Molecular Ions Resulted in Mass Spectrometer for 1,3-*bis*(phenylselanyl)-azulenes and Their Oxidized Products

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The reported results in this paper confirm the previous statement on the limited validity of the EE rule for the molecular ion generation when ESI method was used in mass spectrometer. Thus, the ratio $[M]^{\cdot +}/[M+1]^+$ *increases with the molecule oxidizability until the absence of the protonated form; therefore, in several cases the base peak fragment is not always an EE fragment. In addition to the basic fragmentation of the compounds with one selenium atom in the molecule, the presence of the second such atom, especially in higher oxidation states, complicates the splitting in the mass spectrometer.*

Key words: azulene, selenium compounds, mass spectra, isotopes

In the paper devoted to the even electron rule in electrospray mass spectra Thurman and collab. [1,2] make the following observations. “The base peak fragment is almost always an EE ion; the majority of the fragment ions were EE ions; the ESI mass spectrum was simpler than the EI mass spectrum. “

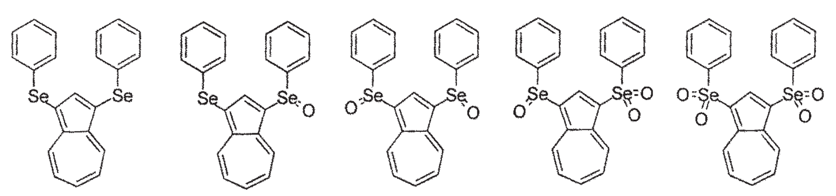
In connection with these observations we have already reported [3] the behaviour of the unsubstituted and substituted 1-(phenylselanyl)azulenes in the mass spectrometer using ESI mode. We have highlighted the peculiar behaviour of these compounds due to their strong reductive character, as well as to the numerous selenium stable isotopes, which participate to the molecule building (*m/z*: 74 (1.8); 76 (18.1); 77 (15.3); 78 (47.4); 80 (100); 82 (19.0)). The protonated 1-(phenylselanyl)azulenes are stable in the mass spectrometer being analyzed using electrospray method in a positive mode. On this occasion we have found that in all recorded mass spectra the molecular ion, $[M]^{\cdot +}$ has also been observed in the more or less abundance together with the $[M+1]^+$ cation. This ascertainment seems to infringe the observations of Thurman. However, this behaviour can be explained by the ability of azulene to lose an electron generating a stable azulenium cation. Similar behaviour has also been observed for other easily oxidizable polyaromatic systems, such as pyrene or antracene that, instead of the protonated molecular peak, generate the molecular radical cation [4].

In the previous paper we have obtained the 1,3-bis(phenylselanyl)azulene, **1**, (scheme 1) together with the mono substituted compound when azulene reacted with PhSeCl [2]. Further, the compound **1** was oxidized with $NaIO_4$ in methanol/water at reflux to 1,3-*bis*(phenylseleninyl)azulene, **3**. Using the same reagent however in dioxane/water at reflux, instead of the attempted 1,3-*bis* (phenylselenonyl)azulene, **5**, a complex reaction mixture was obtained from which 1-(phenylseleninyl)-3-(phenylselenonyl)azulene, **4**, was separated. The reduced amount obtained allowed us to record only its ^{1}H-NMR and mass spectra. Later, after the careful chromatographic separation of the reaction mixture, very small eluted fractions which contained the individual compounds **2 – 5** were obtained. We have considered that a careful analyse of the behaviour of these azulene derivatives with two selenium atoms in molecule in the mass spectrometer using ESI mode may contribute to our previous statements on the validity of EE-rule for these compounds.

Experimental part

Reagents, instrumentation and methods

Varian 1200 L/MS/MS triple quadrupole mass spectrometer fitted with an electrospray (ESI) ionization interface was used. The substances were dissolved in methanol or in methanol containing 1 % of ammonium formate to the 1 mmol/L and were directly infused into the interface by a Prostar 240 chromatographic pump and the flow was set to 20μL/min. The used drying gas was air at a pressure of 18 psi and 150 °C and the nebulising gas was nitrogen to 40 psi. The capillary voltage had been established to the potential +5000 V for positive ionization. Thus protonated molecular ion obtained was selected by the first quadrupole. Into the second quadrupole the protonated molecular ion was fragmented by collision with an inert gas (argon) to 1 mtorr pressure. Prior to these experiments it was performed the tuning of mass spectrometer using PPG.



