Proton-Ionizable Crown Compounds. 6. Synthesis and Structural Studies of New Crown Compounds Containing Sulfonamide Groups [1]

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Two new aza crown ethers, each containing two proton-ionizable sulfonamide groups, have been synthesized by reacting *o*-phenylenediamine with a *bis*-sulfonyl chloride. These compounds transport alkali metal cations in a water-methylene chloride-water liquid membrane system at source phase *p*H values above 12. The crystal structure of one of the crown compounds was determined.

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Introduction.

Since Pedersen first reported the synthesis of crown ethers [2], there have been many different modifications of the crowns in order to enhance the cation-complexation properties of these ligands. Pedersen prepared dibenzo- and dicyclohexano-18-crown-6 compounds [2]. Others have prepared crown compounds containing fused heterocyclic aromatic systems, and the cation-complexing properties of some of them have been studied [3-10]. The synthesis and complexing properties of these compounds have been extensively reviewed [4,8,11].

There has been considerable recent interest in crown compounds containing proton-ionizable groups. Most of the proton-ionizable crown ligands have a pendant arm containing a carboxyl or other proton-ionizable group [12-14] or the ionizable group extends into the macrocyclic ring cavity [15,16]. We are particularly interested in crown compounds which have the proton-ionizable function as part of the macrocyclic ring. To this end, we have prepared crown compounds containing the 4-hydoxypyridine (4-pyridone) and triazole subcyclic units (**1** and **2**, Figure 1) [17-20]. These compounds show promise for the coupling of proton transport with the opposite transport of cations in liquid membrane systems. In these compounds, either a cation or a proton is coordinated to the macrocycle ring. The proton-ionizable crown compound containing a 4-pyridone subcyclic unit (**1**) [19,21] transported potassium cations selectively over other alkali metal cations in a 1 *M* aqueous potassium hydroxide-methylene chloride-aqueous nitric acid (*p*H 1.5 and ~6) bulk membrane system

Scheme 1. Preparation of Intermediates and Macrocycles. Reagents and Conditions: i, KOH/1-Butanol; ii, Chlorosulfonic Acid at 0°; iii, Chloroform/Pyridine at −70°, *o*-Phenylenediamine.

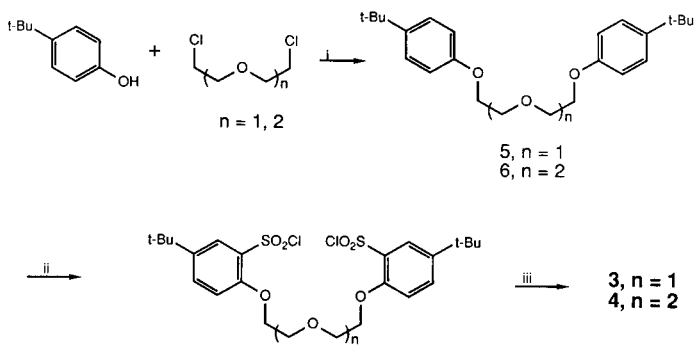
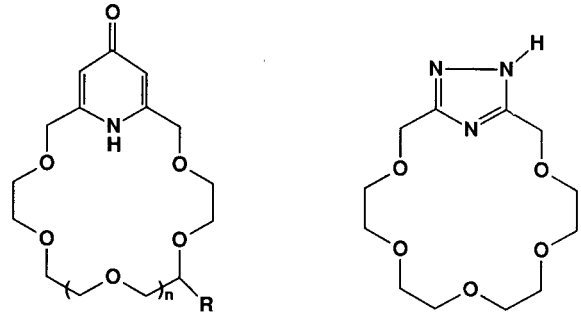


FIGURE 1. Structure of Crown Compounds



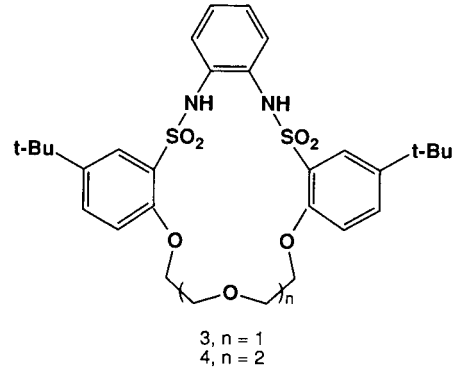
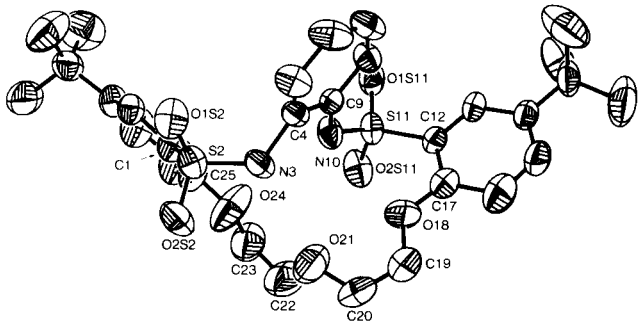


