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ESI-MS spectra of 3-cyano-4-(substituted phenyl)-6-phenyl-2(1*H*)-pyridinones

ALEKSANDAR D. MARINKOVIĆ*#, TATJANA M. VASILJEVIĆ#, MILA D. LAUŠEVIĆ# and BRATISLAV Ž. JOVANOVIĆ#

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P.O. Box 3503, 11120 Belgrade, Serbia

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Abstract: Twelve 3-cyano-4-(substituted phenyl)-6-phenyl-2(1*H*)-pyridinones were investigated by tandem mass spectrometry using positive as well as negative electrospray ionization. The influence of the electron affinity of the substituent and the steric effect on the fragmentation is discussed. Pyridinones with a substituent of low proton affinity show loss of water, HCN or benzene from the pyridinone ring in the first step of MS^2 fragmentations. Oppositely, if a substituent with high proton affinity is present on the phenyl ring in the 4-position of pyridinone, the fragmentation paths are complex, depending mainly on the substituent proton acceptor ability. Elimination of neutral molecules CO, HCN, H_2O, PhH (benzene) or Ph and CN radicals are fragmentation processes common for all compounds in the subsequent steps of the fragmentations.

Keywords: electrospray ionization; substituted pyridinones; tandem mass spectrometry.

INTRODUCTION

The interest in various 3-cyano-4-(substituted phenyl)-6-phenyl-2(1*H*)-pyridinone derivatives stems largely from their unique properties, which enable their use not only in the production of dyes, pigments, fuel and oil additives, but also for the development of medicinal products having a broad spectrum of biological activities.

An excellent review on the synthesis, reactivity and biological activity of 3--cyanopyridine-2(1*H*)-chalcogenones has been published.[1] Substances that improve the blood circulation and cardiotonic activity were also mentioned. Among the other types of biological activities of this class of compounds, it is worth mentioning analgetic and antihypertensive, anti-anaphylactic, diuretic and sodio-

* Corresponding author. E-mail: marinko@tmf.bg.ac.rs
# Serbian Chemical Society member.
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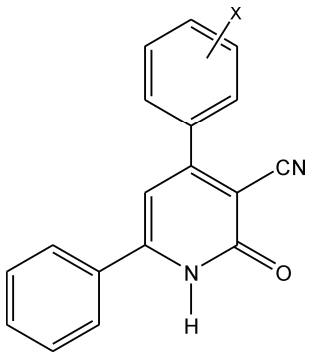
diuretic, anti-oxidant, antiviral, and antimicrobial compounds.[1,2] Biologically degradable agrochemical products, plant growth regulators, pesticides and herbicides are also produced from derivatives of pyridinones.[3–5] Various tautomeric forms of these molecules determine their chemical behaviour and some additional information in the study of their properties can be seen from their MS^2 spectra.

One of the classic studies of lactim/lactam tautomerism is the determination of the 2-hydroxypyridine (2HP)/2-pyridinone (2PYR) equilibrium. UV/Vis,[6,7] mass spectrometric,[8] photoelectron,[9] low-temperature matrix isolation and IR spectroscopic[10] measurements revealed that 2-hydroxypyridine exists in the gas phase and in inert matrices under equilibrium conditions mainly in the lactim form. Considering the equilibrium in solvents of different polarity, it was found that increasing the solvent polarity shifted the equilibrium towards the pyridinone (lactam) form. Furthermore, the hydrogen bonding ability of the solvent plays an important role, since hydrogen-bond donors tend to stabilize the oxo form (lactam), whereas hydrogen-bond acceptors stabilize the hydroxy form (lactim).

In order to determine the structure–fragmentation relation, the fragmentations of selected pyridinones in an ion source as well as in an ion trap were analyzed. The investigated pyridinones had the following structural formulae:



where X is: H (**1**); 4-CH_3 (**2**); 3-CH_3 (**3**); 3-Cl (4); 4-Cl (**5**); 2,4-di-Cl (**6**); 4-CN (**7**); 3-OPh (**8**); 4-OCH_3 (**9**); 3,4-di-OCH_3 (**10**); 3-NO_2 (**11**) and 4-$N(CH_3)_2$ (**12**).

The effect of the phenyl substituent in the 4-position of the pyridinone ring, steric and tautomerism effects on the fragmentation patterns are discussed.

EXPERIMENTAL

Twelve 3-cyano-4-(substituted phenyl)-6-phenyl-2(1*H*)-pyridinones were synthesized following a procedure described in the literature.[11,12] An exception was 3-cyano-4-(4-cyanophenyl)-6-phenyl-2(1*H*)-pyridinone which was synthesized by microwave irradiation of a mixture of 4-cyanobenzalacetophenone, ammonium acetate and ethyl cyanoacetate at 600 W for 6 min.