1 2 3 4 5

Scheme 1

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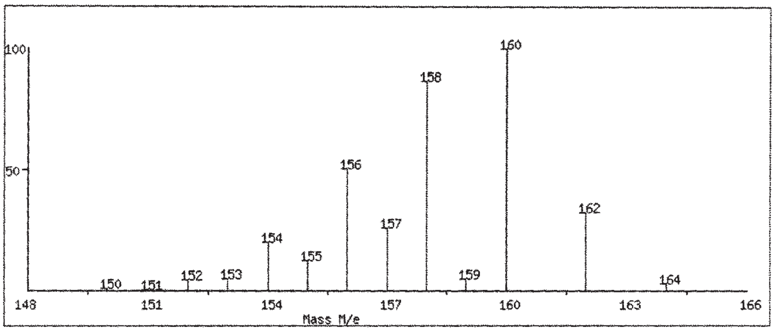


Fig. 1. The calculated isotopic distribution of the Se_2^+ ion

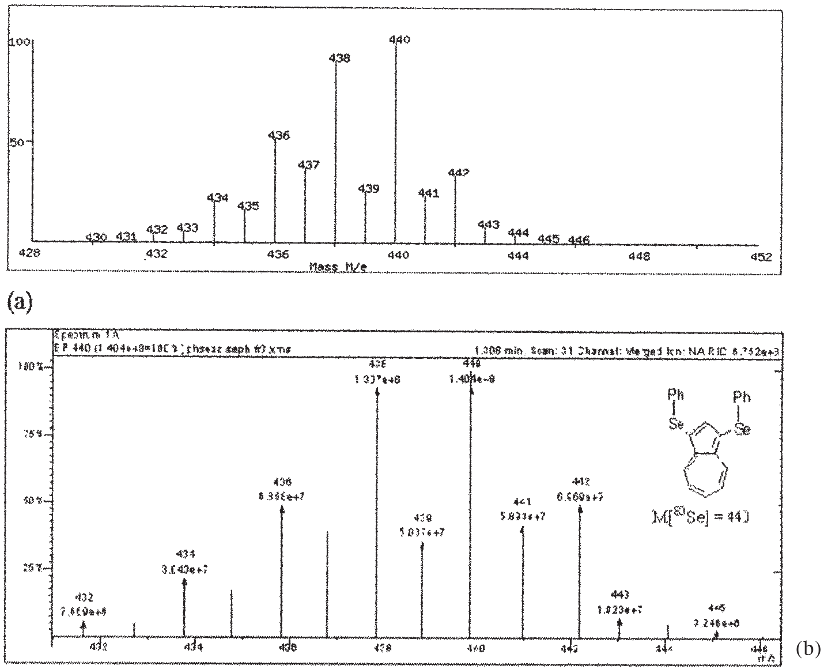


Fig. 2. (a) Calculated isotopic distribution, for [M$^+$] of 1,3-di(phenylselanyl)azulene, 1, and (b) its recorded molecular ion in mass spectrum

Results and discussions

The presence of two selenium atoms, with their rich isotopic distribution in the molecule, in the compounds **1-5** dramatically increases the number of peaks for the fragments which contains Se atoms (if compared to the splitting of monoselenium derivatives). Thus, at the resolution 0.1, results the following calculated isotopic distribution for the fragments containing two selenium atoms [5] m(x2Se)/z: 150 (0.6); 151 (0.5); 152 (4.2); 153 (4.7); 154 (19.6); 155 (12.3); **156 (50.4)**; 157 (26.0); **158 (86.2)**; 159 (4.9); **160 (100)**; 162 (32.1); 164 (3.0) (represented also graphically in the fig. 1).

