Synthesis, Characterization and Electron Impact Mass Spectrometry of Schiff Bases Rearranging to Oxazoline, Thiazoline and Thiazole Derivatives

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A series of oxazoline compounds have been prepared by reaction of 2,6-diformyl-4-chlorophenol, 2,6-diformylpyridine or 2,5-diformylthiophen with *o*-aminophenol or *o*-aminothiophenol respectively. The oxazoline derivatives are stable both in solid state and in solution while the thiazoline derivatives easily oxidize to the corresponding thiazoles. Physico-chemical data confirm this oxidation process. The 70 eV electron impact induced decomposition pathways of these compounds, obtained with the aid of exact mass measurements, B/E linked scans and collisional spectroscopy, are discussed in detail.

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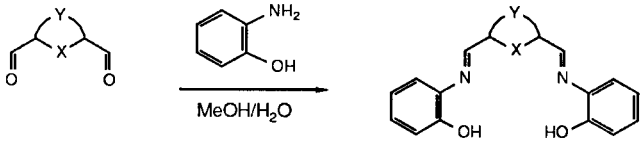
Introduction.

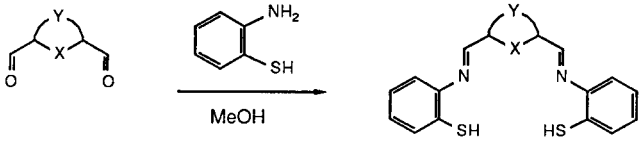
Schiff bases play a central role in inorganic chemistry owing to their interesting properties; they are easily obtainable, generally as solid stable compounds, give rise to complexes which can mimic some of the active sites of metallo-proteins or metalloenzymes [1-7]. A wide range of different Schiff bases, often containing additional donor groups in order to enhance their coordination ability, have been consequently synthesized [8-10].

The usual approach to the synthesis of Schiff bases employs the condensation, in alcoholic solution (sometimes in other organic solvents or water) of aldehydes or ketones with primary aliphatic or aromatic amines. The reaction of formyl derivatives of the type OHC-R-CHO (R = 2,6-disubstituted-pyridine, 4-chloro-2,6-disubstituted-phenol, 2,5-disubstituted-thiophen or furan) with *o*-aminophenol or *o*-aminothiophenol leads to the compounds **1-3** for the former and **4-6** for the latter [4] (see Scheme 1).

Scheme 1

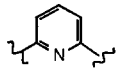


1 - 3

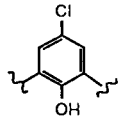


4 - 6

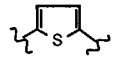
1,4, Y = C_3H_3, X = N



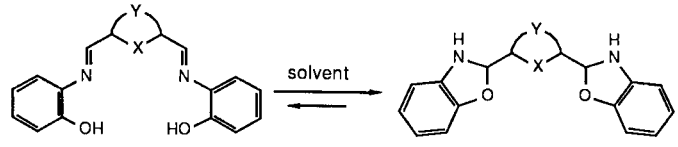
2,5, Y = CH - CCl - CH, X = C - OH



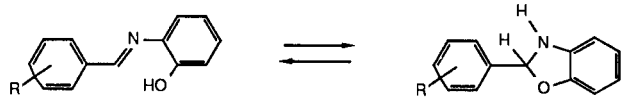
3,6, Y = C_2H_2, X = S



Spectroscopic data give evidence that in the condensed phase compounds **1-3** undergo an equilibrium of the type:

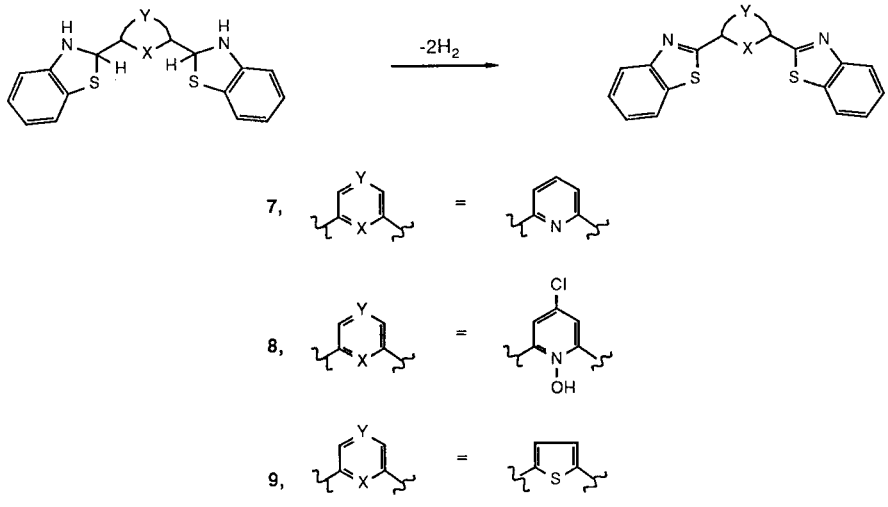


as found for similar systems [11] as:

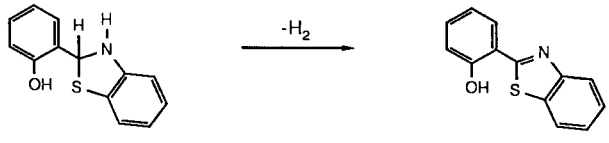


For compounds **4-6** not only the isomerization to thiazoline derivatives takes place, but a 4H· loss is also observed in condensed phase; a reasonable mechanism for this 4H· loss could involve an oxidation with 2 H_2 loss of the type in Scheme 2.

Scheme 2



The oxidation of oxazoline or thiazoline compounds to the oxazole or thiazole analogues has already been chemically or photochemically induced [11]. Recently the X-ray structure of the complex $(AsPh_4)TcOCl_3$ (**11**) has been reported, the ligand being obtained by slow oxidation in air and in solution of the corresponding thiazoline [12].