The new compounds which, to the best of our knowledge, have not been described in the literature, are as follows: 3-cyano-4-(3-phenoxyphenyl)-6-phenyl-2(1*H*)-pyridinone, m. p. 244––246 °C and 3-cyano-4-(4-cyanophenyl)-6-phenyl-2(1*H*)-pyridinone, m.p. 323–325 °C. In addition, the compounds 3-cyano-4-(3-nitrophenyl)-6-phenyl-2(1*H*)-pyridinone, m.p. > 330 °C

and 3-cyano-4-[4-(dimethylamino)phenyl]-6-phenyl-2(1*H*)-pyridinone (m.p. 313–315 °C), although comercially available, have not been considered in the literature. All new-synthesized compounds had satisfactory elemental (C, H, N) composition. Their structures were confirmed by melting point, infrared spectroscopy, ^{1}H- and ^{13}C-NMR and mass spectrometry data.

Mass spectra were obtained using a LCQ Advantage (Thermo, San Jose, CA, USA) quadrupole ion trap mass spectrometer. The electrospray ionisation technique was used in the positive and negative ion mode. The solutions of the pyridinone samples (0.10 mg/ml in CH_3OH) were injected directly into the ESI source by a syringe pump, at a flow rate of 5.0 µl min^{-1} and analysed under the following conditions: capillary temperature 250 °C; sheath gas flow 38 au (N_2); source voltage 4.5 kV; capillary voltage 35 V and –26 V in the positive and negative ionisation mode, respectively. In order to obtain MS^2 spectra, the ions of interest were isolated and fragmented in the collision with helium, with a collision energy in the range 30–50 %. The data obtained were processed using Xcalibur^{TM} 1.2 software.

RESULTS AND DISCUSSION

Mass spectra

The typical peaks that appear in the ESI$^+$-MS spectra of all the investigated pyridinones are protonated molecular ion $[M+H]^+$, the corresponding adduct ion with sodium $[M+Na]^+$ and cluster ions: $[2M+Na]^+$, $[2M–H+2Na]^+$, $[2M–2H+ +3Na]^+$. Two peak groups were also observed, which correspond to multi-charged cluster ions.

The negative ion mass spectra of the investigated pyridinones exhibit far fewer ions than the positive MS. In addition to the deprotonated (quasi-molecular) ion $[M–H]^–$, the only prominent ions present in the negative ion MS are $[2M–2H+ +Na]^–$ and $[3M–3H+2Na]^–$. Compared to the positive ion MS, the total ion current was at least ten fold lower in the negative ion MS, which could easily be explained by the high proton affinity of the studied compounds.

Fragmentation reactions of $[M+H]^+$ ions: MS^2 and pseudo-MS^3 spectra

In order to understand the influence of the different substituents on the phenyl ring of the pyridinone on the stability of the ions in the gas phase, collision-induced dissociation (CID) of the protonated molecular ion was studied. A prominent protonated molecular ion, present in the spectra of all pyridinones, was isolated in the ion trap and subjected to collision with He in order to obtain the MS^2 spectrum. Subsequently, in-source collision-induced dissociation (ISD) of the protonated molecular ion was studied and it was compared to the CID in the ion trap. As the ISD and CID spectra of the quasimolecular ions showed only negligible differences in the intensity of the peaks, it was possible to perform a pseudo-MS^3 CID of the daughter ions generated in the ion source. Mass spectral data for investigated pyridinones in the positive ion mode are presented in Table I. The CID spectrum of the protonated molecular ion of 4-(3-chlorophenyl)-3-cyano-6-phenyl-2(1*H*)-pyridinone is presented in Fig. 1a, as an example of a MS^2 spectrum.

TABLE I. Mass spectral data of the 3-cyano-4-(substituted phenyl)-6-phenyl-2(1*H*)-pyridinones in the positive mode

