



*Dedicated to Professor Alexandru T. Balaban
on the occasion of his 80th anniversary*

BENZO- AND DIBENZO-CROWN ETHERS SUBSTITUTED WITH (AZULENE-1-YL)-IMINO OR (AZULENE-1-YL)-CARBONYL GROUPS

Alexandru C. RAZUS,* Liviu BIRZAN, Victorita TECUCEANU, Mihaela CRISTEA
and Anamaria HANGANU

Roumanian Academy, Institute of Organic Chemistry,
Spl. Independentei, 202B, 060023 Bucharest, P.O. Box 35-108, Roumania

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The synthesis of two new classes of benzo and dibenzo-crown ethers linked on azulenyl moieties by imine or keto group was reported. The imines were obtained by the condensation of (azulene-1-yl)-carbaldehydes with benzo-crown ethers substituted by amino group. The Friedel-Crafts acylation was used for the ketones generation. The products were unequivocally characterized.

INTRODUCTION

The crown ethers have been largely studied because of the important role that these products play in the chemical and biomedical purposes. Since, generally, the crown ethers are colorless compounds, it was of interest to us to investigate several compounds from this large class which contain in the molecule chromophores such as azulene moiety. To this end we have choice as starting reagents the commercially available benzo-crown or dibenzo-crown ethers due to their capacity to be functionalized into benzene ring (for instance, by the electrophilic reactions). We have already described the synthesis and several physico-chemical properties of mono and bis [(azulene-1-yl) azo] benzo- and dibenzo-crown ethers, as well as the similar compound with [(azulene-1-yl) vinyl] substituents (compounds **I**, **II** and **III**, respectively, in Scheme 1).¹ In this paper we reported new crown ethers substituted with (azulene-1-yl)-imino or (azulene-1-yl)-carbonyl groups (compounds with general formula **IV** and **V** in Scheme 1).

RESULTS AND DISCUSSION

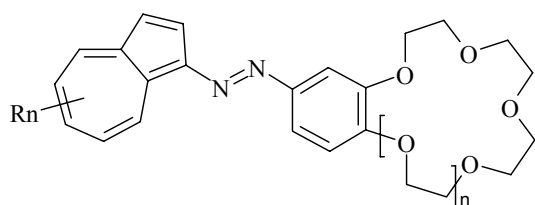
The imines **3** or **4** are obtained by condensation between amino group of the crown ethers **1** or **2** and azulene-1-carbaldehydes without solvent or catalyst (Scheme 2). This green methodology, already reported by us,² involves the heating of the two reagents for 2-3 hours for the mixture homogenization. The mixture was then allowed to room temperature for 2-3 days and the imine resulted in almost quantitative yield as green crystals. The imine crystallization was improved by an atmosphere of diethyl ether at the surface of the reaction mixture.

The second class of the synthesized compounds has a keto function between the azulenyl and the crown ether moieties (compounds **7** and **8** in Scheme 3). We have considered two ways for generation of these products, namely the bis acylation of aromatic moieties of the crown ether **5** or the acylation of azulenes. The first synthetically route involved as the acylation agent the (azulene-1-yl)-carboxylic acid chloride obtained from the corresponding acid. However, the reaction in the presence of polyphosphoric acid occurred with the polymerization of acid chloride due to the

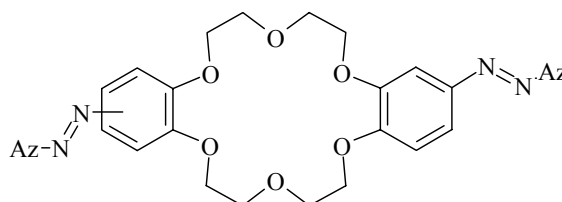
* Corresponding author: acrazus@cco.ro

remained reactive position 3 in azulene moiety. For the azulene acylation, we have obtained first the diacid **6** in the sequence: bis acylation of ether **5** with acetic acid,³ followed by the oxidation of acetyl groups with bromine in the presence of the sodium hydroxide.⁴ Further, the diacid **6** was transformed into the bis acyl chloride using thionyl

