Fragmentation of Azulen-1-yl Diazenes and bis-diazenes in Mass Spectrometer

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The fragmentation in the electrospray ionization mass spectrometry of several azulen-1-yl diazenes and bis diazenes was analyzed and some general features of fragmentation were evidenced.

Keywords: mass spectroscopy, mass fragmentations, azulen-1-yl diazenes, azulen-1-yl bis diazenes

Mass spectrometry is an important tool both for determination of the molecular weight of the compounds and for establishing some structural peculiarities which are reflected by the fragmentations in the mass spectrometer. We have already reported the fragmentation of several (azulen-1-yl)-azoarenes by electron ionization procedure (on mass spectrometer Finnigan MAT 311-A/ 100 MS) [1]. The progress realized by using triple quadrupole mass spectrometer fitted with an electrospray (ESI) ionization interface which is coupled to HPLC (HPLC-MS) suggested us the reexamination of the behaviour of some (azulene-1-yl)-azobenzene in these conditions (VG Analytical 7070 E-HF mass spectrometer) and also to extend the study on several azulenyl diazenes. For recording the protonated molecular ion, the collision energy was less than 20 eV, whereas for molecular fragmentation it was increased to 30 eV.

Results and discussion

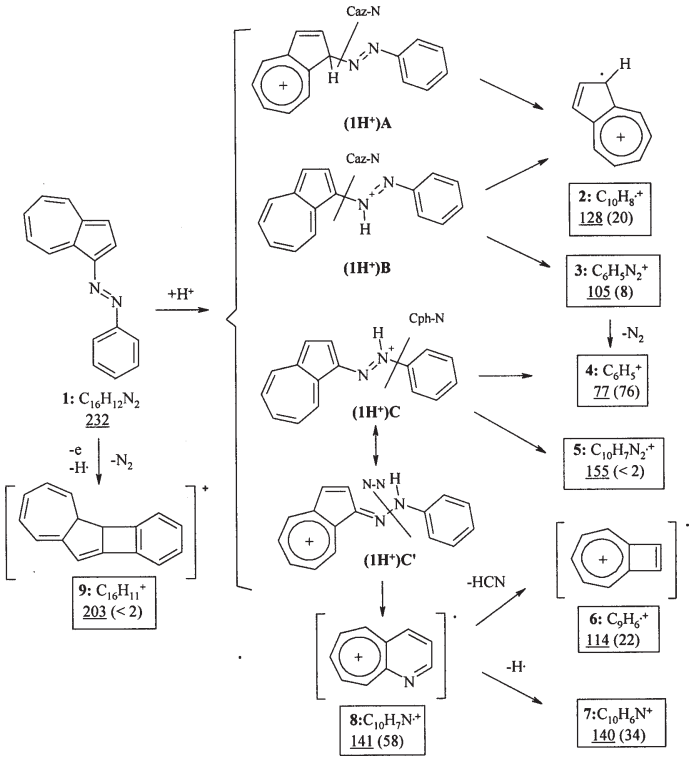
Azulen-1-yl-azobenzene

The protonated molecular peak of azulene-1-yl-azobenzene has an abundance of 100 % even for collision energy of 30 eV when a large number of fragments of various abundances are generated. Generally, only the fragments (cations or radical cations) with abundance of 5-10 % were further considered as significant for the knowledge of the cleavage mechanism (scheme 1 shows the *m/z* and the fragments abundance).

As results from scheme 1, there are three main possibilities for the bound cleavages, namely, between azulenyl and azo groups (Caz-N), between phenyl and azo groups (Cph-N) or between two nitrogen atoms (N-N) due to the decreased double bond character as a consequence of conjugation. The elimination of a nitrogen molecule generates only a small amount of polycondensed product **9**.

From the abundances of fragments **6**, **7** and **8** it seems that the most favored cleavage takes place between the two nitrogen atoms (N-N). The explanation of this breaking route is given by the faster protonation of the electron rich nitrogen atom, (**1H⁺)C'**, than that of the position 1 of azulene, (**1H⁺)A**, despite the generation of the stable tropylium cation in the last case. At the same time, the stability of the obtained fragments **7** and **8** with high aromatic character contributes to this fragmentation.

