond.

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