Compound	X	$[M+H]^+$ (precursor ions for MS^2)	MS^2 spectrum (precursor ions for MS^3)	Fragment ions and relative abundances (in parentheses) in pseudo MS^3
1	H	273	255^{a1}[a](100)	228^{a2}(30); 201^{a3}(3)
			195^{c1}(20)	167^{c2}(53); 140^{c3}(10)
2	4-CH_3	287	269^{a1}(100)	242^{a2}(26); 215^{a3}(5)
			260^{b1}(13)	242^{a2}(30); 234^{b4}(3); 215^{a3}(3) 227^{a5}(61);
			242^{a2}(14)	215^{a3}(67)
			209^{c1}(23)	181^{c2}(14); 154^{c3}(15)
3	3-CH_3	287	269^{a1}(77)	254^{a4}(12); 242^{a2}(100); 215^{a3}(12); 191^{a6}(8)
			260^{b1}(26)	242^{a2}(20); 232^{b2}(3)
			244^{d2}(7)	–
			242^{a2}(12)	227^{a5}(25); 215^{a3}(54)
			209^{c1}(5)	181^{c2}(100); 154^{c3}(37)
4	3-Cl	307	289^{a1}(100)	262^{a2}(19); 254^{a4}(31); 227^{a5}(9)
			272^{d1}(29)	255^{d4}(15); 244^{d2}(100)
			254^{a4}(7)	227^{a5}(19)
			229^{c1}(14)	201^{c2}(30); 174^{c3}(18)
5	4-Cl	307	289^{a1}(100)	262^{a2}(16); 254^{a4}(40); 227^{a5}(15)
			272^{d1}(26)	255^{d4}(15); 244^{d2}(100)
			254^{a4}(4)	227^{a5}(88)
			229^{c1}(25)	202^{c5}(6); 201^{c2}(38); 174^{c3}(65)
6	2,4-di-Cl	341	323^{a1}(100)	288^{a4}(100); 261^{a5}(15)
			306^{d1}(59)	289^{d4}(6); 278^{d2}(29); 271^{d6}(9)
			288^{a4}(19)	261^{a5}(12); 253^{a7}(100)
			263^{c1}(60)	236^{c5}(6); 228^{c4}(63); 208^{c3}(16)
7	4-CN	298	280^{a1}(100)	253^{a2}(12)
			253^{a2}(4)	226^{a3}(10)
			220^{c1}(12)	–
8	3-OPh	365	348(100)	320(18)
			337 (18)	–
			320(10)	292(23)
			287 (13)	–
			272^{d1}(25)	255^{d4}(10); 244^{d2}(36)
			262^{c6}(18)	–
			254^{a4}(13)	–
9	4-OCH_3	303	288(100)	260(100); 216(3)
			260(10)	242(3); 232(17); 182(5)
10	3,4-di-OCH_3	333	318(100)	289(13); 271(3); 261(15); 241(2); 211(9)
			289(28)	271(3); 261(15); 211(7)
			272(13)	244(28); 141(4)
11	3-NO_2	318	288(6)	260(100); 232(3)
			272^{d1}(100)	254^{d4b}(11); 244^{d2}(100); 217^{d3}(6); 169^{d5}(4)
			260(9)	242(14); 232(38); 217(9); 156(6)
12	4-$N(CH_3)_2$	316	300(100)	282(36); 273(51); 256(11); 222(46)
			273(5)	258(18); 256(11); 246(9); 195(9)

[a]Superscript of the *m/z* values defines the corresponding structure in Schemes 1–3; [b]Compound 11 follows the path d1 – d4 but water loss, instead of hydroxyl radical, was observed

