Conformers and Rotamers of (±)-*trans*-2,3-Bis(2-naphthyl)-15-crown-5 and -18-crown-6 and Their Alkali Metal Complexes

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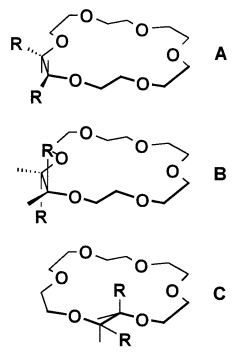
The conformations of (±)-*trans*-2,3-Bis(1-naphthyl)-15-crown-5 (**1**) and -18-crown-6 (**2**) are investigated by MM2 and dynamic ^{1}H-NMR spectroscopy. The most stable conformation is the diequatorial one in both the free ligands and the alkali metal complexes **1**·$NaClO_4$ and **2**·$KClO_4$. Three rotamers, *pseudo-aa, pseudo-ee,* and *pseudo-ae,* with respect to the spatial arrangement of the naphthyl groups, were found as calculated minima by MM2 and experimentally by low-temperature NMR, with fair agreement of the rotational barriers. In the cation-reinforced crowns the rotation rates are significantly diminished. The distribution of the rotamers depends on the size of the crown and its state, free or complexed.

The conformations of crown ethers are quite different in their free states and complexes. Well known examples are the oblong shape of 18-crown-6 and the typical crown arrangement in the potassium complex.[1] In 2,3-disubstituted crown ethers the substituents can be located at *gauche* or *anti* sites of the oblong macrocycle, and the resulting subconformations for the *trans* arrangement of the substituents are the diequatorial (A), diaxial (B), and axial-equatorial (C) ones (Scheme 1). The *trans* substitution is particularly interesting due to the chiral C_2 symmetry,[2][3] and analog conformations apply for the *cis* substitution patterns. The relative importance of the conformations A and B depends on the nature of the substituents. If, for instance, transannular interactions or synergistic effects with guest molecules are possible, the diaxial arrangement will be preferred.[4] The X-ray crystal-structures of the *trans-syn-trans* and *trans-syn-cis* isomers[5] of the 2,3,11,12-tetraphenyl-18-crown-6 series of stereoisomers[3] provide an example of the behavior of noninteracting substituents in both free ligands and sodium complexes.

Here we report on the conformations of (±)-*trans*-2,3-bis(2-naphthyl)-15-crown-5 (**1**) and the homologous 18-crown-6 derivative **2.** In these two crown ethers there is an additional conformational bias, namely the mutual rotation of the vicinal 1-naphthyl groups, a phenomenon which we have previously investigated for the corresponding 2,3-dihydro crown ethers.[6] The question was to which extent complexation would influence the rotation rate of a single naphthyl group and the equilibrium distribution of possible rotamers.

Scheme 1



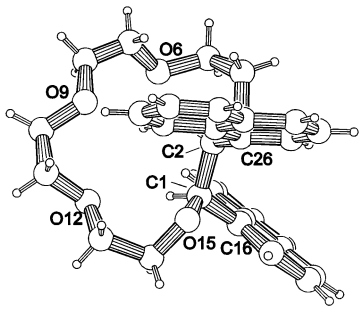
Although, in the crystal,[7] **1** has an axial-equatorial arrangement of the naphthyl groups at a close-to-*anti* conformation ($\psi_{(O-C-C-O)} \approx 21°$) of the crown site (Figure 1), we can show that the only significant conformation in *solution* is the *diequatorial* one in both the free ligands and the complexes of **1** and **2**.