10 **11**

Pursuing our interest in mass spectrometry of Schiff bases [13,14] we have undertaken the study of the electron impact (ei) induced mass spectrometric behaviour of compounds **1-11** with the aid of exact mass measurements, B/E linked scans [15], collisional spectroscopy [16] and deuterium labelling experiments.

EXPERIMENTAL

Materials.

2,6-Diformyl-4-chlorophenol [17], 2,6-diformylpyridine [18] and 2,5-diformylthiophen [19] were prepared according to literature and their purity was checked by melting points, elemental analysis, ir, ^1H nmr and hplc measurements. *o*-Aminophenol was a commercial product and was used without further purification, *o*-aminothiophenol was purified by distillation, maintained under nitrogen and handled both in air and in nitrogen.

Synthesis.

Compound **1**.

To a hot water (50 ml) solution of *o*-aminophenol (812 mg, 7.4 mmoles), 2,6-diformylpyridine (500 mg, 3.7 mmoles) in hot water (100 ml) was added. The yellow suspension obtained in a few minutes was refluxed for 1 hour, the solid was filtered, washed with methanol. The crude product was recrystallized from methanol, filtered and dried *in vacuo*, mp 197-198°.

Anal. Calcd. for $C_{19}H_{15}N_3O_2$: C, 71.92; H, 4.73; N, 13.25. Found: C, 72.30; H, 4.75; N, 13.24.

Compound **2**.

To a methanolic (90 ml) solution of *o*-aminophenol (610 mg, 5.6 mmoles), 2,6-diformyl-4-chlorophenol (520 mg, 2.8 mmoles) in methanol (20 ml) was added dropwise under reflux.

After a few minutes a red product was obtained. The suspension was stirred for 1 hour. The precipitate was filtered, washed with methanol and dried *in vacuo*, mp 230-237°.

Anal. Calcd. for $C_{20}H_{15}ClN_2O_3$: C, 65.48; H, 4.09; N, 7.64. Found: C, 65.49; H, 4.09; N, 7.43.

Compound **3**.

Compound **3** was prepared by the same procedure used for the synthesis of **2**, 2,5-diformylthiophenol was used instead of 2,6-diformylpyridine, mp 182-183°.

Anal. Calcd. for $C_{18}H_{14}N_2O_2S$: C, 65.84; H, 4.35; N, 8.70. Found: C, 65.96; H, 4.30; N, 8.36.

Compound **4**.

The synthesis was carried out in a nitrogen atmosphere by adding to a methanolic (10 ml) solution of *o*-aminothiophenol (62 mg, 0.48 mmole), 2,6-diformylpyridine (32 mg, 0.24 mmole) dissolved in methanol (25 ml). The solution was stirred for 1 hour and the white precipitate obtained was filtered, washed with methanol and dried *in vacuo*, mp 112-118°.

Anal. Calcd. for $C_{19}H_{15}N_3S_2$: C, 65.30; H, 4.40; N, 12.05. Found: C, 65.16; H, 4.34; N, 11.94.

Compound **5**.

Compound **5** was prepared by the same procedure used for the synthesis of **4**, 2,6-diformyl-4-chlorophenol was used instead of 2,6-diformylpyridine, mp >300°.

Anal. Calcd. for $C_{20}H_{15}ClN_2OS_2$: C, 60.22; H, 3.79; N, 7.02. Found: C, 60.00; H, 3.70; N, 6.92.

Compound **6**.

Compound **6** was prepared by the same procedure used for the synthesis of **4**, 2,5-diformylthiophen was used instead of 2,6-diformylpyridine, mp 108-115°.

Anal. Calcd. for $C_{18}H_{14}N_2S_3$: C, 60.98; H, 3.98; N, 7.90. Found: C, 61.26; H, 3.98; N, 7.88.

The purity of all the compounds was checked with hplc techniques indicating the absence of side products.

Compounds **4**, **5** and **6** undergo an almost quantitative oxidation reaction to the corresponding *bis*-thiazole derivatives **7**, **8**, and **9** in air. In addition, from a slow evaporation of the mother liquors of **4**, **5** and **6**, precipitates of the *bis*-thiazole derivatives **7**, **8**, and **9** were also obtained.

Physico-chemical Measurements.

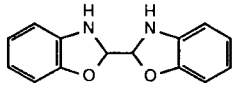
The ir spectra were carried out as nujol mulls or potassium bromide pellets using a Perkin-Elmer 580 model infrared spectrometer equipped with a data station. The ^{1}H nmr spectra were recorded by a Varian FT 90 model nmr spectrometer. The hplc measurements were performed by using a Hewlett Packard 1090 model chromatographer equipped with a uv 600 - 220 nm detector.

Mass Spectrometric Measurements.

All mass spectrometric measurements were performed on a VG ZAB 2F instrument operating in ei conditions (70 eV, 200 μA). The samples were introduced in direct electron impact (dei) conditions with a source temperature of 200°. Exact mass measurements were performed with the peak matching technique at 10,000 resolution (10% valley definition). Metastable transitions were detected either by B/E linked scans [15] or by mass analyzed ion kinetic energy spectra (MIKES). Collisionally activated decompositions (CAD) [16] were obtained by 8 keV ions colliding with air in the second field-free region. The pressure in the collision cell was such to reduce the main beam signal by 50%. The mass spectra were recorded in a range of ion source temperature from 80 to 240°. No changes in relative abundances were observed, proving that no thermal decomposition occur at those temperatures.

Results and Discussion.

The reaction of 2,6-diformylpyridine, 2,6-diformyl-4-chlorophenol and 2,5-diformylthiophen with *o*-aminophenol in a 1:2 molar ratio and in alcoholic or water solutions leads to the red or yellow compounds **1**, **2** and **3**. For these compounds the oxazoline structure is the most likely, as already suggested, on the basis of ir and nmr data, for the product **12** obtained by condensation of glyoxal and *o*-aminophenol [20].