It is difficult to establish if the high amount of phenyl cation, **4**, results on either (**1H⁺)B** - **3** - **4** or (**1H⁺)C** - **4** routes or on both. Despite the stability of the cation **8**, the

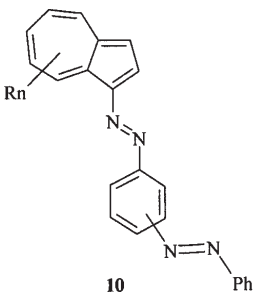


Scheme 1

elimination of the stable molecule HCN is observed, a reaction frequently encountered in mass spectrometry for pyridinic or quinolinic systems.

2. 3- and 4-(Azulen-1-yl)-azo(azobenzene),[2] 10

Recently, we have reported the synthesis of a new class of bis diazenes with one substituted or unsubstituted azulen-1-yl group, 3- and 4-(azulen-1-yl)-azo (azobenzene)s, **10**, scheme 2 [3].



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isomer with 3-Ph-N=N-
or
isomer with 4-Ph-N=N-

Rn = H, 4,6,8-Me_3, 3,8-Me_2-5-iPr and 4,8-Me_2-6-tBu

Scheme 2

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For a better understanding of the complex behaviour of these compounds in the mass spectrometry we focused our attention to the parent compounds, namely 3- and 4-(azulen-1-yl)-azo(azobenzene), **10** (Rn = H). In scheme 3 are shown the *m/z* values of the obtained fragments with their abundances (if it overpasses 5-10%). From the obtained data several conclusions connected to the proposed fragmentation mechanism can be drawn.

Both isomeric molecules present the peak corresponding to $[M+1]^+$ ion , but for *meta* isomer its abundance is lower. The cleavage of cations *meta* and *para* **10H$^+$** generates practically the same fragments (cations or radical cations), but their intensities are different according to the analyzed isomer.

The *m/z* values for some of the common fragments differ between the two isomers by one unit due to the acceptance or lose of one hydrogen atom.

The fragments formed by nitrogen elimination, **11 – 14**, and these with the preservation of azulene-1-yl moiety seem to be representative in the case of *meta* isomer rather than for *para* isomer. The nitrogen elimination must occur from a cyclic moiety [4] such as the radical cation **11**. While the stability of this intermediate is higher in the case of the strongly conjugated isomer *meta*, it is diminished in the case of the *para* isomer where the conjugation of the electronic system is far lower. Cation **13** decays to cation **14** by elimination of a stable HCN molecule.The breaking of the bond between the central phenylene moiety and the azo group of the terminal phenyl group generates the radical cations of type **1**$^{\cdot+}$ for both isomers but fragmentation of this radical cations differs depending of the isomer. The breaking of the bond formed by (azulene-1-yl) azo and phenylene moieties takes place in a small percent and only for the *para* isomer.

The abundance of the cations **3** and **4** for the *para* isomer reflects the weakness of the azo bond between phenyl and phenylene groups belonging to this isomer.

The generation of the cation **8** and the elimination of HCN to fragment **6** are favorable for the *para* isomer as compared to the *meta* isomer.

If azulen-1-yl moiety is substituted with alkyl groups, such as 4,6,8-trimethylazulen-1-yl (scheme 2), the elimination of the alkyl groups and the fragmentations which are described in scheme 3 are concurrent. Hence, in this case are generated both the fragments shown in Scheme 3 as well as those in which the azulen-1-yl moiety preserve its alkyl substituents.