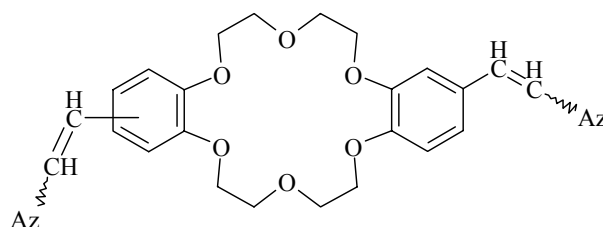
chloride.⁵ Interestingly, in the subsequent acylation only one from the two reactive position of azulene, position 1 and 3, was substituted. The compound **8** was obtained in the aim to polymerize or copolymerize the compound by chemical or electrochemical methods.



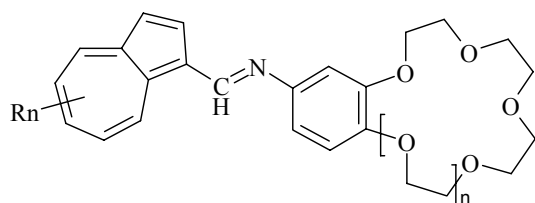
I: Rn = H, 4,6,8-Me₃, 3,8-Me₂-5-*i*Pr or 4,6,8-Me₃-2(or 3)-CO₂H (or CO₂Me)
n = 1 or 2



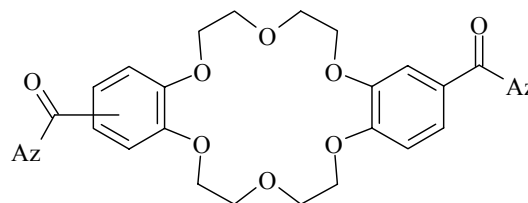
II: Az = azulenyl or azulenyl substituted with 4,6,8-Me₃, 3,8-Me₂-5-*i*Pr or 4,6,8-Me₃-2(or 3)-CO₂H (or CO₂Me)



III: Az = azulenyl

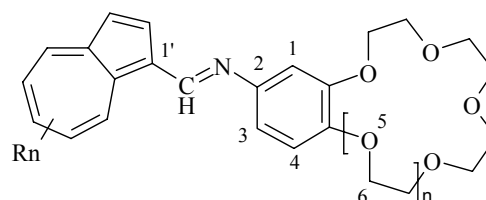
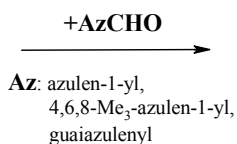
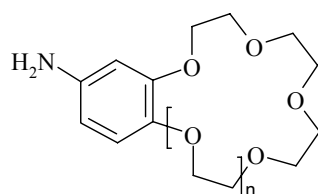


IV



V

Scheme 1



1: n=1, (3-amino-15-benzo-crown 5)
 2: n=2, (3-amino-18-benzo-crown 6)

Rn

Compound / yield (%)
 n = 1 n = 2

H	3 (Az) / 90	4 (Az) / 89
4,6,8-Me ₃	3 (TMA) / 48	4 (TMA) / 35
3,8-Me ₂ -5- <i>i</i> Pr	3 (Gu) / 60	4 (Gu) / 77

Scheme 2

for the product elution. The yield in the product was 28%. The same procedure was used also for the synthesis of the product **8** and the yield was only 10%.

