

Some Considerations Regarding the ^1H and ^{13}C Spectra of 4-(1-azulenyl)-2,6-bis(2-heteroaryl-vinyl)-pyrylium and Pyridinium and their Corresponding Pyridines

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The ^1H and ^{13}C NMR spectra of several 2,6-diheteroarylvinyl heterocycles containing 4-azulenyl moiety were recorded and their proton and carbon chemical shifts were compared with those of the compounds without double bond between the heterocycles. The influence of the nature of central and side heterocycles, molecule polarization and anisotropic effects were revealed. The highest chemical shifts were recorded for the pyrylium salts and the lowest at pyridines, but in the case of the pyridinium salts, the protons chemical shifts at the central heterocycle are more shielded due to a peculiar anisotropy of the attached vinyl groups.

Keywords: azulene, heterocycles, NMR chemical shifts

The theoretical importance and the technical applications of azulene-1-yl substituted heterocycles stimulated their extensive study. Both the electron deficiency at the charged heteroaromatic rings and electron donor property of azulene-1-yl moiety increase the stability of the entire system. As result of the charge distribution, such molecules acquire valuable push-pull properties with interest in optoelectronics [1,2], for example, in the NLO-field [3]. At the same time the polyazulene films based on these compounds work as sensors for anions or cations [4]. In our own study, we reported the synthesis and characterization of six membered heterocycles **1** – **3** with 1-azuleny moieties in 4 position and with 2-furyl or 2-thienyl groups in positions 2 and 6 [5]. This concern was followed by the extensive research of their vinylogous compounds **4** – **6** [6]. During the characterization of the two compounds series, the NMR spectra were recorded and we thought that the complexity of the obtained data requires more

attention. Therefore in this paper the NMR data coming from these compounds series were examined.

Experimental part

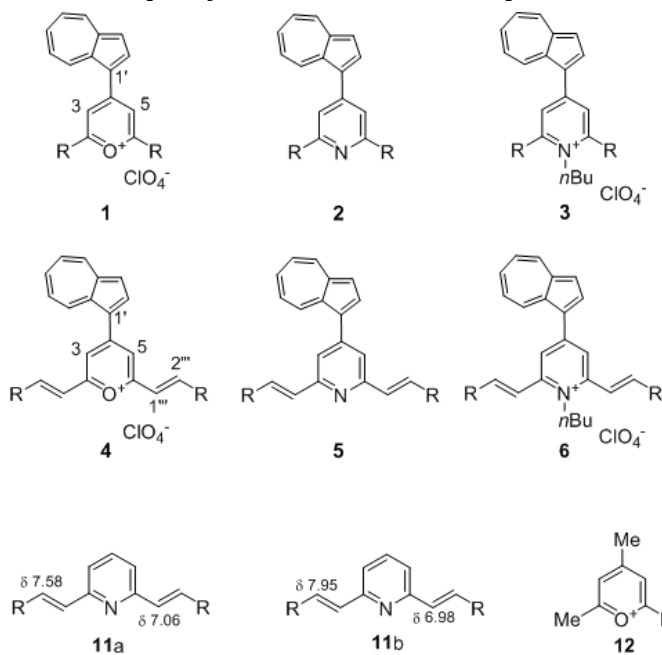
^1H - and ^{13}C -NMR: Bruker Avance III Ultrashield Plus 500 MHz (^1H : 500 MHz, ^{13}C : 125.78 MHz) and Gemini 300 (^1H : 300 MHz, ^{13}C : 75.47 MHz), in CDCl_3 for pyridines and dimethylsulfoxide ($\text{DMSO}-d_6$) for ionic compounds (if there is no other specification in the table, as $\text{acetone}-d_6$); TMS was used as internal standard in CDCl_3 ; signals were assigned on the basis of COSY, HETCOR and HMBC experiments.