Syntheses

1-Naphthaldehyde was converted into (*E*)-2-naphthostilbene by the McMurry reaction[8] and subsequently oxidized by the catalytic Sharpless oxidation with OsO_4/NMO[9] to give the racemic diol **3** whose (*R,R*) enantiomer was recently obtained by asymmetric Sharpless dihydroxylation.[10] The (*R,R*)-acetonide **4** was investigated by CD spectroscopy, and its most stable conformation was calculated by force-field (MMX) methods.[10][11] The ring closure

  1434−193X/98/0202−0403 $ 17.50+.50/0

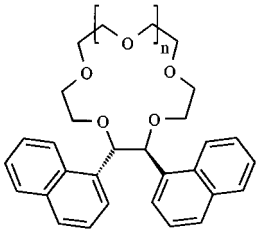
Figure 1. PLUTON presentation of the structure of **1** in the crystal[a]



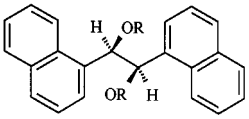
[a] Selected bond lengths [pm], bond angles and dihedral angles [°]: C1−C2 1.549; C1−C16 1.518; C1−O15 1.424; C2−O3 1.427; C2−C26 1.520; C1−C2−O3 105.3; C2−C1−O1 106.0; O15−C1−C2−O3 21.5; C16−C1−C2−C26 86.55. The crystals of **1** shows a thermal disorder in the range of C4 to O10, of which only the major structure is shown.

of **3** with the corresponding oligoethylene glycol dimesylates in THF/KOH gave crown ethers **1** and **2** in 54 and 40% yield.[12] The dimethyl ether **5** was prepared as a reference compound by reaction of **1** with dimethyl sulfate.

Scheme 2



1: n = 1
2: n = 2

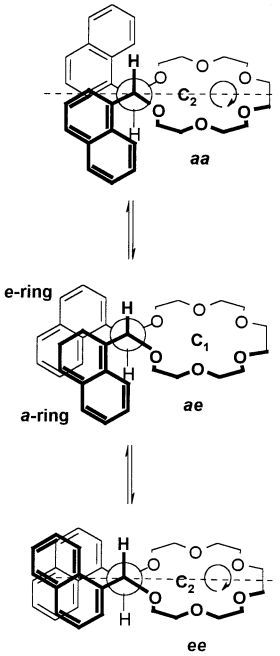


3: R = H
4: R,R = >C(CH$_3$)$_2$
5: R = CH$_3$

MM2 Calculations on the Naphthyl Rotations at the Free Ligands 3 and 4

A schematic representation of the subconformations, or rotamers, of the diequatorial main conformation of **2** is given in Scheme 3. It was assumed that each of the naphthyl rings could, by rotation, assume either an "*out-of-plane*" or an "*in-plane*" position with respect to the mean plane of the crown ether. We may call these *pseudo-axial (a)* and *pseudo-equatorial (e)* rotation states. Hence there are two C_2-symmetric rotamers, *pseudo-aa* and *pseudo-ee* and an asymmetric *pseudo-ae* rotamer in which the two naphthyl rings are in different spatial environment. All three rotamers are inherently chiral [shown here in the (*R*) configuration]. Starting from the *ae* rotamer in Scheme 3, the rotation of the *a*-naphthyl group (in front) around the bond to the crown ether leads to the *ee* rotamer, and likewise the rotation of the *e*-naphthyl group (in the back) gives the *aa* rotamer. A direct interconversion of *aa* and *ee* in a single rotational process is not possible.

Scheme 3



As in our previous work[6] the conformations of crown ethers **1** and **2** were MM2-optimized in the diequatorial conformation at the hydronaphthoin moiety for all three rotamers. Then, beginning with the *ae* rotamer each of the two naphthyl groups was stepwise rotated until the transition state leading to *aa* or *ee* was reached. The second naphthyl group was allowed to yield but it did not invert during this process. At the transition states the Naph−CH−CH−Naph dihedral angle at the hydrobenzoin moiety is widened from 60 to ca. 80°.

