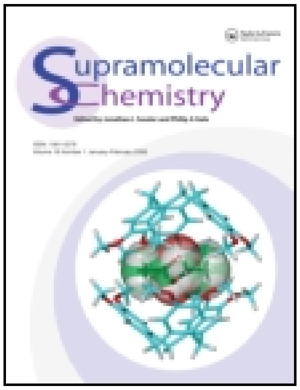

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Synthesis and structures of partially unsaturated thiacrown ethers with hydroxyl groups

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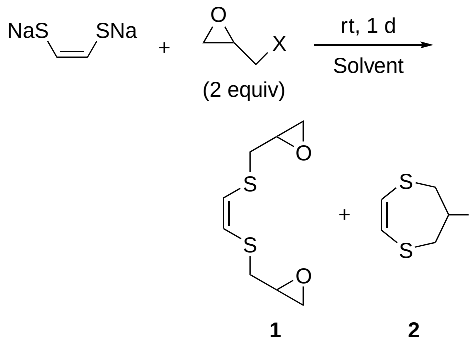
Partially unsaturated 14- and 28-membered thiacrown ethers possessing hydroxyl groups were synthesised. The crystal structures of some geometrical isomers of the macrocycles were determined by X-ray crystallographic analysis and six oxygen atoms of the 14-membered *trans*-thiacrown ether were found to gather through hydrogen bonds in the crystalline state. The redox behaviours of the 14-membered thiacrown ethers were examined and the *Z,E*-isomerisation reactions were found to occur upon heating.

Keywords: thiacrown ether; unsaturated cyclic compound; crystal structure; cyclic voltammetry; *Z,E*-isomerisation

Introduction

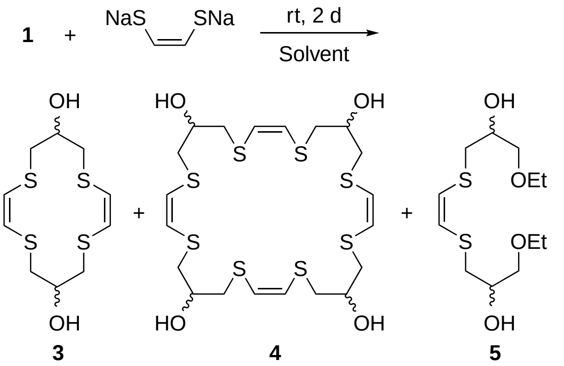
Thiacrown ether was synthesised for the first time in 1934 by Meadow and Reid (*1*), and thiacrown ethers of various sizes were isolated thereafter (*2*). Thiacrown ethers with various substituents have also been studied (*3*). On the other hand, few unsaturated thiacrown ethers have been synthesised (*4*, *5*). Previously, we synthesised unsaturated thia- and selenacrown ethers with *cis*-geometry across the carbon–carbon double bonds and studied their inclusion behaviours and reactivities (*5*, *6*). Partially unsaturated chalcogenocrown ethers with *cis*-double bonds are also interesting compounds on comparison of their conformation, electrochemical properties and inclusion behaviours with those of saturated and unsaturated counterparts. Some partially unsaturated thiacrown ethers

Table 1. Reactions of disodium *cis*-ethenedithiolate with 2 equiv. of epihalohydrin.



			Yield (%)	
Run	X	Solvent	**1**	**2**
1	C1	MeCN	9	31
2	Br	MeCN	43	12
3	Cl	EtOH	–	22
4	Br	EtOH	7	88

Table 2. Reactions of epoxide **1** with disodium *cis*-ethenedithiolate.



	Solvent		Yield (%)[a]		
Run	MeCN:EtOH	ml/mmol	**3**	**4**	**5**
1	1:0	3	–	–	–
2	0:1	3	0.3	1	3
3	1:1	10	2	11	–
4	1:1	25	5	7	–
5	6:1	25	5	8	–
6	1:10	25	1	<0.1	19
7[b]	1:10	25	0.3	<0.1	11

[a] NMR yield.
[b] 0.05 equiv. of Cs_2CO_3 was added.