Product characterization

[1-Azulen-1-yl-meth-(E)-ylidene]-(6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-benzocyclopentadecen-2-yl)-amine, 3(Az). Green crystals, mp 81 °C. UV-Vis (THF): 224 (4.46), 227 (4.46), 229 (4.46), 235 (4.45), 278 sh (4.32), 306 (4.52), 329 sh (4.29), 397 (4.34), 576 (2.27). ¹H-NMR (CDCl₃), δ (ppm): 3.78 (bs, 8 H, CH₂), 3.92-3.96 (m, 4 H, CH₂), 4.16-4.20 (m, 2 H, CH₂), 4.20-4.24 (m, 2 H, CH₂), 6.87 (dd, ³J = 8.4 Hz, ⁴J = 2.1 Hz, 1 H, 3-H), 6.92 (d, ³J = 8.4 Hz, 1 H, 4-H), 6.93 (d, ⁴J = 2.0 Hz, 1 H, 1-H), 7.33 (t, ³J = 9.7 Hz, 1 H, 5'-H), 7.39 (d, ³J = 4.2 Hz, 1 H, 3'-H), 7.40 (t, ³J = 9.7 Hz, 1 H, 7'-H), 7.72 (t, ³J = 9.8 Hz, 1 H, 6'-H), 8.35 (d, ³J = 4.0 Hz, 1 H, 2'-H), 8.39 (d, ³J = 9.7 Hz, 1 H, 4'-H), 9.00 (s, 1 H, CH=N), 9.39 (d, ³J = 9.8 Hz, 1 H, 8'-H). ¹³C-NMR (CDCl₃), δ (ppm): 68.85 (CH₂), 69.59 (CH₂), 69.73 (CH₂), 70.46 (CH₂), 70.59 (CH₂), 71.05 (CH₂), 71.10 (CH₂), 107.9 (C4), 112.5 (C3), 114.9 (C1), 119.1 (C3'), 125.5 (Cq), 126.0 (C5'), 126.3 (C7'), 136.1 (C8'), 137.9 (C2'), 138.8 (C4'), 138.9 (C6'), 144.7 (Cq), 147.0 (C-N), 147.6 (Cq), 149.6 (Cq), 153.8 (C=N). MS [ESI]: 422 [M+1]. Calcd. for C₂₅H₂₇NO₅: C, 71.24; H, 6.46; N, 3.32. Found: C, 71.26; H, 6.50; N, 3.28.

[1-Azulen-1-yl-meth-(E)-ylidene]-(6,7,9,10,12,13,15,16,18,19-decahydro-5,8,11,14,17,20-hexaoxa-benzocyclooctadecen-2-yl)-amine, 4(Az). Green crystals, mp 82 °C. UV-Vis (THF): 227 (4.51), 229 (4.51), 235 (4.51), 278 sh (4.39), 306 (4.61), 325 sh (4.40), 396 (4.41), 567 (2.39), 584 (2.39). ¹H-NMR (CDCl₃), δ (ppm): 3.70 (s, 4 H, CH₂), 3.72-3.75 (m, 4 H, CH₂), 3.77-3.80 (m, 4 H, CH₂), 3.92-3.95 (m, 2 H, CH₂), 3.95-3.97 (m, 2 H, CH₂), 4.17-4.22 (m, 2 H, CH₂), 4.23-4.26 (m, 2 H, CH₂), 6.86 (dd, ³J = 9.4 Hz, ⁴J = 2.2 Hz, 1 H, 3-H), 6.92 (d, ³J = 8.5 Hz, 1 H, 4-H), 6.93 (d, ⁴J = 2.1 Hz, 1 H, 1-H), 7.32 (t, ³J = 9.7 Hz, 1 H, 5'-H), 7.40 (d, ³J = 4.2 Hz, 1 H, 3'-H), 7.41 (t, ³J = 9.8 Hz, 1 H, 7'-H), 7.72 (t, ³J = 9.8 Hz, 1 H, 6'-H), 8.35 (d, ³J = 4.0 Hz, 1 H, 2'-H), 8.39 (d, ³J = 9.5 Hz, 1 H, 4'-H), 9.00 (s, 1 H, CH=N), 9.38 (d, ³J = 9.8 Hz, 1 H, 8'-H). ¹³C-NMR (CDCl₃), δ (ppm): 68.95 (CH₂), 69.57 (CH₂), 69.61 (CH₂), 69.73 (CH₂), 70.71 (CH₂), 70.73 (CH₂), 70.81 (CH₂), 107.9 (C4), 112.6 (C3), 114.9 (C1), 119.1 (C3'), 125.5 (Cq), 125.9 (C5'), 126.2 (C7'), 136.0 (C8'), 137.8 (C2'), 138.6 (C4'), 138.8 (C6'), 144.7 (Cq), 146.9 (C-N), 147.5 (Cq), 149.4 (Cq), 153.8 (C=N). MS [ESI]: 466 [M+1]. Calcd. for C₂₇H₃₁NO₆: C, 69.66; H, 6.71; N, 3.01. Found: C, 69.62; H, 6.75; N, 3.02.

