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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

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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). 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).

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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, 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

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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-iPr or 4.6.8-Me₃-2(or 3)-CO₂H (or CO₂Me) n = 1 or 2

$$Az^{-N} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

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

III: Az = azulenyl

Scheme 1

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

Rn
$$\frac{\text{Compound / yield (\%)}}{\text{n = 1}}$$
 $\frac{\text{n = 2}}{\text{n = 2}}$
H $\frac{3(\text{Az})/90}{4,6,8-\text{Me}_3}$ $\frac{3(\text{TMA})/48}{3(\text{TMA})/48}$ $\frac{4(\text{TMA})/35}{4(\text{Gu})/77}$

Scheme 2

EXPERIMENTAL

Reagents and instrumentation. Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. ¹H- and ¹³C-NMR: Bruker Avance DRX4 (1H: 400 MHz, 13C: 100.62 MHz) spectrometers; chemical shifts (δ) are expressed in ppm, and J values are given in Hz; TMS was used as internal standard in CDCl₃ as solvent;⁶ several signals were assigned on the basis of COSY and HETCOR experiments. Mass spectra: Varian 1200 L/MS/MS triple quadrupole mass spectrometer using direct injection in ESI mode. Column chromatography: silica gel [70-230 mesh (ASTM)]. Dichloromethane (DCM) was distilled over CaH₂ and for the Friedel-Crafts acylation DCM was redistilled on P₂O₅; ethyl acetate was distilled over Na₂CO₃ and diethyl ether was stored on NaOH and freshly distilled on LiAlH₄. UV-Vis spectra in methanol: Varian Carey 100 Bio spectrophotometer. The nomenclature was obtained by use of the ACD/I-Lab web service (ACD/IUPAC Name Free 7.06) and the atoms numbering were indicated in Scheme 2 and 3.

2,13(14)-Diacetil-benzo-18-crown-6 (mp 197 °C; lit.⁷ 197-200 °C) and the diacid 6 (mp 301 °C; lit.⁴ 301-303 °C) as well as the azulene-1-carbaldehydes⁸ were obtained as described in the literature.

Compounds synthesis

Condensation of benzo-crown amines with azulene-1-carbaldehydes. Azulene-1-carbaldehyde (1 mmol) and aminobenzocrown ether 1 or 2 (1 mmol) were mixed and

heated at 60 °C for 3-4 hours for the reagents homogenization. When the pattern aldehyde was used the crown ether was dissolved by the oily azulene-1-carbaldehyde. Then, the reaction mixture was cooled and the oily product was let to stay for 2-3 days into a dessicator, near a crystallizer with a small quantity of diethyl ether. During this time, the imine crystallizes, usually as green crystals. The yield in imines was almost quantitative and for an analytical sample the products were crystallized from ethyl alcohol.