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The ir spectra of **1**, **2** and **3** show sharp absorption bands (as singlets or doublets) in the range 3362-3421 cm^{-1} attributable to ν N-H. The appearance of sharp bands in this region was already assumed as indicative of the oxazoline formation [20].

These compounds react with metal ions (in the presence of base) in the tautomeric Schiff base forms as found for thorium(IV) and uranyl(VI) with **2** and **12** respectively [21,22].

The same reaction occurs with the analogous compounds **4**, **5**, **6**, obtained by condensation of the above diformylprecursors with *o*-aminothiophenol. These products, obtained by this condensation reaction, carried out in alcoholic solution, and under a nitrogen atmosphere, show, in their ir spectrum, ν N-H in the range 3251-3338 cm^{-1} and N-H at 1582 cm^{-1}, indicative of the formation of thiazoline compounds. In addition, mass spectra clearly indicate the parent peak $M^{+\cdot}$ although a detailed study of their mass spectra is precluded by the presence of the $[M-4]^{+\cdot}$ peaks due to the more volatile oxidized products.

The shape of the ir spectra are considerably different and are also indicative of these changes; for instance the disappearance of the absorption bands associated with the N-H groups are clearly detectable in the spectra of the *bis*-thiazole derivatives.

These compounds however are not stable in air for long periods of time and a fast oxidation to the corresponding thiazole derivatives occurs. Mass spectra carried out at different times indicate the progressive disappearance of the parent peaks $M^{+\cdot}$ and the appearance of the $[M-4]^{+\cdot}$ peaks.

As an example, the ir spectra of reduced **5** and oxidized **8** forms are reported in the Figure 1.

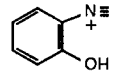
The same oxidation reaction was observed for **5** by heating the sample at about 280-290°.

It must be noted that this reaction was observed only with the compounds **4**, **5** and **6** derived from *o*-aminothiophenol. Analogously the related compound **10**, obtained by condensation of salicylaldehyde and *o*-aminothiophenol, shows the $M^{+\cdot}$ at m/z 229, and, in its ir spectrum, exhibits ν N-H at 3254 cm^{-1}; such a band is absent in the oxidized product **11**, with $M^{+\cdot}$ at m/z 227.

The most abundant and significant ionic species arising from electron impact ionization of compounds **1-3** are reported in Table 1.

Table 1

EI Mass Spectra of Compounds **1-3**; m/z (relative abundance)

Ionic Species	1	2	3
$M^{+\cdot}$	317(94)	366(41)	322(100)
$[M-H]^+$	316(10)	365(6)	321(12)
$[M-2H]^{+\cdot}$	315(15)	364(4)	–
$[M-3H]^+$	314(8)	363(5)	–
$[M-4H]^{+\cdot}$	313(8)	362(1)	–
$[M-OH]^+$	300(8)	–	305(1)
$[M-C_6H_5O]^+$	224(13)	273(7)	229(11)
$[M-C_6H_5ON]^{+\cdot}$	210(100)	259(19)	215(11)
$[M-C_6H_6ON]^+$	209(4)	258(100)	214(12)
$[M-C_7H_5NO]^{+\cdot}$	198(38)	247(5)	203(19)
$[M-C_7H_6NO]^+$	197(34)	246(4)	202(31)
$[M-C_7H_7NO]^{+\cdot}$	196(40)	245(3)	201(4)
$[M-C_6H_6ON-CO]^+$	181(8)	230(3)	186(16)
	120(56)	120(18)	120(40)
$[M-C_7H_5NO-CO]^{+\cdot}$	170(26)	–	–
$[M-C_7H_6NO-CO]^+$	169(30)	–	–
$[M-C_7H_7NO-CO]^{+\cdot}$	168(8)	–	–
$[M-C_7H_5NO-C_6H_5O]^+$	105(16)	154(3)	110(9)

