Journal of Molecular Structure 996 (2011) 17–23

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis and structure of new crown ethers with 1,4-phenylene and 1,4-naphthylene units

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ARTICLE INFO

Article history:
Received 13 November 2010
Received in revised form 24 January 2011
Accepted 24 January 2011
Available online 31 January 2011

Keywords:
Macrocycles
Crown ethers
Podands
X-ray structure
NMR

ABSTRACT

The synthesis of monomers and dimers of some new crown ether type macrocycles with 1,4-phenylene and 1,4-naphthylene units are reported. The structural investigations of the compounds were carried out by NMR spectra, MS measurements and the single crystal X-ray solid state molecular structure of one compound.

1. Introduction

The synthesis and the structural investigations of crown ether type macrocycles became an important target in organic chemistry after the first work reported in this area by Pedersen in 1967 [1]. Crown ether type macrocycles are successfully used in the construction of sensors, as hosts for the chemoselective recognition of different guests [2], they can ensure the solubility of salts [3] or they can increase the activity of catalysts [4].

A further application of crown ether type macrocycles should be connected to their deposition on different surfaces (e.g. gold 1.1.1) in order to obtain materials which are sensitive to different guest species (e.g. alkali cations). For this purpose the target macrocycles has to exhibit appropriate substituents which can themselves (or after transformations) interact with the surface and can facilitate the deposition of the macrocycles. Another feature concerning the structure of these target macrocycles is correlated to the presence of groups which can insure the organization of the macrocycles on the surface. Extended aromatic groups (e.g. naphthalene or anthracene units), via π–π stacking, are important candidates for the obtaining of organized (self-assembled) monolayers (SAM's) [5].

The unsubstituted *ortho,ortho'*-dibenzocrown ethers are well known and they are commercially available [1,6] Their *meta, meta'* or *para, para'* isomers were already obtained [7] but they are not so widely used as the classic dibenzo crown ethers. Crown ethers with 1,4-naphthylene or substituted phenylene units are not common. We focused in this work on the synthesis of crown ether type macrocycles (I, Chart 1) exhibiting 2,3-dimethyl-1,4-phenylene and 1,4-naphthylene units. In our opinion the 1,4-phenylene unit could be functionalized in order to facilitate the deposition of the macrocycles on different surfaces, while the 1,4-naphthylene units could insure the self organization of the macrocycles and thus, the target compounds could be important intermediates for the access to macrocycles based organized monolayers.

2. Experimental

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded at rt in $CDCl_3$ on a Bruker 300 MHz spectrometer, using the solvent line as reference.

The crystal of **14b** was studied on a Bruker AXS X8-APEX II diffractometer with graphite monochromatized Mo Kα radiation. Data were collected at room temperature (297 K). The structure was refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used [8,9] The drawings were created with Ortep [10] and Diamond programs [11]. The structural data

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doi:10.1016/j.molstruc.2011.01.052

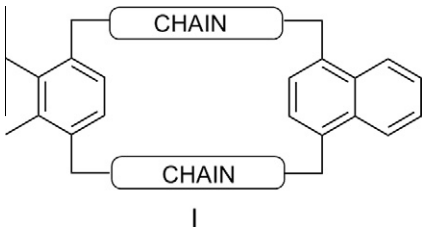
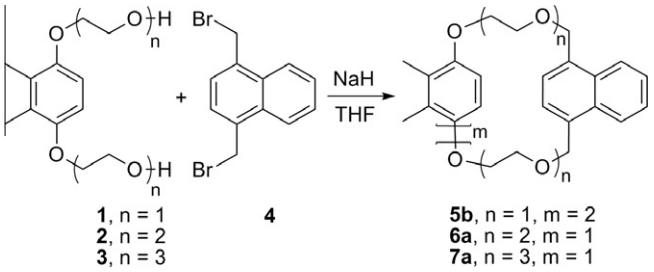
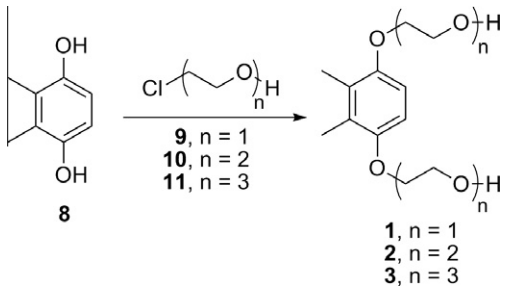


Chart 1. Model of target macrocycles (the chains contain polyethyleneglycol units of various lengths).