Figure 2. Computer Drawing of **3** With All Hydrogen Atoms Omitted For Clarity.



[22,23]. The transport of potassium was found to be dependent on the *p*H of the source phase with the best transport at *p*H values greater than 12. This *p*H value is slightly higher than the pK_a value (10.98) for the ionization of the proton from the unsubstituted analog of **1** [21].

We now report the preparation of two new crown compounds containing proton-ionizable sulfonamide groups (compounds **3** and **4**). These compounds are much more effective than **1** in transporting alkali metal cations through a methylene chloride membrane at source phase *p*H values of 14. A structural study of **3** is also included in this paper.

Results and Discussion.

Compounds **3** and **4** were prepared by the procedure shown in Scheme 1. Intermediates **5** and **6** were isolated in high yields. The yields of the macrocyclic compounds **3** and **4** were more moderate. The structures proposed for **3** and **4** are consistent with data obtained from ir, nmr and fd mass spectra and in the case of **3**, a crystal-structural determination. The combustion analyses for these compounds are consistent for compounds with about 0.5 moles of water. Indeed most of our crown compounds have contained water of hydration. Water was observed in the nmr spectrum for **3**.

The conformation of **3** is shown in Figure 2. The positional and isotropic thermal parameters for the non-hydrogen atoms and HN3 and HN10 are included in Table I. Bond lengths for **3** are given in Table II. There is a good agreement between the lengths of chemically similar bonds. The unusually short lengths reported in the "polyether" portion of the molecule are likely the result of a slight disorder. This is supported by the unusually large thermal motion of those atoms (see Table I). It was not possible to resolve the disorder in the difference maps. The aromatic rings of the molecule are nearly mutually perpendicular with the dihedral angles between the least-square planes of the benzene rings being, between C1 benzene and C4 benzene, 86.0°; between C1 benzene and C12 benzene, 83.6°; and between C4 benzene and C12 benzene, 80.1°. It was possible to locate positions for the hydrogens

Table I

Positional Parameters (× 10^4) and Thermal Parameters (× 10^3) for **3** with e.s.d. Values in Parentheses. Hydrogen atoms bonded to carbons are omitted.

atom	x	y	z	Ueq [a]
C1	12170(5)	1469(4)	3853(3)	55(2)
S2	12949(1)	355(1)	2951(1)	55(1)
O1S2	14357(3)	420(3)	2568(2)	70(1)
O2S2	12721(4)	−715(3)	3380(2)	78(2)
N3	12074(4)	633(3)	2061(3)	50(2)
HN3	11339(23)	504(34)	2224(27)	34(13) [b]
C4	12255(4)	1406(3)	1244(3)	44(2)
C5	13546(5)	1174(4)	596(3)	62(2)
C6	13755(5)	1844(4)	−240(4)	72(2)
C7	12673(6)	2740(4)	−442(4)	67(2)
C8	11375(5)	3010(4)	198(3)	57(2)
C9	11162(5)	2342(4)	1052(3)	45(2)
N10	9853(4)	2607(3)	1733(3)	59(2)
HN10	9656(33)	2072(20)	2006(22)	46(10) [b]
S11	8372(1)	3525(1)	1561(1)	55(1)
O1S11	8595(4)	4665(3)	1393(2)	75(2)
O2S11	7340(3)	3331(3)	2385(2)	76(2)
C12	8018(4)	3112(4)	452(3)	48(2)
C13	7688(4)	3941(4)	−263(3)	50(2)
C14	7351(5)	3671(4)	−1128(3)	56(2)
CT1	6973(6)	4603(5)	−1904(3)	74(2)
CT11	8311(7)	4906(7)	−2431(5)	154(5)
CT12	6211(12)	4271(8)	−2611(7)	212(7)
CT13	6051(8)	5759(6)	−1452(5)	134(4)
C15	7388(6)	2520(5)	−1245(4)	83(3)
C16	7718(6)	1671(5)	−544(4)	94(3)
C17	8040(6)	1960(4)	315(4)	75(3)
O18	8473(5)	1151(4)	1009(3)	123(3)
C19	7884(9)	328(7)	1307(6)	148(5)
C20	8331(9)	−362(7)	2075(5)	144(5)
O21	8972(5)	110(4)	2681(3)	113(2)
C22	8237(7)	360(7)	3624(5)	120(4)
C23	8677(7)	1150(6)	4162(4)	108(4)
O24	9975(4)	1189(5)	3815(3)	124(3)
C25	10722(5)	1762(5)	4219(4)	70(2)
C26	10139(6)	2607(5)	4947(4)	95(3)
C27	11031(7)	3084(5)	5328(4)	86(3)
C28	12485(6)	2783(4)	5007(3)	62(2)
CT2	13394(6)	3297(4)	5517(4)	74(3)
CT21	13298(8)	2856(7)	6584(4)	134(5)
CT22	14923(6)	3004(7)	4995(5)	126(4)
CT23	12838(9)	4628(5)	5587(5)	135(4)
C29	13029(5)	1978(4)	4242(3)	54(2)

