

Synthesis of Novel Crown Ethers Derived from 3,3'-Dimethyl-2,2'-Bithienylene and Preparation of α,ω -Bis-(3-methylenethienyl) Ethers

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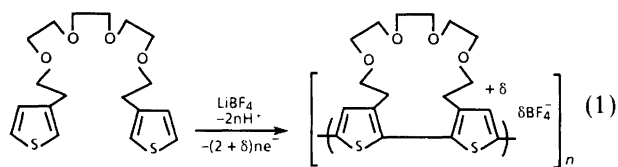
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The synthesis of a series of crown ethers and podands derived from 3,3'-dimethyl-2,2'-bithienylene is described. Their structures are ascertained by elemental analyses and ¹H NMR and mass spectra. To corroborate further the structure assignments X-ray structures of two members of this series, 7,9,10,12-tetrahydrodithieno[3,2-*f*:2',3'-*h*][1,4]dioxecine (**3a**) and 7,9,10,12,19,21,22,24-octahydro-tetrathieno[3,2-*f*:2',3'-*h*:3'',2''-*p*:2''',3'''-*r*][1,4,11,14]tetraoxacycloicosine (**5a**), are reported.

Dedicated to Professor Salo Gronowitz on the occasion of his 65th birthday.

Since the recognition of the unusual alkali- and alkaline-earth-metal ion complexing properties of crown ethers by Pedersen^{1,2} considerable work has been done on this class of compound. However, only a few articles containing crown ethers derived from thiophene have appeared.^{3–12} In addition, all these thiophene-based crown ethers incorporated only monomeric thiophene units into the crown. A recent paper¹³ in which it was claimed that a polymeric crown ether schematically derived from 2,2'-dithienylene was formed electrochemically by oxidation of an α,ω -bis-3-thienyl oligoether according to eqn. (1) prompts us



to publish some of our results on the actual chemical synthesis of monomeric crown ethers with 3,3-bis(bromomethyl)-2,2'-bithiophene (**1**) and 3-bromomethylthiophene (**2**) as starting materials. These compounds constitute part of our continuing work on the synthesis of conductive polymers and our studies of their applications.^{14–17}

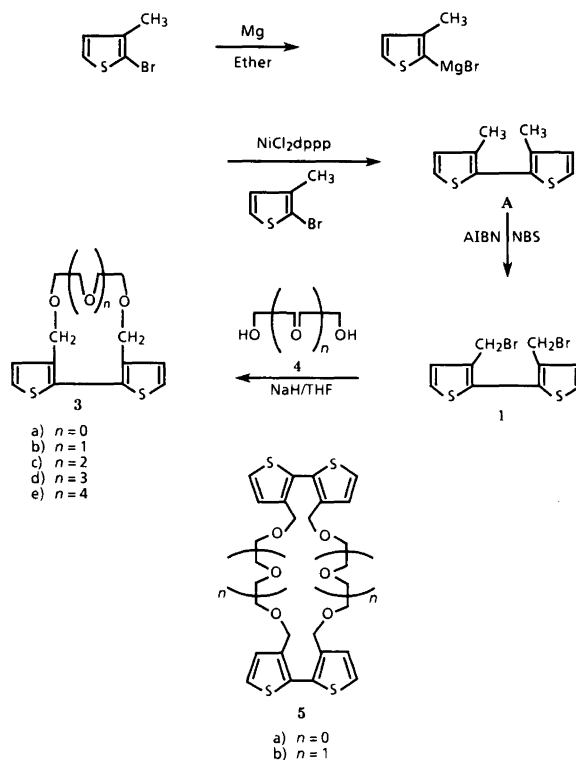
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Results and discussion

The starting material for the synthesis of crown ethers of type **3** was prepared either according to Gronowitz by a Cu(II)-induced oxidative coupling of 2-lithio-3-methylthiophene¹⁸ or by a Kumada coupling reaction¹⁹ of



Scheme 1.

Table 1. Structure determination summaries.