Scheme 1. Synthesis of macrocycles **5b**, **6a** and **7a.**



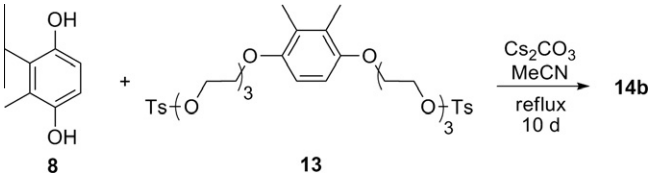
Scheme 2. Synthesis of podands **1**–**3.**

was deposited at the Cambridge Crystallographic Data Center, deposition number is CCDC 799290 (**14b**).

Electrospray ionization mass spectra ESI (ESI^+) were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonic GmbH, Bremen, Germany) equipped with a standard ESI/APCI source.

Melting points were measured with a Kleinfeld melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was conducted on silica gel 60 F254 TLC plates purchased from Merck. Preparative column chromatography was performed using PharmPrep 60 CC (40–63 μm) silica gel purchased from Merck.

Solvents were dried and distilled under argon using standard procedures before use. Chemicals of commercial grade were used without further purification.



Scheme 4. Synthesis of dimer macrocycle **14b.**

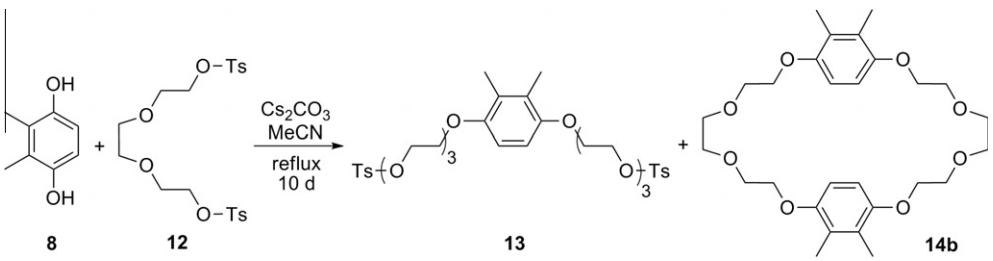
The geometries of the cations of complex **7a(Cs^+)** were optimized at density functional theory level using B3LYP functional as implemented in GAMESS 2010 R2 software package [12,13]. For all atoms the LANL2DZ basis set was used as published on EMSL database [14–18]. Frequency calculations confirmed that the optimized geometries are energy minima (no negative frequencies were obtained).

2.1. Procedure for the synthesis of *1*

Sodium hydroxide (1.6 g, 40 mmol) was solved in a mixture of ethanol (20 ml) and water (5 ml) and added to the ethanolic solution of 2,3-dimethylbenzene-1,4-diol (1.38 g, 10 mmol, 20 ml ethanol) forming a dark red solution that was allowed to stir for 30 min. 2-Chloroethanol (3.22 g, 30 mmol) was then added under stirring and the obtained solution was refluxed for 1 day, and the formation of a precipitate was observed. After cooling to room temperature, the solvent was removed in vacuo affording a red solid that was dissolved in EtOAc (100 ml) and washed with water (2×75 ml). The aqueous phase was further extracted with EtOAc (2×75 ml). The combined organic phases were washed with brine (50 ml), dried over $MgSO_4$ and the solvent was evaporated in vacuo. Purification of the residue by column chromatography (EtOAc/petroleum ether 1:1; $R_f = 0.42$) gave **1** as a off-white powder (1.7 g, 7.5 mmol, yield 76%). 2,3-Dimethyl-1,4-bis(1′,4′-dioxabutane-1′-yl)-benzene **1**. White solid (1.7 g, 76%, 7.5 mmol, m.p. = 117–119 °C). ^1H NMR $\delta = 1.92$ (s, 2H, OH), 2.18 (s, 6H, CH_3), 3.95 (m, 4H, H-3′), 4.02 (m, 4H, H-2′), 6.67 ppm (s, 2H, H-5, H-6). ^{13}C NMR $\delta = 12.2$ (CH_3), 61.8 (C-3′), 70.4 (C-2′), 109.9 (C-5, C-6), 127.3 ppm (C-2, C-3), 151.2 (C-1, C-4). MS (ESI) m/z (rel. int.%) 249 $[M + Na]^+$ (100). Anal. Calcd for $C_{12}H_{18}O_4$ (226.27): C, 67.30; H, 8.02; found: C, 67.49; H, 7.89.

2.2. Procedure for the synthesis of *2*

A solution of 2,3-dimethylbenzene-1,4-diol (1.38 g, 10 mmol) in dry DMF (50 ml) was added over 30 min to a stirred suspension of K_2CO_3 (8.28 g, 60 mmol) in dry DMF (75 ml) under argon. After an additional 30 min, a solution of 5-chloro-3-oxa-1-pentanol (3.74 g, 30 mmol) in dry DMF (30 ml) was added over 30 min, and the temperature was raised to 80 °C. Stirring and heating were continued for 2 days. After cooling to room temperature, the reaction mixture was filtered and the solid residue was washed with DMF (20 ml).