Table 1. MM2-calculated enthalpies of formation for the three rotamers of **1** and **2** and their mutual transition states in comparison with experimental free enthalpies from dynamic ^{1}H-NMR experiments

	energies [kcal/mol]					
	1			**2**		
rotamer	*aa*	*ae*	*ee*	*aa*	*ae*	*ee*
ΔH_f	−103.89	−104.37	−104.67	−144.07	−144.44	−145.07
ΔH_f (*TS*)		−92.62	−90.24		−135.35	−131.90
$\Delta H^{\neq}_{ae\rightarrow aa}$		14.13			12.54	
$\Delta G^{\neq}_{ae\rightarrow aa}$		13.3 ± 0.5			12.8 ± 0.5	
$\Delta H^{\neq}_{ae\rightarrow ee}$			11.75			8.89
$\Delta G^{\neq}_{ae\rightarrow ee}$			11.6 ± 0.5[a]			10.2 ± 0.5
$\Delta G^{\neq}_{ae\rightarrow ee}$[a]			13.3 ± 0.5			12.8 ± 0.5[a]

[a] Data for the *ae*-to-*ee* transition of **1**·$NaClO_4$ and **2**·$KClO_4$.

The data obtained from the MM2 calculations in terms of enthalpies of formation are given in Table 1. As may be

anticipated from the schematic drawing in Scheme 3, the transition state for the *ae* → *aa* conversion is significantly higher than for the *ae* → *ee* one, for both crown-ether sizes. Furthermore, the barriers are substantially higher in the smaller crown ether **1**. For the five-membered ring of acetonide **4**, a close-to-eclipsed C_2-symmetric conformation with an inward naphthalene rotation state similar to the *ee* was calculated by MMX.[11]

Variable-Temperature ^{1}H-NMR Spectroscopy

Due to the MM2 results the three rotamers should be detectable by low-temperature ^{1}H-NMR spectroscopy, and the free activation energies for the *ae* → *aa* and *ae* → *ee* interconversions should be accessible. This is indeed the case for **1** and **2**, and even more distinct for the complexes **1** · $NaClO_4$ and **2** · $KClO_4$.

these displays two different sets of naphthalene protons and two separate α protons with a vicinal coupling of 9.5 Hz. These findings correspond to the two C_2-symmetric *aa* and *ee* rotamers with homotopic naphthyl rings, and one asymmetric *ae* rotamer with heterotopic ones. As predicted by the force-field calculation there are two subsequent freezing processes at low temperature: At first the *aa* rotamer is separated from the *ae*/*aa* equilibrium and at fairly low temperature the *ae* and *ee* rotamers can be distinguished. The low-temperature spectra are particularly well developed for **1** · $NaClO_4$ (Figure 3).

The identity of the subconformations with respect to both *the main diequatorial conformation* and *the three rotamers* is unequivocally proved by the chemical shifts of the naphthyl ptotons and the multiplicity of the α protons (Table 2):

Table 2. Chemical shifts of the α and naphthalene protons of averaged spectra and single rotamers of **1** and **2** and their complexes in comparison to **4** and **5**

compound	rotamer (%)	α-H (s/d)	2-H (d)	3-H (t)	4-H (d)	5-H (d)	6-H (dt)	7-H (dt)	8-H (d)
2 [a,b]		5.48	7.16	7.05	7.45	7.59	7.26	7.21	8.44
5 [b,c]		5.34	7.15	7.10	7.53	7.66	7.33	7.26	8.14
5 [d]	*aa*	5.38	6.42	6.78	7.52	7.81	7.50	7.59	8.92
1	*aa (20)*	5.65	6.55	6.81	[e]	7.81	[e]	[e]	8.98
	ee (42)	5.72	7.11	7.14	[e]	[e]	[e]	[e]	8.04
a ring	*ae (38)*[h]	6.14	6.64	6.66	[e]	[e]	[e]	[e]	9.21
e ring	*ae*[h]	5.02	7.40	7.20	[e]	[e]	[e]	[e]	7.91
2	*aa (55)*	5.64	6.33	6.75	7.57	7.82	[e]	[e]	9.15
	ee (5)	5.78	7.22	[e]	[e]	[e]	[e]	[e]	[e]
a ring	*ae (40)*[h]	6.04	6.52	6.58	[e]	[e]	[e]	[e]	9.31
e ring	*ae*[h]	5.03	7.36	7.09	[e]	[e]	[e]	[e]	7.92
1 · $NaClO_4$ [f]	*aa (24)*	5.69	6.37	6.82	[e]	7.86	[e]	[e]	8.99
	ee (24)	5.71	7.12	7.14	[e]	[e]	[e]	[e]	8.13
a ring	*ae (52)*[h]	6.15	6.51	6.60	[e]	[e]	[e]	[e]	9.17
e ring	*ae*[h]	5.06	7.35	7.05	[e]	[e]	[e]	[e]	7.97
2 · $KClO_4$	*aa (40)*	5.69	6.28	6.74	7.55	7.82	[e]	[e]	8.90
	ee (12)	5.80	7.22	[e]	[e]	[e]	[e]	[e]	8.05
a ring	*ae (48)*[h]	6.15	6.52	6.61	[e]	[e]	[e]	[e]	9.17
e ring	*ae*[h]	5.12	7.38	7.10	[e]	[e]	[e]	[e]	7.90
4 [b,g]		5.74	7.81	7.49	7.79	7.71	7.22	6.88	7.20