(6,7,9,10,12,13,15,16-Octahydro-5,8,11,14,17-pentaoxa-benzocyclopentadecen-2-yl)-[1-(4,6,8-trimethyl-azulen-1-yl)-meth-(E)-ylidene]-amine, 3(TMA). Brown crystals, mp 94 °C. UV-Vis (THF): 227 (4.51), 229 (4.51), 247 (4.55), 299 (4.55), 315 (4.58), 328 (4.53), 403 (4.39), 522 (2.96). ¹H-NMR (CDCl₃), δ (ppm): 2.62 (s, 3 H, Me_{6'}), 2.88 (s, 3 H, Me_{4'}), 3.09 (s, 3 H, Me_{8'}), 3.74 (bs, 8 H, CH₂), 3.91-3.95 (m, 4 H, CH₂), 4.15-4.18 (m, 2 H, CH₂), 4.18-4.21 (m, 2 H, CH₂), 6.78 (dd, ³J = 8.4 Hz, ⁴J = 2.4 Hz, 1 H, 3-H), 6.89 (d, ⁴J = 2.7 Hz, 1 H, 1-H), 6.90 (d, ³J = 8.6 Hz, 1 H, 4-H), 7.16 (s, 2 H, 5'-H, 7'-H), 7.38 (d, ³J = 4.4 Hz, 1 H, 3'-H), 8.40 (d, ³J = 4.4 Hz, 1 H, 2'-H), 9.28 (s, 1 H, CH=N). ¹³C-NMR (CDCl₃), δ (ppm): 25.76 (Me_{4'}), 28.33 (Me_{6'}), 30.37 (Me_{8'}), 68.86 (CH₂), 69.59 (CH₂), 69.71 (CH₂), 69.74 (CH₂), 70.50 (CH₂), 70.63 (CH₂), 71.03 (CH₂), 71.08 (CH₂), 108.4 (C1), 112.2 (C3), 115.1 (C4), 117.4 (C3'), 128.5 (Cq), 129.9 (C5'), 131.3 (C7'), 135.2 (C2'), 135.3 (Cq), 140.9 (Cq), 146.5 (Cq), 146.6 (Cq), 146.9 (Cq), 148.0 (Cq), 149.6 (Cq), 157.0 (C=N). MS [ESI]: 464

[M+1]. Calcd. for C₂₈H₃₃NO₅: C, 72.55; H, 7.18; N, 3.02. Found: C, 72.56; H, 7.16; N, 3.00.

(6,7,9,10,12,13,15,16,18,19-Decahydro-5,8,11,14,17,20-hexaoxa-benzocycloocta decen-2-yl)-[1-(4,6,8-trimethyl-azulen-1-yl)-meth-(E)-ylidene]-amine, 4(TMA). Brown crystals, mp 65 °C. UV-Vis (THF): 227 (4.39), 229 (4.39), 232 (4.39), 247 (4.43), 298 sh (4.42), 316 (4.50), 332 sh (4.44), 404 (4.34), 546 (2.91). ¹H-NMR (CDCl₃), δ (ppm): 2.62 (s, 3 H, Me_{6'}), 2.88 (s, 3 H, Me_{4'}), 3.09 (s, 3 H, Me_{8'}), 3.69 (s, 4 H, CH₂), 3.72-3.75 (m, 4 H, CH₂), 3.77-3.80 (m, 4 H, CH₂), 3.93-3.95 (m, 2 H, CH₂), 3.95-3.97 (m, 2 H, CH₂), 4.17-4.19 (m, 2 H, CH₂), 4.20-4.22 (m, 2 H, CH₂), 6.79 (dd, ³J = 8.4 Hz, ⁴J = 2.0 Hz, 1 H, 3-H), 6.89 (bs, 1 H, 1-H), 6.90 (d, ³J = 8.6 Hz, 1 H, 4-H), 7.16 (s, 2 H, 5'-H, 7'-H), 7.37 (d, ³J = 4.4 Hz, 1 H, 3'-H), 8.40 (d, ³J = 4.2 Hz, 1 H, 2'-H), 9.28 (s, 1 H, CH=N). ¹³C-NMR (CDCl₃), δ (ppm): 25.68 (Me_{4'}), 28.27 (Me_{6'}), 30.37 (Me_{8'}), 68.96 (CH₂), 69.61 (CH₂), 69.71 (CH₂), 70.71 (CH₂), 70.75 (CH₂), 70.81 (CH₂), 108.4 (C1), 112.3 (C3), 115.1 (C4), 117.3 (C3'), 128.5 (Cq), 129.8 (C5'), 131.2 (C7'), 135.1 (C2'), 135.2 (Cq), 140.8 (Cq), 146.4 (Cq), 146.5 (Cq), 146.7 (Cq), 146.8 (Cq), 147.9 (Cq), 156.8 (C=N). MS [ESI]: 508 [M+1]. Calcd. for C₃₀H₃₇NO₆: C, 70.98; H, 7.35; N, 2.76. Found: C, 70.95; H, 7.38; N, 2.78.