Scheme 3. Synthesis of ditosylated podand **13** and macrocycle **14b.**

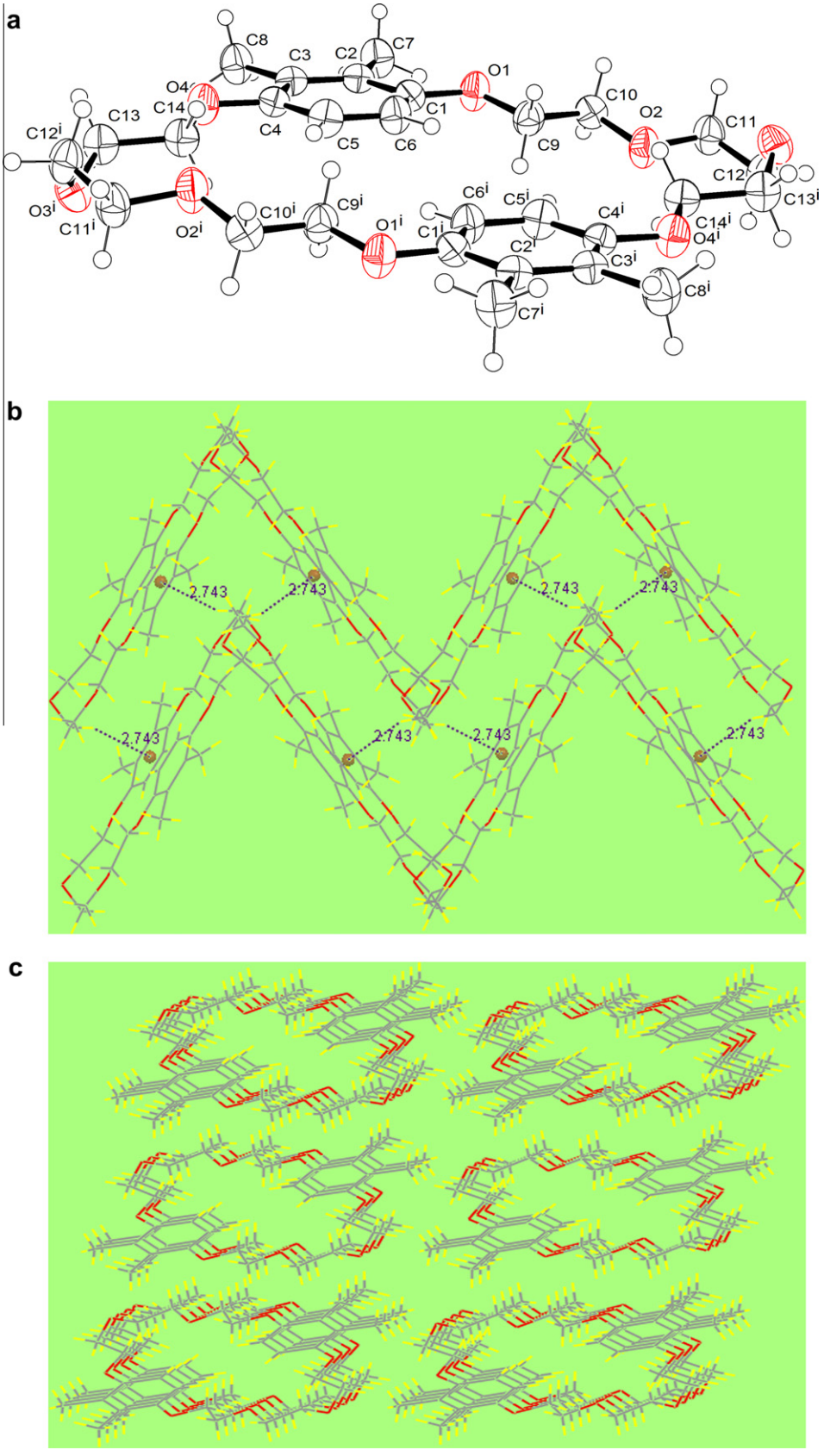


Fig. 1. X-ray diffraction investigations of compound **14b**: (a) Ortep diagram, (b) View of the zig-zag disposition of the neighboring molecules in sheets, with a dihedral angle of 60°, (c) View of the lattice along b crystallographic axis.