[a] Equivalent isotropic thermal parameters are defined as 1/3 of the trace of the orthogonalised U_{ij} tensor. [b] Value is the normal isotropic thermal parameter U.

Table II

Important Bond Distances (Å) Between Atoms in **3**

C1-S2	1.770(6)	S11-O2S11	1.424(4)
S2-O1S2	1.427(4)	S11-C12	1.768(6)
S2-O2S2	1.423(5)	C12-C17	1.386(8)
S2-N3	1.623(6)	C17-O18	1.362(7)
N3-HN3	0.78(3)	O18-C19	1.281(11)
N3-C4	1.420(6)	C19-C20	1.371(11)
C4-C5	1.381(6)	C20-O21	1.384(11)
C4-C9	1.386(6)	O21-C22	1.361(8)
C9-N10	1.416(6)	C22-C23	1.444(12)
N10-HN10	0.77(3)	C23-O24	1.307(9)
N10-S11	1.637(5)	O24-C25	1.360(9)
S11-O1S11	1.428(5)	C25-C1	1.390(70)

Other Bonds

Average C-C aromatic	1.381(8)
Average C-C aliphatic	1.515(11)

Table III

Crystal and Experimental Data for **3**

Formula	$C_{30}H_{38}N_2O_7S_2$
Mr	602.7
F(000)	640
$\mu(cm^{-1})$	2.1
Crystal size (mm)	$0.2\times0.2\times0.3$
Space Group	$P\bar{1}$
a(Å)	10.071(10)
b(Å)	11.866(13)
c(Å)	13.791(12)
α(deg)	86.33(8)
β(deg)	77.87(8)
γ(deg)	73.83(8)
V(Å^3)	1548(3)
Z	2
d x (gcm^{-3})	1.29
sin θ/λ	0.60
total data	5731
observed unique data	3018
unobserved data	2375
Rm	0.015
R	0.065
Rw	0.063
ρ max eÅ^{-3}	0.28
ρ min eÅ^{-3}	−0.26

bonded to N3 and N10, HN3 and HN10, respectively. It is significant that both hydrogens point into the cavity of the ligand. The SO_2 groups are approximately perpendicular (114.3° for S2 sulfonyl and 100.2° for S11 sulfonyl) to the least-squares plane containing the heteroatoms of the ligand. The oxygen atoms of both groups are directed away from the cavity of the ligand. The polyether portion of the molecule containing atoms C17, O18 . . . O24, C25 has the same formula as one-half of a dibenzo-18-crown-6 molecule though the conformation of these atoms differs considerably from that of the simple crown.