Acylation procedure. The dicarboxylic acid 6 (224 mg, 0.5 mmol) dissolved in anhydrous benzene (4.7 mL) was treated with an excess of thionyl chloride (0.3125 ml, 4.3 mmol) and the solution was refluxed 3 hours in an inert atmosphere. The excess of thionyl chloride was vaporized under vacuum and the obtained diacid chloride was dissolved in dry DCM (8 mL). The excess of thionyl chloride was evaporated under vacuum and the obtained diacid dichloride was dissolved in dry DCM (8 mL). To this solution cooled at 0 °C, under inert atmosphere, a solution of azulene (128 mg, 1 mmol) in dry DCM (1 mL) was added and then a great excess of SnCl₄ (0.25 mL) was also added slowly with a syringe. The stirring at 0 °C was continued for 15 minutes and then at room temperature for 30 minutes when the color of reaction mixture turned from blue to red and, finally, to red-brown. The reaction mixture was dissolved in DCM and a solution of HCl 10% was added. The organic layer was separated and washed two times with water and then was dried over Na₂SO₄. The solvent was removed and the residue was chromatographed on alumina with a mixture of petroleum ether-DCM for the elution of azulene and DCM-ethyl acetate (with ester gradient) 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]-(6,7,9,10,12,13,15,16octahydro-5,8,11,14,17-pentaoxa-benzocyclopentadecen-2yl)-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 $(dd, {}^{3}J = 8.4 \text{ Hz}, {}^{4}J = 2.1 \text{ Hz}, 1 \text{ H}, 3-\text{H}), 6.92 (d, {}^{3}J = 8.4 \text{ Hz}, 1 \text{ H}, 4-\text{H}), 6.93 (d, {}^{4}J = 2.0 \text{ Hz}, 1 \text{ H}, 1-\text{H}), 7.33 (t, {}^{3}J = 9.7 \text{ Hz}, 1 \text{ Hz})$ 1 H, 5'-H), 7.39 (d, ${}^{3}J = 4.2 \text{ Hz}$, 1 H, 3'-H), 7.40 (t, ${}^{3}J = 9.7$ Hz, 1 H, 7'-H), 7.72 (t, ${}^{3}J = 9.8$ Hz, 1 H, 6'-H), 8.35 (d, ${}^{3}J =$ 4.0 Hz, 1 H, 2'-H), 8.39 (d, ${}^{3}J = 9.7$ Hz, 1 H, 4'-H), 9.00 (s, 1 H, CH=N), 9.39 (d, ${}^{3}J = 9.8$ Hz, 1 H, 8'-H). ${}^{13}C$ -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-5,8,11,14,17,20hexaoxa-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, $^{3}J = 9.4$ Hz, $^{4}J = 2.2 \text{ Hz}, 1 \text{ H}, 3\text{-H}), 6.92 (d, {}^{3}J = 8.5 \text{ Hz}, 1 \text{ H}, 4\text{-H}), 6.93$ $(d, {}^{4}J = 2.1 \text{ Hz}, 1 \text{ H}, 1 \text{-H}), 7.32 (t, {}^{3}J = 9.7 \text{ Hz}, 1 \text{ H}, 5' \text{-H}), 7.40$ $(d, {}^{3}J = 4.2 \text{ Hz}, 1 \text{ H}, 3'-\text{H}), 7.41 (t, {}^{3}J = 9.8 \text{ Hz}, 1 \text{ H}, 7'-\text{H}),$ 7.72 (t, ${}^{3}J = 9.8 \text{ Hz}$, 1 H, 6'-H), 8.35 (d, ${}^{3}J = 4.0 \text{ Hz}$, 1 H, 2'-H), 8.39 (d, ${}^{3}J$ = 9.5 Hz, 1 H, 4'-H), 9.00 (s, 1 H, CH=N), 9.38 (d, ${}^{3}J$ = 9.8 Hz, 1 H, 8'-H). ${}^{13}C$ -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-pentaoxabenzocyclopentadecen-2-yl)-[1-(4,6,8-trimethyl-azulen-1yl)-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, Me₆), 2.88 (s, 3 H, $Me_{4'}$), 3.09 (s, 3 H, $Me_{8'}$), 3.74 (bs, 8 H, CH_2), 3.91-3.95 (m, 4 H, CH₂), 4.15-4.18 (m, 2 H, CH₂), 4.18-4.21 (m, 2 H, CH₂), $6.78 \text{ (dd, }^{3}\text{J} = 8.4 \text{ Hz, }^{4}\text{J} = 2.4 \text{ Hz, }^{1}\text{ H, }3\text{-H), }6.89 \text{ (d, }^{4}\text{J} = 2.7)$ Hz, 1 H, 1-H), 6.90 (d, ${}^{3}J = 8.6$ Hz, 1 H, 4-H), 7.16 (s, 2 H, 5'-H, 7'-H), 7.38 (d, ${}^{3}J$ = 4.4 Hz, 1 H, 3'-H), 8.40 (d, ${}^{3}J$ = 4.4 Hz, 1 H, 2'-H), 9.28 (s, 1 H, CH=N). ${}^{13}C$ -NMR (CDCl₃), δ (ppm): 25.76 (Me₄), 28.33 (Me₆), 30.37 (Me₈), 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 $C_{28}H_{33}NO_5$: 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-5,8,11,14,17,20hexaoxa-benzocycloocta decen-2-yl)-[1-(4,6,8-trimethylazulen-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, ${}^{3}J = 8.4$ Hz, ${}^{4}J =$ 2.0 Hz, 1 H, 3-H), 6.89 (bs, 1 H, 1-H), 6.90 (d, ${}^{3}J = 8.6$ Hz, 1 H, 4-H), 7.16 (s, 2 H, 5'-H, 7'-H), 7.37 (d, ${}^{3}J = 4.4$ Hz, 1 H, 3'-H), 8.40 (d, ${}^{3}J = 4.2$ Hz, 1 H, 2'-H), 9.28 (s, 1 H, CH=N). ¹³C-NMR (CDCl₃), δ (ppm): 25.68 (Me₄), 28.27 (Me₆), 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-5,8,11,14,17pentaoxa-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). 1 H-NMR (CDCl₃), δ (ppm): 1.37 (d, 3 J = 6.9 Hz, 6 H, Me_2 CH), 2.61 (s, 3 H, $Me_{3'}$), 3.06 (s, 3 H, $Me_{8'}$), 3.08 (hept, $^{3}J = 6.9 \text{ Hz}, 1 \text{ H}, \text{Me}_{2}\text{C}H), 3.77 \text{ (bs, } 8 \text{ H}, \text{CH}_{2}), 3.91-3.95 \text{ (m,}$ 4 H, CH₂), 4.15-4.18 (m, 2 H, CH₂), 4.18-4.21 (m, 2 H, CH₂), $6.78 \text{ (dd, }^{3}\text{J} = 8.4 \text{ Hz, }^{4}\text{J} = 2.4 \text{ Hz, } 1 \text{ H, } 3\text{-H), } 6.89 \text{ (d, }^{4}\text{J} =$ 2.5 Hz, 1 H, 1-H), $6.90 \text{ (d, }^{3}\text{J} = 8.6 \text{ Hz}$, 1 H, 4-H), $7.13 \text{ (d, }^{3}\text{J} =$ 10.7 Hz, 1 H, 7'-H), 7.40 (dd, ${}^{3}J = 10.6$ Hz, ${}^{4}J = 1.9$ Hz, 1 H, 6'-H), 8.16 (d, ${}^{4}J = 1.9$ 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 $((CH_3)_{3'})$, 24.42 $((CH_3)_2CH)$, 29.43 $((CH_3)_{8'})$, 37.86 (Me_2CH) , 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-5,8,11,14,17,20hexaoxa-benzocycloocta decen-2-yl)-[1-(5-isopropyl-3,8dimethyl-azulen-1-yl-meth-(E)-ylidene]-amine, 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, Me₃), 3.07 (s, 3 H, Me₈), 3.08 (hept, ${}^{3}J = 6.9 \text{ Hz}$, 1 H, MeCH), 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, ${}^{3}J = 8.4$ Hz, ${}^{4}J = 2.4$ Hz, 1 H, 3-H), 6.90 (d, ${}^{4}J = 2.5$ Hz, 1 H, 1-H), 6.91 (d, ${}^{3}J = 8.6$ Hz, 1 H, 4-H), 7.14 (d, ${}^{3}J = 10.7$ Hz, 1 H, 7'-H), 7.42 (dd, ${}^{3}J =$ 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 $(CDCl_3)$, δ (ppm): 12.93 ($(CH_3)_{3'}$), 24.49 ($(CH_3)_2CH$), 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 $C_{32}H_{41}NO_6$: C, 71.75; H, 7.72; N, 2.61. Found: C, 71.71; H, 7.75; N, 2.59.

