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4-(azulen-1-yl)-2,6-diphenylchalcogenopyrylium Perchlorates; Synthesis and Characterization

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Abstract*. 2,6-Diphenyl substituted thio- and seleno-pyrylium salts with azulen-1-yl moieties in 4-position were prepared from phenylacetylene going through chalcogenopyrones and 4-chloro-chalcogenopyrylium salts as intermediates. The final step of synthesis involves the electrophile substitution in 1-position of azulenes with the obtained chloro-derivatives and the products isolation as stable perchlorates. The electronic and magnetic spectra of products are presented and compared with those of the corresponding pyrylium salts.*

Keywords*: chalcogenopyrylium salts, azulene, chalcogenopyran-4-ones, NMR spectra, electronic spectra, solvatochromism*

1.Introduction

Our research on the synthesis and properties of some azulenes substituted with heteroaryl moieties, which started in 2006, [1] has been recently reviewed in the literature together with other related topics [2,3]. The discussed compounds contain as heterocycle, among others, pyrylium, pyridine or pyridinium moieties. The introduction of the good electron donor azulen-1-yl group at 4-position of six-membered heterocycle, mainly when this is charged, ensure high stability for the resulted system. Therefore, we considered interesting to enlarged the study of such systems with a new classes, namely chalcogeno-pyrylium derivatives with 4-position occupied by azulen-1-yl group. The special physico-chemical properties of chalcogenopyrylium salts as well as their overwhelming applications which can be divided in technical [4,5] and mainly biological applications [4,6,7] represented still a major reason for our interest on the synthesis of this compound classes. The comprehensive reviews elaborated by Doddi in 1994 [4] and more recently, in 2012, by Fernández-Lodeiro [6] regarded the preparation, properties and application of chalcogenopyrylium (thio-, seleno- and telluro-pyrylium) salts.

Materials and methods

Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. Some difficulties were encountered at the elemental analysis due to tendency of perchlorates to violent decomposing. ^{1}H- and ^{13}C-NMR: Bruker Avance DRX4 (^{1}H: 400 MHz, ^{13}C: 100.62 MHz) spectrometers; the atoms numbering were assigned as in Scheme 4. IR: Beckmann IR 5A. Mass spectra: Varian 1200L Triple Quadrupole LC/MS/MS spectrometer by direct injection in ESI. Uv-vis: Specord UV-Vis spectrometer (C. Zeiss Jena).Column chromatography: silica gel [70-230 mesh (ASTM)]. Dichloromethane (DCM) was distilled over CaH_2, ethyl acetate was distilled over Na_2CO_3 and diethyl ether was conserved on NaOH and freshly distilled on $LiAlH_4$. The nomenclature was obtained by use of the ACD/I-Lab web service (ACD/IUPAC Name Free 7.06).

General synthetic procedure

The azulenic compound (0.2 mmol) and 4-chloro-2,6-diphenyl-chalcogenopyrylium perchlorate (0.1 mmol) [7,8] were added in chloroform (2 mL) and the reaction mixture was stirred at reflux for

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1h in the case of thiopyrylium salts and at 70°C for selenopyrylium salts and then the reaction mixture was cooled at room temperature. The precipitation attempt with ether did not give good results because the unreacted chloro-chalcogenopyrylium salt precipitate together with the products. Therefore, the reaction mixture was directly deposited on a silica gel column and the desired compound was eluted with a mixture DCM-EtOAc 10% (increasing ester amount). (If the compound is retained on column, it can be eluted with acetone containing several drops of perchloric acid). The first fraction represented the unreacted azulene compound and then eluted a yellowish band with undefined nature. Finally, the desired products are coming out as bluish (or greenish) solutions (yields are in Table 1). The attempt to work with dichlorophosphates (generated in reaction of pyranones with PCl_5) instead of perchlorates failed because this are not always stable on the column. In some cases the elution system is benzene-acetone.

