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MASS SPECTROMETRY OF AROMATIC CYCLIC IMIDES AND AMIDES. PART I: ELECTRON IONIZATION INDUCED DECOMPOSITION OF *N*-SUBSTITUTED 2,3-PYRIDINE-DICARBOXIMIDES

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Abstract – The behaviour of a series of *N*-substituted 2,3-pyridinedicarboximides (**1-14**) under electron impact mass spectrometry at 70eV is analyzed. Compounds under study were divided into three groups according to their substitution patterns, namely *N*-aryl, *N*-alkyl and *N*-functionalized alkyl derivatives, which in turn determine the dominant fragmentations. The proposed fragmentation patterns are supported by high resolution, B/E and B^2/E linked-scan mass spectrometric data of some selected compounds. Results are compared in some cases to data reported for the related phthalimides.

INTRODUCTION

From its early days, mass spectrometry has been effectively employed for the structural characterization of aromatic cyclic imides. In particular, dissociation of phthalimides under electron impact[1-9] has been thoroughly studied. However, analogous imides with pyridine nucleus have received less attention. Following previous research of our group on the characterization of nitrogen containing heterocycles by mass spectrometry,[10] mass spectral analysis of a series of 2,3-pyridinedicarboximides (quinolinimides) has been undertaken. Although they proved to be interesting as synthetic intermediates[11-13] and biological activity was observed for some of them,[14] there are only a few reports concerning the mass spectrometry of such compounds. Typically, fragmentation occurs mainly upon expulsion of neutral molecules. Therefore, the main ions of non substituted quinolinimide come from fragmentation of molecular ion by successive losses of HNCO, CO and HCN.[3,15] Besides, Bentley and Johnston have reported spectra of *N*-methyl and *N*-phenylquinolinimide where fragmentation occurs mainly by losses of CO_2, CO and isocyanates (RNCO) from molecular ion.[3] These authors analyzed the results in relation to decarboxylation and decarbonylation processes and comparing them to those of other imides, specially

phthalimides and cinchomeronimides.

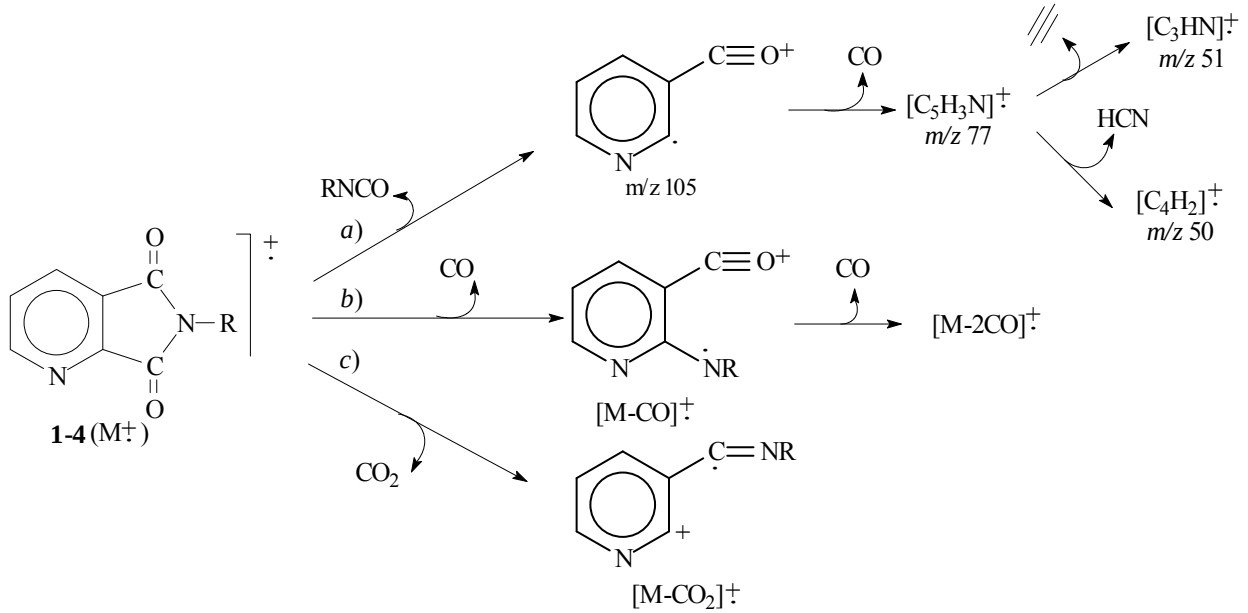
We present here a study of electron impact mass spectrometry of a series of *N*-substituted quinolinimides. Fragmentation patterns show remarkable differences depending on the type of susbstituents. For a better analysis of their fragmentation, compounds under study were divided into three groups according to their substitution patterns: *N*-aryl substituted quinolinimides (**1-4**), *N*-alkyl or benzyl substituted quinolinimides (**5-9**) and *N*-substituted compounds with functionalized alkyl groups, namely quinolinimidoacetic acid (**10**) and their amides (**11-14**).

Proposed fragmentation pathways are supported by high resolution data and B/E and B^2/E linked scan experiments of selected compounds. Results are compared in some cases to data reported for related phthalimides.

RESULTS AND DISCUSSION

N-Aryl-2,3-pyridinedicarboximides (1-4) (Table 1)

Relative abundance of the molecular ion varies depending on the aryl group substitution. Thus, for compounds **1** and **2** is the base ion, whereas in the spectrum of *o*-nitrophenyl derivative (**3**) it appears with low abundance, due to an initial loss of a nitro group being $[M\text{-}NO_2]^+$ the base peak. Spectra are in general simple and display few peaks. Three main fragmentation routes (Scheme 1) were observed.



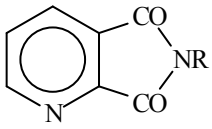
Scheme 1. Fragmentation pathways of *N*-aryl-2,3-pyridinedicarboximides (**1-4**) under EI conditions

Route ***a*** involves initial loss of aryl isocyanate (ArNCO) leading to ions at *m/z* 105, 77 (base ion for compound **4**), 51 and 50.

The successive loss of two molecules of CO (Route ***b***) is observed in all compounds except for the

o-nitrophenyl derivative (**3**), that undergoes previous loss of a nitro group. Decarbonylation favoured by the presence of pyridine nitrogen is a characteristic feature of these compounds which is not observed for analogous *N*-arylphthalimides.[1] Specially the first loss of CO is the most favoured process for 2-pyridyl derivative (**4**) and leads to a prominent ion at *m/z* 197 (77%). Formation of a highly conjugated tricyclic ion (Scheme 2), supports the relative abundance of such ion.