Since the transport of metal ions by ligand 3 takes place only at *p*H values above 12 (see below), it seems likely that the hydrogens on the nitrogens must be removed prior to complexation and that the nitrogen atoms are coordinating atoms. Also, since the oxygen atoms of crown complexes are generally involved in coordination of metal ions it seems reasonable that O18, O21 and O24 are involved in coordinating a cation. The role of the SO_2 groups is not clear. The stereochemical constraints of being bonded to benzene rings tend to force the sulfur atoms into the cavity of the ligand where they are available to interact with the cation. However, the highly electronegative oxygen atoms would reduce the electron density near the sulfur atoms. It has been shown that potassium and rubidium ions will interact with sulfur donor atoms though likely not as strongly as with oxygen atoms [24]. Unfortunately, it has not been possible to prepare single crystals of the potassium complex of the ligand at the high *p*H values for complexation so the role of the sulfur atoms cannot be determined.

Compounds **3** and **4** were tested as carriers for cations in a water-methylene chloride-water bulk liquid membrane system using transport cells patterned after the Shulman Bridge and which have been described [25]. Compound **3** transported all alkali metal cations at source phase *p*H values of 12 or higher. The transport of potassium ions by **3** was more efficient than any other ligand we have tested. A complete report of cation transport using these new macrocyclic ligands will be reported when the work is completed.

EXPERIMENTAL

Infrared (ir) spectra were obtained on a Beckman Acculab 2 spectrometer. The proton nuclear magnetic resonance (nmr) spectra were obtained in a JEOL FX-90Q spectrometer. Field desorption (fd) mass spectra were obtained on Varian MAT 711 System. Crystal structure determinations were done on a Nicolet R3 autodiffractometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Starting materials were purchased from commercial sources where available.

1,5-Bis(4-*t*-butylphenoxy)-3-oxapentane (**5**).

A mixture of 45 g (0.3 mole) of p-*t*-butylphenol, 21.5 g (0.15 mole) of dichloroethyl ether, 18.6 g (0.33 mole) of potassium hydroxide and 50 ml of 1-butanol was stirred under reflux for 18 hours. After cooling, the potassium chloride was filtered and washed with acetone. The combined filtrates were evaporated under reduced pressure. The oily residue was dissolved in 200 ml of methylene chloride and washed with 5% aqueous potassium hydroxide and water. The organic solution was dried over anhy-

drous magnesium sulfate and filtered. The filtrate was evaporated under vacuum to give 52 g (94%) of a viscous oil which failed to crystallize (lit mp 34-35° [26]); nmr (carbon tetrachloride): δ 1.27 (s, 18H), 3.8 (t, J = 4 Hz, 4H), 4.0 (t, J = 4 Hz, 4H), 6.7 (d, J = 9 Hz, 4H), 7.2 (d, J = 9 Hz, 4H). This material was not further purified but was used to prepare **7**.

1,8-Bis(4-*t*-butylphenoxy)-3,6-dioxaoctane (**6**).

This compound was prepared as above using 1,8-dichloro-3,6-dioxaoctane to give a viscous oil (lit mp 32° [26]) in a 94% yield; nmr (carbon tetrachloride): δ 1.27 (s, 18H), 3.60 (s, 4H), 3.77 (m, 4H), 3.97 (m, 4H); 6.75 (d, J = 7 Hz, 4H), 7.20 (d, J = 7 Hz, 4H). This material was used to prepare **8** without further purification.

1,5-Bis(4-*t*-butyl-2-chlorosulfonylphenoxy)-3-oxapentane (**7**).

To 45 ml of stirring chlorosulfonic acid at 0° was added 22 g (59.5 mmoles) of **5** over a 30 minute period. The resulting mixture was stirred at 0° for an additional 2.5 hours. The mixture was then diluted with 200 ml of chloroform and poured onto 300 g of cracked ice. The aqueous layer was saturated with sodium chloride. The separated organic layer was washed twice with saturated brine and neutralized with saturated aqueous sodium bicarbonate. Ethyl ether (30 ml) was added to the mixture and the organic layer was separated and dried over anhydrous magnesium sulfate. The filtered organic phase was evaporated under reduced pressure to give 32 g (94%) of a crude solid. Part of the solid was recrystallized from dry ether, mp 123-125°; nmr (dimethyl sulfoxide-d_6): δ 1.24 (s, 18H), 3.80 (m, 4H), 4.10 (m, 4H), 6.92 (d, J = 9 Hz, 2H), 7.30 (2d, J = 9 Hz and J = 2.5 Hz, 2H), 7.72 (d, J = 2.5 Hz, 2H). This material was used without further purification to prepare **3**.

1,8-Bis(4-*t*-butyl-2-chlorosulfonylphenoxy)-3,6-dioxaoctane (**8**).