The first compound to be discussed, 1,3-di(phenylselanyl)azulene, **1**, contains two phenylselanyl groups, symmetrically substituted at the azulenic moiety. While in figure 2 (b) is represented the complex structure of the signals belonging to the molecular ion of compound **1,** in the figure 2 (a) are simulated the signals of radical cation belonging to the same compound, taking into account the above discussed isotopic distribution. The almost identical placed signals and their similar abundance proved the exclusive generation of radical cation generated from the compound **1** and, at the same time, the absence of the protonated molecular ion.

However, if in spectrometer the compound **1** is infused in a reductive and slightly acidic medium, as MeOH containing 1 % $HCOONH_4$, the protonated molecular ion is obtained. In this case the formic acid prevents the premature oxidation of compound while the ammonium ion induces its easier protonation.

The oxidation of at least one selenium atom of the bis selanylated azulene **1** to the Se (IV), as for the 1-phenylseleninyl-3-phenylselanylazulene, **2**, makes that this compound to no longer be oxidized in the mass spectrometer. Instead of the radical cation, the protonated molecular ion would be expected to be generated in ESI mode. Therefore, we have calculated the isotopic distribution for the molecular radical cation of compound **2**, and the obtained result was compared with the recorded structure for the molecular ion obtained with mass spectrometer (fig. 3 (a) and (b)). The calculated abundances for the radical cation, $[M]^{\cdot+}$, contains the intense signal at m/z = 456 for the compound with two ^{80}Se however also a weaker signal at m/z = 455 corresponding to compound with ^{80}Se and ^{79}Se. The recorded mass spectrum of compound **2** contains both these signals but in reversed ratios which proves the presence of protonated molecular ion, $[M+1]^+$, of the compound **2** (the ratio ^{80}Se/^{78}Se is almost 1).

Switching to the compound in which both selenium atoms are linked by oxygen, as in the case of 1,3-bis(phenylseleninyl)azulene **3,** the molecular peak is only an EE ion. Thus, as can be easy seen in figure 4, the obtained experimental values of mass signals are with one unit higher than the calculated values for the radical cation of **3.** At the same time, one can notice the absence of signal corresponding to the radical cation (m/z = 472). This behaviour can be explained by the low aptitude toward oxidation of the compound **3**. As a peculiarity of this system, it is interesting to note the presence in high abundance of the protonated dimer of compound **3** in mass spectrum. The same behaviour was also encountered when we have studied the behavior of 1-(phenylseleninyl)-azulene [1].

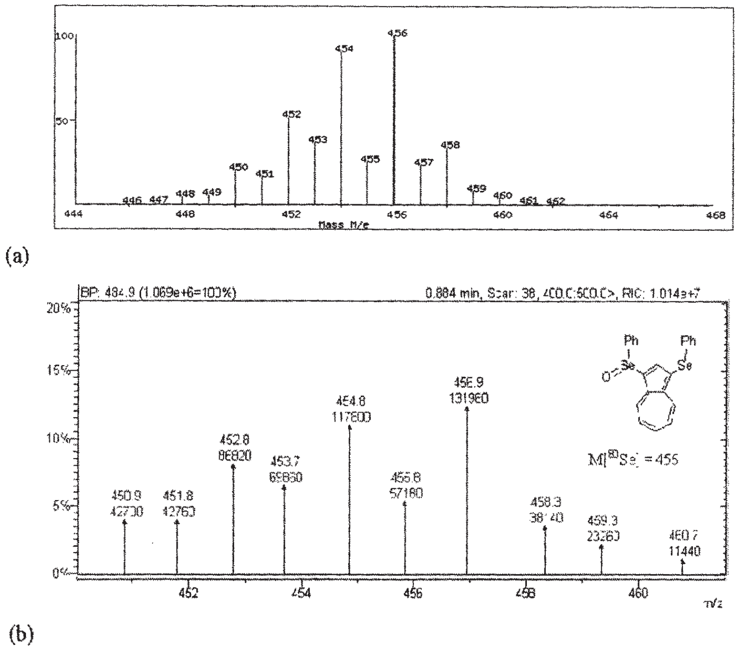


Fig.3. (a) Calculated isotopic distribution for $[M+1]^+$ of 1-phenylseleninyl-3-phenylselanylazulene, **2**, and (b) its recorded molecular ion in mass spectrum