Products characterization

4-(Azulen-1-yl)-2,6-diphenyl-thiopyrylium perchlorate, **7.** Dark green crystals, mp. 275°C. UV spectrum (MeOH), λ_{max} (log ε): 225 (4.37), 258 (4.32), 301 (4.39), 394 (4.14), 562 (4.38), 582 (4.32). IR spectrum, KBr, ν, cm^{-1} : 614 (m), 687 (m), 749 (m), 872 (m), 921 (m), 968 (m), 999 (m), 1069 (s), 1187 (m), 1260 (m), 1380 (s), 1461 (s), 1489 (s), 1565 (s), 1727 (m), 2856 (m), 2923 (m), 2957 (m). ^{1}H-NMR spectrum, (400 MHz, acetone-d_6), δ, ppm (*J*, Hz): 7.61 (1 H, d, *J* = 4.4, 3'-H), 7.78 (2 H, t, *J* = 7.0, 4''-H), 7.81 (4 H, t, *J* = 7.0, 3''-H, 5''-H), 7.98 (1 H, t, *J* = 9.8, 5'-H), 8.07 (1 H, t, *J* = 9.8, 7'-H), 8.25 (4 H, d, *J* = 8.2, 2''-H, 6''-H), 8.27 (1 H, t, *J* = 9.8, 6'-H), 8.88 (1 H, d, *J* = 9.9, 4'-H), 8.89 (1 H, d, *J* = 4.4, 2'-H), 9.12 (2 H, s, 3-H, 5-H), 9.46 (1 H, d, *J* = 9.6, 8'-H). ^{13}C-NMR spectrum, (100.62 MHz, acetone-d_6), δ, ppm (*J*, Hz): 125.2 (C-3'), 128.2 (C-1'), 129.9 (C-2'', C-6''), 131.3 (C-3, C-5), 131.7 (C-3'', C-5''), 132.4 (C-1''), 133.7 (C-5'), 134.0 (C-7'), 134.5 (C-4''), 139.5 (C-8'), 142.0 (C-4'), 142.5 (C-2'), 143.4 (C-3a'), 144.0 (C-6'), 151.5 (C-8a'), 153.7 (C-4), 164.7 (C-2, C-6). Mass spectrum, *m*/*z* (*I*rel, %): 375 $[M]^+$ (100%), 376 (30%), 377 (7%). Found for $C_{27}H_{19}ClO_4S$, %: C 68.26; H 4.05. Calculated, %: C 68.28; H 4.03.

4-(Azulen-1-yl)-2,6-diphenyl-selenopyrylium perchlorate, **10**. Dark green crystals, mp 302°C. UV spectrum (MeOH), λ_{max} (log ε): 225 (4.39), 261 (4.37), 305 (4.41), 407 (4.11), 576sh (4.35), 600 (4.36). IR spectrum, KBr, ν, cm^{-1}: 614 (m), 685 (m), 747 (m), 869 (m), 913 (m), 989 (m), 1069 (s), 1187 (m), 1224 (m), 1260 (m), 1379 (s), 1461 (s), 1488 (s), 1565 (s), 1641 (m), 1737 (m), 2856 (m), 2923 (m), 2957 (m). ^{1}H-NMR spectrum, (400 MHz, acetone-d_6), δ, ppm (*J*, Hz): 7.57 (1 H, d, *J* = 4.4, 3'-H), 7.74 (2 H, t, *J* = 7.0, 4''-H), 7.76 (4 H, t, *J* = 7.0, 3''-H, 5''-H), 7.99 (1 H, t, *J* = 9.8, 5'-H), 8.08 (1 H, t, *J* = 9.8, 7'-H), 8.20 (4 H, d, *J* = 8.2, 2''-H, 6''-H), 8.24 (1 H, t, *J* = 9.8, 6'-H), 8.86 (1 H, d, *J* = 9.9, 4'-H), 8.88 (1 H, d, *J* = 4.4, 2'-H), 9.05 (2 H, s, 3-H, 5-H), 9.43 (1 H, d, *J* = 9.6, 8'-H). ^{13}C-NMR spectrum, (100.62 MHz, acetone-d_6), δ, ppm (*J*, Hz): 124.8 (C-3'), 128.5 (C-1', C-2'', C-6''), 130.3 (C-3, C-5), 131.0 (C-3'', C-5''), 131.6 (C-1''), 133.2 (C-5'), 133.4 (C-7'), 133.7 (C-4''), 139.1 (C-8'), 141.3 (C-4'), 141.8 (C-2'), 142.8 (C-3a'), 143.4 (C-6'), 151.1 (C-4, C-8a'), 162.4 (C-2, C-6). Mass spectrum, *m*/*z* (*I*rel, %): 417 $[M]^+$ (2%), 419 (18.5%), 420 (20.5%), 421 (52%), 422 (14%), 423 (100%), 424 (29%), 425 (21%), 426 (5%). Found for $C_{27}H_{19}ClO_4Se$, %: C 62.12; H 3.68. Calculated, %: C 62.14; H 3.67.