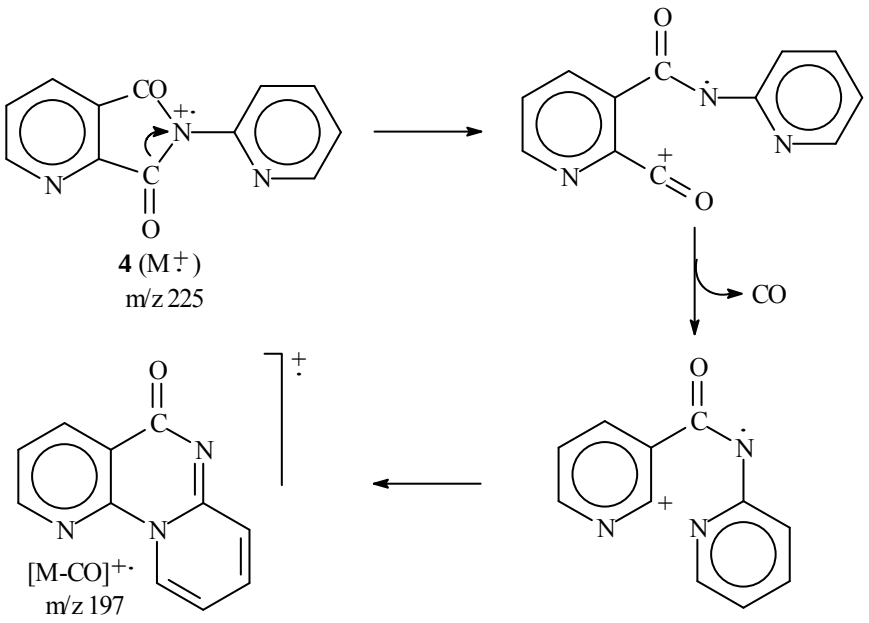
Table 1. Select fragments in the EI mass spectra of *N*-aryl-2,3-pyridinedicarboximides (**1-4**) [*m/z* (% relative abundance)]



Ion	**1** [b] R= C_6H_5	**2** R= 4-ClC_6H_4	**3** R= 2-$NO_2C_6H_4$	**4** R= 2-C_5H_4N
$[M]^{+\cdot}$	224 (100)	258 (100), 260 (33)	269 (6)	225.0539 (52) [c]
$[M-CO]^{+\cdot}$	196 (7)	230 (7), 232 (2)	241 (-)	197.0579 (77) [d]
$[M-CO_2]^{+\cdot}$	180 (26)	214 (27), 216 (8)	225 (-)	181 (1)
$[M-2CO]^{+\cdot}$	168 (5)	202 (5), 204 (2)	213 (-)	169.0652 (16) [e]
$[M-RNCO]^{+\cdot}$	105 (28)	105 (48)	105 (31)	105.0227 (72) [f]
m/z 77	(36)	(62)	(72)	77.0276 (100) [g]
m/z 51	(10)	(13)	(22)	(49)
m/z 50	(14)	(46)	(55)	(63)
Others		179 (22) $[M-CO_2-Cl]^+$	223 (100) $[M-NO_2]^+$	224.0475 (33) $[M-1]^+$ [h]
[a]		167 (8) $[M-2CO-Cl]^+$	195 (38)	198.0420 (24) $[M-HCN]^{+\cdot}$ [i]
		76 (21)	$[M-NO_2-CO]^+$	121 (28)
			167 (13)	94 (19)
			$[M-NO_2-2CO]^+$	78 (63)
			140 (22)	76 (24)
			76 (26)	67 (20)
			63 (17)	

[a] Characteristic peaks and/or with relative abundances higher than 15% are depicted. [b] *m/z* and relative abundances are similar to those obtained by Johnstone.[3] [c] Calcd. for $C_{12}H_7N_3O_2$: 225.0538. [d] Calcd. for $C_{11}H_7N_3O$: 197.0589. [e] Calcd. for $C_{10}H_7N_3$: 169.0640. [f] Calcd. for C_6H_3NO: 105.0215. [g] Calcd. for C_5H_3N: 77.0265. [h] Calcd. for $C_{12}H_6N_3O_2$: 224.0460. [i] Calcd. for $C_{11}H_6N_2O_2$: 198.0429.

Loss of CO_2 (Route ***c***) is only important for compounds **1** and **2**. This fact shows that, as in phthalimides,[3,6] decarboxylation only occurs when there is no other more energetically favoured pathway. Loss of Cl in compound **2** occurs after decarbonylation and decarboxylation.