Results and discussions

Considerations on ^1H -NMR spectra

The studied compounds **4** – **6** possess four proton kinds: a) azulene-1-yl protons, b) protons attached to the central heterocycle, c) those belonging to five-membered heterocycles and d) vinylic protons. It seems to be interesting to compare proton chemical shifts of the compounds belonging to this series with those already determined for the corresponding compounds without carbon double bond between the heterocycles, compounds **1** – **3** [5]. Several considerations regarding the NMR spectra of the 4-(azulene-1-yl)pyrylium salts with 2-(azulene-1-yl)vinyl substituents in 2- and 6-positions, **4e**, may be also of interest [7].

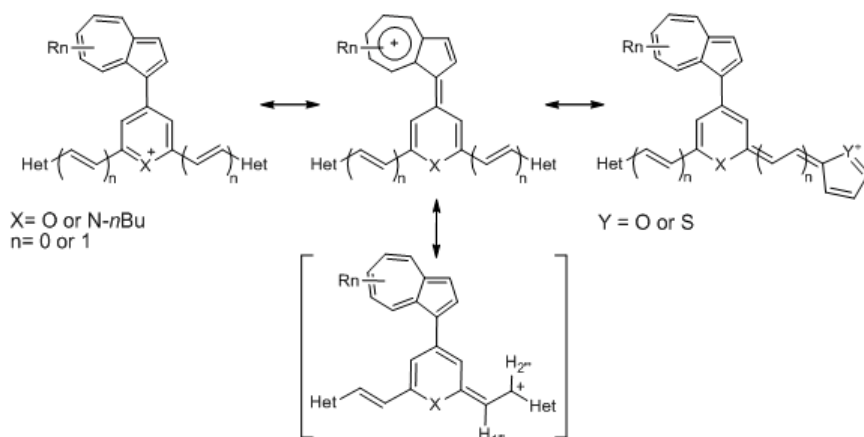
Similar δ values for azuleny protons were found for pyrylium salts **1** and for their vinylogous compounds, **4**, whatever the nature of heterocycles (table 1). These values are also comparable with those reported for the pyrylium salt 2,6-disubstituted with phenyl, **1d**, except the moderate deshielding of 2'-H for the last compound. Generally, the deshielding of azuleny protons was heightened by the increase in net positive charge densities of the moiety linked to azulene 1'-position, as in 1-phenylazulene < 4-(azulene-1-yl)pyridines < 4-(azulene-1-yl)pyridinium salts < 4-(azulene-1-yl)pyrylium salts. The alkyl substituent at nitrogen in pyridinium salts decreases the positive charge at central heterocycle and approach the behavior of these salts on the pyridines. Usually, the protons in positions 4', 6' and 8' are more deshielded in the last compounds. This behavior is motivated by the strong conjugation of the azuleny



a: R = 2-furyl; b: R = 2-thienyl; c: R = 3-thienyl
d: R = phenyl; e: R = 1-azulenyl

Scheme 1. The investigated compounds

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Scheme 2. The main resonance structures of the 4-azulenyl-2,6-bis(heteroarylvinyl)pyrylium or pyridinium salts

moiety with the charged heterocycles, which decreases the electron density at azulene seven-ring with generation of stable tropylium cation (scheme 2). The azulenyl protons are unaffected by the change in the five membered heterocycles because these moieties are further than away. The protons of 4-azulenyl moiety are shielded to some extent by the replacement of heteroaryl with azulenyl moieties. Therefore, their chemical shifts in **4e** [7], are lower than those observed for the other compounds **4a-c** (scheme 1). The possible explanation could be the higher efficiency of azulene-1-yl moieties as electron donor.

The δ values of protons 3-H and 5-H, at the central heterocycle, are influenced by the heteroatom, by the azulene system linked in 4-position as well as by the nature of the substituents in 2- and 6- positions. Regarding the values from table 2, the deshielding generally follows the decrease in electron density at the heterocycle according to sequence pyridine < pyridinium salt < pyrylium salt. The stronger anisotropic effect of phenyl in compounds **1d** – **3d** than that of heteroaryl in compounds **1a,b**–**3a,b** deshields more the protons 3-H and 5-H for the first series. It should be noted the lower deshielding power of 1-furyl as compared with 2-thienyl due to the difference between the anisotropic effects of these heterocycles. When the heteroaryl moieties are not directly substituted at the central heterocycle, but by the carbon double bond insertion,

as for the compounds **4a,b,c**–**6a,b,c**, the δ values of the protons 3-H and 5-H do not depend on the heterocycle attached to the double bond. The decrease in positive charge due to the influence of two azulene-1-yl groups in compound **4e** shields the protons 3 and 5 in this pyrylium salt (at 8.04 ppm).