[1-(5-Isopropyl-3,8-dimethyl-azulen-1-yl)-meth-(E)-ylidene]-(6,7,9,10,12,13,15,16-octa hydro-5,8,11,14,17-pentaoxa-benzocyclopentadecen-2-yl)-amine, 3(Gu). Green crystals, mp 100 °C. UV-Vis (THF): 212 (4.39), 224 (4.46), 250 (4.47), 292 (4.44), 318 (4.57), 340 sh (4.40), 414 (4.52), 594 (2.71). ¹H-NMR (CDCl₃), δ (ppm): 1.37 (d, ³J = 6.9 Hz, 6 H, Me₂CH), 2.61 (s, 3 H, Me_{3'}), 3.06 (s, 3 H, Me_{8'}), 3.08 (hept, ³J = 6.9 Hz, 1 H, Me₂CH), 3.77 (bs, 8 H, CH₂), 3.91-3.95 (m, 4 H, CH₂), 4.15-4.18 (m, 2 H, CH₂), 4.18-4.21 (m, 2 H, CH₂), 6.78 (dd, ³J = 8.4 Hz, ⁴J = 2.4 Hz, 1 H, 3-H), 6.89 (d, ⁴J = 2.5 Hz, 1 H, 1-H), 6.90 (d, ³J = 8.6 Hz, 1 H, 4-H), 7.13 (d, ³J = 10.7 Hz, 1 H, 7'-H), 7.40 (dd, ³J = 10.6 Hz, ⁴J = 1.9 Hz, 1 H, 6'-H), 8.16 (d, ⁴J = 1.9 Hz, 1 H, 4'-H), 8.39 (s, 1 H, 2'-H), 9.28 (s, 1 H, CH=N). ¹³C-NMR (CDCl₃), δ (ppm): 12.87 ((CH₃)₃), 24.42 ((CH₃)₂CH), 29.43 ((CH₃)_{8'}), 37.86 (Me₂CH), 69.59 (CH₂), 69.72 (CH₂), 70.49 (CH₂), 70.63 (CH₂), 71.03 (CH₂), 71.07 (CH₂), 108.4 (C1), 112.1 (C3), 115.1 (C4), 125.7 (Cq), 127.0 (Cq), 129.7 (C7'), 134.3 (C4'), 135.1 (C6'), 136.5 (Cq), 137.8 (C2'), 142.4 (Cq), 144.0 (Cq), 145.3 (Cq), 146.8 (Cq), 148.1 (Cq), 149.6 (Cq), 156.0 (C=N). MS [ESI]: 492 [M+1]. Calcd. for C₃₀H₃₇NO₅: C, 73.29; H, 7.59; N, 2.85. Found: C, 73.25; H, 7.61; N, 2.86.