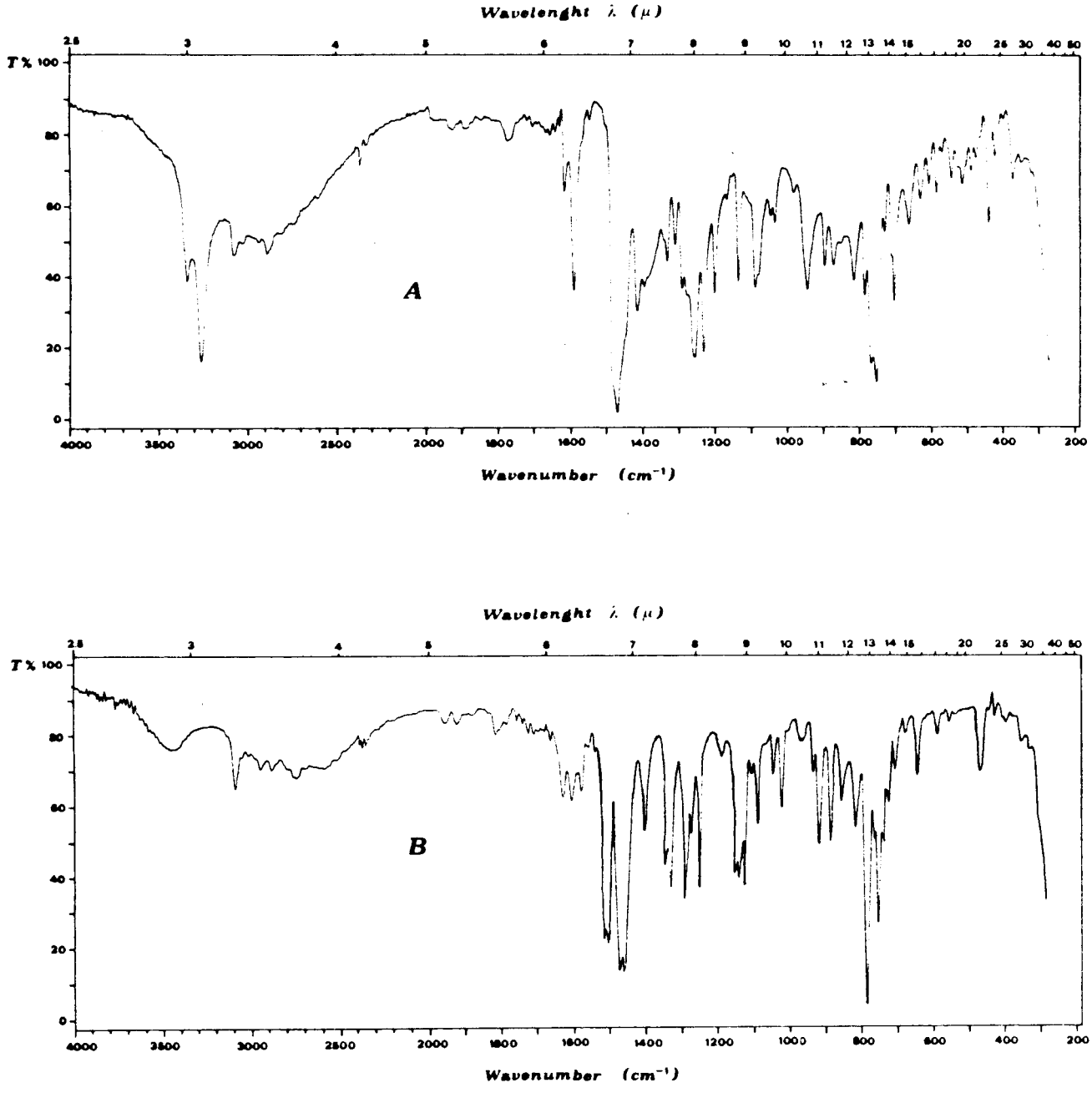
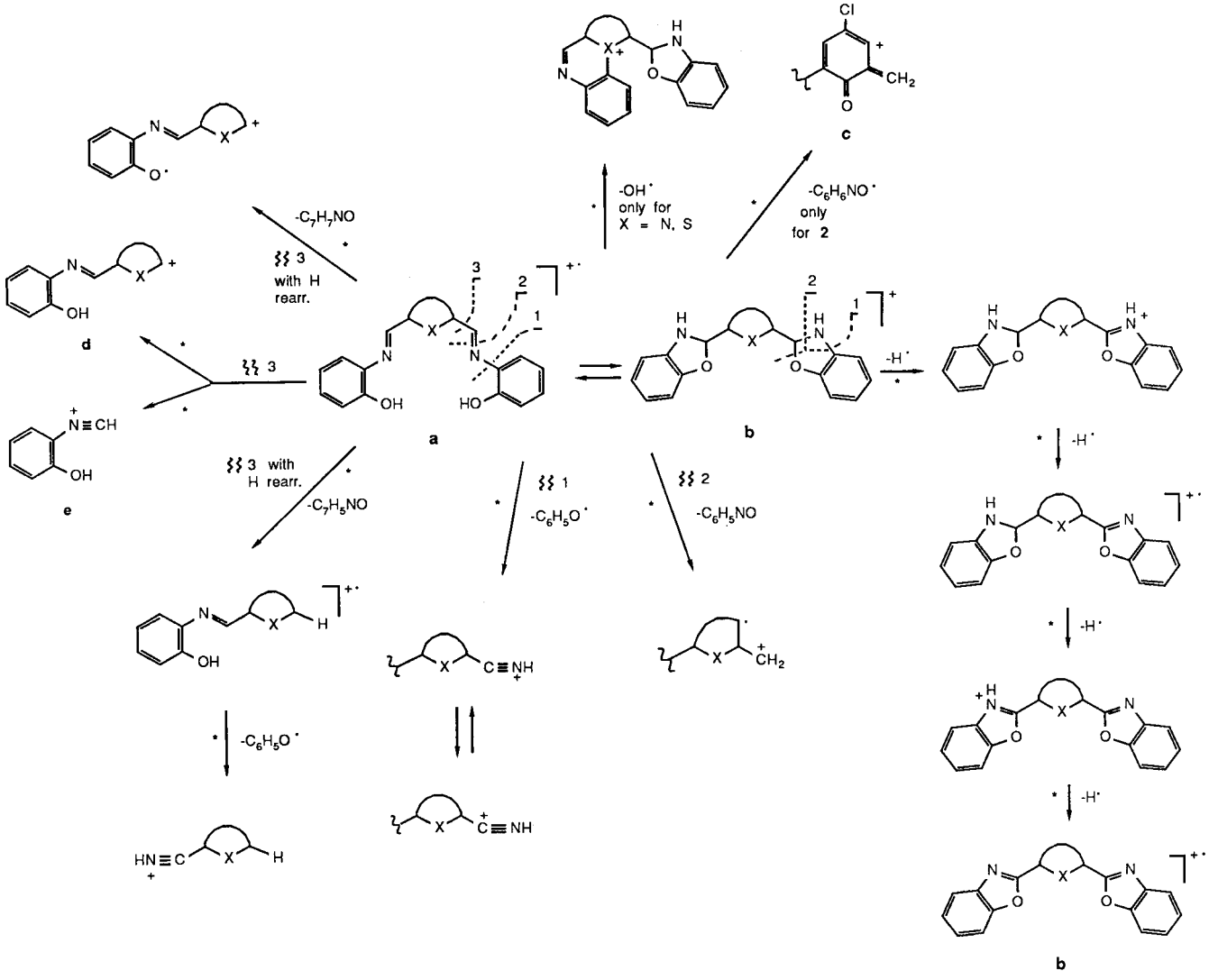


Figure 1. (a) Infrared spectrum of the compound **5**; [b] Infrared spectrum of the compound **8**.