[14-(Azulene-1-carbonyl)-6,7,9,10,17,18,20,21octahydro-5,8,11,16,19,22-hexaoxa-dibenzo[a,j] cyclooctadecene-2-yl]-azulen-1-yl-methanone, 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, 4 J = 1.9 Hz, 2 H, 4-H, 13- or 14-H), 7.31 (d, 3 J = 4.1 Hz, 2 H, 3'-H), 7.44 (dd, ${}^{3}J = 8.3$ Hz, ${}^{4}J = 1.9$ Hz, 2 H, 3-H, 14- or 13-H), 7.48 (t, ${}^{3}J = 9.8 \text{ Hz}$, 2 H, 5'-H), 7.49 (d, ${}^{4}J = 1.9 \text{ Hz}$, 2 H, 1-H, 12- or 15-H), 7.58 (t, ${}^{3}J = 9.8$ Hz, 2 H, 7'-H), 7.83 (t, ${}^{3}J =$ 9.8 Hz, 2 H, 6'-H), 8.11 (d, ${}^{3}J$ = 4.1 Hz, 2 H, 2'-H), 8.50 (d, ${}^{3}J$ = 9.6 Hz, 2 H, 4'-H), 9.57 (d, ${}^{3}J$ = 9.8 Hz, 2 H, 8-H). ${}^{13}C$ -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-Carbethoxy-2-cyano-vinyl)-azulene-1carbonyl]-6,7,9,10,17,18,20,21-octahydro-5,8,11,16,19,22hexaoxa-dibenzo[a,j]cyclooctadecene-2-carbonyl}-azulen-1-yl}-2-cyano-acrylic acid ethyl ester, 8. Reddish-brown crystals, m.p. 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). ${}^{1}\text{H-NMR}$ (CDCl₃), δ (ppm): 1.88 (t, ${}^{3}\text{J} = 7.0 \text{ Hz}$, 6 H, CH₃CH₂), 4.05 (bs, 8 H, CH₂), 4.25 (bs, 8 H, CH₂), 4.40 (q, 3 J = 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, ${}^{3}J = 9.8$ Hz, 2 H, 5'-H), 7,85 (t, ${}^{3}J = 9.8$ Hz, 2 H, 7'-H), 8.07 (t, ${}^{3}J = 9.8$ Hz, 2 H, 6'-H), 8.86 (s, 2 H, CH=), 8.87 (d, ${}^{3}J=$ 9.8 Hz, 2 H, 4'-H), 9.25 (s, 2 H, 2'-H), 9.63 (d, ${}^{3}J = 9.8$ Hz, 2 H, 8'-H). ${}^{1}H$ -NMR (DMSO-d₆), δ (ppm): 1.88 (t, ${}^{3}J = 7.0$ Hz, 6 H, $CH_{3}CH_{2}$), 3.89 (bs, 8 H, CH_2), 4.08 (bs, 8 H, CH_2), 4.33 (q, $^3J = 7.1 Hz$, 4 H, CH_3CH_2), 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, ${}^{3}J =$ 9.8 Hz, 2 H, 5'-H), 8.07 (t, ${}^{3}J = 9.8$ Hz, 2 H, 7'-H), 8.34 (t, ${}^{3}J$ = 9.7 Hz, 2 H, 6'-H), 8.91 (s, 2 H, CH=), 9.08 (s, 2 H, 2'-H), 9.25 (d, ${}^{3}J = 10.0 \text{ Hz}$, 2 H, 4'-H), 9.54 (d, ${}^{3}J = 10.0 \text{ Hz}$, 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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