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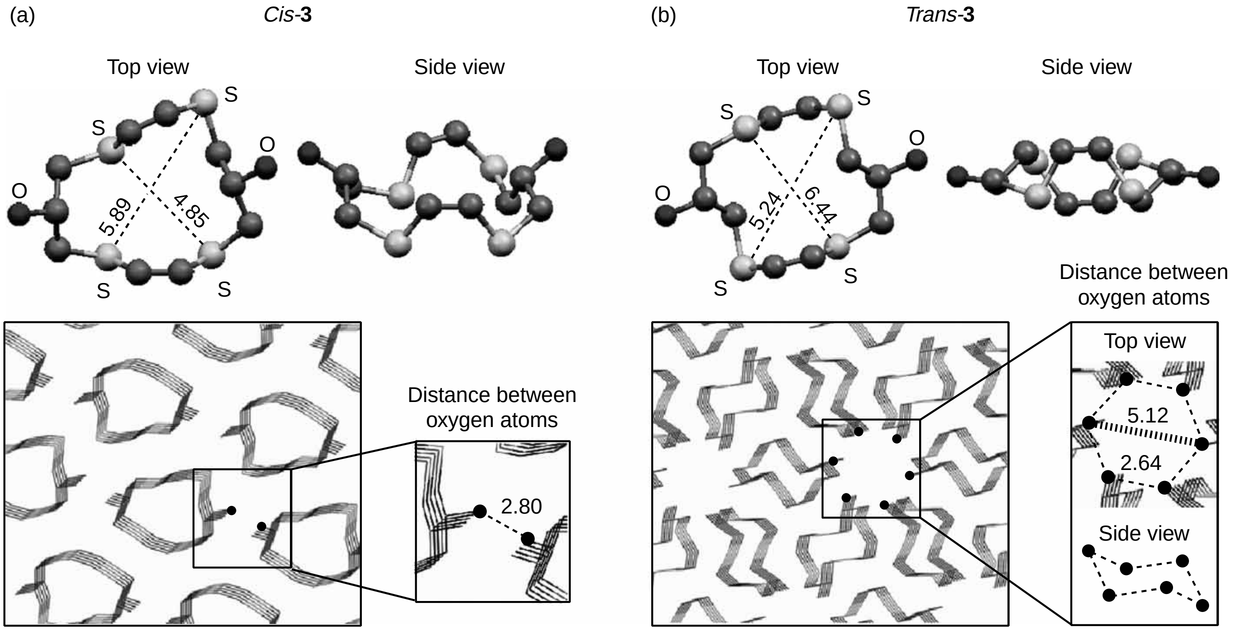

Figure 1. Crystal structures of *cis*- and *trans*-**3** with selected atomic distances (Å). Hydrogen atoms are omitted for the sake of clarity.

have been synthesised (*7–9*). Recently, we succeeded in synthesising 14- and 28-membered partially unsaturated thiacrown ethers possessing hydroxyl groups. We report here the synthesis, crystal structures and some fundamental properties of partially unsaturated thiacrown ethers with hydroxyl groups.

Results and discussion

First of all, the direct synthesis of the title compounds was examined. The reaction of disodium *cis*-ethenedithiolate with 1 equiv. of epichlorohydrin in acetonitrile did not afford the title compound but gave 1:2 adduct **1** and seven-membered cyclic compound **2** (*10*). The reaction with epibromohydrin also gave the same products. Therefore, the reaction conditions for synthesising 1:2 adduct **1**, which was expected to be a suitable precursor for the title compounds, were examined. The reaction of *cis*-ethenedithiolate with 2 equiv. of epibromohydrin in acetonitrile afforded 1:2 adduct **1** in 43% yield (Table 1, run 2), whereas cyclic compound **2** was the main product in the reaction with epichlorohydrin (run 1). In ethanol, the reaction with epichlorohydrin did not give **1** (run 3) and the reaction with epibromohydrin yielded cyclic product **2** in good yield (run 4). These results indicated that ethanol increased the reactivity of the epoxide moiety.

The reaction of epoxide **1** with *cis*-ethenedithiolate was examined in mixed solvents of acetonitrile and ethanol because epoxide **1** was soluble in acetonitrile and insoluble in ethanol, whereas *cis*-ethenedithiolate was soluble in ethanol and slightly soluble in acetonitrile. In ethanol or the