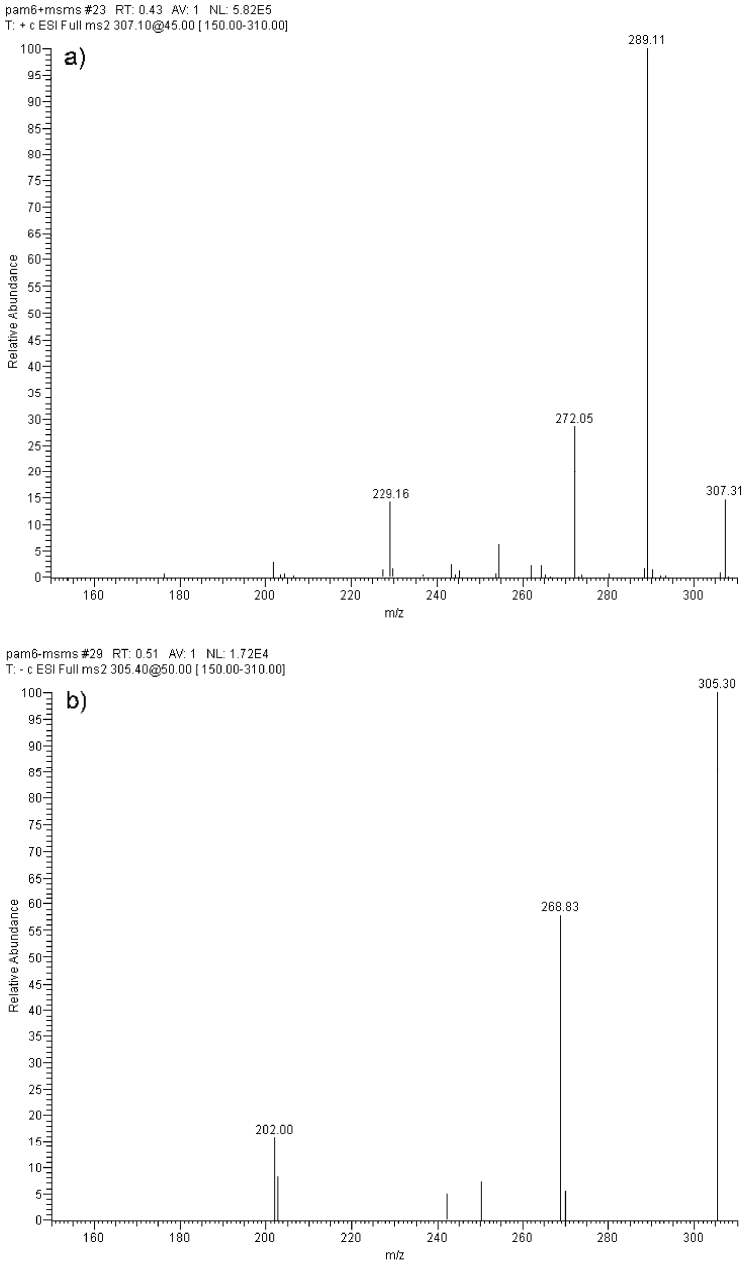


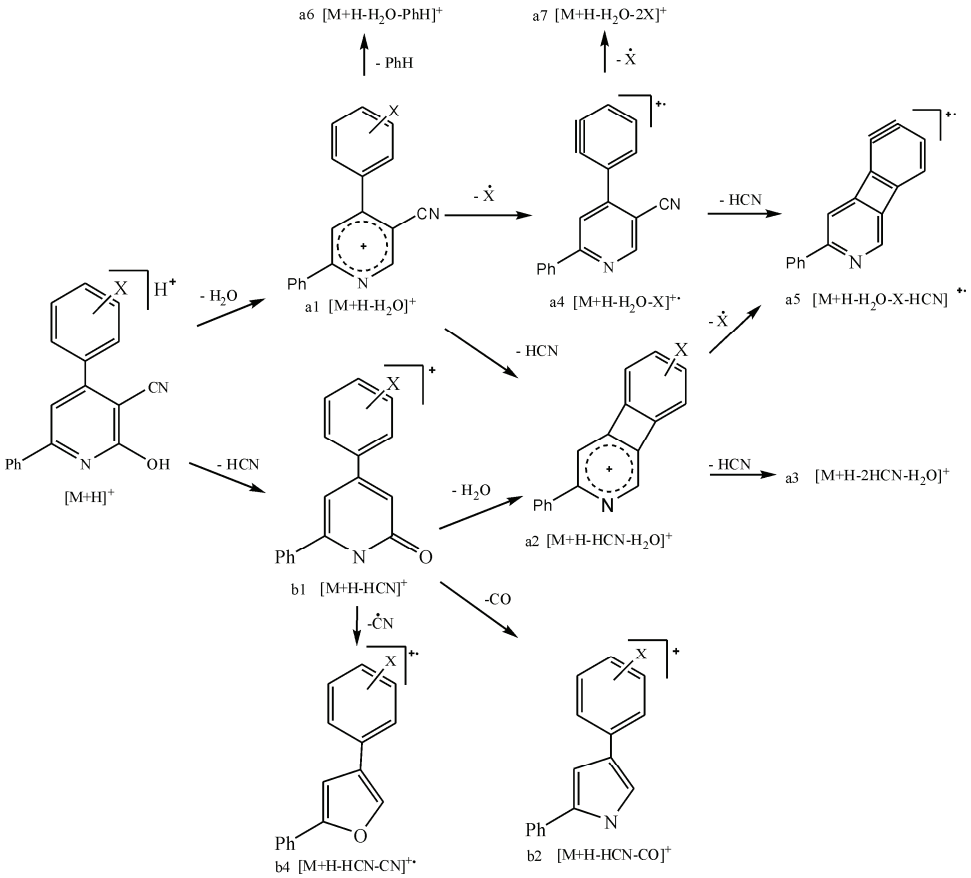
Fig. 1. MS^2 spectra of a) $[M+H]^+$ and b) $[M–H]^–$ obtained from 4-(3-chlorophenyl)- 3-cyano-6-phenyl-2(1*H*)-pyridinone.

The fragmentation pathways of the corresponding protonated molecular ions of the compounds investigated in MS^2 and quasi-MS^3 are presented in Schemes

1–3 and the mass spectral data in Table I. The LCQ Advantage spectrometer does not allow exact mass measurement, therefore the exact composition of the detected ions and lost neutral fragments could not be determined. The proposed structures are based on literature data and chemical logic.

Based on CID and ISD/CID mass spectral data from Table I, two main fragentation paths of the investigated pyridinones could be defined.

