Some Considerations Regarding the NMR Spectra of 1-phenylselanylazulene Derivatives

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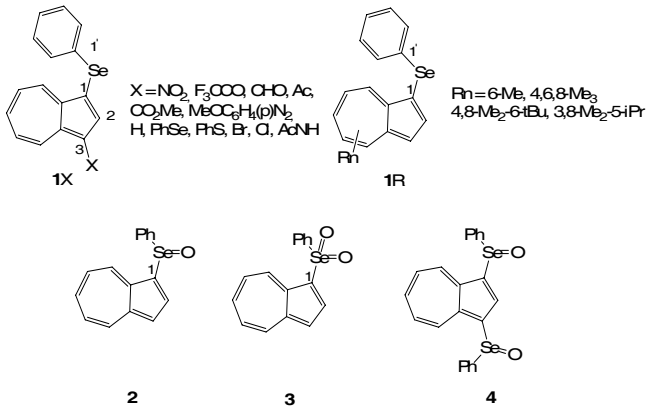
1-Phenylselanylazulene derivatives were characterized using ^{1}H, ^{13}C and ^{77}Se-NMR spectroscopy. Their chemical shifts are in accordance with the electronic charge on the individual atoms being influenced both by the substituents effects and by selenium oxidation state. For the investigated compounds, good correlation between δ values of azulenyl H-6 and C-6 and Hammett's constants was observed.

Keywords: NMR, selenium compounds, azulene, Hammett correlation

The nuclear magnetic resonance is one of the most widely used procedures for the compounds identification and characterization. While the ^{1}H and ^{13}C spectra are commonly used for almost all organic materials, those resulted from other paramagnetic elements, as ^{77}Se can be also used for determining the compounds structure.

During our study on the azulene compounds containing in the molecule chalcogen atoms [1] we have paid special attention to the selenium compounds [2,3] due to their peculiar structure and properties as well as for their potential medical purposes [4]. The target of this paper is to analyse the NMR spectra of 1-phenylselanylazulene, compound **1**H and of several of its derivatives. The spectra of the compounds which, in addition to phenylselenium group, either possess in position 3 other substituents-compounds **1**X, or are substituted with alkyl groups, **1**Rn are also commented. In addition, we considered interesting to discuss the spectra of the compounds in which the selenium atom(s) is oxidized, as in compounds **2-4** from scheme 1.



Scheme 1

Experimental part

^{1}H, ^{13}C, and ^{77}Se NMR spectra were measured in $CDCl_3$ at 400, 100, and 76 MHz, respectively, using a Bruker AMX 400 NMR spectrometer. Both ^{1}H and ^{13}C were detected directly while ^{77}Se was detected indirectly. As external standard, Me_2Se was used. Also 2D COSY and ^{13}C-^{1}H HMBC and HMQC experiments were performed.

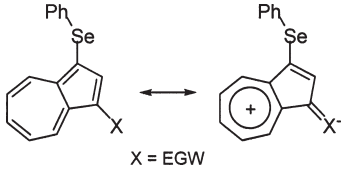
Results and discussions

Azulen-1-yl is a good polarizable system, which can interact with electron accepting functional groups yielding efficient pull-push π-conjugated systems. In consequence, this polarization modifies the normal values for ^{13}C, and mainly for ^{1}H, chemical shifts belonging to the azulene derivatives, as can be seen intable 1.

The δ values of phenyl protons in azulene-1-yl(phenyl)selane, compound **1**H, (multiplet at 7.08 - 7.14 ppm in table 1) are lower compared to the phenyl protons of (4-methoxyphenyl)(phenyl)selane (H-2 and -6 = 7.4; H-3 and -5 = 7.3; H-4 = 7.3 ppm). That means that the phenyl ring of the first compound is more negatively polarized than in the latter compound. At the same time, the phenylselanyl group induces a deshielding effect on the δ values of azulenyl protons. This effect is more important at the closest protons, H-2, H-3 and H-8 due to the inductive effect produced by PhSe group. The enhanced deshielding of H-8 could be the result of the supplementary anisotropic influence of the aromatic system of the phenyl ring on this proton. The other azulenyl protons are deshielded although to a much lesser extent.

The substitution in position 3 of compound **1**H induces supplementary effect along the influence of PhSe group. As expected, whereas the electron withdrawing groups (EWG) deshielded all azulenyl protons of **1**X those rich in electrons have only a slightly shielding effect.