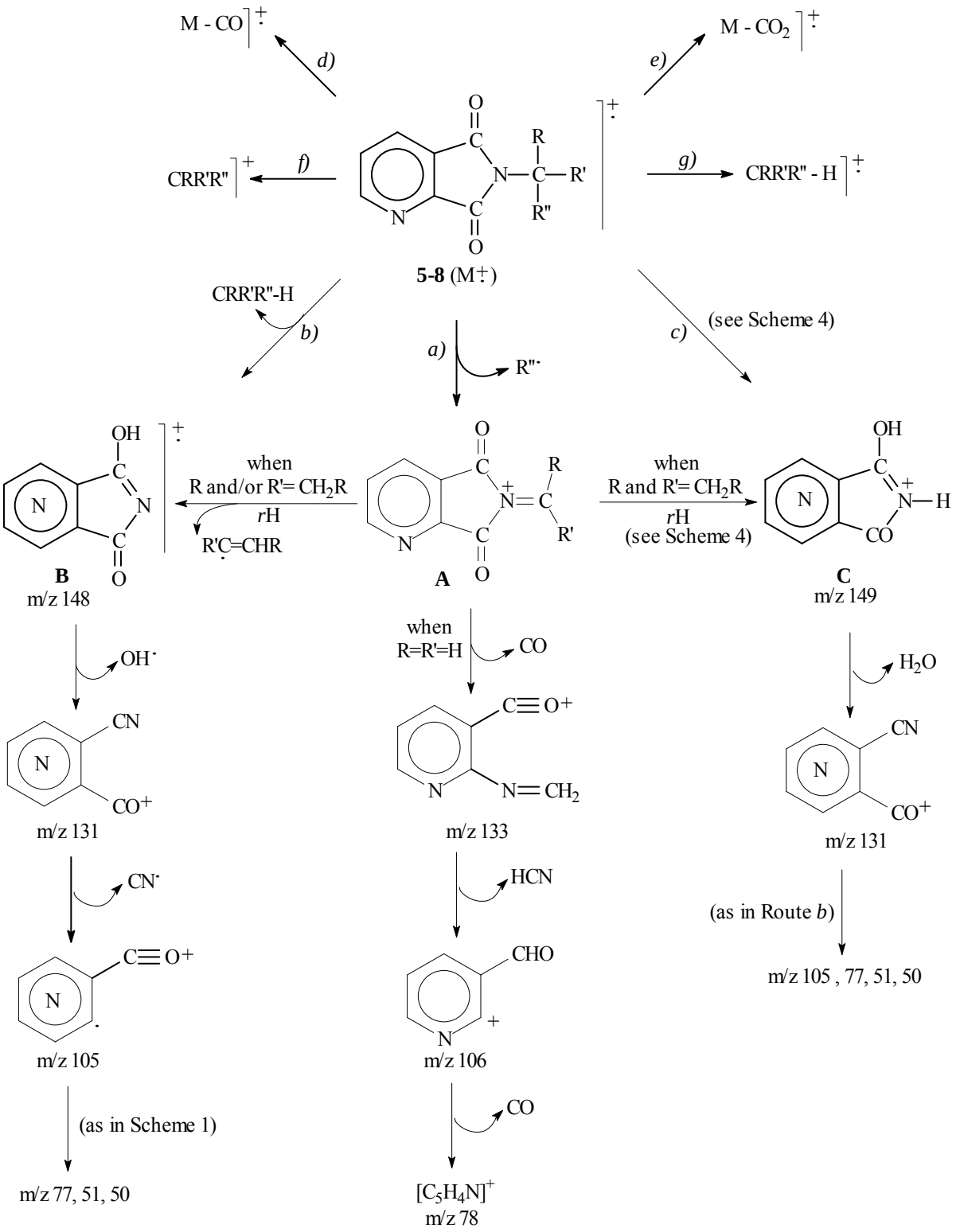
Scheme 2. Possible mechanism for the decarbonylation of compound **4** molecular ion leading to a tricyclic ion (M-CO)

***N*-Alkyl-2,3-pyridinedicarboximides (5-9)** (Table 2)

The molecular ion is generally abundant being the base ion in the *N*-methyl derivative (**5**). The increase in branching leads to a decrease in $[M]^{+\cdot}$ relative abundance and more complex spectra are observed.

Main fragmentation pathways are depicted in Scheme 3. Route ***a*** corresponds to the α-cleavage to imide nitrogen leading to iminium ion **A**, base ion in *N*-ethyl- and *N*-isopropylquinolinimide (**6** and **7**) spectra and almost negligible in *N*-benzyl derivative (**9**). Subsequent fragmentation of ions **A** depends on methylene carbon substitution. B/E linked-scan experiment shows that non substituted iminium ion obtained from compound **6** (**A**, R=R'=H, *m/z* 161) undergoes initial degradation losing CO and originating *m/z* 133 ion. Further loss of HCN and CO leads to characteristic ions at *m/z* 106 and 78. Initial loss of HCN, as it occurs in iminium ions generated from analogous phthalimides,[2,5] is not observed. This fact shows again the importance of pyridine nitrogen atom in favouring decarbonylation reactions.

Formation of *m/z* 148 ion (**B**) is probably due to a McLafferty rearrangement (Route ***b***) as the result of a hydrogen transfer from the alkyl side chain to the carbonyl group with charge retention on the imide moiety. Thus, the required presence of hydrogen on a β-carbon to imide nitrogen is responsible for the appearance of such ions in compounds **6** (70%), **7** (52%) and **8** (79%) and their absence in **5** and **9**. Additional source of ions **B** are the iminium ions **A** which can transfer a hydrogen from an alkyl side chain. B/E linked-scan data support this hypothesis, showing that iminium ion **A** (R=H, R'=Me, *m/z* 175) generated from compound **7** leads to *m/z* 148. Fragmentation follows with sequential loss of OH, CN (also confirmed by B/E linked scan spectrum) and CO leading to ions at *m/z* 131, 105 and 77.