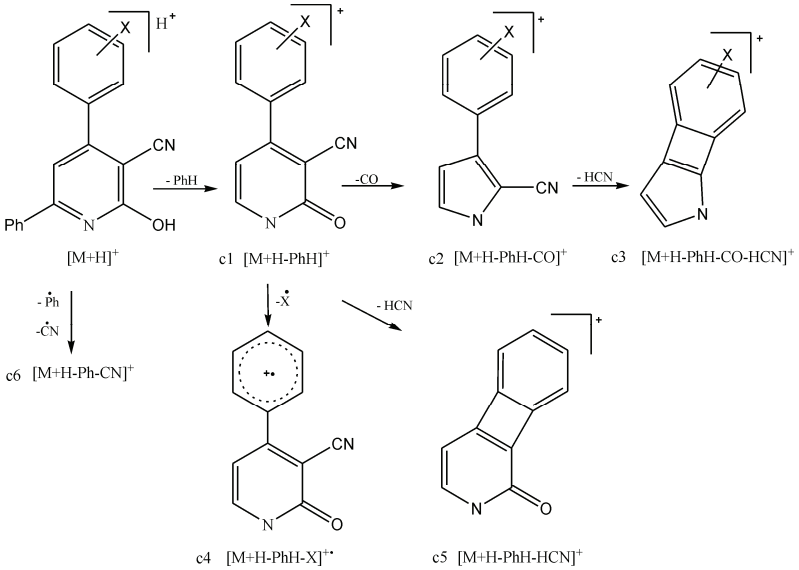
The first fragmentation pattern includes loss of a water molecule, HCN or benzene (PhH) as the first step of the MS^2 fragmentation. These loses were observed for compounds **1**–**7** and are presented in Schemes 1 and 2. The pyridinone ring of these compounds is destabilized by protonation on either the nitrogen or oxygen, thus the fragmentation occurs primarily at the pyridinone structure.



Scheme 1. Proposed fragmentation pathways of $[M+H]^+$ for the loss of H_2O or HCN in the first step.

A completely different fragmentation pattern was observed for compounds **8**–**12** (Table I). The electron-donor substituents are readily protonated, inducing

destabilization of the phenyl ring in the 4-position of pyridinone (compounds **8**–**10** and **12**). In this way, the fragmentation processes occur primarily through the substituted phenyl ring. Loss of a hydroxyl radical (*m*/*z* 348), not water, from $[M+H]^+$ of compound **8** in the MS^2 corroborates the postulate that protonation of the substituent is the main process. It could probably be because of the large phenoxy substituent, which induces a characteristic spatial arrangement of this molecule and electronic character of the C(2)–OH bond, which is more susceptible to homolytic cleavage.



Scheme 2. Proposed fragmentation pathways of $[M+H]^+$ for the loss of a PhH molecule in the first step.

The solvent (methanol) is a hydrogen bond acceptor and donor and significantly influences the appropriate equilibrium of the tautomeric forms of the investigated pyridinones (67 mmol/mol for 2HYP/2PYR).[13] The hydroxy tautomeric form of pyridinone is readily protonated under ESI^+ conditions, water elimination occurs easily, being the main fragmentation path under MS^2 conditions for compounds **1**–**7** (Scheme 2). After water loss, further fragmentations depend on the electronic character of the substituents. For compounds with electron-donor substituents, the fragmentations follow a1-a2-a3 path, while for compounds with electron-acceptor substituents abundant ions a4 and a5 are given (Scheme 1).

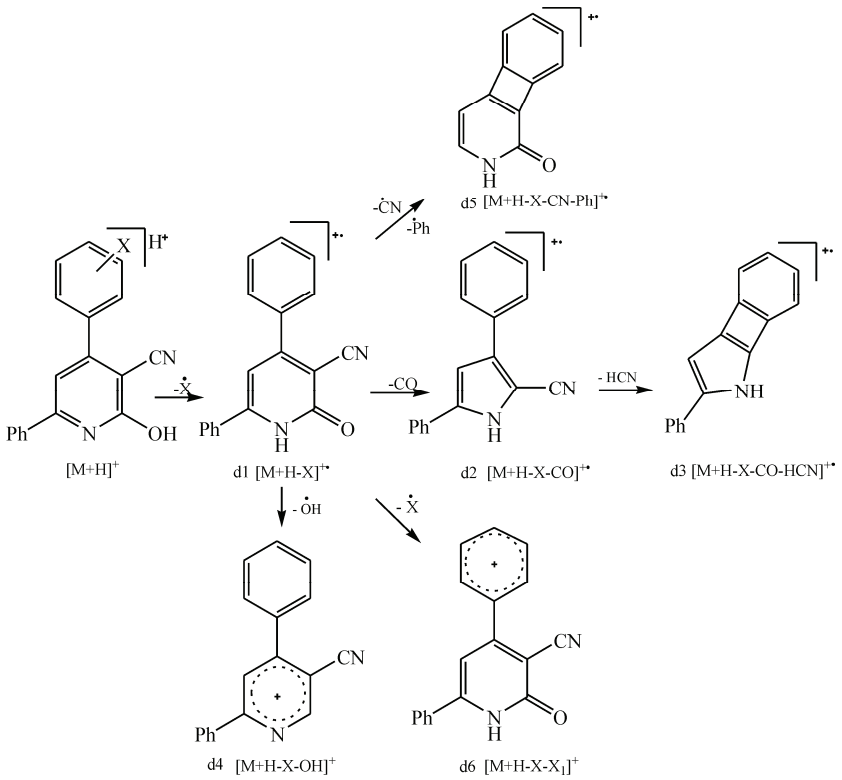
The loss of HCN (fragmentation "route b", Scheme 1) followed by either the loss of CO or a CN radical was observed only for compounds **2** and **3**, in which a non-polar and weak electron donor methyl group is the substituent on the phenyl ring. In this case, the pyridinone ring is destabilized and by either loss of CO or a CN radical decomposes, probably to form a five-membered, heterosubstituted