4-(3,8-Dimethyl-5-isopropyl-azulen-1-yl)-2,6-diphenyl-thiopyrylium perchlorate, **8**. Dark green crystals, mp >300°C. UV spectrum (MeOH), λ_{max} (log ε): 244 (4.37), 263 (4.32), 311sh (4.17), 396 (4.13), 635 (4.40). IR spectrum, KBr, ν, cm^{-1}: 616 (m), 689 (m), 761 (m), 882 (m), 964 (m), 1005 (m), 1075 (s), 1187 (m), 1224 (m), 1312 (m), 1355 (s), 1393 (s), 1438 (m), 1464 (m), 1489 (s), 1532 (s), 1574 (m), 1642 (m), 1707 (m), 2362 (m), 2853 (s), 2921 (s), 2956 (m). ^{1}H-NMR spectrum, (400 MHz, acetone-d_6), δ, ppm (*J*, Hz): 1.40 (6 H, d, *J* = 6.9, iPr), 2.59 (3 H, s, Me_3), 2.90 (3 H, s, Me_8), 3.22 (1 H, sept, *J* = 6.9 Hz, iPr), 7.48 (1 H, t, *J* = 9.6, 7'-H), 7.60 (4 H, t, *J* = 7.0, 3 "-H, 5''-H), 7.61 (2 H, t, *J* = 7.0, 4''-H), 7.84 (4 H, d, *J* = 8.2, 2''-H, 6''-H), 7.87 (1 H, t, *J* = 9.8, 6'-H), 8.10 (2 H, s, 3-H, 5-H), 8.12 (1 H, s, 4'-H), 8.27 (1 H, s, 2'-H). ^{13}C-NMR spectrum, (100.62 MHz, acetone-d_6), δ, ppm (*J*, Hz):

13.26 (3'-Me), 24.42 (*Me*CH), 30.28 (8'-Me), 38.79 (*Me*CH), 127.0 (C-1'), 129.5 (C-3, C-5), 130.3 (C-2", C-6"), 132.3 (C-1"), 132.7 (C-3", C-5"), 134.8 (C-4"), 135.3 (C-7'), 137.6 (C-3', C-4'), 139.1 (C-6'), 141.6 (C-3a'), 142.3 (C-2'), 149.1 (C-5'), 152.5 (C-8a'), 154.3 (C-8'), 155.4 (C-4), 165.2 (C-2, C-6). Mass spectrum, *m/z* (*I*rel, %): 445 [M^+] (100%), 446 (35%), 447 (10%). Found for $C_{32}H_{29}ClO_4S$, %: C 70.49; H 5.38. Calculated, %: C 70.51; H 5.36.