[a] Averaged spectrum in $C_2H_2Cl_4$ at 383 K. – [b] Confirmed by ^{1}H-^{1}H-COSY and/or NOE. – [c] Averaged spectrum in [D_8]THF at 295 K. – [d] In [D_8]THF at 183 K, other rotamers not resolved. – [e] Signals not discernable due to peak overlapping or low signal intensity. – [f] Spectra in CD_2Cl_2/$CDCl_3$ mixture. – [g] In $CDCl_2$: δ(CH_3) = 1.84. – [h] ^3J [(Hα(a),Hα(e)] = 9.40 ± 0.15 Hz.

The general temperature behavior is illustrated by the high-, medium-, and low-temperature spectra of the free ligand **2**. An averaged ^{1}H-NMR spectrum of **2** in $C_2D_2Cl_4$ is obtained at 383 K (Figure 2a, Table 2), with sharp naphthalene proton signals and crown ether protons with two ABCD parts due to the C_2 symmetry, and a singlet for the far ethylene protons. Signal broadening well above room temperature begins at the 2-H, 3-H, and 8-H resonances. On further cooling, in CD_2Cl_2, at ca. 265 K a complete broadening of all naphthalene protons signals occurs and at 245 K a new sharp naphthalene spectrum emerges from the background (Figure 2b). Further cooling down to 183 K brings forth two new additional naphthalene spectra (Figure 2c, shown for the $KClO_4$ complex of **2**). One of

1. One can rule out any conformations with *diaxial* naphthalene positions because in this case strong mutual anisotropic magnetic influences of the vicinal naphthalene rings should be fairly absent.

2. A conformation with *axial-equatorial* standing of the naphthyl groups (see **C** in Scheme 1) would require heterotopic α protons for *all* rotamers, with coupling constants between 3 to 6 Hz and not a large one of 9.4 ± 0.15 Hz as observed for all *ae* cases (see Table 2).

3. The same types of spectra appear in the free ligands as they do in the complexes, thus there are no different sets of conformers and rotamers.

4. The shielding or deshielding of particular naphthalene protons are in accordance with the geometry of the postu-

Figure 2. ^{1}H-NMR spectra of **2**; a: in $C_2H_2Cl_2$ at 383 K, b: in CD_2Cl_2 at 213 K, c: **2**·$KClO_4$ in CD_2Cl_2 at 203 K