	Compound 3a	Compound 5a
Crystal data		
Formula	C ₁₂ H ₁₂ O ₂ S ₂	C ₂₄ H ₂₄ O ₄ S ₄
Color and habit	Colorless plates	Colorless rectangular prisms
Size/mm	0.25 × 0.50 × 0.50	0.10 × 0.20 × 0.20
Space group	<i>P</i> 4 ₁ 2 ₁ 2 (No. 92)	<i>C</i> 2/ <i>c</i> (No. 15)
Unit cell dimensions (<i>a</i> , <i>b</i> , <i>c</i> in Å) (angles in deg)	<i>a</i> = 6.9270(5) <i>c</i> = 25.0785(36)	<i>a</i> = 18.128(3) <i>b</i> = 10.643(2) <i>β</i> = 120.76(1) <i>c</i> = 14.561(3)
<i>V</i> /Å ³	1203.3(2)	2414.0(6)
<i>Z</i> (molecules/cell)	4	4
Molecular weight	252.36	504.69
Density, calc. (g cm ⁻³)	1.39	1.39
<i>F</i> (000) (e ⁻)	528	1056
Data collection		
Diffractometer	Nicolet R3m	Nicolet R3m
Radiation	Mo (0.71073)	Mo (0.71073)
Monochromator	Highly oriented graphite crystal	Highly oriented graphite crystal
<i>T</i> /K	294	294
<i>h</i> , <i>k</i> , <i>l</i> limits	-9-0, -9-0, -28-0	-21-21, 0-13, 0-17
2 θ range/deg	3-45	3-45
Scan type	θ	$\theta/2\theta$
Scan speed/deg min ⁻¹	Variable; 2.0-8.0	Variable; 1.5-4.0
Scan range/deg	0.6 on either side of <i>K</i> _{α2}	0.8 on either side of <i>K</i> _{α2}
Background measurement	Stationary crystal and counter at beginning and end of scan; total background time to scan time ratio of 0.5	Stationary crystal and counter at beginning and end of scan; total background time to scan time ratio of 0.5
Standard reflections	3 measured every 37	3 measured every 37
Reflections collected	1960 total (790 independent)	1776 total (1591 independent)
Reflections observed	724; <i>F</i> > 6 σ (<i>F</i>)	980; <i>F</i> > 6 σ (<i>F</i>)
Absorption coefficient/cm ⁻¹	4.06	3.68
Number of psi scan refls.	No absorption correction	No absorption correction
Min./max. transmission	No absorption correction	No absorption correction
Refinement		
System used	Micro VAX II; Nicolet SHELXS/SHFLXTL PLUS	Micro VAX II; Nicolet SHELXS/SHFLXTL PLUS
Solution	Direct methods (TREF)	Direct methods (TREF)
Final residuals	<i>R</i> (<i>F</i>) = 0.0246 <i>wR</i> (<i>F</i>) = 0.0291	<i>R</i> (<i>F</i>) = 0.0341 <i>wR</i> (<i>F</i>) = 0.0310
Goodness-of-fit	<i>S</i> = 2.17	<i>S</i> = 1.25
Largest Shift/esd	0.001	0.001
Number of variables	97	193
Data-to-parameter ratio	7.5:1	5.1:1
Max./min. excursions	0.24 and -0.26 e ⁻ Å ⁻³	0.18 and -0.16 e ⁻ Å ⁻³

Table 2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (10³ Å²) for compound 3a.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
C(1)	8008(5)	6621(5)	132(1)	73(1)
O(2)	7023(3)	5296(3)	462(1)	63(1)
C(3)	6628(4)	3497(4)	205(1)	53(1)
C(4)	4950(4)	2539(3)	468(1)	44(1)
C(5)	3149(3)	2398(3)	253(1)	40(1)
S(6)	1639(1)	1052(1)	660(1)	63(1)
C(7)	3421(6)	721(4)	1111(1)	74(1)
C(8)	5063(6)	1564(5)	966(1)	64(1)

^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

2-bromo-3-methylthiophene to yield 3,3'-dimethyl-2,2'-bithiophene²⁰ followed by NBS sidechain bromination. Reaction of equimolar amounts of α,ω -dialkoxides derived from the polyethylene glycols **4** (*n* = 0-4) gave the desired crown ethers **3a-e** (Scheme 1). In the case of **4a** and **4b** two compounds were collected by chromatography to give the 1:1 cyclic products, **3a** and **3b**, and the 2:2 cyclic products, **5a** and **5b**. Compounds **3a** and **3b** as well as **5a** and **5b** gave identical elemental analyses and ¹H NMR spectra. Mass spectroscopy proved to be a useful technique for the structure determination of these compounds via the chemical ionization method. The selectivity toward formation of type **5**