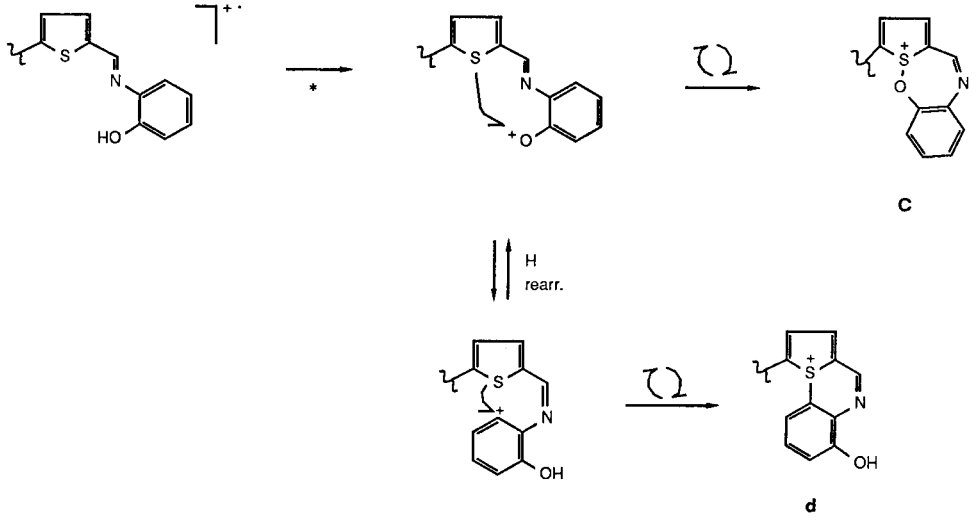
All compounds **1-3** exhibit abundant molecular ions giving evidence for their stability. Sequential losses of H$^{\cdot}$, 2H$^{\cdot}$, 3H$^{\cdot}$, 4H$^{\cdot}$ are present for both compounds **1** and **2** while only a single H$^{\cdot}$ loss is observed for **3**. This fragmentation pathway can reasonably originate from the formation of oxazole-like ions **b** (see right part of Scheme 3). The structure of a *bis*-benzoxazole derivative **b'** can be assigned to the $[M\text{-}4H]^{+\cdot}$ species.

The absence of such processes for compound **3** is to be emphasized. First of all, deuterium labelling of the phenolic hydrogen proves its implication in the primary H$^{\cdot}$ loss. This could be due to the stability of $[M\text{-}H]^{+}$ ions, which originate by a condensation reaction on the thiophen sulphur atom. In Scheme 4 we propose two possible mechanisms. We are inclined towards the formation of ions **d** which require extensive H rearrangements but lead to a more stable aromatic ion.

Scheme 3



Scheme 4



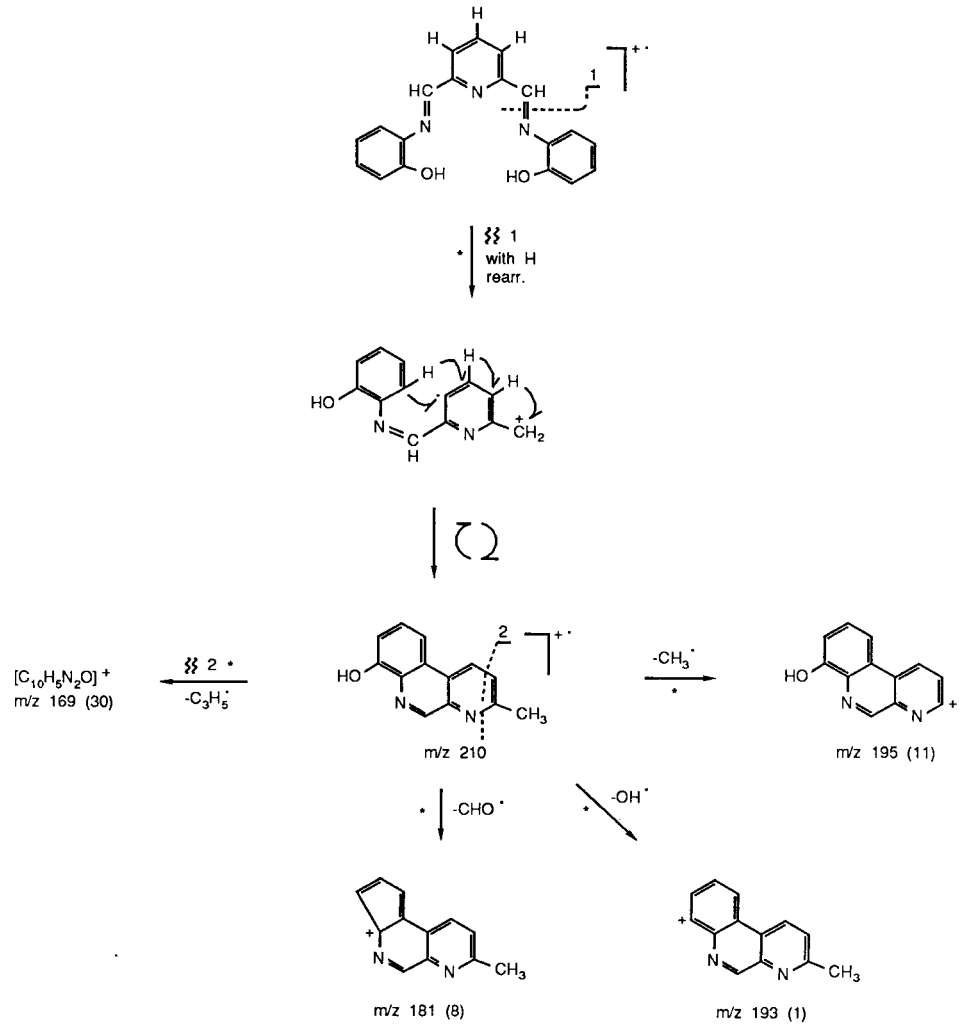
Primary hydroxyl radical loss is abundant in the ei spectrum of compound **1** only, (8% *vs* 0% and 1% for compounds **2** and **3** respectively) leading to a condensation product on the pyridine nitrogen as evidenced by the presence in the ion source of a molecular species structured as the Schiff base (structure **a** of Scheme 3).