4-(3,8-Dimethyl-5-isopropyl-azulen-1-yl)-2,6-diphenyl-selenopyrylium perchlorate, **11.** Dark green crystals, mp >300°C. UV spectrum (MeOH), λ_{max} (log ε): 245 (4.40), 266 (4.33), 281 (4.32), 325 (4.01), 411 (4.11), 660 (4.45). IR spectrum, KBr, ν, cm^{-1}: 561 (m), 615 (m), 689 (m), 759 (m), 877 (m), 961 (m), 994 (m), 1075 (s), 1190 (m), 1252 (m), 1310 (m), 1354 (s), 1390 (s), 1434 (m), 1467 (m), 1489 (s), 1531 (s), 1573 (m), 1644 (w), 2362 (m), 2859 (m), 2919 (m), 2955 (m). ^{1}H-NMR spectrum, (400 MHz, acetone-d_6), δ, ppm (*J*, Hz): 1.43 (6 H, d, *J* = 6.9, iPr), 2.60 (3 H, s, Me_3), 2.91 (3 H, s, Me_8), 3.25 (1 H, sept, *J* = 6.9, iPr), 7.28 (1 H, t, *J* = 9.6, 7'-H), 7.60 (4 H, t, *J* = 7.0, 3"-H, 5"-H), 7.61 (2 H, t, *J* = 7.0, 4"-H), 7.80 (4 H, d, *J* = 8.2, 2"-H, 6"-H), 7.81 (1 H, t, *J* = 9.8, 6'-H), 7.95 (2 H, s, 3-H, 5-H), 8.14 (1 H, s, 4'-H), 8.30 (1 H, s, 2'-H). ^{13}C-NMR spectrum, (100.62 MHz, acetone-d_6), δ, ppm (*J*, Hz): 13.15 ($Me_{3'}$), 24.43 (*Me*CH), 30.16 ($Me_{8'}$), 38.85 (*Me*CH), 127.0 (C-1'), 127.6 (C-2", C-6"), 130.1 (C-3, C-5), 130.4 (C-3", C-5"), 130.8 (C-1"), 132.6 (C-4"), 135.5 (C-7'), 137.0 (C-3'), 138.1 (C-4'), 139.5 (C-6'), 141.6 (C-2', C-3a'), 145.8 (C-5'), 150.8 (C-8a'), 152.6 (C-4), 155.1 (C-8'), 164.9 (C-2, C-6). Mass spectrum, *m/z* (*I*rel, %): 489 [M^+] (18%), 490 (22%), 491 (48%), 492 (17%), 493 (100%), 494 (35%), 495 (17%). Found for $C_{32}H_{29}ClO_4Se$, %: C 64.93; H 4.96. Calculated, %: C 64.92; H 4.94.

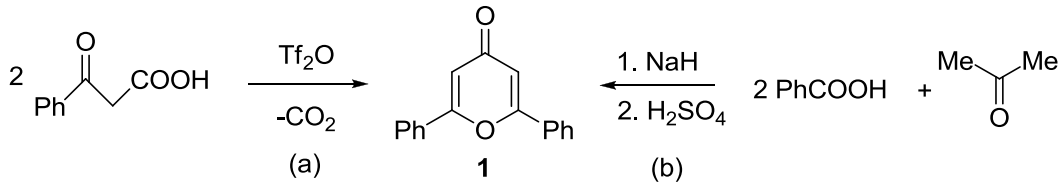
2,6-Diphenyl-4-(4,6,8-trimethyl-azulen-1-yl)-thiopyrylium perchlorate, **9.** Dark green crystals, mp 291 °C. UV spectrum (MeOH), λ_{max} (log ε): 258 (4.42), 283 (4.41), 396 (4.11), 599 (4.34). IR spectrum, KBr, ν, cm^{-1}: 615 (m), 688 (m), 731 (m), 763 (m), 883 (m), 934 (m), 1001 (m), 1067 (s), 1193 (m), 1214 (m), 1271 (m), 1301 (s), 1379 (m), 1405 (m), 1443 (s), 1485 (s), 1568 (s), 1641 (m), 1724 (m), 2856 (m), 2923 (m), 2957 (m). ^{1}H-NMR spectrum, (400 MHz, acetone-d_6), δ, ppm (*J*, Hz): 2.75 (3 H, s, 6'-Me), 2.84 (3 H, s, $Me_{4'}$), 2.88 (3 H, s, $Me_{8'}$), 7.38 (1 H, d, ^3J = 4.8, 3'-H), 7.48 (2 H, t, *J* = 7.1, 4"-H), 7.61 (4 H, t, *J* = 7.6, 3"-H, 5"-H), 7.62 (1 H, s, 5'-H), 7.74 (1 H, s, 7'-H), 7.87 (4 H, d, *J* = 7.0, 2"-H, 6"-H), 8.09 (1 H, d, *J* = 4.4, 2'-H), 8.18 (2 H, s, 3-H, 5-H). ^{13}C-NMR spectrum, (100.62 MHz, acetone-d_6), δ, ppm (*J*, Hz): 25.88 ($Me_{8'}$), 29.07 ($Me_{6'}$), 30.01 ($Me_{4'}$), 116.0 (C-3, C-5), 121.1 (C-3'), 126.0 (C-1'), 127.9 (C-2", C-6"), 130.3 (C-3", C-5"), 131.0 (C-1"), 132.9 (C-4"), 136.9 (C-5'), 137.0 (C-7'), 139.6 (C-2'), 141.5 (C-3a'), 149.1 (C-8'), 149.5 (C-8a'), 150.7 (C-4'), 151.5 (C-6'), 156.4 (C-4), 166.7 (C-2, C-6). Mass spectrum, *m/z* (*I*rel, %): 417[M^+] (100%), 418 (33%), 419 (5%). Found for $C_{30}H_{25}ClO_4S$, %: C 69.67; H 4.88. Calculated, %: C, 69.69; H, 4.87.