ring (ions b2 and b4, Scheme 1). The disubstituted compound **6** follows the path a1(*m*/*z* 323)-a4 (*m*/*z* 288) by loosing only one chlorine radical in this fragmentation step.

The loss of a PhH molecule is a common fragmentation observed for compounds **1**–**7**, and the fragmentation mainly follows the path through the c1-c2-c3 sequence (Scheme 2). The intensities of the corresponding ions depend on their electronic properties. Pyridinones having a weak electron-donor or one chlorine substituent (compounds **1**–**5**) further fragment by the loss of CO and HCN from the pyridinone ring to the c3 ion. An exception is compound **6**, in which the two chlorine atoms contribute to strong electron acceptor properties. Compound **6** follows either the path to the c3 ion without a trace of the c2 ion or by elimination of Cl or HCN from the c1 ion yielding the c4 and c5 ions. The significant abundance of the c4 ion in the pseudo MS^3 of compound **6** indicates the stabilisation of this ion by the positive resonance effect of the remaining chlorine atom. The structures of the c4 and c5 ions of the disubstituted chlorine compound **6** contain one and two chlorine atoms, respectively. Compound **7**, in which the substituent is the cyano group with strong electron-acceptor properties, fragments to the c1 ion, showing quasimolecular ion stability.

The complete loss of substituent from $[M+H]^+$ follows the fragmentation paths presented in Scheme 3. This type of fragmentation is influenced by a significant destabilisation of the protonated quasimolecular ions by the electron acceptor-character of the substituent. Compounds **4** and **5** (3-Cl and 4-Cl substituents, respectively) gave a base peak d2 in the pseudo MS^3 spectra, showing a significant pyrrole type fragment stability. Considering the position of the chlorine atom in compounds **4** and **5**, small influences on the fragmentation paths could be observed. On the contrary, the fragmentation of the $[M+H]^+$ ions from compound **6** is somewhat different, indicating that the *ortho* position of the chlorine atom causes rotation of the 4-substituted phenyl ring for certain dihedral angle from a plane of the pyridinone ring. From this point of view, it is clear that the geometry of the investigated compounds also influences the fragmentation paths to some extent. For compound **6**, after the loss of one chlorine from $[M+H]^+$, the second one remains attached in structures d1, d2 and d4.

If substituents with a significant proton acceptor affinity are present in the investigated compounds, the complex fragmentation paths depend mainly on the proton acceptor ability. Compound **9**, (with one methoxy group) and compound **10** (with two methoxy groups) show some similarities but also some differences in the fragmentation paths of their $[M+H]^+$. The methoxy group was fragmented by the loss of a methyl radical, leaving a hydroxy group as a possible site for the expulsion of carbon monoxide (*m*/*z* 232) or loss of a water molecule (*m*/*z* 242). On the contrary, in the case of compound **10**, the loss of a methyl radical is followed by the loss of a formyl radical from the second methoxy group, gene-



Scheme 3. Proposed fragmentation pathways of $[M+H]^+$ for the loss of the substituent in the first step.

rating the *m*/*z* 289 ion. Subsequent fragmentations involving the loss of CO, PhH and H_2O molecules are the usual fragmentations observed for all compounds. Fragmentation of compound **12** is strongly affected by the high proton acceptor affinity of the dimethylamino group. The protonated amino group easily releases methane, providing a base peak *m*/*z* 300 in the MS^2 spectrum of this compound, which after a loss of HCN produces the *m*/*z* 273 ion. The so-created methylimino group is significantly stable and further fragmentation occurs by elimination of either a PhH molecule or loss of an OH radical, producing *m*/*z* 195 and 256 ions, respectively. The nitro group present in compound **11** does not posses proton acceptor affinity but, after the well-known loss of a NO radical, the formed hydroxyl group is a good proton-acceptor (*m*/*z* 288).