The relative abundances of primary decomposition products in the ion source, in the first and in the second field-free regions (comparing the usual ei spectra, the B/E linked scans and the MIKE spectra) (see Table 2) indicate that hydroxyl loss is a slow process. An analogous behaviour is observed for compounds **2** and **3** also. In this case the peak corresponding to $OH^{\cdot}$ loss become well detectable only in B/E and MIKE spectra.

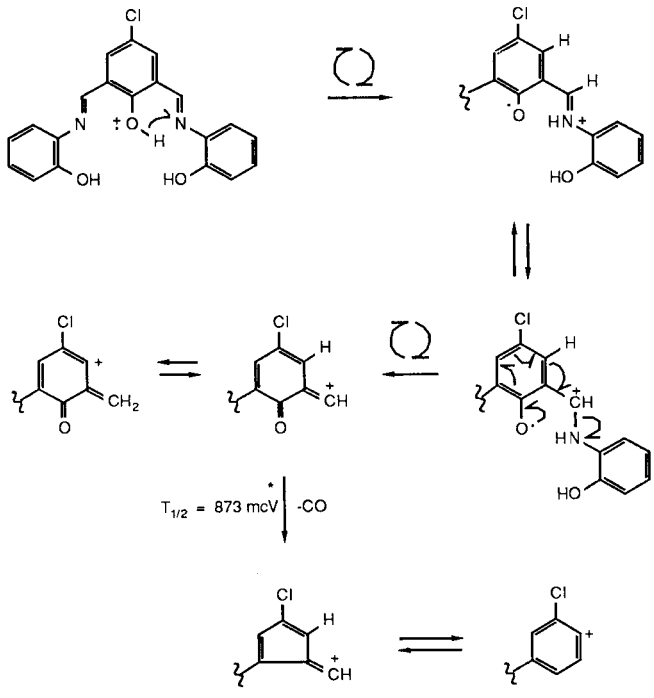
Cleavage 1 of Scheme 3, corresponding to the loss of $C_6H_5O^{\cdot}$ radical leads to quite abundant ionic species reasonably bearing a protonated nitrile group. This fragment ion can originate either from structure **a** through the cleavage of N-C bond or from structure **b** by sequential cleavages of C-O and N-C bonds of the oxazoline ring.

The primary loss of $C_6H_5NO^{\cdot}$ (cleavages 2 of Scheme 3) leads to particularly abundant fragment ions (for compound **1** they give rise to the base peak of the mass spectrum); for this fragmentation process a precursor ion of structure **b** seems to be more reasonable and the high abundance observed in the pyridine-containing compound **1** can be explained by the higher stability of the product ion (see Scheme 5). The proposed structure of ions at m/z 210 for **1** is well supported by the metastable decomposition pattern. For compound **2** the primary loss of $C_6H_6NO^{\cdot}$, corresponding to cleavage 2 with H rearrangemen., is more favoured; first of all this implicates that the phenolic hydrogen is involved in this process and its high abundance can be easily explained by the formation of a quinone-like structure **c** of Scheme 6.

Scheme 5



Scheme 6



Finally cleavage 3 give rise to both complementary ions **d** and **e**, due to the near ionization energy values of the two fragments (Stevenson-Audier rule [23]).

Furthermore the same fragmentation pathway is present with H rearrangement from and to the isonitrile moiety (losses of C_7H_5NO and C_7H_7NO respectively).

In conclusion the fragmentation patterns of compounds **1-3** result in a quite extent dependent upon the heteroatom X present in the diformyl precursor. Condensation reactions on X are always present for X = N, S while in the case of X = C-OH they are obviously inhibited. Some fragmentation pathways can be easily explained by the presence of the equilibrium

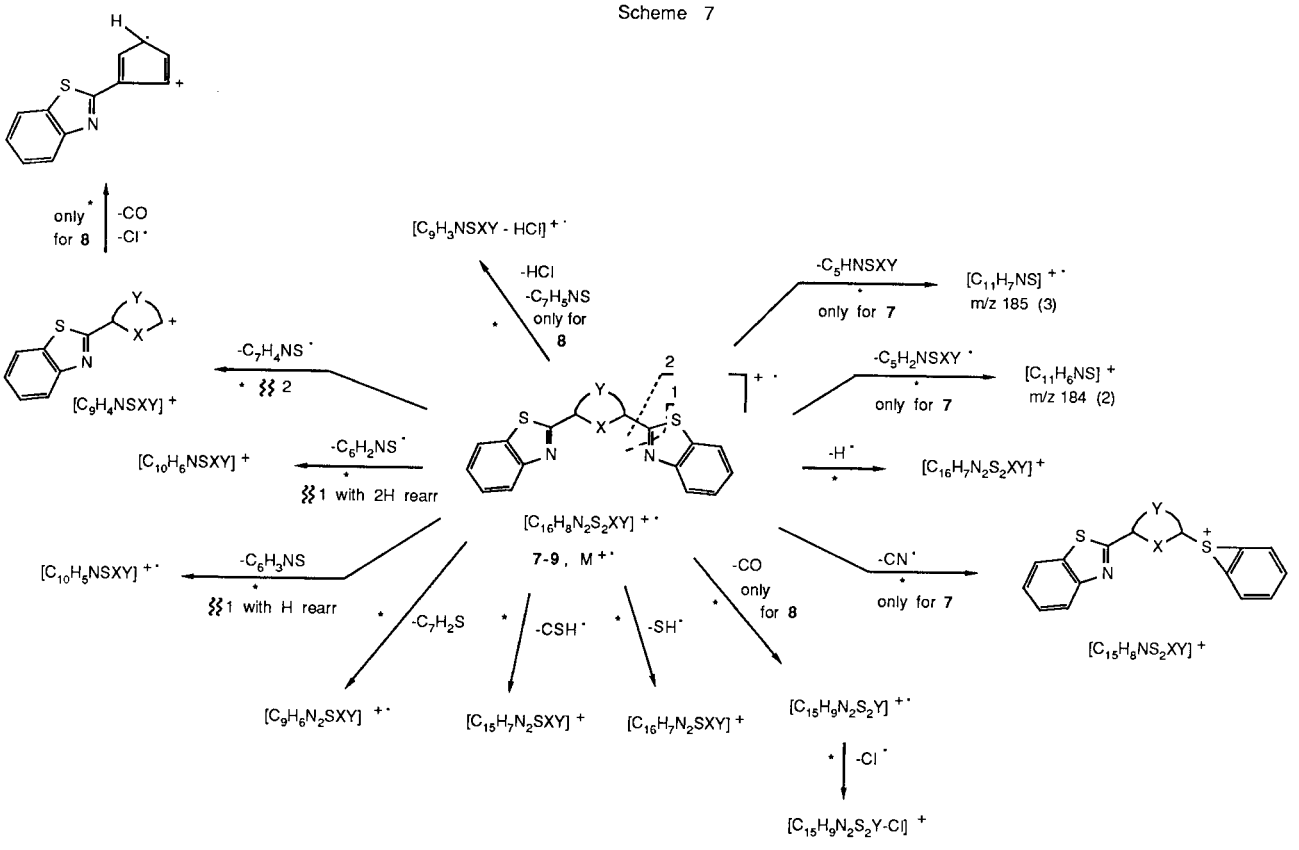
$$\mathbf{a}^{+\cdot} \leftrightarrows \mathbf{b}^{+\cdot}$$