The increase of electron density at the central heterocycle by the contribution of 4-(azulenyl) moiety shields the signals for 3-H and 5-H. This contribution is however affected in some extent when 8-position of azulene is substituted by methyl as in 4,6,8-trimethylazulenyl (TMA) or in guaiazulenyl (Gu). The substituent disturbs the coplanarity of azulene with the heterocycle, lowering their conjugation. Thus, the favorable inductive effect of alkyl groups on the electron donation of azulenyl is diminished by the loss of conjugation at the increase of dihedral angle between this moiety and central heterocycle. At the same time, the decrease in coplanarity lowers the influence of the anisotropic effect of the azulene moiety on the central heterocycle protons. As a result of these influences, the protons 3-H and 5-H are significantly deshielded in compounds with unsubstituted azulene-1-yl moiety than that with alkylated moiety (table 3).

The protons of the five-membered heterocycles (mainly for 2-thienyl) in compounds **3** and **4** are deeply influenced

Table 1
CHEMICAL SHIFTS FOR THE PROTONS 2'-H - 8'-H OF COMPOUNDS **1a** – **6a**, **4e**, AZULENE AND 1-PHENYLAZULENE (δ in ppm)

Compound	2'-H	3'-H	4'-H	5'-H	6'-H	7'-H	8'-H
Azulene	7.81	7.30	8.23	7.05	7.45	7.05	8.23
1-Phenylazulene	8.02	7.43	8.34	7.14	7.58	7.14	8.55
1d (pyrylium) ^a	8.92	7.77	8.89	8.03	8.31	8.14	9.57
1a (pyrylium) ^a	8.72	7.75	8.81	7.94	8.23	8.04	9.38
3a (pyridinium) ^b	8.24	7.46	8.45	7.50	7.86	7.71	8.89
2a (pyridine) ^b	8.17	7.49	8.42	7.27	7.69	7.31	8.72
4a (pyrylium) ^a	8.63	7.68	8.81	7.93	8.22	8.01	9.42
6a (pyridinium) ^c	8.55	7.65	8.71	7.63	8.01	7.67	9.11
5a (pyridine) ^b	8.11	7.48	8.43	7.29	7.69	7.31	8.66
Compound 4e ^a	8.57	7.66	8.72	7.76	7.95	7.82	9.16

^aIn acetone- d_6 , ^bIn $CDCl_3$, ^cIn $DMSO-d_6$

(R)	Pyrylium salt, 1	Pyridinium salt, 3	Pyridine 2	(R)	Pyrylium salt, 4	Pyridinium salt, 6	Pyridine 5
a	8.12	7.80	7.84	a	8.25	8.50	7.48
b	8.62	7.93	7.73	b	8.28	8.50	7.42
d	8.92	8.32	8.18	d	8.22	8.48	7.47

Table 2
CHEMICAL SHIFTS
FOR THE PROTONS
3-H AND 5-H OF
COMPOUNDS 1a,b,d-
3a,b,d and 4a,b,d-
6a,b,d (δ in ppm)

by the central heteroaromatic species. Thus, the positively-charged pyrylium ring, deshields these protons, as compared with the effect of neutral pyridine or even of the pyridinium ring. As can be seen in table 4, this influence is also present when the five-membered heterocycle are separated by C=C bridges from the central ones although it is somewhat reduced. The nature of the azulene-1-yl moiety in position 4 have an insignificant effect on the protons belonging to five membered heterocycles.