2,6-Diphenyl-4-(4,6,8-trimethyl-azulen-1-yl)-selenopyrylium perchlorate, **12**. Dark green crystals, mp >300 °C. UV spectrum (MeOH), λ_{max} (log ε): 224 (4.37), 258 (4.42), 289 (4.41), 409 (4.13), 624 (4.35). IR spectrum, KBr, ν, cm^{-1}: 616 (m), 688 (m), 761 (m), 887 (m), 930 (m), 1001 (m), 1073 (s), 1190 (m), 1274 (m), 1281 (m), 1376 (m), 1404 (m), 1440 (s), 1484 (s), 1567 (s), 1696 (m), 1800 (m), 2362 (m), 2904 (w). ^{1}H-NMR spectrum, (400 MHz, acetone-d_6), δ, ppm (*J*, Hz): 2.68 (3 H, s, $Me_{6'}$), 2.77 (3 H, s, $Me_{4'}$), 2.81 (3 H, s, $Me_{8'}$), 7.32 (1 H, d, ^3J = 4.8, 3'-H), 7.51 (2 H, t, *J* = 7.1, 4"-H), 7.52 (4 H, t, *J* = 7.6, 3"-H, 5"-H), 7.61 (1 H, s, 5'-H), 7.71 (4 H, d, *J* = 7.0 2"-H, 6"-H), 7.74 (1 H, s, 7'-H), 8.02 (1 H, d, *J* = 4.4, 2'-H) 8.07 (2 H, s, 3-H, 5-H). ^{13}C-NMR spectrum, (100.62 MHz, acetone-d_6), δ, ppm (*J*, Hz): 25.92 ($Me_{8'}$), 28.49 ($Me_{6'}$), 30.56 ($Me_{4'}$), 112.0 (C-3, C-5), 121.5 (C-3'), 127.8 (C-2", C-6"), 129.2 (C-1'), 130.5 (C-3", C-5"), 132.8 (C-4"), 134.0 (C-1"), 137.2 (C-5'), 137.3 (C-7'), 139.5 (C-3a'), 139.7 (C-2'), 147.8 (C-8a'), 149.3 (C-8'), 150.9 (C-4'), 151.9 (C-6'), 155.5 (C-4), 167.6 (C-2, C-6). Mass spectrum, *m/z* (*I*rel, %): 461 (18), 462 (21), 463 (48), 464 (16), 465 (100), 466 (33), 467 (17). Found for $C_{30}H_{25}ClO_4Se$, %: C 63.87; H 4.48. Calculated, %: C 63.89; H 4.47.

3.Results and discussions

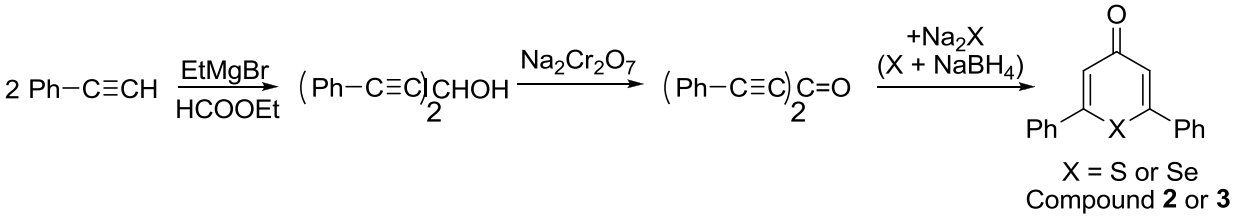
Synthesis

It has been assumed that the known synthesis steps of 2,6-disubstituted 4-(azulen-1-yl)pyrylium salts [2,3] could be adapted for the corresponding chalcogenopyrylium salts. The generation of these pyrylium salts includes the obtaining of 2,6-disubstituted pyran-4-ones, their transformation in the corresponding 4-chloropyrylium salts and finally the electrophilic reaction with azulenes. However, first step, the known synthesis of 2,6-diphenylpyran-4-one shown in Scheme 1 (route (a) [8] or route (b) [1]) do not work for the chalcogenopyrones while the last two steps can be used to the achieving chalcogenopyrylium salts.