(see Scheme 3) already described in solution chemistry.

The mass spectra of compounds **7-9** (the oxidized form), are reported in Table 3, while the related common fragmentation pattern, as obtained by B/E linked scans and exact mass measurements, is reported in Scheme 7.

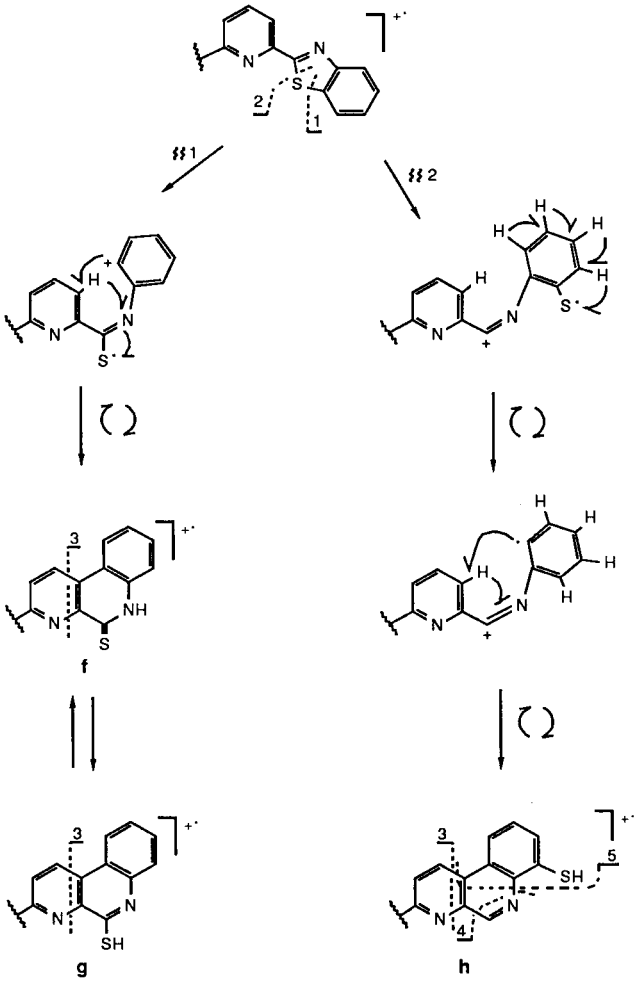
For all compounds, the molecular ion give rise to the base peak, while the $[M-H]^+$ species is particularly abundant for **8** only, presumably due to the presence of the phenolic hydroxyl group.

Scheme 7



Some primary decomposition pathways are in agreement with the proposed molecular structure as indicated in Scheme 7. So, for example $[C_9H_4NSXY]^+$ ions can easily originate from cleavage 2, while $[C_{10}H_6NSXY]^+$ and $[C_{10}H_5NSXY]^+$ ionic species can arise from cleavage 1 with $2H^\cdot$ and $H^\cdot$ rearrangements respectively. On the contrary some other ei induced fragmentations seem to suggest the presence of molecular species differently structured. The primary losses of $SH^\cdot$ and $CSH^\cdot$, observed for all the compounds, can be explained invoking the presence of molecular species containing a thiophenolic moiety. Such structure(s) require condensation and extensive skeletal rearrangements. In fact the losses of C_9H_6NS and C_9H_7NS for compound **7** and of C_4HNSXY for compound **8** cannot arise from molecular ions of the same structure as the neutral moiety. Hence we propose an ei induced skeletal rearrangement of the molecular species **7** as that reported in Scheme 8.

Scheme 8



Structures **f**, **g** and **h** are in agreement either with the observed losses or to the high abundances of $M^{+\cdot}$. In fact the ions at m/z 185 and 184 in the mass spectrum of compound **7** can originate from structures **f-h** through the cleavage of the pyridine ring (cleavage 3 of Scheme 8). Such fragmentations can be justified only from the presence of extensively rearranged molecular ions. A simple disubstituted pyridine would not result in the observed fragmentation process.

Furthermore the observed losses of $SH^\cdot$ and $CSH^\cdot$ can originate from ions **h**. Again the $CN^\cdot$ loss can arise from ions **h** (cleavage 4 of Scheme 8), while the primary loss of C_7H_2S can be due to cleavage 5 (Scheme 8) with $2H^\cdot$ rearrangement.