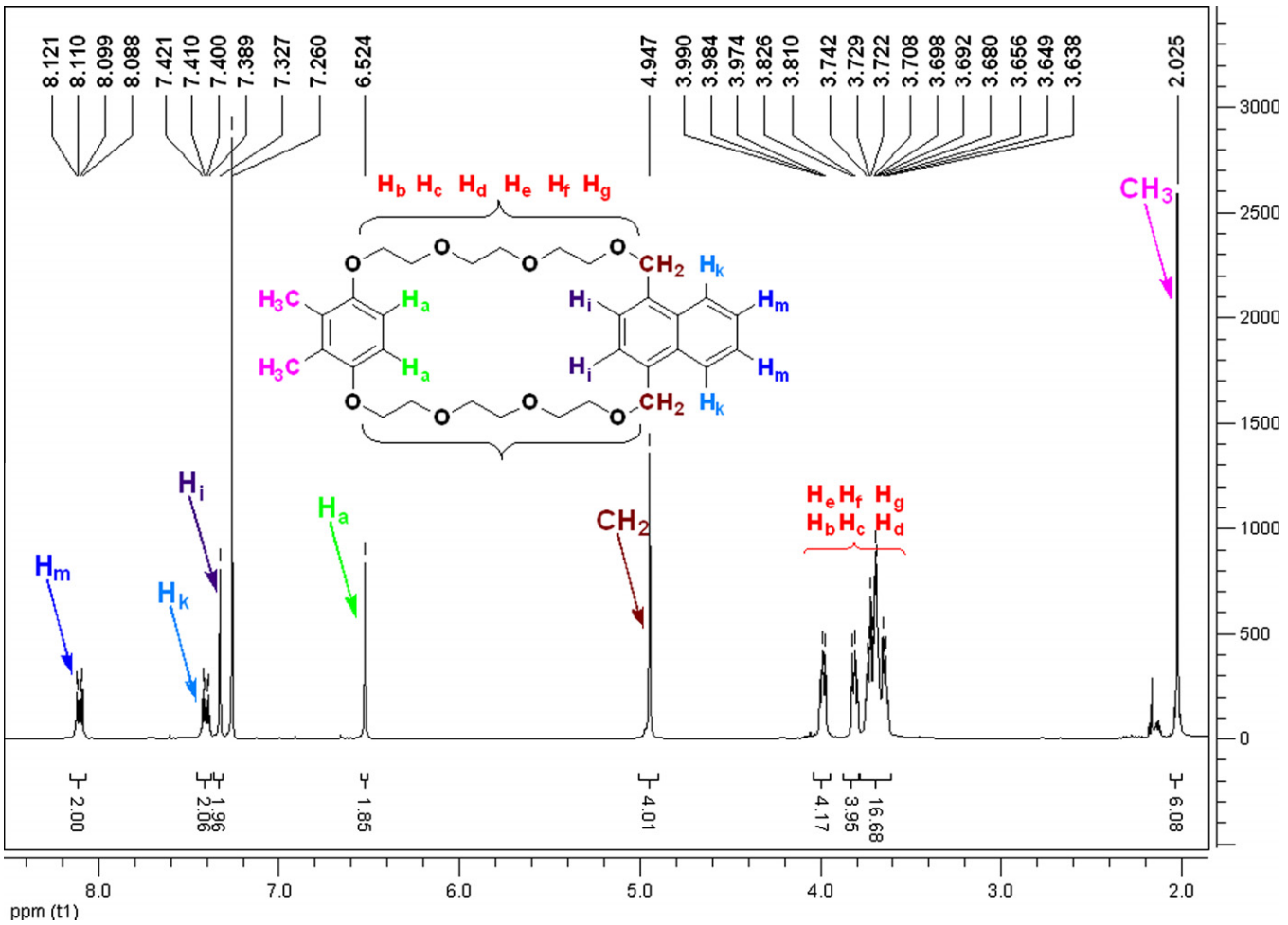


Fig. 2. ^{1}H NMR spectrum ($CDCl_3$, fragment) of compound **7a.**

The solvent was removed in vacuo and the residue was partitioned between CH_2Cl_2 (150 ml) and a saturated solution of NaCl (70 ml). The pH was adjusted to 5 with 2 N HCl. The organic phase was separated and the aqueous phase was washed with CH_2Cl_2 (2 × 50 ml). The combined organic solutions were washed with H_2O (80 ml), dried ($MgSO_4$), and concentrated in vacuo affording **2** as a yellow oil (1.31 g, 4.17 mmol, 42%).

2,3-Dimethyl-1,4-bis(1′,4′,7′-trioxaheptane-1′-yl)-benzene **2**. White solid (1.31 g, 42%, 4.17 mmol). ^{1}H NMR δ = 1.92 (s, 2H, OH), 2.17 (s, 6H, CH_3), 3.68 (m, 4H, H-6′), 3.76 (m, 4H, H-5′), 3.86 (m, 4H, H-3′), 4.07 (m, 4H, H-2′), 6.67 ppm (s, 2H, H-5, H-6); ^{13}C NMR δ = 12.2 (CH_3), 61.7 (C-5′), 68.8 (C-2′), 69.9 (C-3′), 72.5 (C-6′), 110.0 (C-5, C-6), 127.4 (C-2, C-3), 151.3 ppm (C-1, C-4). MS (ESI) m/z (rel. int.%) 337 $[M + Na]^+$ (100). Anal. Calcd for $C_{16}H_{26}O_6$ (314.37): C, 61.13; H, 8.34; found: C, 61.37; H, 8.59.