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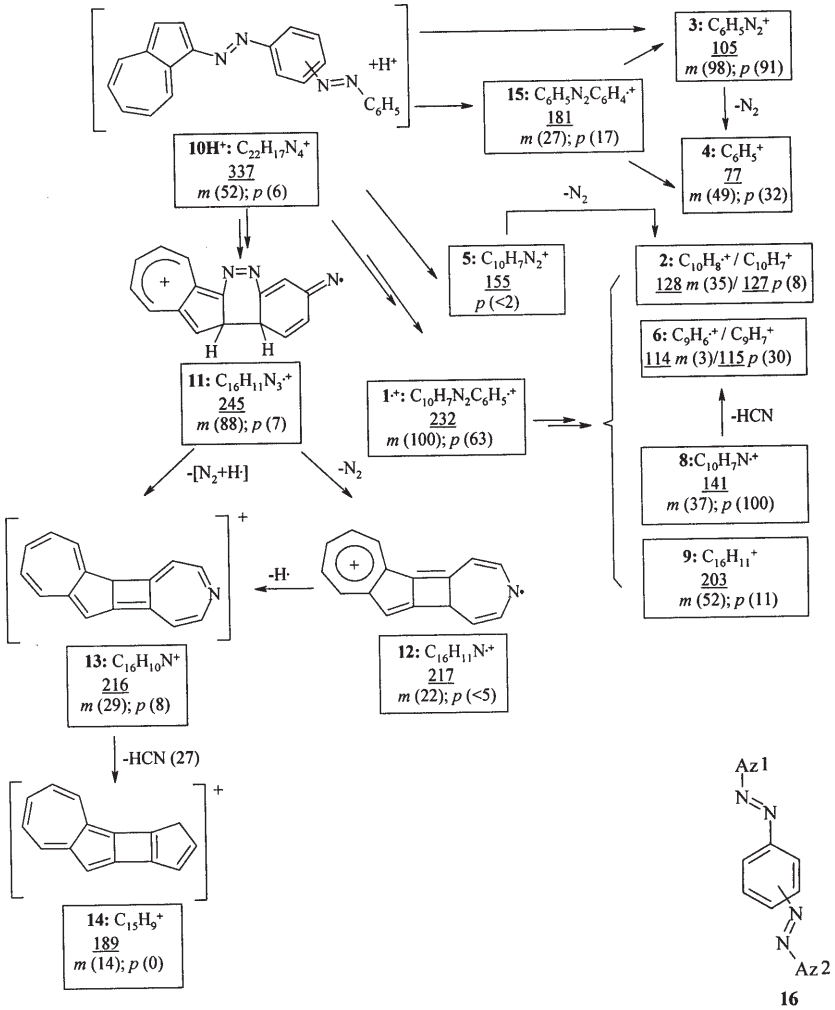
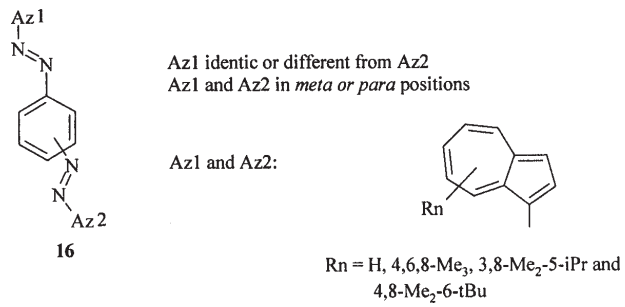
bis Aromatic diazenes containing two azulen-1-yl moieties: 1,3- and 1,4-bis [(E)-1-azulen-1-yl-2-diazenyl]benzenes

Further on, our study regarding the fragmentation of the aromatic bis diazenes was continued by synthesis and characterization of bis diazene derivatives which contain two azulene-1-yl groups, **16**, (scheme 4) [5]. Our interest is to analyze the fragmentation paths in the mass spectrometer of these compounds which posses identical or different azulenic moieties, namely, **16** (Az1 = Az2) or **16** (Az1 ≠ Az2). The results are reported herein.



Scheme 3



Scheme 4

Starting isomer	Fragments, recorded *m/z* depending of isomer and the fragments abundance								
	11	**1H$^+$**	**12; 13**	**9**	**14**	**5**	**8**	**2**	**6**
	m 244; *p* 246	*m* 232; *p* 230	*m* and *p* 218	*m* 204; *p* 202	*m* and *p* 191	*m* and *p* 155	*m* and *p* 141	*m* and *p* 127	*m* and *p* 114
meta	49	40	46	28	14	9	37(33)	100	13
para	18	15	20	35	<5	52	31	100	<5

Table 1
FRAGMENTS ABUNDANCE IN THE MASS SPECTRA OF **16H$^+$** WITH Az1=Az2 AND Rn=H, ISOMERS *META* AND *PARA*

The first remark refers to the absence in the mass spectrum of the signals at m/z = 387, belonging to the protonated molecules, **16H$^+$** (Az1=Az2=azulene-1-yl), when the collision energy overpasses 25 eV. As it was expected, the fragmentation of the bonds of **16H$^+$** follows the same rules (table 1) as those observed for Az-N=N-C_6H_4- group belonging to ion **10H$^+$**. This means that, at the beginning, a rapid bond cleavage between the (azulene-1-yl) azo and phenylene groups takes place. Depending on the studied isomer, sometimes a difference of either one or even two mass units appears ongoing from fragments of the isomers of **16H$^+$** to the fragments resulted in the case of monoazulenic derivatives **10H$^+$**. This phenomenon could be explained by hydrogen atom transfers into the mass spectrometer.