The δ values of H-2 of compounds **1**X are determined by the inductive and electromeric effect of substituent in position 3 as well as by its anisotropic influence. The strong deshielding of the protons on the seven member ring by the EWG in position 3 is decisive produced by the electromeric effects (scheme 2 shows the decrease in electron density of the seven-membered ring) and to a lesser extent by inductive one. From table 1 can be easily seen that the more powerful deshielding groups are nitro and trifluoroacetyl. The higher protons deshielding is encountered at the positions 4, 6 and 8 with the higher



Scheme 2

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X	Protons position						
	2	3	4	5	6	7	8
Azulene	7.81	7.30	8.23	7.05	7.45	7.05	8.23
H	8.12	7.50	8.42	7.30	7.70	7.32	8.72
NO_2	8.68	-	9.81	7.86	8.05	7.75	8.93
$COCF_3$	8.60	-	9.95	7.88	8.04	7.78	8.90
CHO	8.46	-	9.69	7.72	7.94	7.64	8.85
Ac	8.50	-	9.96	7.71	7.90	7.59	8.83
CO_2Me	8.48	-	9.62	7.54	7.77	7.44	8.71
$MeOPhN_2$	8.52	-	9.35	7.38	7.78	7.48	8.68
PhSe	8.28	-	8.76	7.42	7.77	7.42	8.76
PhS	8.23	-	8.75	7.41	7.78	7.43	8.75
Br	8.03	-	8.43	7.38	7.73	7.34	8.65
Cl	7.90	-	8.31	7.35	7.76	7.36	8.71
AcNH*	8.47	-	8.60	7.23	7.73	7.24	8.48
	8.37	-	8.59	7.11	7.61	7.18	8.11
$PhCO_2$	8.18	-	8.38	7.22	7.68	7.25	8.69
Comp. **2**	7.92	7.37	8.45	7.39	7.78	7.43	8.90
Comp. **3**	8.30	7.43	8.59	7.58	7.95	7.65	9.49
Comp. **4****	7.85	-	9.06	7.57	7.92	7.57	9.06
	8.03	-	9.07	7.59	7.95	7.59	9.07

Syn and *anti* isomers. **Pair of diastereoisomers.

Table 1
^{1}H CHEMICAL SHIFTS OF AZULENE AND OF AZULENE-1-YL MOIETY IN 3-SUSBTITUTED 1-PHENYLSELANYLAZULENES, 1X, AND FOR COMPOUNDS 2-4, (δ IN ppm) IN $CDCl_3$

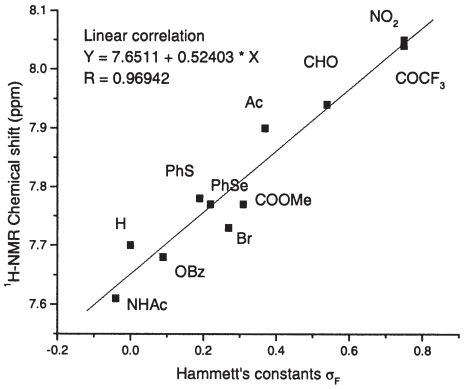

Fig. 1. Correlation between δ value of proton H-6 in ^{1}H-NMR and Hammett's constants for compounds 1X

positive charge in seven-membered ring. As shown in figure 1, the chemical shifts of the protons H-6 in compounds **1**X are correlated with the Hammett's constants with very good results.

With some exceptions the EWGs in compounds **1**X deshield in some extent the δ value of phenyl protons in PhSe of and the donating substituents X lower the δ values of these protons.

When the second PhSe group is substituted at position 3, compound **1**PhSe, the supplementary deshielding of the azulenyl protons is lower. One explanation of this behavior is that the introduction of the second PhSe group (as well as of PhS in **1**PhS) in a symmetric position causes the molecular dipole compensation among the two substituents.

The δ values of almost all azulenyl protons in compound **2** are not very different from these belonging to the compound **1**H which indicates a close effect of PhSe and PhSeO groups. The smaller influence of PhSeO on the H-2 and H-8 can be explained by the change in molecular geometry that modifies the anisotropic effect of the phenyl group on these protons. The much stronger –E effect of $PhSeO_2$ on the azulenyl protons is reflected by the higher deshielding of all azulenyl protons. It is interesting to note the dramatically deshielding of the H-8 where probably vigorously acts the anisotropic effect of the Se=O and of the phenyl group.

An interesting spectrum belongs to 1,3-bis(phenylselanilyl)azulene, **4**, which presents two diastereoisomers pairs, one being *meso*. Their stability at the NMR scale

R	Protons position							
	2	3	4	5	6	7	8	Ph
H	8.12	7.50	8.42	7.30	7.70	7.32	8.72	7.08-7.14
6-Me	8.02	7.44	8.27	7.20	2.66*	7.21	8.58	7.10-7.17
4,6,8-Me_3	7.74	7.39	3.25*	7.06	2.61*	7.08	2.89*	7.10-7.21
4,8-Me_2-6-tBu	7.81	7.41	3.33*	7.34	1.50*	7.37	2.97*	7.13-7.25
3,8-Me_2-5-iPr	7.79	2.84*	8.37	3.22*	7.55	7.14	2.97*	7.36-7.42

*Methyl group.