2.3. Procedure for the synthesis of **3**

A solution of 2,3-dimethylbenzene-1,4-diol (1.38 g, 10 mmol) in dry *t*-butyl alcohol (50 ml) was added to a solution of potassium *t*-butoxide (2.8 g, 25 mmol) in dry *t*-butyl alcohol (40 ml) under argon. The mixture was refluxed for 4 h, then 8-chloro-3,6-dioxa-1-octanol (4.22 g, 25 mmol) was added over 30 min and the reflux was continued for 24 h. After cooling to room temperature, the reaction mixture was filtered and the solid residue washed with CH_2Cl_2 (3 × 50 ml). The combined organic solutions were evaporated in vacuo, and the residue was solved in CH_2Cl_2 (150 ml), was washed with 2 N HCl (30 ml) and H_2O (2 × 50 ml). The organic phase was dried ($MgSO_4$), filtered and the solvent was evaporated in vacuo. Purification of the residue by column chromatography (EtOAc; R_f = 0.27) gave **3** as a yellow oil (1.87 g, 4.65 mmol, 46%).

2,3-Dimethyl-1,4-bis(1′,4′,7′,10′-tetraoxadecane-1′-yl)-benzene **3**. Yellow oil (1.87 g, 46%, 4.65 mmol).^{1}H NMR δ = 2.15 (s, 6H, CH_3), 3.59–4.07 (m, 24H, H-2′, H-3,′ H-5′, H-6′, H-8′, H-9′), 6.64 ppm (s, 2H, H-5, H-6); ^{13}C NMR δ = 12.2 (CH_3), 61.6, 68.7, 70.0, 70.8, 72.5 (C-1′, C-2′, C-4′, C-5′, C-7′, C-8′), 110.0 (C-5, C-6), 127.2 (C-2, C-3), 151.2 ppm (C-1, C-4). MS (ESI) m/z (rel. int.%) 425 $[M + Na]^+$ (100). Anal. Calcd for $C_{20}H_{34}O_8$ (402.48): C, 59.68; H, 8.51; found: C, 59.36; H, 8.71.

2.4. General procedure for the synthesis of macrocycles **5b**, **6a** and **7a**

A solution of **1**, **2** or **3** (1 mmol) in dry THF (20 ml) was added to a suspension of NaH (powder 97%, 3 mmol) in dry THF (250 ml) and the mixture was refluxed for 3 h. Then a solution of 1,4-dibromomethylnaphthalene (1 mmol) in dry THF (120 ml) was added dropwise to the refluxing suspension over 60 h. The reddish mixture was refluxed for another 48 h. After removal of the solvent, H_2O (50 ml) was added and the mixture was extracted with $CHCl_3$ (4 × 50 ml). The combined organic phases were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1.5:1) to afford the desired compound.

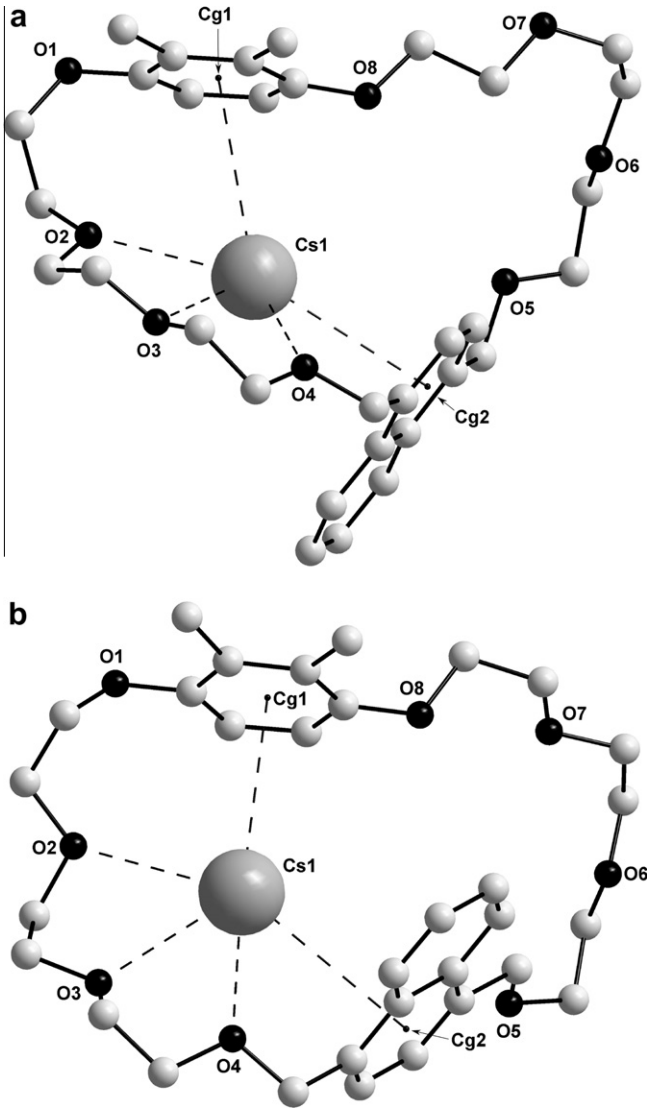


Fig. 3. Optimized geometries [models **A** (a) and **B** (b)] of the complex **7a(Cs$^+$)**. Hydrogen atoms were omitted for clarity.