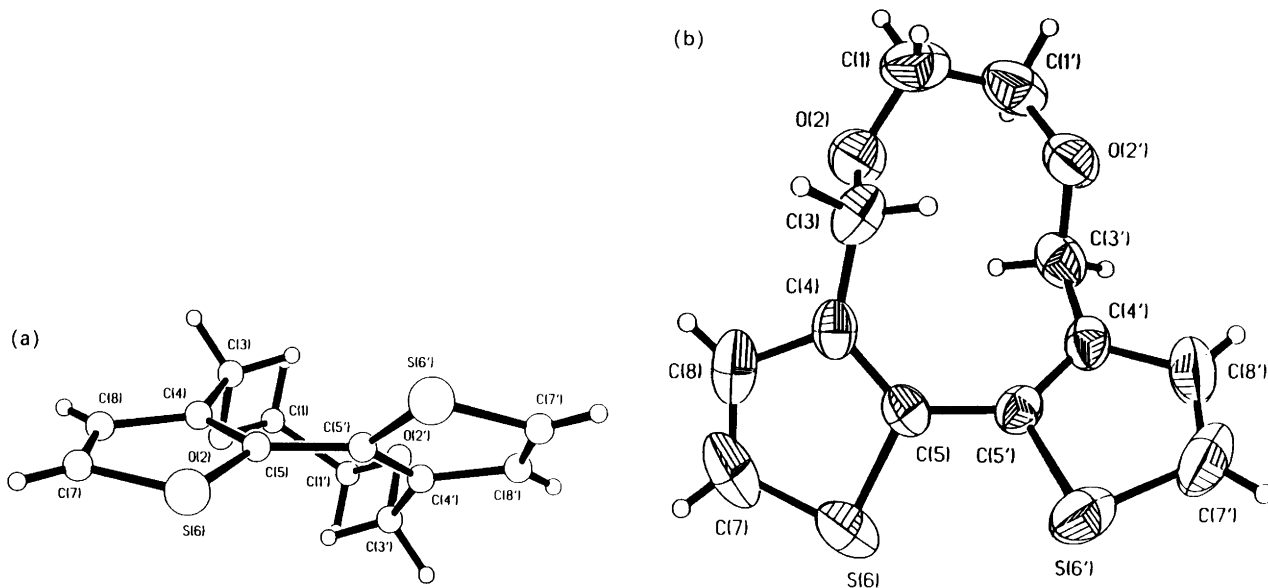


Fig. 1. (a) Pluto drawing of 7,9,10,12-tetrahydrodithieno[3,2-*f*:2',3'-*h*][1,4]dioxecine **3a**. (b) ORTEP drawing of **3a**.

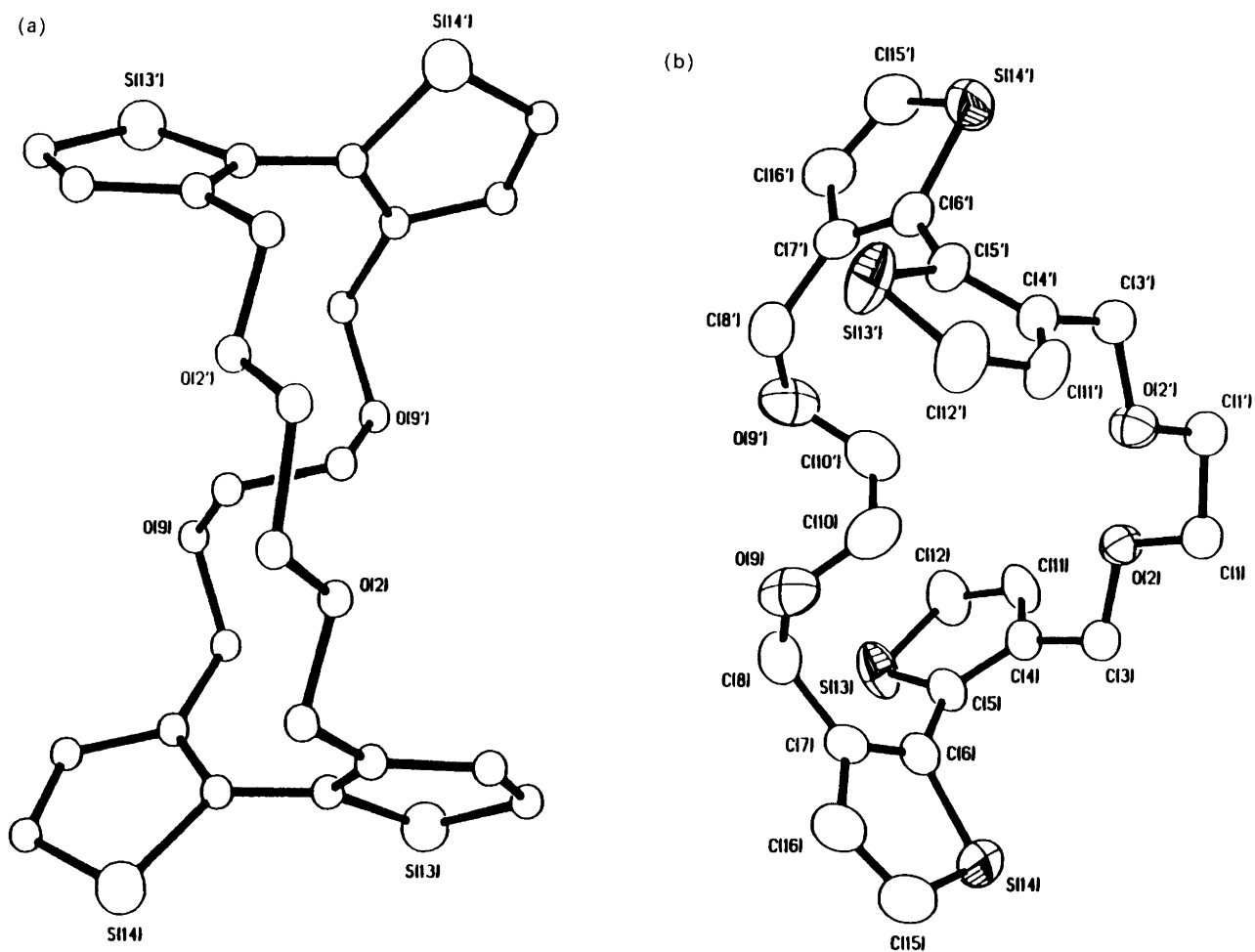
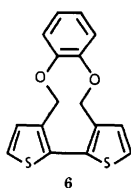