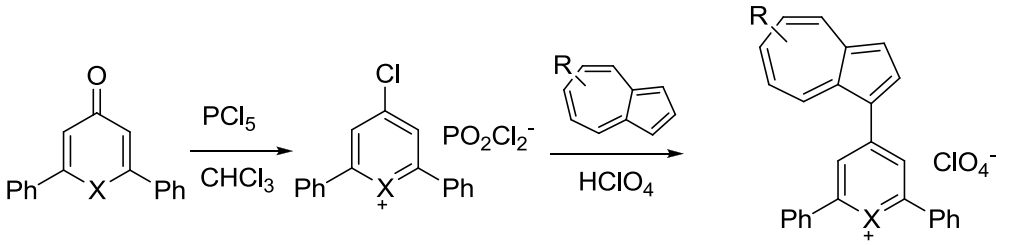
Scheme 1. Preparation of 2,6-diphenyl-4H-pyran-4-one

The synthesis of chalcogenopyrylium salts starts with the preparation of 1,7-diphenylhepta-1,6-diyn-4-one described in literature [9] (however, *n*BuLi was replaced by EtMgBr and MnO_2 by $Na_2Cr_2O_7$ as in Scheme 2, without decreasing the yield). Further, the ketone was cyclized in the presence of Na_2X (generated by reduction of X with $NaBH_4$) to the chalcogenopyranones **2** and **3** [10].



Scheme 2. Preparation of 2,6-diphenyl-4*H*-chalcogenopyran-4-one

As well as for pyranones, by treating with PCl_5 the chalcogenopyranones are transformed into the corresponding 4-chloro-chalcogenopyrylium salts. These salts are the key intermediates for the electrophilic substitution of azulenes, which takes place in hot chloroform for 1 h. Finally, the counterion is change from $PO_2Cl_2^-$ to ClO_4^- by treating the reaction mixture with perchloric acid (Scheme 3). Pure salts were obtained by the chromatography of the reaction mixture on silica gel column. The good yields obtained for the products **7**-**12**, reported in Table 1, are compared with those already found for the 4-(azulen-1-yl)-2,6-diphenylpyrylium salts **4**-**6** [1].



R = (a) H, (b) 1,4-Me_2-7-*i*Pr, or (c) 4,6,8-Me_3
Compounds **4**, **5**, or **6** with X = O; R (a), (b) or (c)
Compounds **7**, **8**, or **9** with X = S; R (a), (b) or (c)
Compounds **10**, **11**, or **12** with X = Se; R (a), (b) or (c)

Scheme 3. Syntheses of 4-(azulen-1-yl)-2,6-diphenyl-pyrylium and -chalcogenopyrylium perchlorates

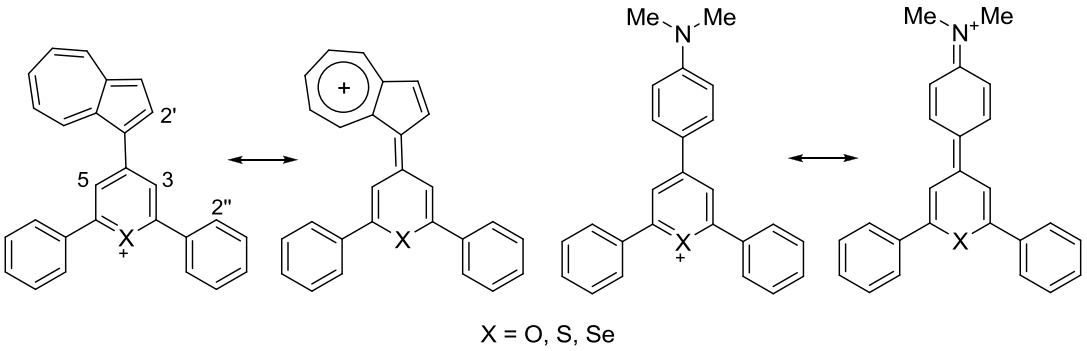
Table 1. Yields (in %) for synthesis of pyrylium and chalcogenopyrylium salts, **4** – **12**, starting from the pyranones