8,9-Dimethyl-3,6,11,14-tetraoxatetracyclo[14,6,2^{1,16},2^{7,10},0^{17,22}] hexacosane-1(26),7,9,16(25), 17(22),18,20,23-octaene **5b**. White solid (0.08 g, 21%, 0.21 mmol, m.p. = 168 °C). ^{1}H NMR: δ = 2.03 (s, 12H, CH_3), 3.86 (t, J = 4.4 Hz, 8H, H-4, H-13, H-26, H-35), 4.05 (t, J = 4.4 Hz, 8H, H-5, H-12, H-27, H-34), 5.06 (s, 8H, H-2, H-15, H-24, H-37), 6.51 (s, 4H, H-45, H-46, H-47, H-48), 7.48 (s, 4H, H-49, H-50, H-51, H-52), 7.49 (m, 4H, H-19, H-20, H-41, H-42), 8.12 ppm (m, 4H, H-18, H-21, H-40, H-43). ^{13}C NMR: δ 12.22 (CH_3), 68.72, 68.86, 71.48 (C-2, C-4, C-5, C-12, C-13, C-15, C-24, C-26, C-27, C-34, C-35, C-37), 109.49 (C-45, C-46, C-47, C-48), 124.46 (C-49, C-50, C-51, C-52), 125.47 (C-18, C-21, C-40, C-43), 125.96 (C-19, C-20, C-41, C-42), 127.15 (C-8, C-9, C-30, C-31), 131.79 (C-17, C-22, C-39, C-44), 133.99 (C-1, C-16, C-23, C-38), 151.19 ppm (C-7, C-10, C-29, C-32). MS (ESI) m/z (rel int.%) = 379.3 [M + H]$^+$ (100). Anal. Calcd for $C_{24}H_{26}O_4$ (378.46): C, 76.17; H, 6.92; found: C, 75.88; H, 7.11.

11,12-Dimethyl-3,6,9,14,17,20-hexaoxatetracyclo[20,6,2^{1,22}, 2^{10,13},0^{23,28}]dotricosan-1(32),10, 12,22(31),23(28),24,26,29-octaene **6a**. White solid (0.11 g, 24%, 0.24 mmol, m.p. = 120–121 °C). ^{1}H NMR δ = 2.12 (s, 6H, CH_3), 3.66 (m, 8 H), 3.86 (t, J = 4.5 Hz, 4H, H-7, H-16), 4.02 (t, J = 4.5 Hz, 4H, H-8, H-15), 4.99 (s, 4H, H-2, H-21), 6.58 (s, 2H, H-29, H-30), 7.41 (s, 2H, H-31, H-32), 7.45 (dd, J = 6.6, 3.3 Hz, 2H, H-25, H-26), 8.05 ppm (dd, J = 6.6, 3.3 Hz, 2H, H-24, H-27). ^{13}C NMR δ = 11.7 (CH_3), 69.5, 70.3, 70.4, 71.3, 71.6 (C-2, C-4, C-5, C-7, C-8, C-15, C-16, C-18, C-19, C-21), 111.1 (C-29, C-30), 124.2 (C-31, C-32), 125.1 (C-24, C-27), 125.8 (C-25, C-26), 127.1 (C-11, C-12), 131.5 (C-23, C-28), 133.7 (C-1, C-22), 151.6 ppm (C-10, C-13). MS (ESI) m/z (rel. int.%) 489.3 [M + Na]$^+$ (100), 505.3 [M + K]$^+$ (40). Anal. Calcd for $C_{28}H_{34}O_6$ (466.57): C, 72.08; H, 7.35; found: C, 72.41; H, 7.19.