Table 2
^{1}H CHEMICAL SHIFTS OF AZULENE-1-YL MOIETY IN SOME ALKYLATED 1-PHENYLSELANYLAZULENES, 1R (δ IN ppm) IN $CDCl_3$

X	Carbon atoms													
	1	2	3	3a	4	5	6	7	8	8a	2',6'	3',5'	4'	1'
Azulene	118.0	136.9	118.0	140.1	136.4	122.6	137.1	122.6	136.4	140.1	-	-	-	-
H	112.3	144.7	118.2	141.8	136.9	124.4	138.3	124.5	137.3	142.1	129.0	128.8	125.6	134.9
NO_2	113.0	141.8	134.6	144.5	138.2	130.6	141.9	132.1	141.3	135.3	130.0	129.4	126.7	132.4
$COCF_3$	115.3	148.6	117.3	145.1	139.8	132.8	141.6	131.2	140.2	148.0	129.3	129.3	126.4	132.8
CHO	114.5	149.7	125.9	141.5	138.1	130.9	141.5	129.5	139.9	147.0	129.4	129.2	126.2	133.2
Ac	112.6	148.4	125.1	141.5	139.8	130.7	140.5	128.7	139.4	146.2	129.2	128.9	126.0	133.8
Br	111.9	144.8	104.3	138.0	136.4	124.9	140.1	125.1	138.3	141.6	129.1	129.1	126.0	134.2
CO_2Me	112.7	147.8	116.9	142.2	138.0	128.0	140.0	129.0	139.0	145.7	129.1	129.1	125.9	133.8
PhS	112.6	150.6	116.0	143.2	136.2	125.9	139.6	126.0	138.1	143.7	129.1	129.1	126.1	134.2
$PhCO_2$	109.1	135.1	137.9	129.2	132.6	124.2	139.6	123.6	138.7	137.5	129.1	129.1	125.8	134.5
NHAc*	109.3	136.2	126.7	128.5	133.6	122.6	139.9	123.5	137.2	137.3	129.2	128.6	125.9	133.9
	111.1	140.0	126.1	130.6	133.5	125.1	141.7	125.6	138.6	140.3	129.1	129.1	1259	134.2
PhSe	113.0	151.7	113.0	143.5	137.8	125.9	139.4	125.9	137.8	143.5	129.1	129.1	125.9	134.3

Syn and *anti* isomers.

Table 3
^{13}C CHEMICAL SHIFTS OF SOME 3-SUBSTITUTED 1 PHENYL SELANYLAZULENES, 1X IN $CDCL_3$

X	NO_2	$COCF_3$	CHO	Ac	CO_2Me	PhSe	PhS	Br	$PhCO_2$	H	NHAc
δ	253.9	248.8	245.7	241.5	241.4	241.4	241.2	243.8	242.5	238.0	236.5

Table 4
^{77}Se CHEMICAL SHIFTS OF SOME 3-SUBSTITUTED 1-PHENYL-SELANYLAZULENES, 1X, (δ IN ppm) IN $CDCl_3$

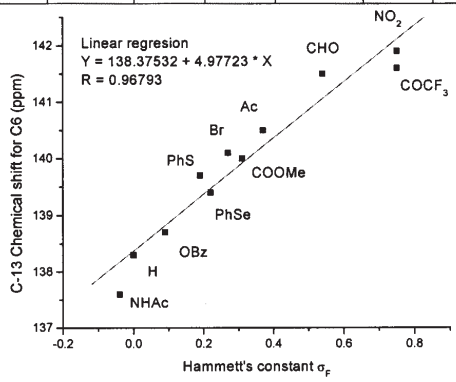

Fig. 2. Correlation between δ value of C(6) in ^{13}C-NMR and Hammett's constants for compounds 1X

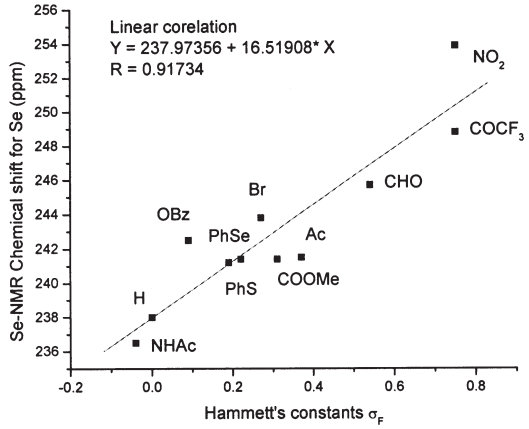

Fig. 3. Correlation between ^{77}Se-NMR and Hammett's constants for compounds 1X

enable us to record the ^1H-NMR spectrum that has a pair of chemical shifts of equal intensity for each proton, as can be seen in the table 1.