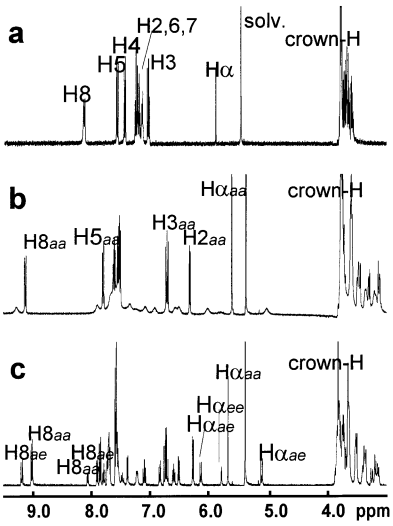
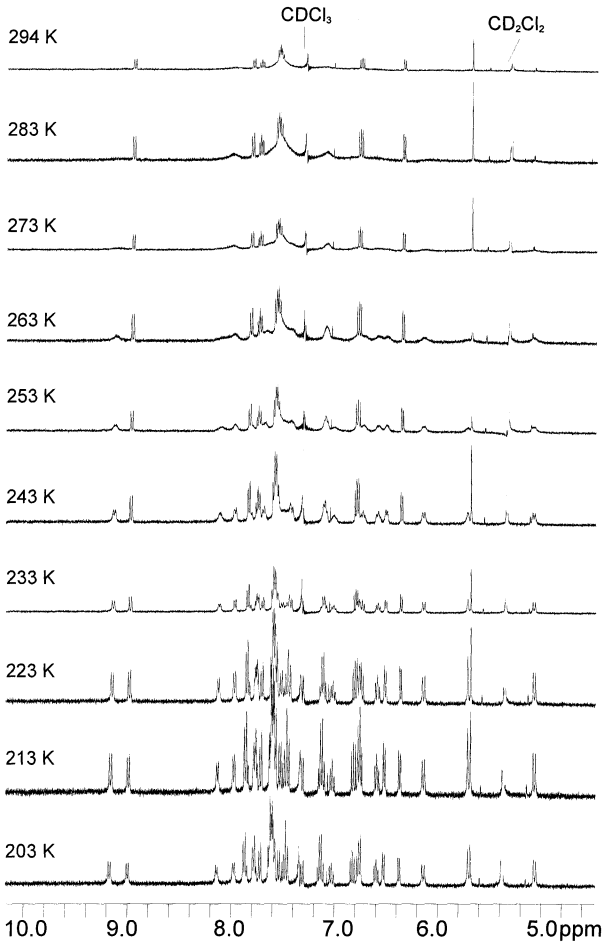


Figure 3. Naphthalene and α protons of **1**·$NaClO_4$ in the ^{1}H-NMR spectra in a CD_2Cl_2/$CHCl_3$ mixture from 294 to 203 K



lated rotamers (Scheme 3 and Table 2). Typical for the *aa* forms is the upfield shift of the 2-H signal and the strong downfield shift of the 8-H signal. In comparison, in the *ee* form, the 2-H signal is shifted 0.5 ppm downfield and that of 8-H is shifted ca. 1 ppm upfield with respect to the *aa* one. In the *ae* rotamers both types of naphthalene rings are present. Furthermore, in these rotamers, the coupling constant of the vicinal α protons clearly indicates their diaxial positions.

From the integration of the final low-temperature spectra the ratio of the three rotamers can be determined for each case. Even in the dimethoxy compound **5**, the *aa* form can be detected at 173 K, the *ee* and *ae* rotamers being unresolved, however.

The appearance of the aliphatic crown-ether protons is rather complex. The high-temperature spectrum of **2**, e.g., shows a singlet at δ = 3.77 for the far $-O-[CH_2]_2-O-$ group. Due to the C_2 symmetry the remaining ethylene protons appear as two ABCD spectra which extend over the range of δ = 3.55−3.85. Typical in all spectra is one *upfield*-shifted proton signal in each $-OCH_2-$ group adjacent to the naphthyl substituent, sensing the shielding cone of the aromatic ring; the next upfield signal is usually one of the protons in the preceding CH_2 group. Although changes and broadenings of the spectra occur at low temperature, different conformations are not resolved.

The acetonide **4** displays a completely different set of naphthalene protons (see Table 2). As proved by COSY- and NOE-derived spectra, 2-H is the most downfield-shifted proton signal and the entire chemical-shift range is very similar to that of 1-(methoxymethyl)naphthalene, a model compound for a single naphthalene ring with a similar electronic situation.[13] A slight broadening of the 8-H proton signal (the most upfield-shifted in the set) indicates some hindrance of the rotation of the naphthyl groups across the dioxolane ring. A substantial broadening of the spectrum, albeit without resolution, is beginning only at 183 K. In conclusion, the naphthyl groups in **5** with a mutual dihedral angle of ca. 120° can rotate quite freely on the time scale of the 250-MHz spectrum.