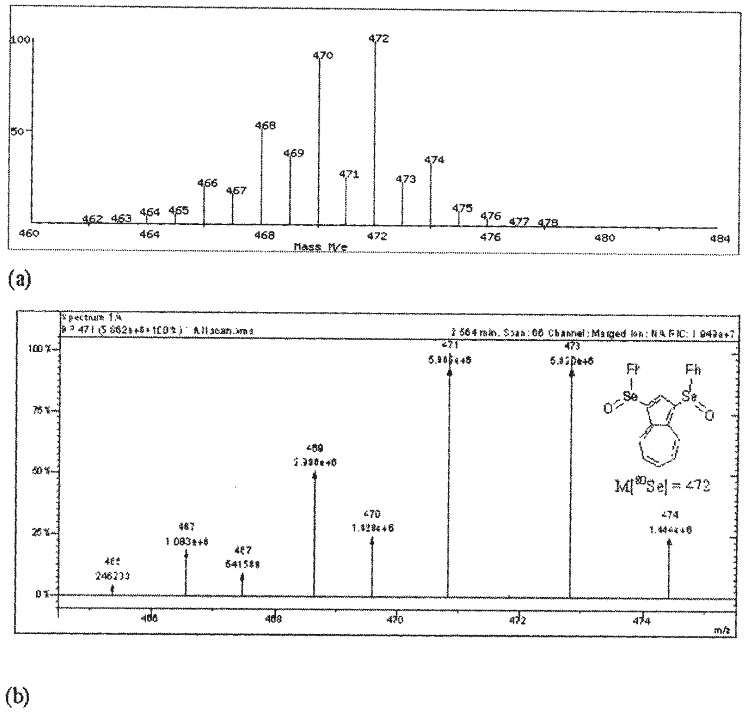


Fig. 4. (a) Calculated isotopic distribution for $[M+1]^+$ of 1,3 bis(phenylseleninyl)azulene, **3**, and (b) its recorded molecular ion in mass spectrum

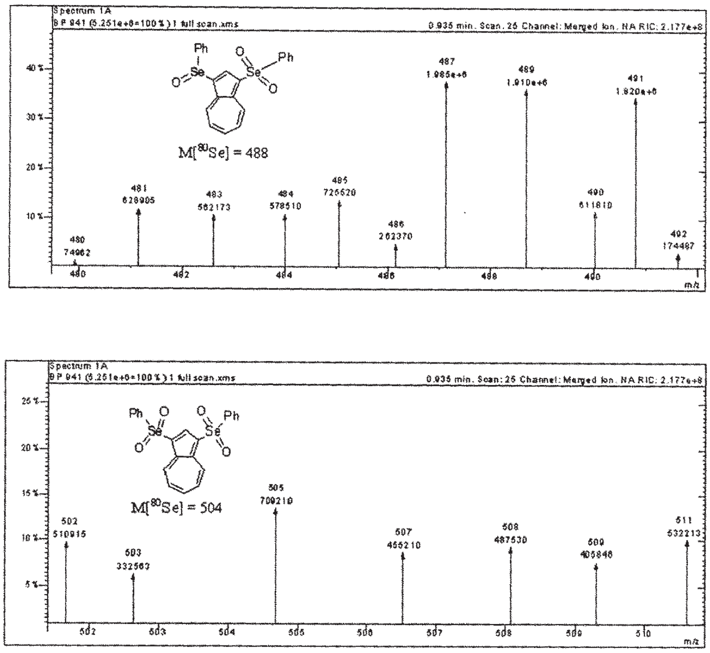


Fig. 5. Isotopic composition of the protonated molecular ion of 1-phenylseleninyl-3-phenylselenonyl-azulene, **4** and 1,3-diphenylselenonyl-azulene, **5**