Fig. 2. (a) Pluto drawing of 7,9,10,12,19,21,22,24-octahydrotrithieno[3,2-*f*:2',3'-*h*:3'',2''-*p*:2''',3'''-*r*][1,4,11,14] tetra-oxacycloicosine **5a**. (b) ORTEP drawing of **5a**.

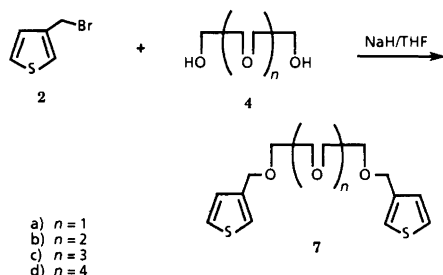
compounds can be explained by a 'template' effect due to the cation.⁷ Alternatively the low yields of compounds **3a** and **3b** in comparison with the significantly higher yields of **3c–3e** could be attributed to strain in the medium-sized rings of the former two compounds.

Unambiguous structural proof for **3a** and **5a** was established by X-ray analysis. A perspective view of the two molecules **3a** and **5a** is presented in Figs. 1 and 2, respectively. A summary of the crystal structure determinations is given in Table 1; final atomic coordinates are given in Tables 2 and 3; bond distances, bond angles and torsion angles are reported in Tables 4, 5 and 6, respectively.

The dimeric thiophene **1** also reacted with catechol under the described conditions to give the expected crown ether **6**.



The podands **7a–d** were synthesized in good yields (Scheme 2) by slightly changing the procedure used for



Scheme 2.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (10^3 \AA^2) for compound **5a**.

Atom	x	y	z	$U(\text{eq})^a$
C(1)	4574(3)	5532(4)	2467(4)	36(2)
O(2)	4556(2)	4496(2)	3066(2)	42(1)
C(3)	3721(3)	4231(4)	2862(4)	40(2)
C(4)	3764(2)	3186(4)	3567(3)	35(2)
C(5)	3332(2)	2075(3)	3204(3)	35(2)
C(6)	2777(2)	1655(4)	2102(3)	36(2)
C(7)	2878(2)	663(4)	1585(3)	38(2)
C(8)	3626(3)	-219(5)	2042(4)	49(3)
O(9)	4162(2)	-42(3)	1602(2)	58(2)
C(10)	4643(3)	1077(6)	1931(4)	60(3)
C(11)	4268(3)	3218(5)	4699(4)	46(2)
C(12)	4216(3)	2171(4)	5172(4)	53(3)
S(13)	3537(1)	1098(1)	4261(1)	54(1)
S(14)	1825(1)	2440(1)	1267(1)	53(1)
C(15)	1591(3)	1443(5)	237(4)	57(3)
C(16)	2195(3)	557(5)	512(4)	50(3)

^a Equivalent isotropic as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Selected bond distances (\AA) for compounds **3a** and **5a**.

3a^a		5a^b	
C(1)–C(1')	1.512(6)	C(1)–O(2)	1.416(4)
C(1)–O(2)	1.412(4)	C(1')–C(1)	1.499(7)
O(2)–C(3)	1.428(3)	O(2)–C(3)	1.414(4)
C(3)–C(4)	1.492(4)	C(3)–C(4)	1.488(5)
C(4)–C(5)	1.363(3)	C(4)–C(5)	1.366(5)
C(4)–C(8)	1.422(3)	C(4)–C(11)	1.418(5)
C(5)–C(5')	1.466(2)	C(5)–C(6)	1.461(5)
C(5)–S(6)	1.733(2)	C(5)–S(13)	1.732(4)
S(6)–C(7)	1.691(4)	C(6)–C(7)	1.363(5)
C(7)–C(8)	1.330(6)	C(6)–S(14)	1.733(4)
		C(7)–C(8)	1.497(5)
		C(7)–C(16)	1.416(5)
		C(8)–O(9)	1.424(5)
		O(9)–C(10)	1.407(6)
		C(10')–C(10)	1.491(9)
		C(11)–C(12)	1.339(6)
		C(12)–S(13)	1.705(4)
		S(14)–C(15)	1.704(5)
		C(15)–C(16)	1.342(6)

^a Symmetry code: $' = (y, x, -z)$. ^b Symmetry code: $' = (1.0 - x, y, 0.5 - z)$.

the preparation of type **3** and type **5** compounds. The podands were purified by column chromatography and were characterized by elemental analysis and ¹H NMR and mass spectroscopy. In the electron-impact mass spectra only weak molecular-ion peaks are observed but intense ion peaks due to the loss of a thienyl radical were present. The base peaks were either due to the

Table 5. Selected bond angles ($^\circ$) for compounds **3a** and **5a**.