The entire abundance of the fragments for the *meta* isomer surpasses that for the *para* isomer (table 1). This may be attributed to the enhanced stability of the *para* isomer for which the fragmentation occurs more difficult. However, an exception to this rule can be observed comparing the abundance of cation **5** resulted from the two isomers. Thus, the breaking of the bond between the azo group and phenylene takes place more rapidly in the case of the *para* isomer. The higher abundance of the radical cation **5** for the *para* isomer is a consequence of the difficult cyclization of this isomer via **16H$^+$** → **11** → **(12, 13, 14)**. Therefore, this radical cation is accumulated in the fragments mixture. At the cleavage of the cation **10H$^+$** in the mass spectrometer the fragment **5** is either absent or of low abundance.

Fragmentation of the cations **16H$^+$** when Az1 = Az2 with alkylated azulenyl moieties, occurs with lose of the alkyl groups simultaneously with other bond cleavages. However, the abundances of the fragments in which the alkyl substituents are preserved surpass those observed in the mass spectrum of **10H$^+$** with alkylated azulenyl moieties.

When **16H$^+$** contains two different azulenyl groups, Az1 ≠ Az2, the signal corresponding to the protonated molecule is also detected only at collision energies lower than 20 eV. The cleavage of **16H$^+$** (Az1≠ Az2) generates two types of fragments of different intensities: (i) the fragments corresponding to alkyl radical elimination and (ii) the common fragments observed for the above discussed systems and described in table 1. Thus, for **16H$^+$** Az1 =azulene-1-yl and Az2 = 4,6,8,trimethylazulen-1-yl, the elimination of one methyl group leads to a fragment of 12 % abundance whereas the elimination of the second methyl occurs only with 4 % abundance.

The comparison of the mass spectra recorded for **16H$^+$**(Az1 =azulene-1-yl and Az2 = 4,6,8,trimethylazulen-1-yl) and **16H$^+$**(Az1 = Az2 = azulene-1-yl) shows the presence of additional fragments with m/z = 182 (100%) and 168 (39%) for the first ion and the absence of fragments **6** and **14**. The first two fragments could represent fragments of type **5** (m/z = 155) that have preserved one or two methyl groups (several hydrogen atom transfer also takes place).

Conclusions

In the mass spectrometer, the protonated molecules **1H$^+$, 10H$^+$** and **16H$^+$** with Az1 = Az2 or Az1≠ Az2 are splitted as follows: (a) between azulene-1-yl and azo groups, (b) between phenyl and azo or (c) between two azo nitrogen atoms when a simple bond character between these nitrogen atoms was generated by the conjugation or resonance effect.

Regardless the broken bond, the preferred fragmentation is that which allows the preservation of the azulene-1-yl moiety in the generated cation or radical cation. This fragmentation is followed by the cleavage in which the phenyl group is preserved.

The elimination of a nitrogen molecule takes place through the cyclic intermediate, which leads to carbocyclic polycondensed systems. Lose of HCN represents another possible elimination of a small stable molecule.

The fragmentations of bis diazenes with only one azulene-1-yl moiety are similar with those observed for compounds possessing two azulenic groups. This fact shows that the presence of the second group does not dramatically influence the fragmentation. When either one or both azulene moieties are substituted with alkyl groups, the elimination of the substituents takes place with a superior rate as compared to other cleavage processes, although both are competitive as results from the recorded m/z values and abundances of the fragments.

A series of differences appear in the case of fragmentation of *meta* or *para* substituted bis diazenes, however, these differences are not in the fragment structure, rather in abundance of the recorded peaks.

Acknowledgment: The financial support of this research, received from the Ministry of Education and Research, Romania, PN-II No. 115/ 2007, is gratefully acknowledged.

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2. *** The IUPAC name of compound **10** is 1-(azulen-1-yl)-2-[3 or 4-(phenyldiazenyl)phenyl]diazene]
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Manuscript received: 21.01.2009