The charge of the central ring is also dissipated on 2''-C by π -conjugation (scheme 2). Therefore, the chemical shifts of these protons depend on the variation in the nature of central heterocycle being higher than that for the corresponding 1''-H, which are deshielded only by inductive effect. At the same time, 2''-H chemical shifts are significantly influenced by the neighbor heterocycle system. Due to the higher anisotropic effect of thiophene, produced by its stronger aromaticity as compared with those of furan, the highest chemical shifts are observed for pyrylium salts and for thiophene derivatives (table 5).

The nature of azulenyl moiety in 4-position has no influence on the vinyl protons. Nevertheless, it is interesting to note that the 4-(azulen-1-yl) moiety in pyridine shields both vinyl protons in compound 5a,b compared to the corresponding unsubstituted 2,6-bis (heteroarylvinyl) pyridines, 11a,b [8].

Considerations on ^{13}C -NMR spectra

The decrease in electron density at both azulenyl and five membered heterocycles (scheme 2) deshields their carbon atoms in the order 4-(azulen-1-yl)pyridines, 4-(azulen-1-yl)pyridinium salts, 4-(azulen-1-yl)pyrylium salts as results from tables 6 and 7. The most deshielding is signaled for the positions 5 and 7 of the azulene moiety and at the position 3 of the side heterocyclic systems in concordance with their resonance structures.

The charge at the double bond is strongly polarized in the case of the pyrylium and pyridinium salts and almost non-polarized in the case of the pyridines. The strong polar solvent DMSO- d_6 , used for spectra registration of the salts also intensified the polarization as compared with CDCl_3 used for pyridines. The C2'' chemical shifts are influenced mainly by the heterocyclic system attached and the linked position. In spite of the positive charge and strong -I and -E effects, the C1'' chemical shifts of the pyrylium salts are the most shielded (116.7 ppm for R = Fu). Contrary, at the most electron rich molecules, pyridines this proton is observed at 126.2 ppm for R = Fu.

The carbon chemical shifts of the heterocycles are not significantly influenced by the introduction of the azulene moiety in 4-position (of course, with the exception of the pyridinic C4).

Azulen-1-yl substituents	Pyrylium salts		Pyridinium salts		Pyridine	
	1b	4b	3b	6b	2b	5b
R = H	8.62	8.28	7.93	8.50	7.73	7.42
R = 4,6,8-Me ₃	8.20	7.80	-	-	7.60	7.25
R = 3,8-Me ₂ -5-iPr	8.08	7.73	-	-	7.58	7.26

Table 3
CHEMICAL SHIFTS
DEPENDENCE OF PROTONS 3-H
AND 5-H ON THE AZULEN-1-YL
SUBSTITUENTS (δ in ppm)

Compound	2''-H	3''-H	4''-H	5''-H
Pyrylium salt: 1a / 4a	-	7.86 / 7.13	6.89 / 6.72	8.30 / 7.88
Pyrylium salt: 1b / 4b	-	8.51 / 7.69	7.49 / 7.27	8.24 / 7.83
Pyridine: 2a / 5a	-	7.22 / 6.56	6.58 / 6.47	7.57 / 7.43
Pyridine: 2b / 5b	-	7.71 / 7.24	7.15 / 7.06	7.44 / 7.27
Pyrylium salt: 4c	8.14	-	7.59	7.70
Pyridine: 5c	7.43	-	7.35	7.45

Table 4
CHEMICAL SHIFTS FOR THE PROTONS OF SIDE
HETEROCYCLES 2''-H - 5''-H (δ in ppm)

(R)	4 (pyrylium)		6 (pyridinium)		5 (pyridine)	
	1 ^{'''} -H	2 ^{'''} -H	1 ^{'''} -H	2 ^{'''} -H	1 ^{'''} -H	2 ^{'''} -H
2-furyl, a	7.21	8.02	7.45	7.86	7.26	7.70
2-thienyl, b	7.28	8.44	7.62	8.00	7.11	7.97
3-thienyl, c	7.43	8.28	7.63	8.00	7.17	7.80

Table 5
CHEMICAL SHIFTS FOR
THE VINYL PROTONS,
1^{'''}-H - 2^{'''}-H (δ in ppm)