3a^a		5a^b	
C(1')–C(1)–O(2)	111.2(2)	O(2)–C(1)–C(1')	108.0(3)
C(1)–O(2)–C(3)	113.3(2)	C(3)–O(2)–C(1)	112.7(3)
O(2)–C(3)–C(4)	109.8(2)	C(4)–C(3)–O(2)	109.4(3)
C(3)–C(4)–C(5)	124.8(2)	C(5)–C(4)–C(3)	124.3(4)
C(3)–C(4)–C(8)	123.8(3)	C(11)–C(4)–C(3)	123.9(4)
C(5)–C(4)–C(8)	111.4(3)	C(11)–C(4)–C(5)	111.8(4)
C(4)–C(5)–C(5')	129.9(1)	C(6)–C(5)–C(4)	128.7(3)
C(4)–C(5)–S(6)	111.0(2)	S(13)–C(5)–C(4)	110.9(3)
C(5')–C(5)–S(6)	119.1(1)	S(13)–C(5)–C(6)	120.4(3)
C(5)–S(6)–C(7)	91.5(1)	C(7)–C(6)–C(5)	129.2(4)
S(6)–C(7)–C(8)	112.4(2)	S(14)–C(6)–C(5)	120.1(3)
C(4)–C(8)–C(7)	113.7(3)	S(14)–C(6)–C(7)	110.6(3)
		C(8)–C(7)–C(6)	126.0(4)
		C(16)–C(7)–C(6)	112.5(4)
		C(16)–C(7)–C(8)	121.5(4)
		O(9)–C(8)–C(7)	112.8(4)
		C(10)–O(9)–C(8)	113.9(4)
		O(9)–C(10)–C(10')	114.4(3)
		C(12)–C(11)–C(4)	113.9(4)
		S(13)–C(12)–C(11)	111.7(4)
		C(12)–S(13)–C(5)	91.8(2)
		C(15)–S(14)–C(6)	91.6(2)
		C(16)–C(15)–S(14)	112.1(4)
		C(15)–C(16)–C(7)	112.1(5)

^a Symmetry codes: $' = (y, x, -a)$. ^b Symmetry codes: $' = (1.0 - x, y, 0.5 - z)$.

Table 6. Torsion angles^a (deg) for compounds **3a** and **5a**.