(6,7,9,10,12,13,15,16,18,19-Decahydro-5,8,11,14,17,20-hexaoxa-benzocycloocta decen-2-yl)-[1-(5-isopropyl-3,8-dimethyl-azulen-1-yl)-meth-(E)-ylidene]-amine, 4(Gu). Green crystals, mp 95 °C. UV-Vis (THF): 215 (4.42), 225 (4.48), 249 (4.48), 291 (4.45), 318 (4.55), 335 sh (4.45), 414 (4.51), 599 (2.90). ¹H-NMR (CDCl₃), δ (ppm): 1.38 (d, ³J = 6.9 Hz, 6 H, Me₂CH), 2.62 (s, 3 H, Me_{3'}), 3.07 (s, 3 H, Me_{8'}), 3.08 (hept, ³J = 6.9 Hz, 1 H, Me₂CH), 3.70 (s, 4 H, CH₂), 3.72-3.74 (m, 4 H, CH₂), 3.77-3.80 (m, 4 H, CH₂), 3.93-3.96 (m, 2 H, CH₂), 3.95-3.97 (m, 2 H, CH₂), 4.18-4.20 (m, 2 H, CH₂), 4.21-4.23 (m, 2 H, CH₂), 6.80 (dd, ³J = 8.4 Hz, ⁴J = 2.4 Hz, 1 H, 3-H), 6.90 (d, ⁴J = 2.5 Hz, 1 H, 1-H), 6.91 (d, ³J = 8.6 Hz, 1 H, 4-H), 7.14 (d, ³J = 10.7 Hz, 1 H, 7'-H), 7.42 (dd, ³J = 10.6 Hz, ⁴J = 1.9 Hz, 1 H, 6'-H), 8.16 (d, ⁴J = 1.9 Hz, 1 H, 4'-H), 8.39 (s, 1 H, 2'-H), 9.29 (s, 1 H, CH=N). ¹³C-NMR (CDCl₃), δ (ppm): 12.93 ((CH₃)₃), 24.49 ((CH₃)₂CH), 29.51 ((CH₃)_{8'}), 37.93 (Me₂CH), 69.07 (CH₂), 69.74 (CH₂), 69.94 (CH₂), 70.80 (CH₂), 70.83 (CH₂), 70.84 (CH₂), 108.4 (C1), 112.3 (C3), 115.2 (C4), 125.8 (Cq), 127.1 (Cq), 129.8 (C7'), 134.3 (C4'), 135.1 (C6'), 136.6 (Cq), 137.8 (C2'), 142.5 (Cq),

144.0 (Cq), 145.3 (Cq), 146.8 (Cq), 148.1 (Cq), 149.5 (Cq), 156.0 (C=N). MS [ESI]: 536 [M+1]. Calcd. for C₃₂H₄₁NO₆: C, 71.75; H, 7.72; N, 2.61. Found: C, 71.71; H, 7.75; N, 2.59.

[14-(Azulene-1-carbonyl)-6,7,9,10,17,18,20,21-octahydro-5,8,11,16,19,22-hexaoxa-dibenzo[a,j]cyclooctadecene-2-yl]-azulen-1-yl-methanone, 7. Red crystals, mp 138 °C. UV-Vis (dioxane): 224 (4.60), 262 (4.54), 291 sh (4.65), 301 (4.70), 366 (4.29), 377 sh (4.25), 535 (2.46), 566 sh (2.23). ¹H-NMR (CDCl₃), δ (ppm): 3.94-4.02 (m, 8 H, CH₂), 4.15-4.21 (m, 8 H, CH₂), 6.91 (dd, ³J = 8.3 Hz, ⁴J = 1.9 Hz, 2 H, 4-H, 13- or 14-H), 7.31 (d, ³J = 4.1 Hz, 2 H, 3'-H), 7.44 (dd, ³J = 8.3 Hz, ⁴J = 1.9 Hz, 2 H, 3-H, 14- or 13-H), 7.48 (t, ³J = 9.8 Hz, 2 H, 5'-H), 7.49 (d, ⁴J = 1.9 Hz, 2 H, 1-H, 12- or 15-H), 7.58 (t, ³J = 9.8 Hz, 2 H, 7'-H), 7.83 (t, ³J = 9.8 Hz, 2 H, 6'-H), 8.11 (d, ³J = 4.1 Hz, 2 H, 2'-H), 8.50 (d, ³J = 9.6 Hz, 2 H, 4'-H), 9.57 (d, ³J = 9.8 Hz, 2 H, 8-H). ¹³C-NMR (CDCl₃), δ (ppm): 114.1, 117.4, 124.5, 125.6, 127.0, 128.3, 132.6, 134.1, 138.4, 138.9, 139.4, 141.3, 141.9, 144.9, 148.3, 151.7, 191.7. MS [ESI]: 669 [M+1]. Calcd. for C₄₂H₃₆O₈: C, 75.43; H, 5.43. Found: C, 75.36; H, 5.50.