R	O^+ [1]	S^+	Se^+
H	73 (**4**)	86 (**7**)	75 (**10**)
1,4-Me_2-7-*i*Pr	54 (**5**)	64 (**8**)	66 (**11**)
4,6,8-Me_3	90 (**6**)	85 (**9**)	89 (**12**)

The results obtained so far, for tellurium-containing compounds are not conclusive and the research in this direction is underway. The results will be reported as soon as they are satisfactory. Other goal we are considering refers to the substitution of azulen-1-yl moiety with electron donor and acceptor groups.

Optical properties

All azulenic pyrylium and chalcogenopyrylium salts are very beautiful colored compounds. The pyrylium salts have a red-violet color in acetone, while the corresponding thiopyrylium are blue-violet and those of selenium, blue or even green for guaiazulene. The extended π-conjugated electronic system, which includes the tropylium azulenic system, the middle heterocycle and the charged heteroatom (Scheme 4), ensures a strong chromophore system that induces dying properties for the studied compounds. The contribution of the alkyl groups substituted to the seven-membered azulenic ring, which stabilizes the tropylium system, results in the increase of bathochromic effect following the substituent series: H, 4,6,8-Me_3, 1,4-Me_2-7-*i*Pr.



Scheme 4. Resonance structure of compounds **4**, **7, 10** and of the corresponding 4-(*p*-dimethylamino)-substituted compounds

The comparison between the values of λ_{max} of visible absorption of the studied compounds with those of the corresponding pyridines and pyridinium salts reveals, as expected, the lowest values for neutral pyridines (Table 2). The alkyl substituent attached at heterocyclic nitrogen, by its inductive effect, reduces the positive net charge at N in pyridinium salts; therefore, the molecule polarization is much lower than that shown by the pyrylium or chalcogenopyrylium salts inducing a lower value of λ_{max} of visible absorption. Looking at the behavior of the last salts, a bathochromic effect can be noticed in heteroatom order: $O^+ < S^+ < Se^+$. This trend can be empirically associated with the decrease in the electronegativity of heteroatom (O, 3.5; S, 2.5; Se, 2.4) [11]. Another observation can be made by comparing the pyrylium and chalcogenopyrylium salts possessing (azulen-1-yl) moiety in position 4 with those containing 4-dimethylaminophenyl substituent in this position (Scheme 4); the same sequence rule is valid for both series (Table 2).

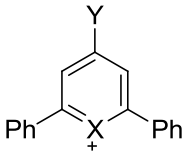


Table 2. Long wavelength absorption maxima of several heteroaromatic salts, λ_{max} (in nm, in MeOH)

Y	X					Ref.
	N	N^+Bu	O	S	Se	
Az*	370	434	530 (**4**)	572** (**7**)	600 (**10**)	For N [12]
4,6,8-Me_3-Az*	374	450	543 (**5**)	599 (**8**)	624 (**11**)	For N^+Bu [13]
1,4-Me_2-7-*i*Pr-Az*	385	475	576 (**6**)	630 (**9**)	660 (**12**)	For O^+ [1]
4-Me_2N-C_6H_4	-	-	550	592	620	4-Me_2N-C_6H_4[11]

*Az = azulen-1-yl. **the middle of the split band

Unlike other chalcogenopyrylium salts, λ_{max} of the compounds substituted with the azulene moieties at position 4 are less sensitive to the dielectric constant of solvent resembling to the behavior of compounds with 4-dimethylaminophenyl substituent in this position [11]. (Scheme 4). Thus, the solvent with lower dielectric constant (dioxane) gives a smaller hypochromic shift relative to the higher dielectric solvents as shown in Table 3 for 4-(azulen-1-yl)-2,6-diphenyl-thiopyrylium perchlorate. The highest wavelength absorption are observed for halogenated (chlorinated) solvents.