3a					5a				
O2	C1	C1'	O2A	-61.3	C1A	C1	O2	C3	-166.3
C1'	C1	O2	C3	96.2	C1	O2	C3	C4	-176.6
C1	O2	C3	C4	-156.2	O2	C3	C4	C5	-121.5
O2	C3	C4	C5	106.7	O2	C3	C4	C11	57.7
O2	C2	C4	C8	-76.7	C3	C4	C5	C6	2.0
C3	C4	C5	C5'	-1.9	C3	C4	C5	S13	-179.7
C3	C4	C5	S6	176.2	C11	C4	C5	C6	-177.3
C8	C4	C5	C5'	-178.9	C11	C4	C5	S13	1.1
C8	C4	C5	S6	-0.8	C4	C5	C6	C7	117.2
C4	C5	C5'	C4A	-49.0	C4	C5	C6	S14	-64.4
C4	C5	C5'	S6A	133.0	S13	C5	C6	C7	-61.1
S6	C5	C5'	C4A	132.9	S13	C5	C6	S14	117.4
S6	C5	C5'	S6A	-45.1	C5	C6	C7	C8	-2.5
C4	C5	S6	C7	0.6	C5	C6	C7	C16	179.7
C5'	C5	S6	C7	179.0	S14	C6	C7	C8	179.0
C5	S6	C7	C8	-0.3	S14	C6	C7	C16	1.1
C3	C4	C8	C7	-176.4	C6	C7	C8	O9	-108.2
C5	C4	C8	C7	0.6	C16	C7	C8	O9	69.4
S6	C7	C8	C4	-0.1	C7	C8	O9	C10	71.1
C3A	O2A	C1'	C1	96.2	C8	O9	C10	C10A	71.5
C3A	C4A	C5'	C5	-1.9	C3	C4	C11	C12	-179.5
C3A	C4A	C5'	S6A	176.2	C5	C4	C11	C12	-0.2
C8A	C4A	C5'	C5	-178.9	C4	C11	C12	S13	-0.8
C8A	C4A	C5'	S6A	-0.8	C4	C5	S13	C12	-1.3
C7A	S6A	C5'	C5	179.0	C6	C5	S13	C12	177.3
C7A	S6A	C5'	C4A	0.6	C11	C12	S13	C5	1.2
C4A	C3A	O2A	C1'	-156.2	C5	C6	S14	C15	-179.6
O2A	C3A	C4A	C5'	106.7	C7	C6	S14	C15	-0.9
O2A	3A	C4A	C8A	-76.7	C6	S14	C15	C16	0.5
C7A	C8A	C4A	C5'	0.6	C6	C7	C16	C15	-0.8
C7A	C8A	C4A	C3A	-176.4	C8	C7	C16	C15	-178.7
C8A	C7A	S6A	C5'	-0.3	S14	C15	C16	C7	0.1
S6A	C7A	C8A	C4A	-0.1	O2A	C1A	C1	O2	70.1
					O9A	C10A	C10	O9	43.5
					C3A	O2A	C1A	C1	-166.3
					C8A	O9A	C10A	C10	71.5
					C4A	C3A	O2A	C1A	-176.6
					C7A	C8A	O9A	C10A	71.1
					C5A	C4A	C3A	O2A	-121.5
					C11A	C4A	C3A	O2A	57.7
					C16A	C7A	C8A	O9A	69.4
					C6A	C7A	C8A	O9A	-108.2
					C6A	C5A	C4A	C3A	2.0
					C6A	C5A	C4A	C11A	-177.3
					S13A	C5A	C4A	C3A	-179.6
					S13A	C5A	C4A	C11A	1.1
					C12A	C11A	C4A	C3A	-179.5
					C12A	C11A	C4A	C5A	-0.2
					C15A	C16A	C7A	C8A	-178.7
					C15A	C16A	C7A	C6A	-0.8
					C5A	C6A	C7A	C8A	-2.5
					C5A	C6A	C7A	C16A	179.7
					S14A	C6A	C7A	C8A	179.0
					S14A	C6A	C7A	C16A	1.1
					C7A	C6A	C5A	C4A	117.2
					C7A	C6A	C5A	S13A	-61.1
					S14A	C6A	C5A	C4A	-64.4
					S14A	C6A	C5A	S13A	117.4
					S12A	S13A	C5A	C4A	-1.3
					C12A	S13A	C5A	C6A	177.3
					S13A	C12A	C11A	C4A	-0.8
					H12A	C12A	C11A	C4A	177.9
					C11A	C12A	S13A	C5A	1.2
					S14A	C15A	C16A	C7A	0.1
					C15A	S14A	C6A	C7A	-0.9
					C15A	S14A	C6A	C5A	-179.6
					C6A	S14A	C15A	C16A	0.5

^a Estimated standard deviations to within 1 deg.

thiopyrylium cation (m/z 97) or protonated ethylene oxide (m/z 45).

Preliminary results of experiments involving crown ethers of type **3** show that the picrate anion extraction from aqueous solution into dichloromethane is dependent on the cation. Thus **3c** with a fairly large cavity extracted K- and Cs-picrates into dichloromethane; however, Napicrate was not extracted into the organic layer by this crown ether. These results, together with the outcome of attempts to polymerize type **3** and **7** compounds electrochemically will be published in a forthcoming paper.

Experimental

Melting points were determined with a Mel Temp apparatus and are uncorrected. UV spectra were run in CH_2Cl_2 on Perkin-Elmer Lambda 5, UV-VIS spectrophotometer. ^1H NMR spectra were recorded on IBM NR-80 and/or Bruker AC-250 MHz spectrometers. Chemical shifts are expressed in δ (ppm) relative to tetramethylsilane as an internal standard and CDCl_3 as the solvent. Elemental analyses were performed at M-H-W Laboratories, Phoenix, Arizona. All reactions were performed under nitrogen. Silica gel 60 (Merck) was used for column chromatography and diethyl ether-petroleum ether (b.p. 37–59°C) mixtures as eluents. The reported yields refer to pure isolated materials. Crystal structure determinations were carried out on a Nicolet R3M four-circle diffractometer.

Preparation of crown ethers 3a–e and 5a, b: general procedure. A solution of equimolar amounts of **1** and the appropriate **4** in THF was added dropwise to a suspension of an excess of NaH in refluxing THF over a period of 3 h and refluxed for an additional 24 h. The excess of NaH was carefully decomposed by addition of H_2O . The solvent THF was removed under vacuum and the residue shaken with dilute HCl and extracted with CH_2Cl_2 . The organic layer was dried over anhydrous MgSO_4 and evaporated to dryness. The residues were purified by column chromatography.