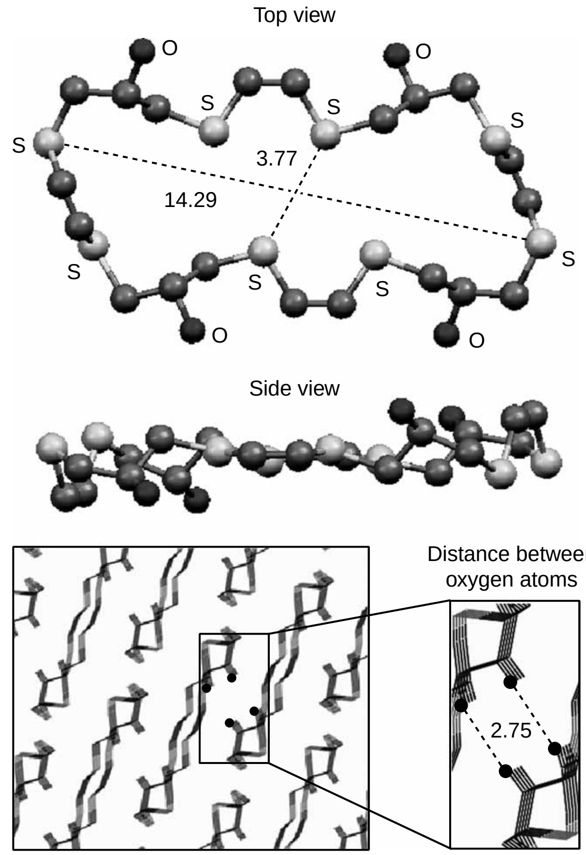

Figure 2. Crystal structure of *1,2-alternate*-**4** with selected atomic distances (Å). Hydrogen atoms are omitted for the sake of clarity.

mixed solvent, 14- and 28-membered thiacrown ethers with hydroxyl groups **3** and **4** were obtained as geometrical mixtures, respectively, whereas the reaction did not proceed in acetonitrile (Table 2). The highest yields of **3** and **4** were obtained in the 1:1 mixed solvent (runs 3 and 4); a low concentration of the 1:1 mixed solvent was effective for the formation of **3** (run 4) while a high concentration furnished **4** in 11% yield (run 3). When the ratio of ethanol was increased, ethylated compound **5** was obtained together with trace amounts of **3** and **4** (runs 2 and 6). When Cs_2CO_3 was added, however, the template effect was not observed (run 7).

14-Membered cyclic products *cis*- and *trans*-**3** were isolated by silica gel column chromatography[1,2] and their single crystals were obtained by recrystallisation from hexane/dichloromethane solutions, respectively. The crystal structures of those compounds were determined by X-ray crystallographic analysis. All of the olefin moieties of *cis*- and *trans*-**3** have the *Z*-geometry. *Cis*-isomer *cis*-**3** shows strain-free geometry in the crystalline state and the distances between sulphur atoms that are positioned diagonally are