The loss of a CO molecule, a typical fragmentation for 2-pyridinones molecular ion under EI condition,[14,15] is only observed for compound **8** with a low abundance of the *m*/*z* 337 ions in the MS^2 spectrum. However, by expulsions of CO from b1, c1, d1, *m*/*z* 288, 260 and 289 ions were also observed in the quasi-MS^3 spectra. This indicates appropriate influences of the tautomeric forms from

the equilibrium in the sample solution to the fragmentation paths of the investigated compounds under ESI^+ condition.

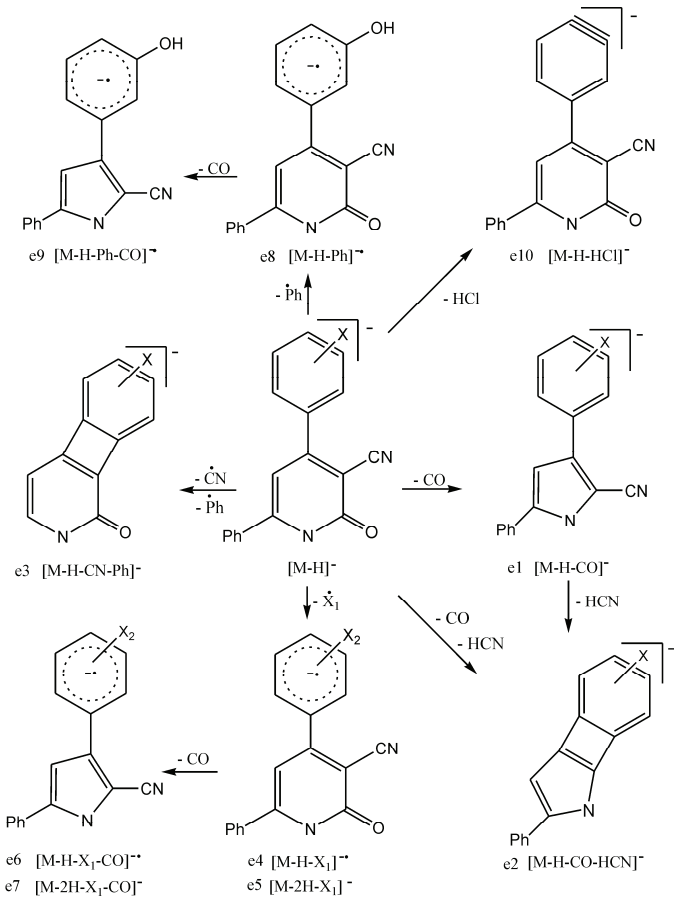
Fragmentation reactions of [M–H]⁻

Contrary to the positive ESI-MS, where elimination of H_2O molecules was favoured, the main fragmentation process in the negative ESI–MS was the elimination of CO molecules, observed for almost all the investigated compounds. An example of the MS/MS spectrum of the $[M–H]^-$ of 4-(3-chlorophenyl)-3-cyano--6-phenyl-2(1*H*)-pyridinone is presented in Fig. 1b. The mass spectral data obtained in the negative ionization mode for $[M–H]^-$ of all investigated compounds are presented in Table II.

TABLE II. Mass spectral data of the 3-cyano-4-(substituted phenyl)-6-phenyl-2(1*H*)-pyridinones in the negative ionization mode (superscripts of the *m*/*z* values define the corresponding structures in Scheme 4)

Compound	X	$[M–H]^-$ (Precursor ions for MS^2)	MS^2 Spectrum
1	H	271(100)	$243e^1$(100)
2	4-CH_3	285(100)	$257e^1$(100)
3	3-CH_3	285(100)	257^{e1}(12)
4	3-Cl	305(100)	269^{e10}(58); 250^{e2}(7); 242^{e6}(5); 202^{e3}(16)
5	4-Cl	305(100)	269^{e10}(7); 250^{e2}(16)
6	2,4-di-Cl	339(100)	303^{e10}(42); 236^{e3}(12)
7	4-CN	296(100)	268^{e1}(17); 241^{e2}(30); 193^{e3}(30)
8	3-OPh	363(100)	286^{e8}(100); 270^{e4}(6); 258^{e9}(12)
9	4-OCH_3	301(100)	286^{e4}(26)
10	3,4-di-OCH_3	331(100)	316^{e4}(100); 315^{e5}(63); 287^{e7}(15)
11	3-NO_2	316(100)	286^{e4}(100); 270^{e4}(78); 258^{e6}(4)
12	4-$N(CH_3)_2$	314(100)	299^{e4}(35); 298^{e5}(8)