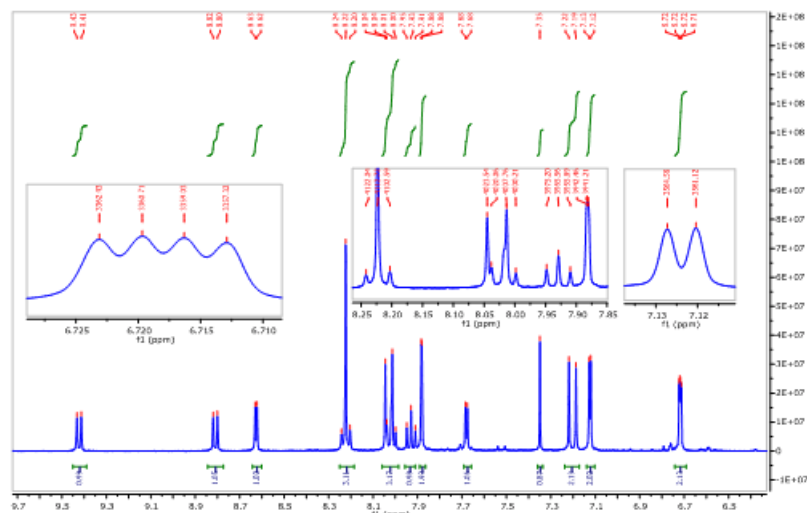


Fig. 1. Proton spectrum of **4a** in DMSO at 500 MHz

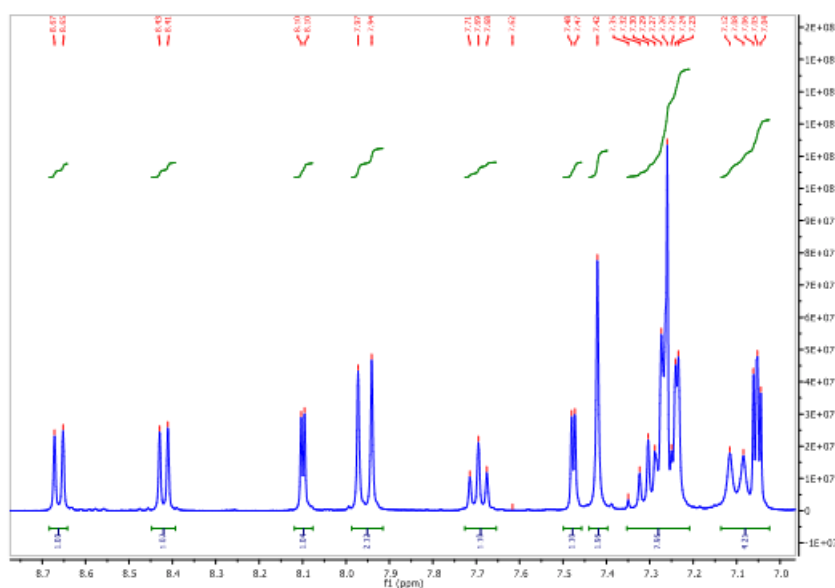


Fig. 2. Proton spectrum of **5b** in CDCl₃ at 500 MHz

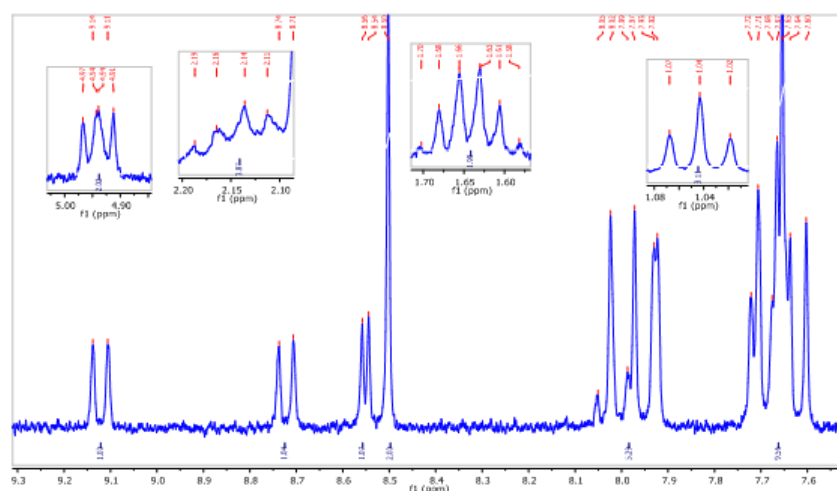


Fig. 3. Proton spectrum of **6b** in DMSO at 500 MHz

Comps.	C1'	C2'	C3'	C3a'	C4'	C5'	C6'	C7'	C8'	C8a'
4a	124.8	141.1	124.5	151.6	141.3	133.4	143.2	133.4	139.2	129.1
4b	124.9	141.1	124.5	151.5	141.3	133.3	143.3	133.3	139.2	129.4
4c	123.9	140.0	123.5	150.5	140.4	132.5	142.3	132.3	138.4	129.3
6a	124.9	139.4	120.8	146.4	140.1	128.2	141.3	128.7	137.1	138.6
6b	123.8	138.4	120.1	145.3	138.7	127.2	140.1	128.5	136.0	138.1
6c	124.9	139.4	120.8	146.4	140.0	128.2	141.3	128.7	137.1	138.6
5a	126.0	137.0	118.2	142.6	137.9	124.4	138.9	124.6	135.3	136.0
5b	126.0	137.0	118.1	142.6	137.8	124.2	138.7	124.5	135.3	135.9
5c	125.2	137.8	118.1	142.6	138.7	124.5	139.7	124.2	135.1	135.3

Table 6
CHEMICAL SHIFTS
OF AZULENE
CARBON ATOMS
C1' - C8' (δ in ppm)

Comps.	C2-6	C3-5	C4	C2''	C3''	C4''	C5''	C1'''	C2'''
4a	165.9	116.4	156.6	152.6	119.1	114.5	147.9	116.7	129.0
4b	166.0	116.3	156.9	133.3	134.2	130.0	132.3	118.1	135.9
4c	165.7	115.4	155.3	131.1	142.2	125.1	128.0	118.2	136.0
12a ^d	152.2	122.8	142.3	150.6	115.4	112.7	145.7	115.5	128.4
6a	153.1	123.1	152.0	152.5	116.3	113.8	146.7	116.6	130.2
6b	151.7	122.4	151.4	139.9	128.9	128.8	132.0	116.5	135.6