Although the processes of conformational and rotational freezing are too complicated as to yield quantitative data for activation energies, a semi-quantitative analysis of the free activation enthalpies for the rotamer conversions is possible. For simplification both processes have been treated as a symmetric first-order one-signal case.

For the first rotamer separation the breakdown of the 8-H signal into a very broad one at δ ≈ 8.2 was taken as the first coalescence temperature T_c1. The frequency difference of the new signals was 350 Hz when the resolved *aa*-8-H signal and the mean frequency of both the later resolved *ee* and *ae* rotamer signals were used. In the second process the breakdown of the signal at δ ≈ 8 was taken as T_c2 and the high-field 8-H signal of the *ea* rotamer and the 8-H signal of the *ee* rotamer gave a frequency difference of 54 Hz. Under these circumstances ΔG^+ values were estimated to be acceptable within a ±0.5 kcal/mol range. The activation parameters thus obtained correspond reasonably well with the results of the MM2 calculations as given in Table 1.

In the two alkali metal complexes the lower temperature process was readily accessible by dynamic NMR. The *aa*

rotamer signals of **1**·$NaClO_4$ and **2**·$KClO_4$ are already completely resolved in the room-temperature spectra. An upper coalescence temperature could not be reached. The reinforcement of the crown ether conformation by cation complexation thus leads to a significant increase of the rotational barriers.

The ratios of the three rotamers in the final low-temperature distribution remarkably depend on the crown-ether size and on its state, free or complexed. The asymmetric *ae* rotamer is present in substantial amount in all four cases with ca. 40% in the free ligands and ca. 50% in the complexes (Table 2). This conformation appears to be the optimal balance of steric and π-stacking effects. Rather striking is the ratio of the *aa* and *ee* rotamers in the smaller and in the larger crown: The *aa*/*ee* ratio in **1** is 1:2 but 10:1 in **2**. In contrast to the distinct minimum of the oblong form of 18-membered crown ethers[14] the 15-crown structures are much less planar as can be seen in Figure 1. Therefore the *aa* form will be disfavored by steric hindrance between the C-8−8-H part of the naphthalene rings with the oligoethylenedioxy loop of **1** (Scheme 3). On complexation and the concomitant flattening of the crown the *aa*/*ee* ratio in the 15-crown becomes 1:1.

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Experimental Section

General: The following analytical instruments were used: Beckman Acculab 1 or 2 (IR), Hitachi U 2000 (UV/Vis), Bruker WM 250 or Bruker ARX 400 (^{1}H-NMR and ^{13}C-NMR spectra; TMS as internal standard in $CDCl_3$ unless noted otherwise); Varian MAT 112 S [EI-MS (70 eV)]; Büchi 510 apparatus (melting points, uncorrected). − Elemental analyses were performed by the Analytical Laboratory of the University of Regensburg.

(E)-1,2-Bis(1-naphthyl)ethene: To a refluxing McMurry reagent prepared from $TiCl_4$ (7.5 ml, 69 mmol), Zn/Cu (10.3 g, 0.16 mol) in THF (750 ml), 1-formylnaphthalene (11.15 g, 68.5 mmol) in THF (150 ml) was added dropwise for 30 min. After 3 h, 10% aqueous $NaCO_3$ (400 ml) and diethyl ether (400 ml) were added to the cooled mixture and the organic phase was separated, washed with brine and dried with Na_2SO_4. The residue obtained after evaporation of the solvent was recrystallized from 2-methoxyethanol: 8.75 g (90%), colorless crystals, m.p. 162−163°C (ref.[10] 163°C). − ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 7.46−7.55 (m, 6 H, naphthyl-H); 7.74−7.87 (m, 6 H, naphthyl-H); 7.90 (s, 2 H, $-C_2H_2-$ethylene); 8.22−8.25 (m, 2 H, naphthyl-H).