The fragmentations of compounds **9**, **10** and **12**, with strong electron-donor substituents, show the loss of a methyl radical. These fragmentations are similar to the corresponding ones in the ESI^+ mode. Phenyl radical loss is the base peak in the spectrum of compound **8**. The substituent in compound **11**, being a strong electron-acceptor, shows the ability to lose a nitrosyl radical in the negative ionization mode. The main fragmentation process for the chloro-substituted compounds is the loss of HCl, probably due to the accommodation of a negative charge on chlorine atom, which extracts the neighbouring proton. Typical fragmentations of the investigated pyridinones in the ESI^- ionisation mode are presented in Scheme 4.



Scheme 4. Proposed fragmentation paths of the $[M–H]^-$ in the MS^2 spectra; e4 and e6 ions: $X_1 = CH_3$ for compounds **9** (*m*/*z* 286; X_2 = OH) and **10** (*m*/*z* 316; X_2 = 3-OH and 4-OCH_3), $X_1 = CH_3$ for compound **12** (*m*/*z* 299; $X_2 = NHCH_3$), X_1 = NO (*m*/*z* 286; X_2 = OH) or NO_2 (*m*/*z* 270; X_2 = H) for compound **11**, X_1 = OPh for compound **8** (*m*/*z* 270; X_2 = H); e5 and e7 ions: $X_1 = CH_4$ for compound **10** (*m*/*z* 315; X_2 = 3-OH and 4-OCH_3), $X_1 = CH_4$ for compound **12** (*m*/*z* 298; $X_2 = NHCH_2$); e10 ion containing one chlorine for the dichloro-substituted compound.

CONCLUSIONS

The typical peaks appearing in the ESI^+ spectra of all pyridinones are the protonated molecular ion $[M+H]^+$, the corresponding molecular ion adducts with sodium $[M+Na]^+$ and cluster ions $[2M+Na]^+$, $[2M–H+2Na]^+$ and $[2M–2H+3Na]^+$. The negative ESI-MS spectra exhibit far fewer ions, which are, apart from $[M–H]^-$, $[2M–2H+Na]^-$ and $[3M–3H+2Na]^-$.

Different factors influence the fragmentation pattern of the investigated pyridinones in the positive ionization mode. The position and proton affinity of the substituents play an important role in the fragmentation processes in the MS^2 and

MS^3 spectra. Pyridinones with a substituent of low proton affinity show loss of water, HCN or benzene from the pyridinone ring in the first step of MS^2 fragmentations. Conversely, if a substituent with a high proton affinity is present at the phenyl ring in the 4-position of pyridinone, the complex fragmentation paths depend mainly on the substituent proton acceptor ability. Elimination of neutral molecules CO, HCN, H_2O and PhH (benzene) or Ph and CN radicals are fragmentation processes common for all compounds in the subsequent steps of the fragmentations.

The ionisation mode significantly influences the fragmentations depending on the tautomeric form of the investigated compounds. In ESI^+, water molecule elimination indicates that protonation of the hydroxyl group of the lactam tautomer occurs. On the contrary, in ESI^-, expulsion of a CO molecule indicates deprotonation of the hydroxyl group.

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ИЗВОД

ESI–MS СПЕКТРИ 3-ЦИЈАНО-4-(СУПСТИТУИСАНИ ФЕНИЛ)-6-ФЕНИЛ-2(1*H*)-ПИРИДИНОНА

АЛЕКСАНДАР Д. МАРИНКОВИЋ, ТАТЈАНА М. ВАСИЉЕВИЋ, МИЛА Д. ЛАУШЕВИЋ и БРАТИСЛАВ Ж. ЈОВАНОВИЋ

Технолошко–металуршки факултет, Универзитет у Београду, п.пр. 3503, Карнегијева 4, 11120 Београд

3-Цијано-4-(супституисани фенил)-6-фенил-2(1*H*)-пиридинони су испитивани тандем масеном спектрометријом коришћењем позитивне и негативне електроспреј јонизације. Испитиван је утицај супституената и стерног ефекта на фрагментације. Пиридинони који имају супституенте малог афинитета према протону показују губитак воде, HCN или бензена из пиридинонског прстена у првом кораку MS^2 фрагментација. Супротно, ако је супституент са високим афинитетом према протону присутан на фенилном прстену у 4-положају пиридинона, сложени фрагментациони путеви углавном зависе од јачине те интеракције. Елиминације неутралних молекула CO, HCN, H_2O, PhH (бензен) или Ph и CN радикала су фрагментациони процеси уобичајени за сва испитивана једињења у наредним фрагментационим ступњевима.

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