Table 3. Shift of λ_{max} of 4-(3,8-dimethyl-5-isopropyl-azulen-1-yl)-2,6-diphenyl-thiopyrylium perchlorate, **8**, with the solvent change (in nm)

Solvent	CH_2Cl_2	$CHCl_3$	DMSO	THF	MeOH	Acetone	Dioxane
Absorption	645	645	540	638	636	634	627

NMR and mass spectra

As result of the relationship between the structure of pyranylium salt and their NMR spectra [1] it was established that two effects govern the chemical shifts of azulene protons. One is the azulene conjugation with good electron withdrawing pyrylium moiety that strongly deshielded all azulene protons comparing with those from 1-phenylazulene [14] (Table 4) or 4-(azulen-1-yl)-2,6-diphenyl-pyridine [1]. The second effect consists in the different position of azulene protons towards pyrylium magnetic field. A similar observation is true for the phenyl moieties but to a lesser extent. As shown in Table 4, these rules apply also to chalcogenopyrylium salts investigated here. However, the lower chalcogenopyrylium salts polarization compared with that for the pyrylium salts is reflected in the lower proton chemical shifts of the first series. Obviously, the lowest values for proton chemical shifts at azulene moiety were noticed for the neutral azulen-1-ylpyridine.

Table 4. Chemical shifts for (azulen-1-yl) substituted phenyl and heteroaryls (in ppm)

H	AzPh*	Y = Az		Y = Az	
		X = N	X = O (**4**)	X = S (**7**)	X = Se (**10**)
3 and 5	-	7.95	8.83	9.12	9.05
2’	8.02	8.18	8.92	8.89	8.88
3’	7.43	7.53	7.77	7.61	7.57
4’	8.34	8.44	8.89	8.88	8.86
5’	7.14	7.28	8.03	7.98	7.99
6’	7.58	7.45	8.31	8.27	8.24
7’	7.14	7.29	8.14	8.07	8.08
8’	8.55	8.71	9.57	9.46	9.43

*1-Phenylazulene.

Mass spectroscopy

For the characterization of obtained chalcogenopyrylium salts +ESI procedure was used. It is interesting to stress that in the case of selenium compounds complicated spectra are generated due to the large number of selenium natural isotopes. The most abundant isotope being ^{80}Se, the

highest peak of the positive ion for 4-(azulen-1-yl)-2,6-diphenyl-selenopyrylium ion is observed for this isotope at M = 423 amu (Figure 1).

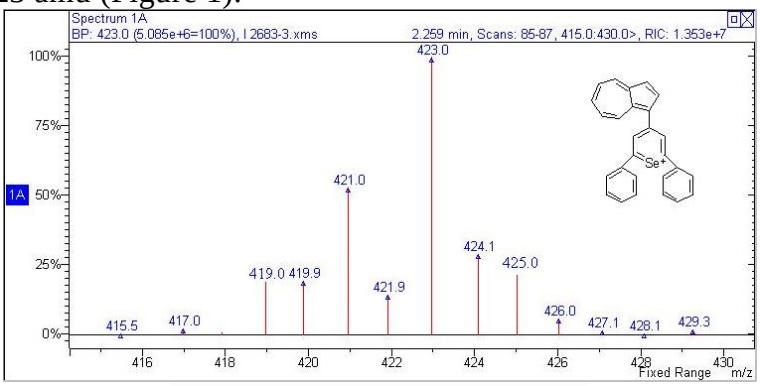


Figure 1. The molecular ion of 4-(azulen-1-yl)-2,6-diphenyl-selenopyrylium perchlorate

4.Conclusions

The series of 1-(heteroaryl)azulenes was enriched with the 4-(azulen-1-yl) -thiopyrylium and selenopyrylium salts. The syntheses of the new salts were carried out in several steps starting from phenyl-acetylene, which was transformed into chalcogenopyranones. Then, the 4-chloro-chalcogeno-pyrylium salts, obtained from the corresponding pyranones, reacted electrophilically, in good yields, with both unsubstituted and substituted azulenes. The attempted products were isolated and characterized as stable perchlorates. Their electronic and magnetic spectra were compared with those of corresponding pyrylium salts. The deeply influence exerted by the electronegativity of the hetero-atom, as well as by the azulene substituents on the spectra, was underlined.

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