Table 2

Absolute Abundances of EI Induced Primary Fragments of Compound **1** Obtained in the Source, in the I and II Field-free Regions

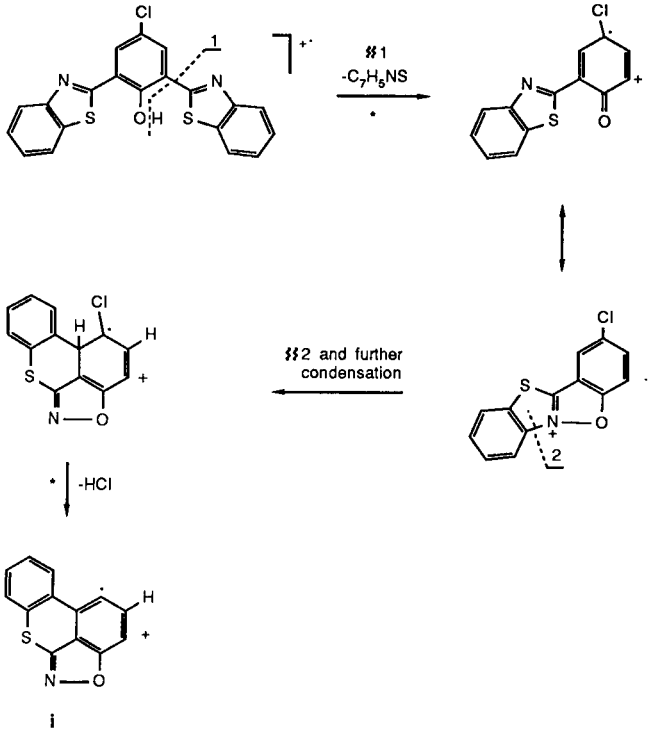
Ionic Species	Ion Source Spectra	B/E I FFR	MIKE II FFR
$[M-H]^+$	6	35	17
$[M-OH]^+$	5	46	54
$[M-C_6H_5O]^+$	7	2	2
$[M-C_6H_5ON]^{+\cdot}$	59	6	23
$[M-C_7H_7ON]^{+\cdot}$	23	11	4

Table 3

EI Mass Spectra of Compounds **7-9**; m/z (relative abundance)

Ionic species	**7**	**8**	**9**
$M^{+\cdot}$	345(100)	394(100)	350(100)
$[M-H]^+$	344(27)	393(1)	349(5)
$[M-CN]^+$	319(5)	-	-
$[M-CO]^{+\cdot}$	-	366(4)	-
$[M-SH]^+$	312(0.5)	361(0.1)	317(7)
$[M-CSH]^+$	300(0.5)	359(0.2)	(305(1)
$[M-CO-Cl]^+$	-	331(10)	-
$[M-C_7H_2S]^{+\cdot}$	-	276(5)	232(15)
$[M-C_6H_2NS]^+$	226(0.5)	275(4)	231(7)
$[M-C_6H_3NS]^{+\cdot}$	-	274(13)	-
$[M-C_7H_4NS]^+$	211(5)	-	216(9)
$[M-C_7H_5NS-HCl]^{+\cdot}$	-	223(3)	-
$[C_{12}H_7NS]^{+\cdot}$	197(1)	197(9)	-
$[C_{11}H_7NS]^{+\cdot}$	185(3)	-	-
$[C_{11}H_6NS]^+$	184(2)	-	-
$[C_7H_5NS]^{+\cdot}$	135(6)	-	135(7)
$[C_6H_7N]^{+\cdot}$	-	93(3)	-
$[C_6H_6N]^+$	92(15)	-	-

Scheme 9



i

The contemporary losses of C_7H_5NS and HCl are observed for compound **8** only, implying the participation of the hydroxyl hydrogen atom. For such a fragmentation pathway we propose the mechanism shown in Scheme 9, leading to the aromatic, highly stable product ion **i**.

Also $[C_{12}H_7NS]^{+\cdot}$ ions are present in the mass spectrum of compound **8** only, and their fragmentation pathway can be explained through sequential losses of CO and Cl$^{\cdot}$ from the $[C_9H_4NSXY]^{+\cdot}$ ions.

An analogous fragmentation route, starting from $M^{+\cdot}$ of **8**, leads to ions at m/z 331(10).

In order to further investigate possible cyclization reactions occurring for 2-aromatic-substituted 1,3-benzothiazoles, we have studied the fragmentation pattern of compound **11**. In this case CO and CHO$^{\cdot}$ primary losses are still present; cleavages of the phenolic benzene ring followed by condensation on the nitrogen atom lead to ionic species at m/z 173 and 186 (see Scheme 10). Analogous reactions to those reported in Scheme 8 for benzothiazoles are not seen.

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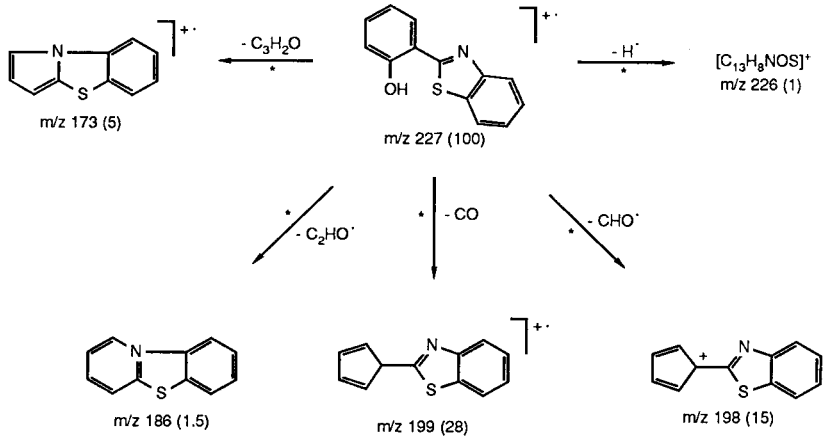
Scheme 10



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