3-{3-[14-[3-(2-Carboxy-2-cyano-vinyl)-azulene-1-carbonyl]-6,7,9,10,17,18,20,21-octahydro-5,8,11,16,19,22-hexaoxa-dibenzo[a,j]cyclooctadecene-2-carbonyl]-azulen-1-yl}-2-cyano-acrylic acid ethyl ester, 8. Reddish-brown crystals, mp. 235 °C. UV-Vis (MeOH): 205 (4.75), 251 (4.43), 279 (4.33), 322 (4.53), 390 (4.36), 410 (4.41), 425 (4.38). ¹H-NMR (CDCl₃), δ (ppm): 1.88 (t, ³J = 7.0 Hz, 6 H, CH₃CH₂), 4.05 (bs, 8 H, CH₂), 4.25 (bs, 8 H, CH₂), 4.40 (q, ³J = 6.9 Hz, 4 H, CH₃CH₂), 6.83-6.94 (m, 2 H, 4-H, 12- or 15-H), 7.54 (s, 2 H, 1-H, 15- or 12-H), 7.53-7.65 (m, 2 H, 3-H, 13- or 14-H), 7.82 (t, ³J = 9.8 Hz, 2 H, 5'-H), 7.85 (t, ³J = 9.8 Hz, 2 H, 7'-H), 8.07 (t, ³J = 9.8 Hz, 2 H, 6'-H), 8.86 (s, 2 H, CH=), 8.87 (d, ³J = 9.8 Hz, 2 H, 4'-H), 9.25 (s, 2 H, 2'-H), 9.63 (d, ³J = 9.8 Hz, 2 H, 8'-H). ¹H-NMR (DMSO-d₆), δ (ppm): 1.88 (t, ³J = 7.0 Hz, 6 H, CH₃CH₂), 3.89 (bs, 8 H, CH₂), 4.08 (bs, 8 H, CH₂), 4.33 (q, ³J = 7.1 Hz, 4 H, CH₃CH₂), 7.02-7.21 (m, 2 H, 4-H, 12- or 15-H), 7.47 (s, 2 H, 1-H, 15- or 12-H), 7.44-7.63 (m, 2 H, 3-H, 13- or 14-H), 8.06 (t, ³J = 9.8 Hz, 2 H, 5'-H), 8.07 (t, ³J = 9.8 Hz, 2 H, 7'-H), 8.34 (t, ³J = 9.7 Hz, 2 H, 6'-H), 8.91 (s, 2 H, CH=), 9.08 (s, 2 H, 2'-H), 9.25 (d, ³J = 10.0 Hz, 2 H, 4'-H), 9.54 (d, ³J = 10.0 Hz, 2 H, 8'-H). MS [ESI]: 915 [M+1]. Calcd. for C₅₄H₄₆O₁₂N₂: C, 70.90; H, 5.03; N, 3.06. Found: C, 70.85; H, 5.12; N, 3.10.

CONCLUSIONS

We have achieved the synthesis of two new classes of benzo and dibenzo-crown ethers linked on azulenyl moieties by imine or keto group. By the condensation of (azulene-1-yl)-carbaldehydes with benzo-crown ethers substituted by amino group the imines **3** or **4** resulted in good yields. The ketones were obtained in the Friedel-Crafts reaction between azulene and the bis acyl chlorid of diacid **6** obtained starting from dibenzo-crown ether **5**.

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