(±)-1,2-Bis(1-naphthyl)-1,2-ethanediol (**3**): A mixture of 1,2-bis(1-naphthyl)ethylene (760 mg, 2.7 mmol), *N*-methylmorpholine *N*-oxide monohydrate (348 mg, 2.5 mmol) in H_2O (2 mml) and OsO_4 (1.7 ml of a 40 mM solution in *t*BuOH[15]) in THF (25 ml) was kept at 4°C for 2 d under occasional shaking. After addition of $Na_2S_2O_5$ (1 g) in water (50 ml), the product was obtained after extraction with ether: 510 mg (60%), colorless crystals, m.p. 173−175°C (ref.[16] 174−175°C). − IR (KBr): $\tilde{\nu}$ = 3390, 3050, 3010, 1600; 1070, 805, 780 cm^{-1}. − ^{1}H NMR (250 MHz, [D$_6$]acetone/TMS): δ = 2.88 (br. s, 2 H, OH); 5.72 (s, 2 H, C*H*OH); 7.17−7.35 (m, 6 H, naphthyl-H); 7.59−7.73 (m, 6 H, naphthyl-H); 7.98 (d, 2 H, naphthyl-H). − EI MS (70 eV); *m*/*z* (%): 314 (4) [M$^+$], 296 (14) [$(C_{10}H_7)_2C_2H_2O^+$], 267 (68) [$(C_{10}H_7)_2CH^+$], 157 (76) [$C_{10}H_7CH_2O^+$], 129 (100) [$C_{10}H_7^+$].

2,3-Bis-(1-naphthyl)-15-crown-5 (**1**) *and 2,3-Bis-(1-naphthyl)-18-crown-6* (**2**). − *General Procedure:* The mixture of diol **3** (322 mg, 1 mmol), the corresponding dimesylate (1 mmol), and powdered NaOH (10 mmol, for **1**) or KOH (10 mmol, for **2**) in THF (15 ml) was refluxed for 48 h. The cooled suspension was filtered and the solids were washed with CH_2Cl_2 (30 ml). The combined organic phases were washed with 2 N HCl and brine and dried with $MgSO_4$. The semicrystalline solids which were obtained after removal of the solvents were purified by recrystallization with CH_3OH.

1: 257 mg (54%), colorless crystals, m.p. 100−101°C. − IR (KBr): $\tilde{\nu}$ = 3060, 2840−2980, 1590, 1450, 770 cm^{-1}. − EI MS (70 eV); *m*/*z* (%): 472 (100) [M$^+$], 156 (72) [$C_{10}H_7CO^+$], 128 (67) [$C_{10}H_7^+$], 45 (44) [$C_2H_4O^+$].− ^{1}H NMR (400 MHz, CD_2Cl_2/TMS, 294 K): δ = 3.41−3.45 (m, 2 H), 3.60−3.68 (m, 4 H), 3.69−3.75 (m, 2 H), 3.75−3.82 (m, 10 H), crown-H; for naphthyl proton signals see Table 2. − $C_{30}H_{32}O_5$ (472.2): calcd. C 76.27, H 6.77; found C 75.87, H 6.84.

2: 195 mg (40%), colorless crystals, m.p. 109−110°C. − IR (KBr): $\tilde{\nu}$ = 3050, 2800−3000, 1590, 1450, 1460, 770 cm^{-1}. − EI MS (70 eV); *m*/*z* (%): 516 (20) [M$^-$], 156 (34) [$C_{10}H_7CO^+$], 128 (34) [$C_{10}H_7^+$], 45 (100) [$C_2H_4O^+$]. − ^{1}H NMR (400 MHz, CD_2Cl_2/TMS, 294 K): δ = 3.33−3.36 (m, 2 H), 3.48−3.52 (m, 2 H), 3.57−3.78 (m, 16 H), crown-H; for naphthyl proton signals see Table 2. − $C_{32}H_{36}O_6$ (516.2): calcd. C 74.39, H 7.02; found C 74.19, H 6.67.