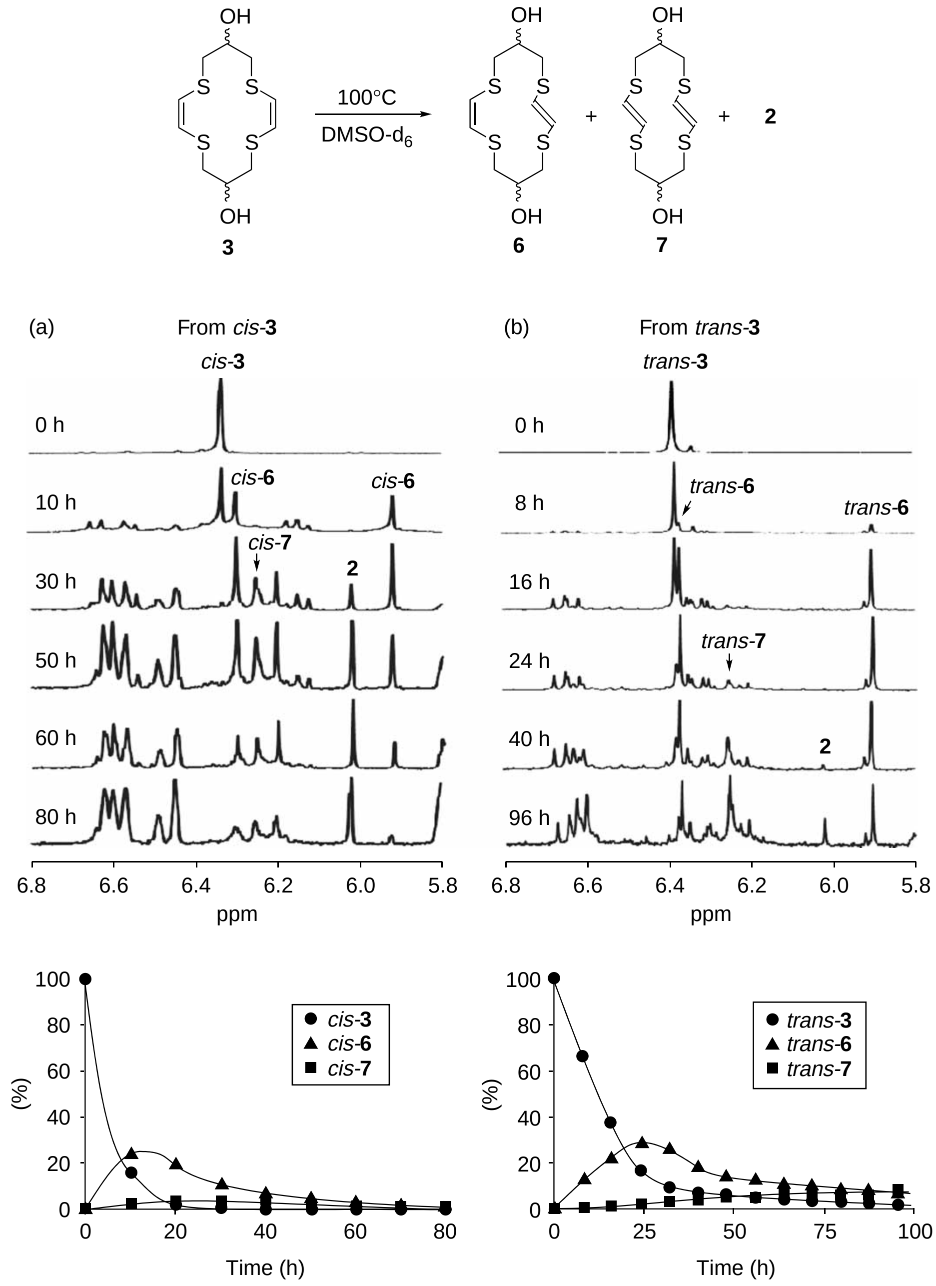

Figure 3. *Z,E*-Isomerization of (a) *cis*-**3** and (b) *trans*-**3** at 100°C in DMSO-d_6 in an NMR tube.

4.85 and 5.89 Å (Figure 1(a)).[3] The olefin moieties of *cis*-**3** are positioned on the same side of the molecular plane and this geometry is similar to that of the benzene-fused derivative (*8*), whereas the olefin moieties of the corresponding non-substituted derivative are directed to the opposite side of the plane (*9*). In the packing structure, the molecules make a columnar structure. The distance between the layers is 5.00 Å and the columns are connected by hydrogen bonds. The *trans*-isomer *trans*-**3** has a centre of symmetry in its molecule and the distances between the opposite sulphur atoms are 5.24 and 6.44 Å (Figure 1(b)).[4] In the packing structure, six oxygen atoms of different molecules are gathered via hydrogen bonds.

A trace amount of one of the 28-membered cyclic isomers *1,2-alternate*-**4** was also obtained as orange blocks by crystallisation from the geometrical mixture in chloroform, and the structure was determined by X-ray crystallographic analysis and ^{1}H NMR spectroscopy.[5] The X-ray analysis shows that all of the olefin moieties of *1,2-alternate*-**4** have the *Z*-geometry and the sulphur atoms are nearly coplanar (Figure 2). [6]The isomer has a symmetrical centre in its molecule and shows a slender structure. The distance between the farthest sulphur atoms is 14.29 Å and that between the nearest is 3.77 Å. Four sulphur atoms are oriented towards the inside of the molecule (endodentate) and another four sulphur atoms on an apsis are exodentate. In the crystalline state, the molecules of *1,2-alternate*-**4** are also connected to each other via hydrogen bonds.

The electrochemical oxidation of *cis*- and *trans*-**3** was examined. The cyclic voltammogram of *cis*-**3** was measured in acetonitrile at a platinum working electrode and two irreversible oxidation peaks at 0.55 and 1.09 V were observed. *Trans*-**3** also showed very similar oxidation peaks. The UV spectra of *cis*- and *trans*-**3** show absorption maxima at 256 and 253 nm, respectively, in acetonitrile.

When the thermal stabilities of 14-membered cyclic compounds *cis*- and *trans*-**3** were examined in an NMR tube, *Z,E*-isomerisation of the olefin moieties was observed. The ^{1}H NMR spectra of *cis*-**3** in DMSO-d_6 are shown in Figure 3. The spectrum slowly changed upon heating at 100°C and new signals assignable to *Z,E*-isomerised products *cis*-**6** and *cis*-**7** appeared together with that of ring-reduced compound **2**, with time. *Trans*-**3** also decomposed upon heating to afford *Z,E*-isomerised products, *trans*-**6** and *trans*-**7**; one of the isomerisation products *trans*-**6** was isolated and identified by ^{1}H and ^{13}C NMR spectra.