14,15-Dimethyl-3,6,9,12,17,20,23,26-octaoxatetracyclo[26,6,2^{1,28}, 2^{13,16},0^{29,34}]octatricosan-1(38),13,15,28(37),29(34),30,32,35-octaene **7a**. Yellowish oil (0.15 g, 28%, 0.28 mmol). ^{1}H NMR δ = 2.03 (s, 6H, CH_3), 3.69 (m, 16 H, H-4, H-5, H-7, H-8, H-21, H-22, H-24, H-25), 3.81 (m, 4H, H-10, H-19), 3.99 (m, 4H, H-11, H-18), 4.95 (s, 4H, H-2, H-27), 6.52 (s, 2H, H-35, H-36), 7.33 (s, 2H, H-37, H-38), 7.41 (dd, J = 6.6, 3.3 Hz, 2H, H-31, H-32), 8.10 ppm (dd, J = 6.6, 3.3 Hz, 2H, H-30, H-33). ^{13}C NMR δ = 12.19 (CH_3), 68.94 (C-11, C-18), 69.49 (C-10, C-19), 69.94, 70.84, 70.93, 71.05 (C-4, C-5, C-7. C-8, C-21, C-22, C-24, C-25), 71.68 (C-2, C-27), 110.00 (C-35, C-36), 124.50 (C-37, C-38), 125.72 (C-30, C-33), 125.82 (C-31, C-32), 127.25 (C-14, C-15), 131.89 (C-29, C-34), 134.03 (C-1, C-28), 151.20 ppm (C-13, C-16). MS (ESI) m/z (rel. int.%) 555.3 [M + H]$^+$(100). Anal. Calcd for $C_{32}H_{42}O_8$ (554.67): C, 69.29; H, 7.63; found: C, 69.12; H, 7.37.

*2.5. Procedure for the synthesis of **14b***

To the mixture of 1.45 mmol of 2,3-dimethyl-hydroquinone (**8**) and 11 mmol of Cs_2CO_3 solved in 350 ml dry acetonitrile, a solution of triethyleneglycoleditosylate (4.35 mmol) in 10 ml acetonitrile was added dropwise with a push-syringe, under argon, over 4 days. After 10 days reflux at 80°C the reaction was worked up by filtering the salt and evaporating the solvent. Acetonitrile was distilled at reduce pressure and the crude product was solubilized in 100 ml water and extracted with dichloromethane (3 x 25 ml). The organic layer was dried ($MgSO_4$) and purified on chromatographic column using hexane: ethyl acetate = 2:1 as eluent (yields 30%; R_f = 0.20).

The same experimental procedure using ditosylated **13** (0.28 mmol), 2,3-dimethylhydroquinone **8** (0.25 mmol), Cs_2CO_3 (1.28 mmol) and dry acetonitril (350 ml) gave macrocycle **14b** in 22% yields.

13,14,27,28-Tetramethyl-2,5,8,11,16,19,22,25-octaoxa-triciclo [24,22^{12,15}]dotricontan-1(28),12,14,27,29,31-hexaene **14b**. White crystals (0.22 g, 30%, 0.43 mmol; m.p. = 135–136 °C). ^{1}H NMR δ = 2.06 (s, 12H, CH_3), 3.75 (s, 8H, H-6, H-7, H-20, H-21), 3.84 (m, 8H), 3.96 (m, 8H), 6.50 ppm (s, 4H, aromatic protons), ^{13}C NMR δ = 12.16 (CH_3), 68.83, 70.15, 71.21 (C-3, C-4, C-6, C-7, C-9, C-10, C-17, C-18, C-20, C-21, C-23, C-24), 110.07 (C-29, C-30, C-31, C-32), 127.09 (C-13, C-14, C-27, C-28), 151.35 ppm (C-1, C-C-12, C-15, C-26). MS (ESI) m/z (rel. int.%) m/z 505.28 (100%). [M + H]$^+$Anal. Calcd for $C_{28}H_{40}O_8$ (504.61): C, 66.65; H, 7.99; found: C, 66.42; H, 8.14.

3. Results and discussion

New crown ether type macrocycles **5**–**7** with 2,3-dimethyl-1,4-phenylene and 1,4-naphthylene units, monomers **6a** and **7a** (m = 1) and the dimer **5b** (m = 2), were obtained in fair yields (21–28%) by the usual procedure for the synthesis of macrocycles starting from diols and dibrominated compounds [19] (Scheme 1). The macrocycles were separated from the raw product by column chromatography. The formation of dimers **6b** and **7b** was not observed (ESI-MS investigations of the corresponding raw products).

Podands **1**–**3** were obtained in good yields (42–76%) using hydroquinone **8** and chloropolyethylene glycols **9**–**11**. Procedures adapted from similar syntheses reported in the literature [20] were

applied (Scheme 2). The synthesis of **1** was carried out in ethanol using NaH as base, while **2** was obtained in DMF and the synthesis of **3** was performed in *t*-butanol using K_2CO_3 instead of NaH.

In the synthesis of **3** starting from diphenol **8** and ditosylated triethyleneglycol **12**, besides ditosylated derivative **13**, the dimer macrocycle **14b** was also obtained in a significant amount.

The yields in macrocycle **14b** (30%) and in ditosylated derivative **13** (49%) were good and compounds **13** and **14b** could be separated by column chromatography (Scheme 3).