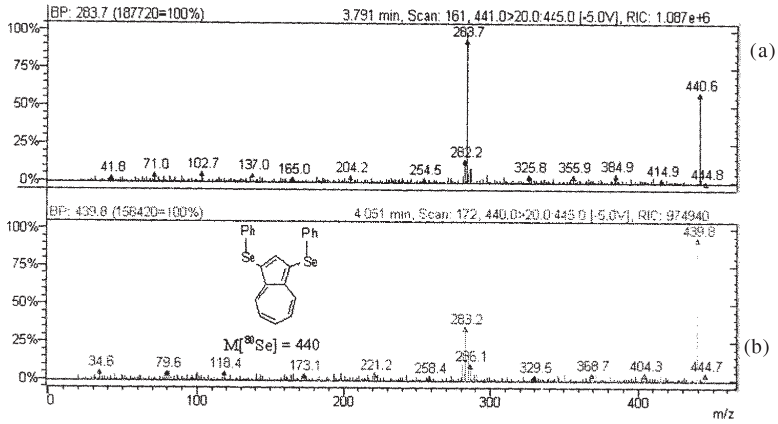
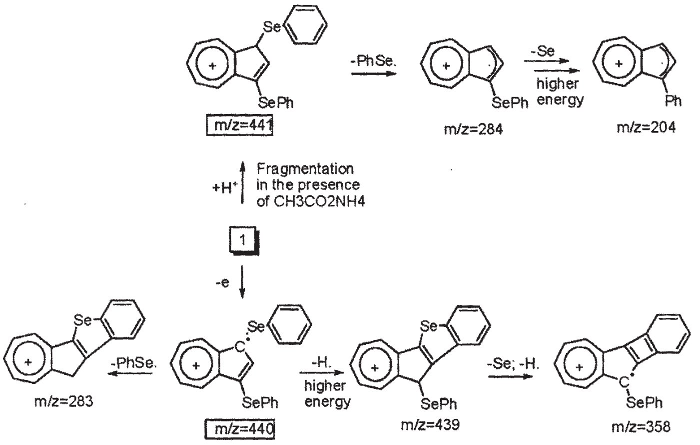


Fig. 6. Fragmentation of the base peaks $[M+1]^+$, and $[M]^{\cdot+}$, belonging to 1,3-*bis*(phenylselanyl)azulene, **1**, at 5 eV, spectrum (a) and spectrum (b), respectively



Scheme 2

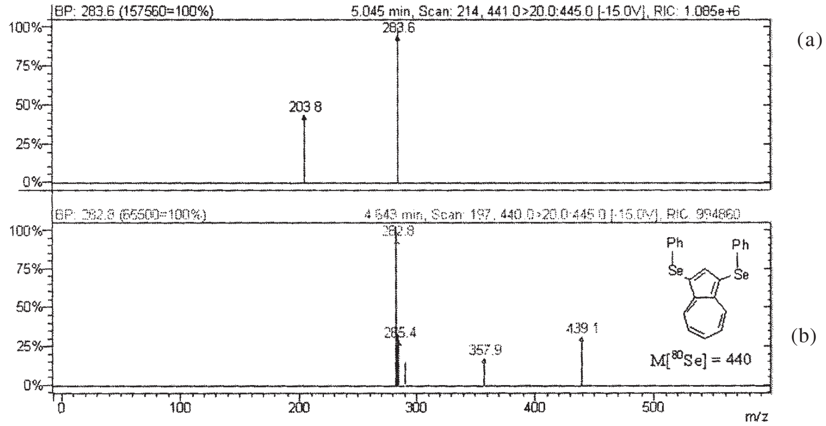


Fig.7.Fragmentation of the base peaks $[M+1]^+$, and $[M]^{\cdot+}$, belonging to 1,3-*bis*(phenylselanyl)azulene, **1**, at 5 eV, spectrum (a) and spectrum (b), respectively

Due to the higher oxidation state of 1-(phenylseleninyl)-3-(phenylselenonyl)-azulene, **4**, and 1,3-diphenylselenonyl-azulene, **5**, it is normal that only the protonated molecular ion (m/z = 489 and m/z = 505, respectively) to be present in their mass spectra, as confirmed in figure 5.