Crown Complex **1**·$NaClO_4$: From the combined solutions of **1** (100 mg, 0.21 mmol) and $NaClO_4$ (26 mg, 0.21 mmol) in THF (1 ml each) the complex precipitated overnight at 4°C: colorless crystals, m.p. > 300°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3050 w, 2880−2930, m, 1600 w, 1050−1190 ss, 780 cm^{-1} s. − FAB MS (glycerol); *m*/*z*: 495 [M − ClO_4^-]. − ^{1}H NMR (400 MHz, CD_2Cl_2/TMS, 294 K): δ = 3.41−3.45 (m, 2 H), 3.60−3.68 (m, 4 H), 3.69−3.75 (m, 2 H), 3.75−3.82 (m, 10 H), crown-H; for naphthyl proton signals see Table 2. − $C_{30}H_{32}O_5$·$NaClO_4$ (594.6): calcd. C 60.56, H 5.38; found C 60.68, H 5.61.

Crown Complex **2**·$KClO_4$: **2** (100 mg, 0.19 mmol) and $KClO_4$ (27 mg, 0.19 mmol) in THF (4 ml) were refluxed until a homogeneous solution was obtained (24 h). The complex precipitated as a microcrystalline powder: 102 mg (96%) m.p. 229−230°C. − IR (KBr): $\tilde{\nu}$ = 3050 w, 2800 w, 1450, 1470 s; 1090 s, 780 cm^{-1} s. − FAB MS (glycerol); *m*/*z*: 555 [M$^+$ − ClO_4^-]. − ^{1}H NMR (400 MHz, CD_2Cl_2/TMS, 294 K): δ = 3.21−3.24 (m, 2 H), 3.33−3.38 (m, 2 H), 3.50−3.52 (m, 2 H), 3.59−3.63 (m, 4 H), 3.65−3.87 (m, 10 H), crown-H; for naphthyl proton signals see Table 2. − $C_{32}H_{36}O_6$·$KClO_4$: (639.0) calcd. C 60.14, H 5.05; found C 60.01, H 4.98.

2,3-Bis-(1-naphthyl)-2,3-dimethoxyethane (**5**): Diol **3** (0.5 mmol) was treated with 2 equivalents of dimethyl sulfate in boiling dry THF (5 ml) with excess KOH for 24 h. After aqueous work-up, the product was extracted with CH_2Cl_2: yield 68 mg, 40%, m.p. 120°C. − ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 3.23 (s, 6 H, OMe), 5.33 (s, 2 H, −C*H*O−), for naphthalene proton signals see Table 2. − MS (EI, 70 eV); *m*/*z* (%): 342 (2.3) [M$^+$], 171 (100) [$C_{12}H_{11}O$], 156 (6) [$C_{11}H_8O$], 128 (13) [$C_{10}H_8$].

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[7] X-ray structure-analysis of **1**: The intensities of reflections were determined with an Enraf Nonius CAD4 diffractometer (room temp., Cu-K_α radiation λ = 1.54184 A). The structures were solved by direct methods and refined with F^2 for all independent reflections. Hydrogen atoms were calculated for assumed geometries; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. Programs: SHELXS-86 for structural determination and SHELXL-93 for refinement. Structural data of **1**: $C_{30}H_{32}O_5$, M = 472.56, crystals from methanol, m.p. 100−101°C; crystal size: 0.50 × 0.30 × 0.10 mm; monoclinic, space group $C2$, a = 22.236(1), b = 7.574(1), c = 15.041(1) A, β = 95.13(1)°; V = 2523.0 A^3, Z = 4, $\rho_{calcd.}$ = 1.44 g cm^{-3}; $F(000)$ = 1008; μ_{Cu} = 0.672 cm^{-1}; Θ_{max} = 27°; 5876 collected, 5115 unique, 4811 observed reflections ($F_o^2 > 2\sigma F_o^2$); $R1$ = 0.0353, $wR2$ = 0.0981, GOF (F^2) = 1.049 for 363 parameters, residual electron density 0.162 and −0.129 e A^{-3}. A thermal disorder exists within the chain from C-4 to C-10 with site-occupation factors of 0.538:0.462. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-100782. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + (0)1223/336-033; e-mail: deposit@chemcrys.cam.ac.uk).
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