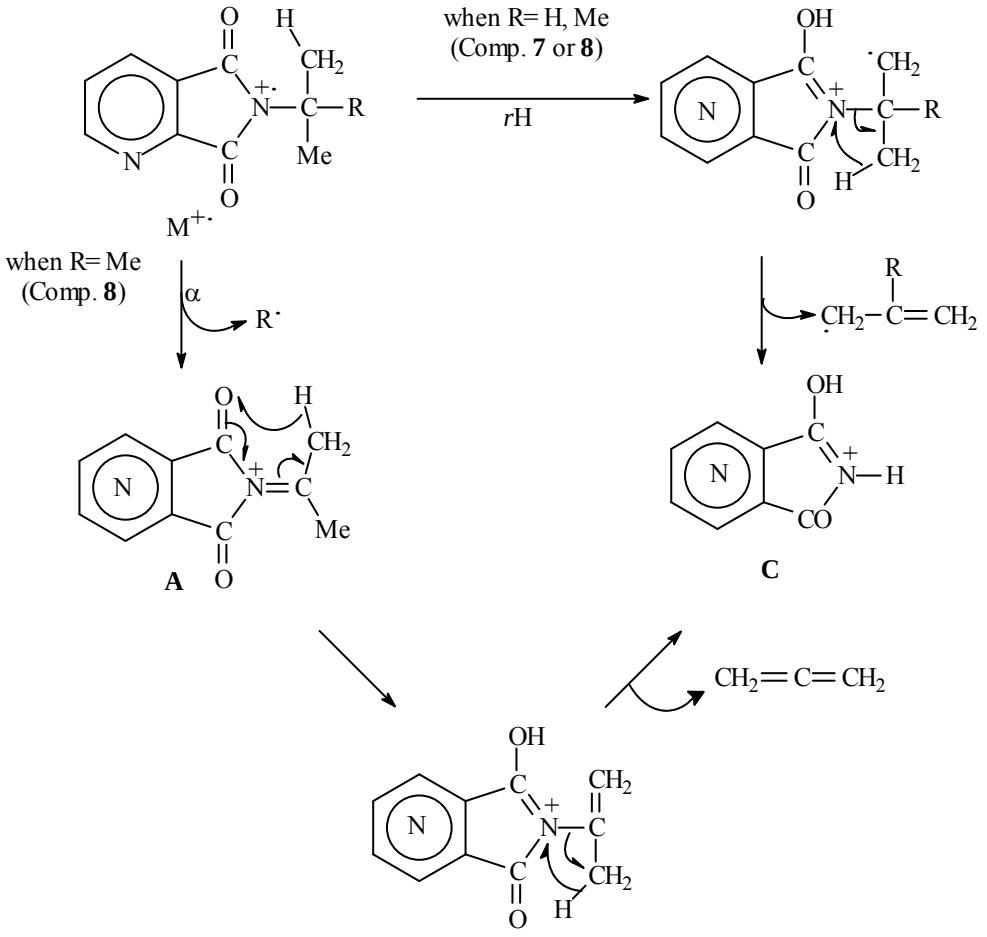


Scheme 3. Fragmentation pathways of *N*-alkyl-2,3-pyridinedicarboximides (**5-8**) under EI conditions

Ions at *m/z* 149 (Route ***c***), compatible with structure **C** (protonated imide) formally arise from the parent ion as a result of a double hydrogen transfer (to oxygen and to nitrogen) with loss of the side chain as allyl radical and charge retention on the imide moiety (Scheme 4). This mechanism requires the presence of at least two alkyl groups located on an α-carbon having hydrogens available for transfer. This explains

the presence of such ions in the spectra of compounds **7** and **8** and its absence in the ones of **5**, **6** and **9**. However, this ion may also come from properly substituted iminium ion **A** having two hydrogens capable to be transferred with the loss of an allene. This was confirmed by a B^2/E experiment of the ion at *m/z* 149 obtained from compound **8**. The fact that in *N*-*tert*-butyl derivative (**8**), the protonated imide **C** is the base ion and in *N*-isopropyl derivative (**7**) shows low abundance (14%), would indicate that its main source should be iminium ion **A**. B/E linked scan experiments show that degradation of ion **C** begins with the loss of water affording ions at *m/z* 131, 105 and 77.

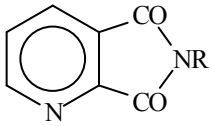
Loss of small molecules from molecular ion are less important pathways. Although expulsion of CO (Route ***d***) originates ions showing low abundance, it is a characteristic feature of all the quinolinimides studied. Loss of CO_2 (Route ***e***) only has some importance in *N*-methyl derivative (**5**), where $[M\text{-}CO_2]^{+\cdot}$ ion (*m/z* 118) appears with a relative abundance of 6%.



Scheme 4. Formation of ion **6** (protonated imide) through hydrogen transfer reactions

Other ions which may appear in spectra are those arising from cleavages with charge retention on an alkyl moiety. Thus, heterolytic cleavage of N-R bond leads to stabilized $[R]^+$ ions (Route ***f***): $[C_4H_9]^+$ (*m/z* 57, 36%) in compound **8** and $[C_7H_7]^+$ (tropylium ion, *m/z* 91, 25%) in **9**.

Table 2. Select fragments in the EI mass spectra of *N*-alkyl-2,3-pyridinedicarboximides (**5-9**) [*m/z* (% relative abundance)]