6c	153.8	123.4	152.2	129.8	139.5	128.5	126.4	119.1	137.7
11a ^d	154.6	120.9	136.9	153.0	110.5	111.8	142.7	120.3	126.1
5a	153.0	121.5	153.0	154.8	110.8	112.0	143.0	126.2	127.8
5b	155.0	121.2	146.2	128.0	127.8	127.8	127.8	125.5	127.8
5c	155.0	120.8	146.2	125.2	130.9	126.3	124.5	127.2	128.2

Table 7
CHEMICAL SHIFTS
OF HETEROCYCLIC
AND VINYLIC
CARBON ATOMS (δ
in ppm)

Where **12a** represents 1-methyl-2,4-bis[2-(furan-2-yl)viny]pyridinium iodide

Conclusions

The ^1H and ^{13}C NMR spectra of several 2,6-diheteroarylvinyl heterocycles containing 4-azulenyl moiety were compared with those of the compounds without double bond between the heterocycles. The chemical shifts of protons as well as of carbon atoms were discussed in terms of the nature of central and side heterocycles, molecule polarization and anisotropic effects. The most sensible protons and carbon chemical shifts at the changes were these of azulenyl seven-member ring and of the vinyl group as a result of the molecule polarizability. According with their electron withdrawing power of the central heterocycle, the highest chemical shifts are for the pyrylium salts and the lowest at pyridines. It is interesting to note that, in the case of pyridinium salts, the protons chemical shifts at the central heterocycle are higher due to a peculiar anisotropy of the attached vinyl groups.

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