The electron repulsive effect of alkyl groups substituted at azulenyl seven-membered ring enhances its negative charge therefore, as can be seen in table 2, induces an important shielding of the protons belonging to this ring. The effect is influenced by the number of the groups and by their positions. At the same time, the phenyl protons are slightly deshielded probably due to a different geometry of the molecules.

The ^{13}C-NMR spectra, presented in table 3, are much less influenced than those of protons by the presence of the PhSe group attached on azulene as well as by the azulenyl substitution at position 3 in compounds **1**H. Thus, the phenyl signals for C(2',6'), C(3',5') and C(4') are between 125.8 and 130.0, near to the value of unsubstituted benzene (128.5 ppm) whereas the signals for C(1') are found between 132.4 and 134.9. The chemical shifts of azulenyl carbon atoms in ^{13}C spectrum of compound **1**H are also close to those of the carbon atoms in the parent azulene. Some difference can be observed at the C(2), where both the inductive effect of PhSe and the anisotropic effect of phenyl deshields the carbon atom. In compounds **1**X the signal for C(1), as well as the δ values of carbon atoms at seven-membered ring, vary also slightly with the substituent at position 3. Obviously, there are several differences between δ values of C(2) and C(3) depending on the influence exerted by substituent X. However, the overlapping of the effects of 1- and 3-substituents make more difficult the possibility to explain correct the obtained δ values.

It was obtained also a good correlation between the chemical shift of azulenyl C(6) and the Hammett's constants for compounds **1**X as results from figure 2.

The alkyl groups deshield strongly the carbon atoms attached to them and shield those from their proximity; however these groups do not have a noticeable effect on other carbon atoms.

The Se oxidation, as in compounds **2-4,** modifies the δ values of the carbon atoms situated closed to it. Azulenyl C(1) is deshielded with 13 ppm by SeO and with 10 ppm by SeO_2 while phenyl C(1') is deshielded with 6, respectively 10 ppm. The other azulenyl carbon atoms are slightly shielded. At the same time, while the phenyl carbon atoms in *ortho* and in *para* to both SeO and SeO_2 groups are deshielded those situated in *meta* remain almost unchanged.

Like the ^1H-NMR spectrum of compound **4** the ^{13}C-NMR spectrum also confirms the presence of optical isomers; almost each carbon atom has two chemical shifts.

As we have mentioned above, the ^{77}Se spectra can be additionally used for structure confirmation. However, the ^{77}Se-NMR spectra registration need concentrated samples of compounds or long acquisition times due to the ^{77}Se both low magnetogyric ratio and natural isotopic abundance. Therefore, a more convenient method uses the inverse proton detection, based on a more abundant element possessing at the same time a high magnetogyric ratio [5].

The chemical shift of ^{77}Se is strongly influenced by the selenium environment, being hard to evaluate. While the δ values of Se in dialkylselenides are small, when Se is involved in the π-conjugation the values increase: 149.5 ppm for PhSeH or even 613 ppm for selenophene. Related compounds with the azulenic compounds **1**, as phenylselanyl-1-naphthalenes have intermediate values: 352.4 [6] or 440-475 depending on the aryls substituents [7,8].

For the analyzed compounds **1**X, δ values of Se are slightly lower than for other diarylselenides (table 4) due to the higher electron density at the five-membered azulenyl ring. As shown in table 4, the azulenyl substituents have some influence on δ values of Se.

A good correlation is observed between their chemical shifts and the Hammett's constants of the substituents, as is presented in figure 3. The alkyl groups attached to azulene moiety shield selenium; for example 6-Me group decreases the chemical shift of selenium to 235.7 ppm.

Whereas for Se(II), as in compound **1**H, the selenium chemical shifts vary around 240 ppm, for selenium with higher oxidation states the chemical shifts increase dramatically. For example, for the compound **2** with Se(IV) the Se chemical shift becomes 830 ppm while for the compound **3** with Se(VI) the δ value increases to 955 ppm.

Conclusions

1-Phenylselanylazulene derivatives were characterized using ^{1}H, ^{13}C and ^{77}Se-NMR spectroscopy. Their chemical shifts are in accordance with the electronic charge on the individual atoms being influenced both by the substituents effects and by selenium oxidation state. For the investigated compounds, good correlation between δ values of azulenyl H-6 and C-6 and Hammett's constants was observed.

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