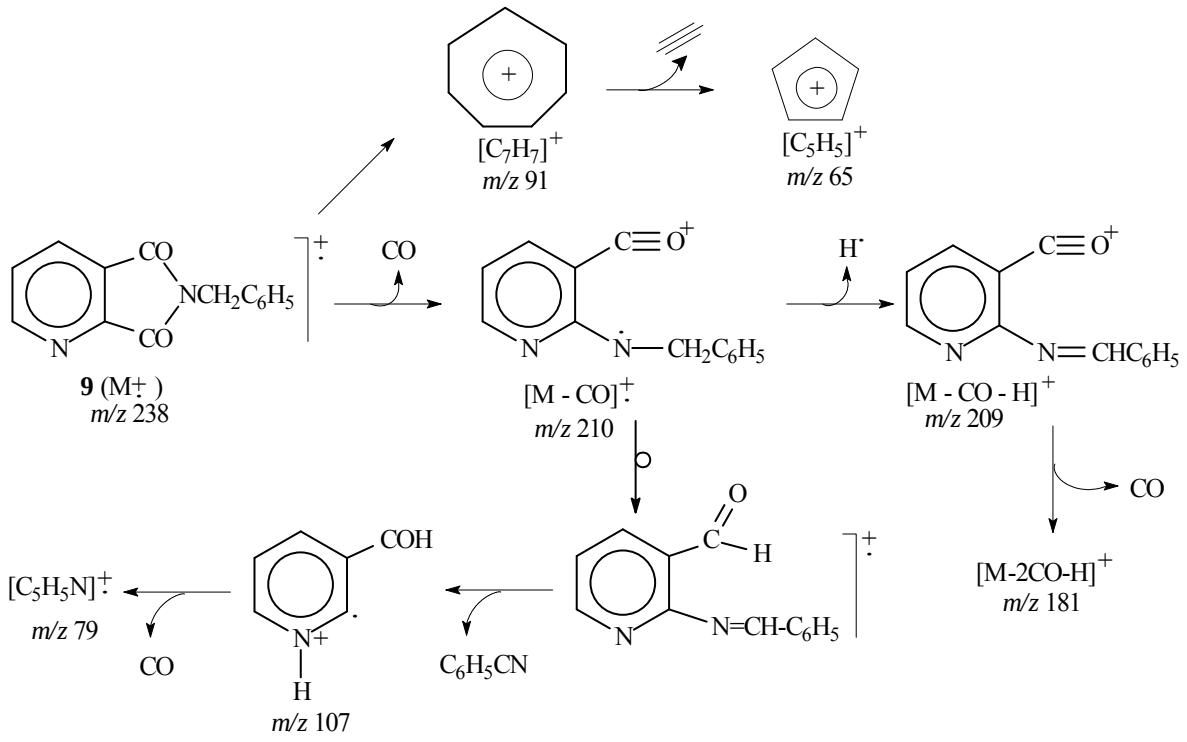


Ion	**5** [b] R= Me	**6** R= C_2H_5	**7** R= $CH(Me)_2$	**8** R= $C(Me)_3$	**9** R= $CH_2C_6H_5$
$M^{+\cdot}$	162 100)	176.0520 (92) [c]	190.0747 (55) [k]	204 (43)	238.0730 (63) [t]
$[M\text{-}CO]^{+\cdot}$	134 (16)	148.0673 (18) [d]	162.0822 (18) [l]	176 (6)	210.0780 (17) [u]
$[M\text{-}CO_2]^{+\cdot}$	118 (6.0)	132 (-)	146 (-)	160 (1)	194 (2)
$[\mathbf{A}]^+$	161 (5)	161.0399 (100) [e]	175.0520 (100) [m]	189 (69)	161 (1)
m/z 149 $[\mathbf{C}]^+$	(-)	(-)	149.0380 (14) [n]	(100)	(-)
m/z 148 $[\mathbf{B}]^{+\cdot}$	(-)	148.0205 (70) [f]	148.0238 (52) [o]	(79)	(-)
m/z 131	(-)	131.0190 (11) [g]	131.0223 (36) [p]	(51)	(-)
m/z 106	(13)	106.0329 (74) [h]	106.0299 (20) [q]	(10)	(35)
m/z 105	(72)	105.0279 (61) [i]	105.0255 (26) [r]	(19)	(10)
m/z 78	(14)	(57)	(46)	(37)	(45)
m/z 77	(61)	(82)	77.0258 (42) [s]	(49)	(40)
m/z 51	(10)	(50)	(26)	(30)	(39)
m/z 50	(23)	(80)	(41)	(57)	(27)
Others		133.0458 (16) [j]	101 (27)	57 (36)	212 (19)
[a]		79 (36)	42 (14) $[C_3H_6]^{+\cdot}$	$C_4H_9]^+$	209.0723 (12)
		76 (28)		56 (38)	$[M\text{-}CO\text{-}H]^+$ [v]
				$[C_4H_8]^{+\cdot}$	181.0782 (40)
				42 (79)	$[M\text{-}2CO\text{-}H]^+$ [w]
					107.0390 (21) [x]
					91 (25) $[C_7H_7]^+$
					79.0434 (100) [y]
					65 (21) $[C_5H_5]^+$

[a] Characteristic peaks and/or with relative abundances higher than 15% are depicted. [b] *m/z* and relative abundances are similar to those obtained by Johnstone.[3] [c] Calcd. for $C_9H_8N_2O_2$: 176.0586. [d] Calcd. for $C_8H_8N_2O$: 148.0637. [e] Calcd. for $C_8H_5N_2O_2$: 161.0351. [f] Calcd. for $C_7H_4N_2O_2$: 148.0273. [g] Calcd. for $C_7H_3N_2O$: 131.0246. [h] Calcd. for C_6H_4NO: 106.0293. [i] Calcd. for C_6H_3NO: 105.0215. [j] Calcd. for $C_7H_5N_2O$: 133.0402 [k] Calcd. for $C_{10}H_{10}N_2O_2$: 190.0742. [l] Calcd. for $C_9H_{10}N_2O$: 162.0794. [m] Calcd. for $C_9H_7N_2O_2$: 175.0508. [n] Calcd. for $C_7H_5N_2O_2$: 149.0351. [o] Calcd. for $C_7H_4N_2O_2$: 148.0273. [p] Calcd. for $C_7H_3N_2O$: 131.0246. [q] Calcd. for C_6H_4NO: 106.0293. [r] Calcd. for C_6H_3NO: 105.0215. [s] Calcd. for C_5H_3N: 77.0265. [t] Calcd. for $C_{14}H_{10}N_2O_2$: 238.0742. [u] Calcd. for $C_{13}H_{10}N_2O$: 210.0793. [v] Calcd. for $C_{13}H_9N_2O$: 209.0715. [w] Calcd. for $C_{12}H_9N_2$: 181.0766. [x] Calcd. for C_6H_5NO: 107.0371. [y] Calcd for C_5H_5N: 79.0422.

On the other hand, hydrogen rearrangement reactions with charge retention in the hydrocarbon moiety (Route ***g***), would originate ions at *m/z* 42 ($[C_3H_6]^{+\cdot}$, 14%) for compound **7** and *m/z* 56 ($[C_4H_8]^{+\cdot}$, 38%) for **8**.

N-Benzylquinolinimide (**9**) shows a fragmentation pattern different from that of all the *N*-alkylquinolinimides studied above. Thus, expulsion of CO is here the dominant primary fragmentation (Scheme 5). As in *N*-benzylphthalimide,[6] further loss of hydrogen leads to an iminium ion at *m/z* 209. Subsequent loss of another molecule of CO accounts for an important ion at *m/z* 181. The base ion is *m/z* 79 (FM: C_5H_5N) and it also arises from $[M\text{-}CO]^{+\cdot}$, as it is demonstrated by B/E and B^2/E linked-scan data. A rearrangement with expulsion of benzonitrile, would intermediately originate an odd-electron ion at *m/z* 107, almost inexistent in quinolinimides (**5**-**8**). Subsequent decarbonylation with a double hydrogen transfer to pyridine nucleus accounts for the *m/z* 79 ion.