Further, it seems interesting to analyze the fragmentation of molecular ion belonging to compound **1** whether it results in the presence, or not, of ammonium formate. The protonated molecule obtained in the first case, eliminates phenylselenium radical generating the base peak fragment with m/z = 284 for ^{80}Se (fig. 6 (a) and scheme 1); this behaviour contradicts the EE rule. It should also be noted that no traces of $PhSe^+$ (m/z = 157) are observed in this case, as would be expected according to the EE rule. The radical cation of **1** eliminates the same fragment and thus yields the cation with the possible condensate structure of dihydroazuleno[2,1-d]benzo[b]selenophene with m/z = 283 (fig. 6 (b) and scheme 1). The elimination from the radical cation occurs slower, possible due its superior stability conferred by its higher symmetry as compared with the protonated species.

At higher energy, the protonate molecule, after $PhSe^{\cdot}$ separation with the generation of the 1-phenylselanyl-azulene radical cation, eliminates selenium atom yielding 1-phenylazulene radical cation (fragment with m/z = 204 in scheme 2). Similar behaviour has already been reported [1] at the fragmentation of radical cation generated from 1-(phenylselanyl)azulene when ESI-method was used. Under the same conditions, the radical cation of **1** eliminates both $PhSe^{\cdot}$ (fragment with m/z = 238), as well as one selenium atom and hydrogen atoms (fragment with m/z = 358) (scheme 1).

The protonation of compound **2** in mass spectrometer occurs at oxygen atom with the charge generation at selenium atom and, at 10 eV, $HO\text{-}Se^+$ bond is broken. After $HO^{\cdot}$ elimination, the fragmentation takes place quite similar with the fragmentation of pattern compound **1** by the Az-Se bond splitting forming the cation m/z =283 (fig. 8). It should be also noted the absence of molecular ion and the presence, as a resulted fragment, of phenylazulene radical cation with m/z =204 at 20 eV.

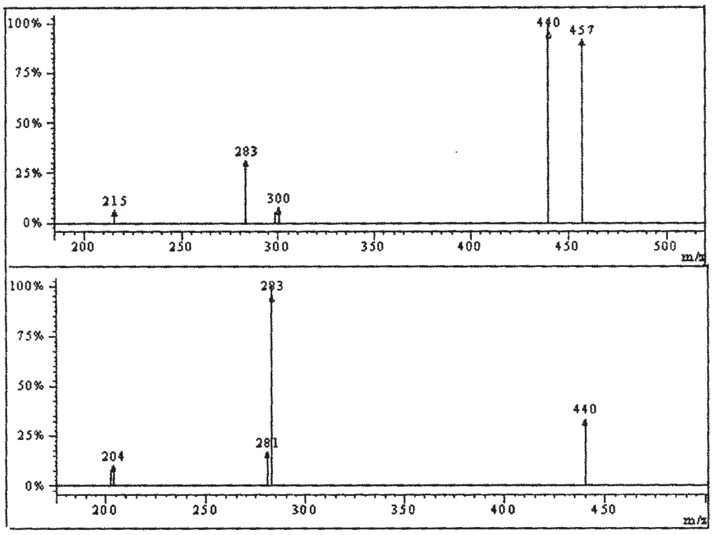
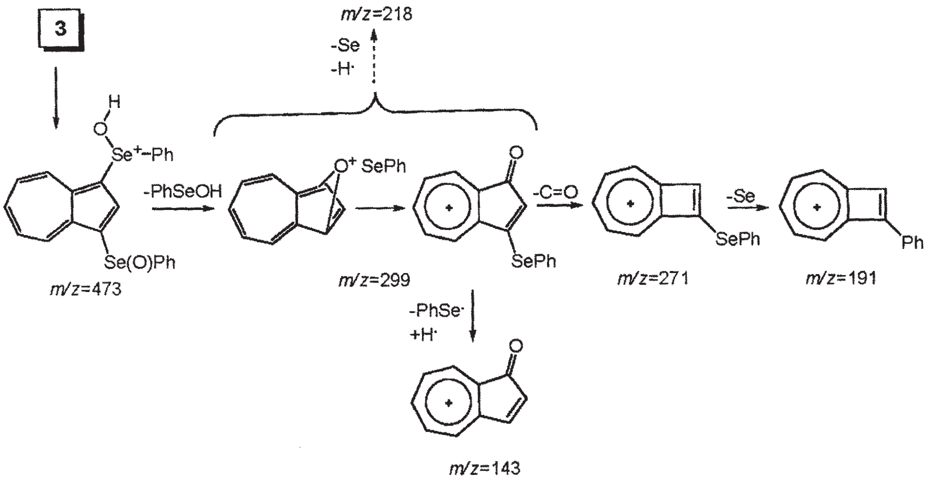