Supplementary Material

General procedures for the presented reactions, spectral data for compounds **1**, **2** and **5**, and method for cyclic voltammetry are available online.

Acknowledgements

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Notes

1. (*Z,Z*)-*cis*-1,4,8,11-Tetrathia-6,13-dihydroxycyclotetradec-2,9-diene (*cis*-**3**): mp 148°C (decomp., colourless needles from hexane-dichloromethane); ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.58 (dd, $J = 14.0, 9.0$ Hz, 4H), 2.95 (dd, $J = 14.0, 3.5$ Hz, 4H), 3.56–3.59 (m, 2H), 3.63 (d, $J = 3.0$ Hz, 2H), 6.39 (s, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 39.3, 68.9, 130.0; MS (EI, 70 eV) *m/z* 296 (M$^+$, 73%), 130 (39%), 103 (100%), 73 (66%); IR (KBr) $\nu_{\max}$ 3426, 2908, 2365, 2346, 1686, 1522, 1412, 1271, 1230, 1027, 996, 808, 756, 687 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_2S_4$, 40.51; H, 5.44. Found: C, 40.37; H, 5.45
2. (*Z,Z*)-*trans*-1,4,8,11-Tetrathia-6,13-dihydroxycyclotetradec-2,9-diene (*trans*-**3**): mp 128°C (decomp., pale yellow blocks from hexane-dichloromethane); ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.71 (dd, $J = 14.0, 8.0$ Hz, 4H), 2.91 (dd, $J = 14.0, 4.8$ Hz, 4H), 3.27 (d, $J = 3.0$ Hz, 2H), 3.75–3.80 (m, 2H), 6.43 (s, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 39.5, 69.7, 129.8; MS (EI, 70 eV) *m/z* 295 (M$^+$ − 1, 69%), 130 (70%), 103 (100%), 73 (99%); IR (KBr) $\nu_{\max}$ 3179, 2916, 2369, 2346, 1684, 1541, 1415, 1300, 1070, 1034, 991, 865, 815, 689, 676 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_2S_4$, 40.51; H, 5.44. Found: C, 40.67; H, 5.52
3. *Cis*-**3**: Compound *cis*-**3** crystallised in the monoclinic space group $P2_1$, with $a = 9.9681(17)$ Å, $b = 4.9997(6)$ Å, $c = 13.2482(19)$ Å, $b = 94.215(7)^{o}$, $V = 658.47(17)$ Å^3, $Z = 2$, and $Dc = 1.495$ g cm^{-3}. 5059 data collected with Mo Kα radiation ($\lambda = 0.71070$ Å) and $Fo > 2.0\sigma$ (I) were used in the least-squares refinement to yield $R = 0.076$, $R_w = 0.213$. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-780250
4. *Trans*-**3**: Compound *trans*-**3** crystallised in the trigonal space group *R*-3, with $a = 20.4290(13)$ Å, $b = 20.4290(13)$ Å, $c = 8.5863(7)$ Å, $V = 3103.3(4)$ Å^3, $Z = 9$, and $Dc = 1.428$ g cm^{-3}. 7623 data collected with Mo Kα radiation ($\lambda = 0.71070$ Å) and $Fo > 2.0\sigma$ (I) were used in the least-squares refinement to yield $R = 0.040$, $R_w = 0.099$. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-780684
5. (*Z,Z,Z,Z*)-*1,2-alternate*-1,4,8,11,15,18,22,25-Octathia-6,13,20,27-tetrahydroxycyclooctacos-2,9,16,23-tetraene (*1,2-alternate*-**4**): ^{1}H NMR (270 MHz, DMSO-d_6) δ 2.78 (dd, $J = 13.5, 6.2$ Hz, 8H), 2.78–2.89 (m, 8H), 3.61–3.72 (m, 4H), 5.27 (d, $J = 5.1$ Hz, 4H), 6.09 (s, 8H)
6. *1,2-Alternate*-**4**: Compound *1,2-alternate*-**4** crystallised in the monoclinic space group $P2_1$/n, with $a = 7.234(2)$ Å, $b = 9.968(3)$ Å, $c = 19.387(5)$ Å, $\beta = 98.563(5)^{o}$, $V = 1382.4(7)$ Å^3, $Z = 2$, and $Dc = 1.425$ g cm^{-3}. 7519 data collected with Mo Kα radiation ($\lambda = 0.71073$ Å) and $Fo > 2.0\sigma$ (I) were used in the least-squares refinement to yield $R = 0.105$, $R_w = 0.284$. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-780685

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