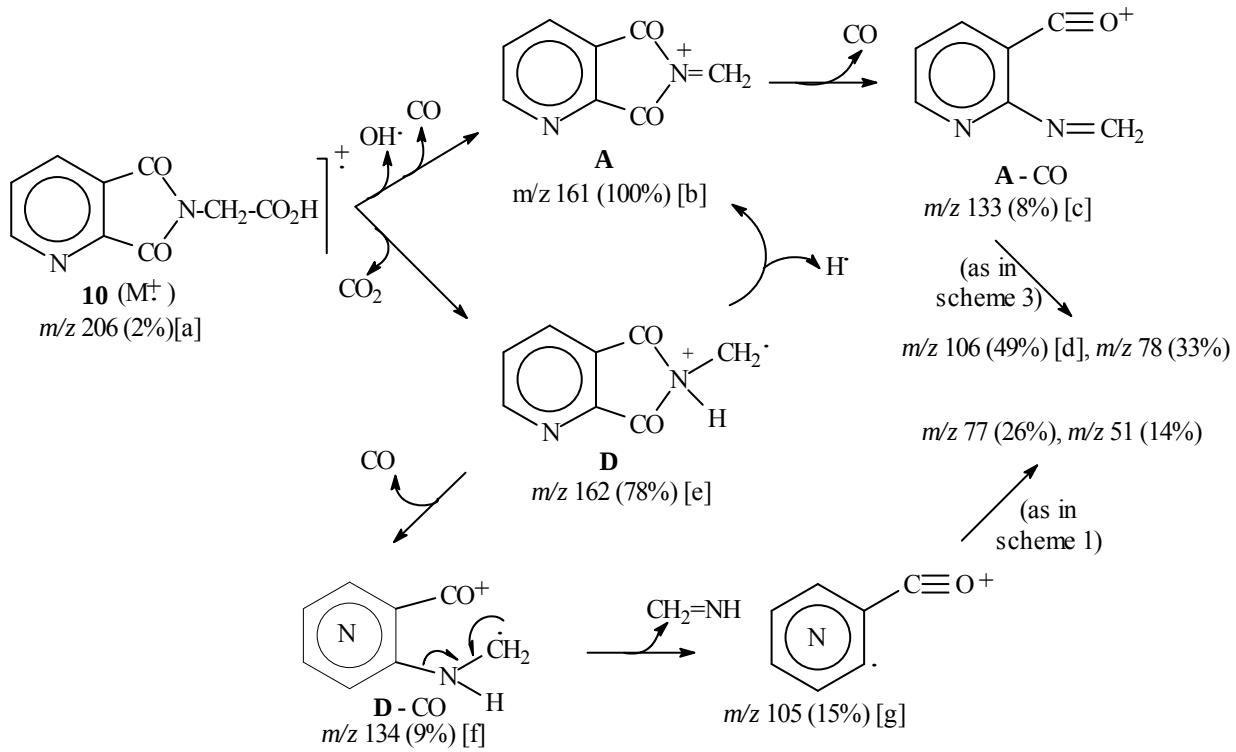


Scheme 5. Fragmentation pathways of *N*-benzyl-2,3-pyridinedicarboximide (**9**) under EI conditions

2,3-Pyridinedicarboximidoacetic acid (**10**)

Mass spectrum of acid (**10**) shows $[M]^{+\cdot}$ of low abundance (2%) and suggests two dominant fragmentation pathways supported on B/E and B^2/E linked-scan experiments (Scheme 6). The first one, leads to iminium ion **A** (R=R'=H, *m/z* 161, 100% at 70 eV) which degradation accounts for ions at *m/z* 133, 106 and 78 (as pointed for compound **6**, Scheme 3). The second one, leading to an important ion at *m/z* 162 with a relative abundance (78%) superior to that expected for an isotopic ion of **A**. HRMS shows that the main ion corresponds to $C_8H_6N_2O_2$ originated from molecular ion decarboxylation. Structure **D**,

arising from a rearrangement which involves carboxyl hydrogen transfer to imide nitrogen with simultaneous cleavage of side chain Cα-Cβ bond, is proposed.[16] Similar rearrangements were observed for other *N*-substituted imides[7,17] and require the presence of a γ-hydrogen. Ion **D** undergoes degradation through two main routes. The first route implies the loss of neutral fragments (CO, CH_2=NH) leading to ions at *m/z* 134 and 105. The second route involves loss of hydrogen radical leads to iminium ion **A**. The latter pathway (*m/z* 162 → *m/z* 161) accounts for differences between relative abundances of ions at *m/z* 162 and 161 in spectra taken at 20 and 70 eV.[18] Thus, at 20 eV the base ion corresponds to ion at *m/z* 162, while at 70 eV transformation 162 → 161 is responsible for an increase in ion *m/z* 161 abundance (100%).



[a] Calcd. for $C_9H_6N_2O_4$: 206.0328; HRMS: *m/z* 206.0310. [b] Calcd. for $C_8H_5N_2O_2$: 161.0351; HRMS: *m/z* 161.0350. [c] Calcd. for $C_7H_5N_2O$: 133.0402; HRMS: *m/z* 133.0407. [d] Calcd. for C_6H_4NO: 106.0293; HRMS: *m/z* 106.0284. [e] Calcd. for $C_8H_6N_2O_2$: 162.0429; HRMS: *m/z* 162.0428. [f] Calcd. for $C_7H_6N_2O$: 134.0480; HRMS: *m/z* 134.0483. [g] Calcd. for C_6H_3NO: 105.0215; HRMS: *m/z* 105.0242.

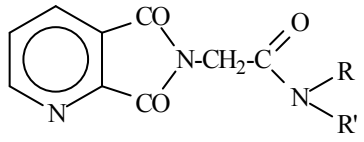
Scheme 6. Fragmentation pathways of 2,3-pyridinedicarboximidoacetic acid (**10**) under EI conditions

2,3-Pyridinedicarboximidoacetamides (**11-14**) (Table 3)

Ions corresponding to $[M]^{+\cdot}$ show variable abundance, being most intense in *N*-arylcarboxamides. Decomposition of amides reflects the strong tendency of carboxamide nitrogen to undergo reactions originating ions with charge retention. Four primary fragmentation pathways are observed in the spectra, depicted in Scheme 7. The importance of each one depends on the amide substitution pattern. Route ***a***

involves an α-cleavage leading to carboxamide ion $[CONRR']^+$. This pathway was by far the most important in *N,N*-disubstituted amides, leading to the base ion in compound **11** and to an abundant ion in compound **12** spectrum (73%). Fragmentation continues with the loss of CO originating $[NRR']^+$, base ion for compound **12**.

Table 3. Select fragments in the EI mass spectra of 2,3-pyridinedicarboximidoacetamides (**11-14**) [*m/z* (% relative abundance)]