Fig.8. Fragmentation of the molecular peaks of **2** at 10 and 20 eV



Scheme 3

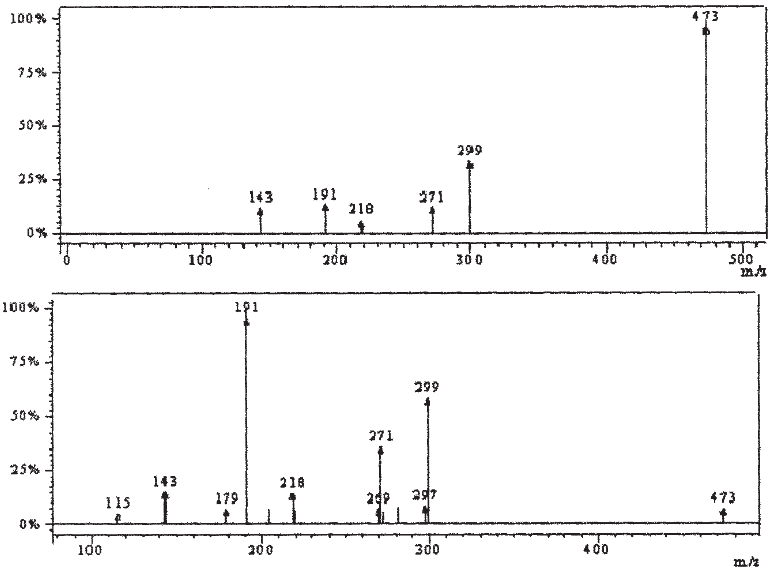


Fig.9. The fragmentation of the molecular peaks of **3** at 10 and 20 eV

Unexpectedly, the fragmentation of protonated bis(phenylseleninyl)azulene, **3**, is different from that of the protonated compound **2**, although in both fragmentation the PhSe(O) substituent is involved. The splitting of protonated compound **3** takes place between azulene and Se^+ and therefore the PhSeOH fragment is eliminated and the cation with m/z =299 results (fig. 9) as major fragment. That indicates that for this cation the bond Az-Se^+ is weaker as the bond HO-Se^+. Thus whereas for the fragmentation of protonated compound **3** the EE rule works, the protonated compound **2** circumvent this rule when ammonium formate is not present. The remained cation, after isomerization as suggested in scheme 3, eliminates PhSe· and a hydrogen atom to cation with m/z = 143 or eliminates successively the C=O molecule and one selenium atom to cations with m/z = 271 and m/z = 191, respectively. The only route in disagreement with the EE rule is that which produces the cation with m/z = 218 obtained after the elimination of hydrogen and selenium atoms. As results from figure 8, the fragmentation of protonate compound **3** at 10 or 20 eV differs only quantitatively.

Conclusions

For the studied compounds the obtained ratio $[M+1]^+/[M]^{\cdot+}$ in mass spectra using ESI method increases with the decrease of the molecule oxidizability until the absence of the radical cations. Another finding concerns the validity of the EE rule for the fragmentation when ESI-method was used. The compounds with high availability to release an electron deviate from the Thurman's observations that the base peak fragment is almost always an EE ion. The reported results in this paper show that the validity of this rule depends in a large extent on the compounds structure and it is not generally valuable.

References

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