The synthesis of new macrocycle **14b** was also performed starting from **8** and **13** using the high dilution procedure, but the yields in macrocyclic compound could not be improved (22%; Scheme 4).

The structure of **14b** could be investigated by the solid state molecular structure obtained by single crystal X-ray diffractometry (Fig. 1a). The ORTEP diagram shows the almost planar structure of the compound; the angle between the two aromatic rings is $\alpha = 0.00°$, the distance between the two planes described by the aromatic units is $d = 0.849$ Å and the distance between the centroids of the two aromatic units is $d' = 6.430$ Å. In the lattice the molecules exhibit a zig-zag arrangement (Fig. 1b) and the angle between two neighboring macrocycles is of 60°. The view of the lattice along the b axis reveals the formations of columns (Fig. 1c). The arrangement of the molecules in the lattice is insured by C–H——π (aromatic) interactions between the hydrogen atoms of the methyl group of a molecule and the centroids of the aromatic rings of the neighboring macrocycles (d∗—*H* = 2.743 Å; Fig. 1b).

The structural investigations in solution revealed only a small number of signals in the NMR spectra of **5b**, **6a**, **7a** and **14b** proving the symmetry of the structures and the flexibility of the chains. Thus, the ^{1}H NMR spectrum of **14b** exhibits singlets for the aromatic protons, the protons of the central ethyleneoxide groups and the methyl groups ($\delta = 6.50$; 7.75; 2.06 ppm), while for the protons of the rest of ethyleneoxide groups there are two multiplets at 3.96 and 3.84 ppm, respectively.

The ^{1}H NMR spectrum of **7a** (Fig. 2) exhibits singlets for the protons of the substituted moiety of the naphthalene ring, the protons of the benzene ring, the methylene protons connected to the naphthalene unit and the methyl groups connected to the benzene ring (7.32, 6.62, 4.94 and 2.02), while the protons of the ethyleneoxide groups give overlapped peaks in the range 3.63–3.99 ppm.

The aromatic protons H_m and H_k display signals (multiplets, $\delta = 7.41$ and 8.10 ppm) corresponding to an AA′BB′ system as it can be observed in symmetrically *ortho*-disubstituted benzenes.

In an ESI-MS experiment, samples obtained by stirring for 30 min at rt the solution obtained from equal volumes of 10^{-5} M solution of **7a** and 10^{-5} M solution of the mixture of alkali cations Na^+, K^+, Rb^+ and Cs^+ (the corresponding triflates were solved in a 1/1 mixture of methanol and water) were investigated. The ESI-MS spectra revealed the peaks for all macrocycle-alkali cation complexes. The highest relative intensities were obtained for the large Rb^+ and Cs^+ cations [M + Rb^+ (551.3; 63%), M + Cs^+ (599.2; 100%)].

In order to estimate the possible structures of the cation complexes of **7a**, theoretical calculations were carried out for its complex with Cs^+.

Two equilibrium geometries (**A** and **B**) were obtained for the structure of the complex of **7a** with Cs^+. Graphical representations of the models **A** and **B** are depicted in Fig. 3a and b, respectively. The coordinates of the equilibrium geometries are provided as Supporting information.

The most important difference between model **A** and model **B** is the conformation adopted by the organic ligand. In model **B** the methyl groups of the 1,4-phenylene unit are oriented towards the naphthalene unit, while in model **A** the methyl groups are oriented in the opposite side. In both calculated structures the organic ligand coordinates to the cesium cation through three oxygen atoms. The calculated Cs···O bond lengths are slightly longer in model **B** (3.203, 3.209, 3.279 Å) than in model **A** (3.136, 3.175, 3.222 Å). In both structures there are contacts shorter than 4.0 Å between the centroids of the aromatic groups and the cesium ion (**A**: 3.777, 3.800 Å; **B**: 3.721, 3.916 Å).

In gas phase the energy found for the model **B** is 2.83 kcal/mol lower than that found for model **A**.

Podands **1**–**3** and **13** were investigated by NMR and mass spectrometry and the data are shown in the experimental part.

4. Conclusions

New macrocycles with cavities of different sizes exhibiting 1,4-phenylene and 1,4-naphthylene units were obtained in fair yields by the reaction of several ditosylated diols exhibiting polyethyleneglycol type chains of different lengths with 1,4-dibromomethyle-naphthalene. The structure of the macrocycles was investigated by NMR spectra, ESI-MS and X-ray diffractometry. In the case of the macrocycle with two 1,4-phenylene units the solid state molecular structure investigation revealed the almost planar structure of the compound and C–H——π interactions between the molecules in the lattice. The ESI-MS investigations of the largest monomeric macrocycle showed the preference for the complexation of Cs^+, the largest alkali cation.

Acknowledgment

This work was supported by CNCSIS–UEFISCDI, project number PN II–IDEI 2278/2008.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.01.052.

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