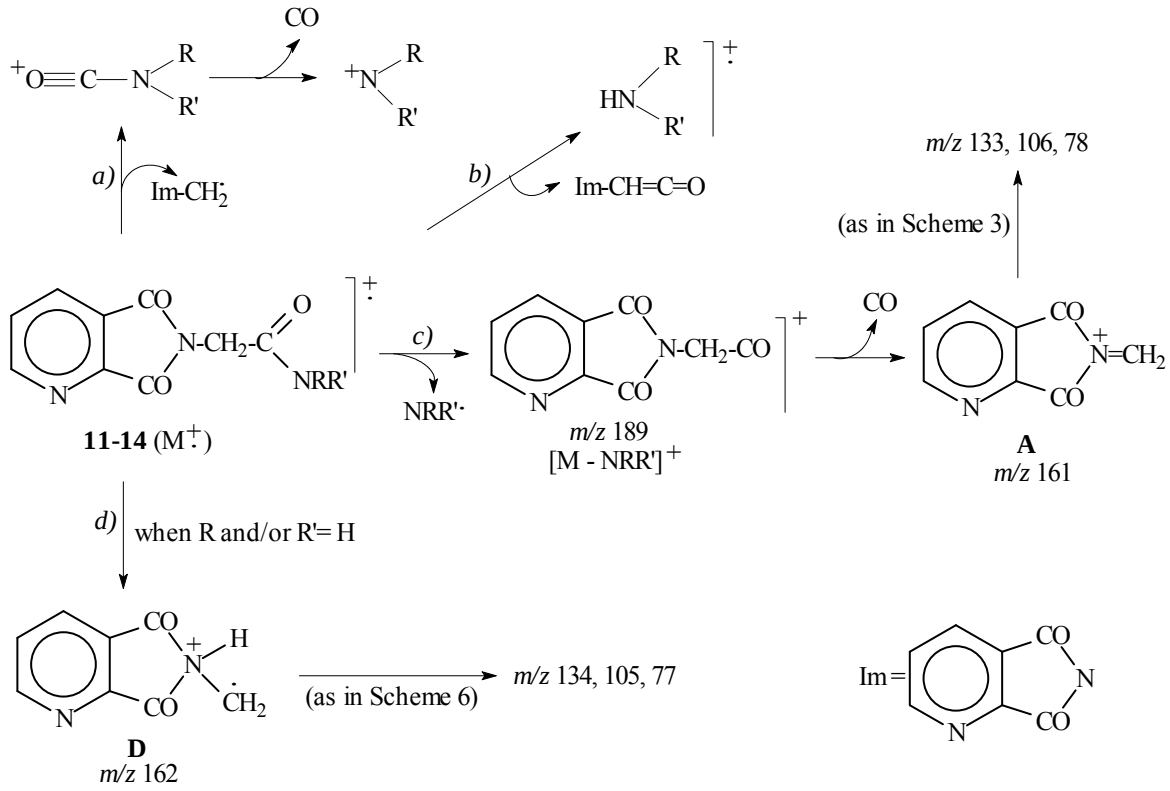


Ion	**11** R= Me, R'= C_6H_5	**12** R=R'= C_2H_5	**13** R= H, R'= C_6H_5	**14** R= H, R'= $CH(Me)_2$
$[M]^{+\cdot}$	295.0962 (56) [c]	261 (10)	281 (30)	247 (1)
$[CONRR']^+$	134.0554 (100) [d]	100 (73)	120 (5)	86 (3)
$[NRR']^+$	106.0607 (22) [e]	72 (100)	92 (-)	58 (14)
$[NHRR']^{+\cdot}$	107.0765 (60) [f]	73 (4)	93 (100)	59 (-)
m/z 189 $[M\text{-}NRR']^+$	(-)	(1)	(1)	(3)
m/z 161 $[\mathbf{A}]^+$	161.0408 (37) [g]	(14)	(80)	(40)
m/z 162 $[\mathbf{D}]^{+\cdot}$ [a]	(-)	(3)	(57)	(100)
m/z 134 $[\mathbf{D}\text{-}CO]^{+\cdot}$	(-)	-	(24)	(33)
m/z 133	133.0462 (10) [h]	(2)	(15)	(8)
m/z 106 [**A**-CO-HCN]	106.0238 (11) [i]	(8)	(67)	(28)
m/z 105	(1)	(4)	(19)	(13)
Others	51 (29)	44 (23)	79 (55)	79 (85)
[b]	50 (19)		78 (68)	78 (38)
			77 (49)	77 (22)
			51 (52)	232 (2) $[M\text{-}Me]^+$
			50 (36)	51 (24)
				50 (20)
				44 (41) $[NHRR'\text{-}Me]^+$
				43 (54) $[C_3H_7]^+$

[a] This ion has similar nominal mass to isotopic peak of ion A. [b] Characteristic peaks and/or with relative abundances higher than 15% are depicted. [c] Calcd. for $C_{16}H_{13}N_3O_3$: 295.0957. [d] Calcd. for C_8H_8NO: 134.0606. [e] Calcd. for C_7H_8N: 106.0657. [f] Calcd. for C_7H_9N: 107.0735. [g] Calcd. for $C_8H_5N_2O_2$: 161.0351. [h] Calcd. for $C_7H_5N_2O$: 133.0402. [i] Calcd. for C_6H_4NO: 106.0293.

Route ***b*** involves CO-N cleavage with hydrogen transfer to nitrogen. Such cleavage is typical of

acetamides[19] leading to odd electron ion $[HNRR']^{+\cdot}$. It is interpreted as the result of a methylene hydrogen transfer to carboxamide nitrogen, subsequent homolytic cleavage with charge retention on nitrogen and expulsion of a substituted ketene. This fragmentation pathway is important in anilides, whose spectra present intense peaks $[HNRR']^{+\cdot}$ (base peak in **13**). Although in *N*-alkylcarboxamides such radical ion is absent or appears with low abundance, ions arising from its further fragmentation are observed, therefore this route cannot be discarded. The spectrum of **14** shows an important ion at *m/z* 44 (41%) resulting from the α-cleavage of $[H_2NCH(Me)_2]^{+\cdot}$ with loss of Me.



Scheme 7. Fragmentation pathways of 2,3-pyridinedicarboximidoacetamides (**11-14**) under EI conditions

Route ***c*** leads to the stabilized iminium ion **A** (R=R'=H, *m/z* 161, 14-80%) probably through an intermediary acyl ion (*m/z* 189) which is generally detected with very low abundance.

In *N*-monosubstituted amides a prominent ion at *m/z* 162 is observed (base ion for **14**) for which the structure **D** is suggested. It is probably originated through a mechanism similar to that proposed for compound **10** and requires in this case a carboxamide hydrogen transfer with loss of RNCO.

SUMMARY

The electron impact mass spectrometry results a proper method for the characterization of *N*-substituted-2,3-pyridinedicarboximides (*N*-substituted quinolinimides). Fragmentation patterns show remarkable differences depending on the type of substituents on nitrogen.

N-Arylquinolinimides (**1-4**) undergo fragmentation mainly through the loss of molecules (ArNCO, CO, CO_2). Decarbonylation favoured by the presence of pyridine nitrogen is a distinctive feature of these compounds from analogous *N*-arylphthalimides.