7,9,10,12-Tetrahydrodithieno[3,2-f:2',3'-h][1,4]-dioxecine (3a). Yield = 0.076 g (10%), m.p. 112°C. Anal. $\text{C}_{12}\text{H}_{12}\text{O}_2\text{S}_2$: C, H. UV (λ_{max}) 250, 276 nm. MS: EI: m/z (%) 252 (M^+ , 55), 207 [$(M^+ - \text{C}_2\text{H}_5\text{O})$, 5], 191 [$(M^+ - \text{C}_2\text{H}_5\text{O}_2)$, 100], 178 [$(M^+ - \text{C}_3\text{H}_6\text{O}_2)$, 12]. ^1H NMR (CDCl_3): δ = 7.35, 7.18 (2 d, 4 H), 4.60 (s, 4 H), 3.75 (s, 4 H).

7,9,10,12,13,15-Hexahydrodithieno[3,2-i:2',3'-k]-[1,4,7]trioxacyclotridecine (3b). Yield = 0.20 g (22.8%), m.p. 142°C. Anal. $\text{C}_{14}\text{H}_{16}\text{O}_3\text{S}_2$: C, H. UV (λ_{max}) 247, 270 nm. MS: EI: m/z (%) 296 (M^+ , 5), 207 [$(M^+ - \text{C}_4\text{H}_9\text{O}_2)$, 9], 192 [$(M^+ - \text{C}_4\text{H}_8\text{O}_3)$, 30], 190 [$(M^+ - \text{C}_4\text{H}_{10}\text{O}_3)$, 100]. ^1H NMR (CDCl_3): δ = 7.40, 7.10 (2 d, 4 H), 4.45 (s, 4 H), 3.55 (s, 8 H).

7,9,10,12,13,15,16,18-Octahydrodithieno[3,2-l:2',3'-n]-[1,4,7,10]tetraoxacyclohexadecine (3c). Yield = 0.6 g

(58.8%), m.p. 121°C. Anal. $\text{C}_{16}\text{H}_{20}\text{O}_4\text{S}_2$: C, H. UV (λ_{max}) 247, 270 nm. MS: EI: m/z (%) 340 (M^+ , 1), 207 [$(M^+ - \text{C}_6\text{H}_{13}\text{O}_3)$, 9], 192 [$(M^+ - \text{C}_6\text{H}_{12}\text{O}_4)$, 85], 190 [$(M^+ - \text{C}_6\text{H}_{14}\text{O}_4)$, 100]. ^1H NMR (CDCl_3): δ = 7.4, 7.2 (2 d, 4 H), 4.50 (s, 4 H), 3.7 (s, 12 H).

7,9,10,12,13,15,16,18,19,21-Decahydrodithieno[3,2-o:2',3'-q][1,4,7,10,13]pentaoxacyclonadecine (3d). Yield = 0.67 g (58%), m.p. 70°C. Anal. $\text{C}_{18}\text{H}_{24}\text{O}_5\text{S}_2$: C, H. UV (λ_{max}) 245, 270 nm. MS: EI: m/z (%) 384 (M^+ , 3), 207 [$(M^+ - \text{C}_8\text{H}_{17}\text{O}_4)$, 5], 192 [$(M^+ - \text{C}_8\text{H}_{16}\text{O}_5)$, 42], 19 [$(M^+ - \text{C}_{10}\text{H}_6\text{S}_2)^+$, 100]. ^1H NMR (CDCl_3): δ = 7.4, 7.1 (2 d, 4 H), 4.45 (s, 4 H), 3.55 (s, 16 H).

7,9,10,12,13,15,16,18,19,21,22,24-Dodecahydrodithieno[3,2-r:2',3'-t][1,4,7,10,13,16]hexaoxacyclododecine (3e). Yield = 0.68 g (53%), oil. Anal. $\text{C}_{20}\text{H}_{28}\text{O}_6\text{S}_2$: C, H. UV (λ_{max}) 247, 270 nm. MS: EI: m/z (%) 428 (M^+ , 8), 207 [$(M^+ - \text{C}_{10}\text{H}_{21}\text{O}_5)$, 7], 192 [$(M^+ - \text{C}_{10}\text{H}_{20}\text{O}_6)$, 25], 190 [$(M^+ - \text{C}_{10}\text{H}_6\text{S}_2)^+$, 100]. ^1H NMR (CDCl_3): δ = 7.4, 7.1 (2 d, 4 H), 4.50 (s, 4 H), 2.6 (s, 20 H).

7,9,10,12,19,21,22,24-Octahydrotetrathieno[3,2-f:2',3'-h:3'',2''-p:2''',3'''-r][1,4,11,14]tetraoxacycloicosine (5a). Isolated by flash-column chromatography from the reaction mixture of **1** and **4a**. Yield = <1%, m.p. 155°C. Anal. $\text{C}_{24}\text{H}_{24}\text{O}_4\text{S}_4$: C, H. UV (λ_{max}) 247, 270 nm. MS: EI: m/z (%) 504 (M^+ , 15), 422 [$(M^+ - \text{C}_2\text{H}_6\text{O}_2)$, 40], 251 (50), 192 (100). ^1H NMR (CDCl_3): δ = 7.35, 7.18 (2 d, 8 H), 4.6 (s, 8 H), 3.75 (s, 8 H).