When nitrogen substituent is a functionalized or non functionalized alkyl group (compounds **5-8**,**10**), main fragmentations lead to total or partial loss of the side chain with charge retention on the imide moiety. Unlike above compounds, expulsion of CO is the dominant primary fragmentation in the spectrum of *N*-benzylquinolinimide (**9**). Decomposition of quinolinimidoacetamides (**11-14**) reflects the strong tendency of carboxamide nitrogen to undergo reactions originating ions with charge retention: $[CONRR']^+$, $[NRR']^+$ and $[HNRR']^{+\cdot}$.

EXPERIMENTAL

Compounds **1-5**,**7-9**[20] **6**,[13] **10**,[21] and **11-14**[12] were synthesized according literature procedures. Mass spectra were obtained operating under electron impact at 70 eV unless otherwise indicated. Low resolution mass spectra were recorded using GC-MS Varian 1200-L triple quadrupole spectrometer (Varian, Walnut Creek, CA, USA). High resolution spectra were obtained with a model VG AutoSpec three sector (EBE) mass spectrometer (Waters, Milford, MA, USA) at a scan rate of 1 scan/4 sec, operating with variable magnetic field at a 8000 resolving power (10% valley definition) using perfluorokerosene (PFK) as the reference compound. B/E and B^2/E linked scan analysis were obtained on the same instrument. The conditions are: ionizing energy, 70 eV; 3500 resolving power (10% valley definition); detector voltage, 250 V; collision gas, argon at a pressure of 1.8 mTorr; precursor ion selected width, 0.5 Da.

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REFERENCES AND NOTES

1. J. L. Cotter and R. A. Dine-Hart, *Chem. Commun.*, 1966, 809.
2. R. T. Aplin and J. H. Jones, *Chem. Commun.*, 1967, 261.
3. T. W. Bentley and R. A. W. Johnstone, *J. Chem. Soc. (C),* 1968, 2354.
4. J. L. Cotter and R. A. Dine-Hart, *Org. Mass Spectrom.,* 1968, **1**, 915.
5. R. T. Aplin and J. H. Jones, *J. Chem. Soc. (C)*, 1968, 1770.
6. J. Sharvit and A. Mandelbaum, *Israel J. Chem.,* 1967, **5**, 33.
7. P. A. Blanc, F. O. Gülaçar, and A. Buchs, *Helv. Chim. Acta,* 1979, **62**, 2230.
8. A. Weisz, D. Andrzejewski, and A. Mandelbaum, *J. Mass Spectrom.*, 1996, **31**, 676.
9. J. Denitz, B. D. A. Monteiro, M. N. Ramos, and R. M. Srivastava, *Heterocyclic Commun.,* 1997, **3**,

115.

10. Among others: A. Salerno, M. E. Hedrera, N. B. D'Accorso, M. Martins Alho, and I. A. Perillo, *J. Heterocycl. Chem.,* 2000, **37**, 57; M. B. García, I. A. Perillo, and L. R. Orelli, *ARKIVOC (i),* 2006, 57; c) L. R. Orelli, M. B. García, I. A. Perillo, L. Tonidantel, and P. Traldi, *Rapid Commun. Mass Spectrom.,* 2006, **20**, 823.
11. Among others: M. Los, Brit. UK Pat. Appl. GB 2 174 395, 1986 (*Chem. Abstr*., 1986, **106**, 213943d); G. J. Hitchings and J. M. Vernon, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1757; K. A. M. Kremer, W.-X. Wu, and D. R. Maulding, R. US 5 905 154, 2000 (*Chem. Abstr*., 1999, **130**, 338097h).
12. M. M. Blanco, C. B. Schapira, G. Levin, and I. A. Perillo, *J. Heterocycl. Chem*., 2005, **42**, 493 and references cited therein.
13. R. L. Jacobs, US Patent 3,525,747, 1970 (*Chem. Abstr.,* 1970, **73**, 98985e).
14. Among others: H. Hiroshi, Jpn. Kokai Tokkyo Koho JP 82 85,386, 1982 (*Chem. Abstr*., 1982, **97**, 198187k); C. Bacha, I. Ferreira, P. Loiseau, E. Schapoval, J.-P. Tarayre, and C. Wolf, *Pharm. Acta Helvet*., 1987, **62**, 292; A. El-Haddad, A. H. Bedair, N. M. Nassar, and A. M. El-Naggar, *Orient. J. Chem.,* 1989, **5**, 118; T. A. Mohamed, M. M. Kandeel, I. M. A. Awad, M. S. K. Youssef, *Collect. Czech. Chem. Commun.,* 1991, **56**, 2999; G. Hamprecht, P. Muenster, M. Gerber, H. Walter, and K.-O. Westphalen, Ger. Offen DE 4,343,922, 1995 (*Chem. Abstr*., 1995, **123**, 256685q); V. Bailleux, L. Vallée, J. P. Nuyts, and J. Vamecq, *Biomed. & Pharmacother.,* 1995, **49**, 75; A. Scozzafava, L. Menabuoni, F. Mincione, F. Briganti, G. Mincione, and C. T. Supuran, *J. Med. Chem.,* 1999, **42**, 2641.
15. L. Spiessens and M. Anteunis, *Bull. Soc. Chim. Belg.,* 1980, **89**, 205.
16. An alternative structure would be that corresponding to *N*-methylquinolinimide (**5**) molecular ion. However, absence of ion at *m/z* 118 (characteristic of compound **5**) in spectrum of compound **10** and in the B/E linked scan spectrum of ion at *m/z* 162, allow us to discard such possibility.
17. H. Budzikiewicz, C. Djerassi, and D. H. Williams, *"Mass Spectrometry of Organic Compounds"*, Holden-Day, Inc., 1967
18. MS of compound **10** at 20 eV: *m/z* (%): 206 (2), 162 (100), 161 (89), 134 (11.3), 133 (5), 106 (23), 105 (6). 78 (7), 77 (3).
19. F. W. McLafferty and F. Tureček, "*Interpretation of Mass Spectra*", University Science Books, 1993.
20. M. M. Blanco, G. L. Levin, C. B. Schapira, and I. A. Perillo, *Heterocycles,* 2002, **57**, 1881.
21. F. C. Lee and L. R. Caswell, *J. Heterocycl. Chem.,* 1971, **8**, 831.