7,9,10,12,13,15,22,24,25,27,28,30-Dodecahydrotetrathieno[3,2-i:2',3'-k:3'',2''-v:2''',3'''-x][1,4,7,14,17,20]-cyclohexaicosine (5b). Isolated by flash-column chromatography from the reaction mixture of **1** and **4b**. Yield = 0.015 g (1.7%), m.p. 157°C. UV (λ_{max}) 246.4, 274 nm. MS: CI: m/z 593 (%) ($M+1$)⁺. ^1H NMR (CDCl_3): δ = 7.30, 7.12 (2 d, 8 H), 4.43 (s, 8 H), 3.70–3.50 (m, 16 H).

7,14-Dihydrobenzo[b]dithieno[3,2-f:2',3'-h][1,4]dioxecine (6). To a refluxing suspension of 0.106 g (4.4×10^{-3} mol) of hexane-washed NaH in dry THF was added dropwise over a period of 15 min a solution of 0.243 g (2.2×10^{-3} mol) catechol in 15 ml dry THF. A solution of 0.77 g (2.2×10^{-3} mol) **1** in 15 ml THF was then added dropwise and the mixture was refluxed for about 24 h before being quenched by addition of wet THF, followed by 0.5 M HCl until a clear solution resulted. After the THF had been distilled off, the aqueous phase was extracted with diethyl ether and dried over anhydrous MgSO_4 . The compound was purified on a silica gel column using hexane as the eluent. Yield 38% after column chromatography. m.p. 140–141°C. Anal. $\text{C}_{16}\text{H}_{12}\text{O}_2\text{S}_2$: C, H. MS: EI: m/z (%) 299.95 (M^+ , 12); 300.95 ($M^+ + 1$, 2). ^1H NMR (CDCl_3): δ = 7.3–6.91 (8 H m).

A trace of a solid, m.p. 191°C (decomp.), which showed a weak peak at 601 in the chemically ionized spectrum, is taken as evidence in support of the formation of a 2:2 dimeric species with $M = 600.52$, in analogy to **5a** and **5b**. This molecular peak was too weak, however, to obtain an exact mass.

Preparation of podands (7a–d): general procedure. Stoichiometric amounts of 3-bromomethylthiophene and the appropriate α,ω -glycol **4** in THF were added dropwise to a refluxing suspension of an excess of NaH (60% dispersion in mineral oil) in THF and reflux was continued overnight. The reaction mixture was allowed to cool to room temperature when water was added. It was then extracted four times with ether and dried over anhydrous magnesium sulfate and evaporated to dryness.

The crude products were purified by column chromatography using 10% ether–petroleum ether as the eluent.

1,9-Bis-(3-thienyl)-2,5,8-tetraoxanonane (7a). Yield = 2.2 g (73.8%), pale-yellow liquid. Anal. $C_{14}H_{18}O_3S_2$: C, H. UV (λ_{max}): 242.8 nm. MS: EI: m/z (%) 298 (M^+ , 1), 201 (6), 97 (96), 45 (100). 1H NMR ($CDCl_3$): δ = 7.05–7.28 (m, 6 H), 4.57 (s, 4 H), 3.58–3.68 (m, 8 H).

1,12-Bis-(3-thienyl)-2,5,8,11-tetraoxadecane (7b). Yield = 2.67 g (77.9%), pale-yellow liquid. Anal. $C_{16}H_{22}O_4S_2$: C, H. UV (λ_{max}): 242.2 nm. MS: EI: m/z (%) 342 (M^+ , 1), 245 (9), 97 (100), 45 (90). 1H NMR ($CDCl_3$): δ = 7.05–7.32 (m, 6 H), 4.57 (s, 4 H), 3.58–3.72 (m, 12 H).

1,15-Bis-(3-thienyl)-2,5,8,11,14-pentaoxapentadecane (7c). Yield = 2.2 g (57%), pale-yellow liquid. Anal. $C_{18}H_{26}O_5S_2$: C, H. UV (λ_{max}): 243 nm. MS: EI: m/z (%) 386 (M^+ , 1), 289 (5), 97 (100), 45 (77). 1H NMR ($CDCl_3$): δ = 7.05–7.32 (m, 6 H), 4.57 (s, 4 H), 3.57–3.67 (m, 16 H).

1,18-Bis-(3-thienyl)-2,5,8,11,14,17-hexaoxaoctadecane (7d). Yield = 2.1 g (49%), pale-yellow liquid. Anal. $C_{20}H_{30}O_6S_2$: C, H. UV (λ_{max}): 244.1 nm. MS: EI: m/z (%) 430 (M^+ , 0.3), 333 (1), 97 (74), 45 (100). 1H NMR ($CDCl_3$): δ = 7.06–7.30 (m, 6 H), 4.57 (s, 4 H), 3.58–3.68 (m, 20 H).

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