This material was prepared as above from **6** to give a crude solid which could not be recrystallized. The crude solid was used without further purification to prepare **4**.

4',5'''-Di-*t*-butyl-8,9,12,13,16,17-tribenzo-11,14-diaza-1,4,7-trioxa-10,15-dithiacycloheptadecane-10,10,15,15-tetraoxide (**3**).

Solutions of 16.2 g (28.6 mmoles) of impure bis-sulfonyl chloride **7** in 50 ml of chloroform and 3.09 g (28.6 mmoles) of *o*-phenylenediamine in anhydrous tetrahydrofuran were added simultaneously over an hour period to a stirring mixture of 100 ml of chloroform and 6 ml of pyridine at −70°. The resulting mixture was stirred for two hours at −70° and then slowly heated to reflux temperature and stirred an additional 30 minutes. The mixture was cooled and extracted twice with 2 *M* aqueous hydrochloric acid and with water. The organic phase was evaporated to give 14 g of crude product. The product was dissolved in a minimal amount of a 1/10 (v/v) mixture of methylene chloride and toluene and chromatographed on a silica gel column using a mixture of methylene chloride and toluene of increasing polarity, then chloroform and acetone of increasing polarity as eluants. The fractions containing a pure substance with a silica gel tlc R_f = 0.75 (chloroform-acetone, 2/1) were combined and evaporated to give a thick oil. The product crystallized when mixed with ether or isopropyl alcohol, 1.5 g (23%), mp 268-271°; ir (potassium bromide): 3440 (water), 3280 (NH), 1485, 1350, 1320, 1250, 1145, 1155, 1055, 905 cm^{-1}; nmr (dimethyl sulfoxide-d_6): δ 1.24 (s, 18H), 2.32 (s, ≈ 2H, water), 4.00 (m, 4H), 4.26 (m, 4H), 6.76-7.72 (m, 10H), 7.65 (s, 1H, NH), 8.94 (s, 1H, NH), the peaks at 2.32, 7.65 and 8.94 disappeared upon addition of dideuteriooxide. An additional 0.5 g of the product was obtained from the mother liquors (2g total, 23%). The water of hydration was removed by dissolving a small sample into a 1/1 mixture of acetic acid and acetone and allowing the solution to evaporate or by crystallization from methyl isobutyl ketone.

Anal. Calcd. for $C_{30}H_{38}N_2S_2O_7 \cdot \frac{1}{2}H_2O$: C, 58.89; H, 6.42; S, 10.48; M^+, 602.27 (anhydrous). Found: C, 59.10; H, 6.50; S, 10.39; M^+, 602.

4',5'''-Di-*t*-butyl-11,12,15,16,19,20-tribenzo-14,17-diaza-1,4,7,10-tetraoxa-13,18-dithiacycloeicosane-13,13,18,18-tetraoxide (**4**).

This compound was prepared as above for **3** using crude bis-sulfonyl chloride **8** and *o*-phenylenediamine to give a 10% yield, mp 302-305°; ir (potassium bromide): 3370, 3220, 1495, 1350, 1325, 1290, 1260, 1160, 1140, 1065, 945 cm^{-1}; nmr (dimethyl sulfoxide-d_6): δ 1.09 (s, 18H), 3.53 (m, 4H), 3.80 (m, 4H), 4.32 (m, 4H), 6.80-7.65 (m, 10H), 7.60 (s, 1H), 8.30 (s, 1H). Compound **4** was recrystallized from dimethylformamide.

Anal. Calcd. for $C_{32}H_{42}N_2S_2O_8 \cdot \frac{1}{2}H_2O$: C, 58.60; H, 6.61; S, 9.78; M^+, 646.82 (anhydrous). Found: C, 58.79; H, 6.59; S, 9.63; M^+, 646.

X-ray Determination.

A suitable crystal of **3** was mounted on the diffractometer which used graphite monochromated Mo radiation (λ = 0.71073 Å). Lattice parameters and the orientation matrix were obtained using a least-squares procedure involving 25 centered reflections 4.0° < 2θ < 20.2°. Crystal and experimental data are summarized in Table III. It was not possible to determine the space group unambiguously from diffraction data as it could be either P1 or $P\bar{1}$. However, the fact that the average $|E^2-1|$ was 1.01 and Z = 2, strongly suggested that the proper space group was the centrosymmetric $P\bar{1}$. This choice was supported by the successful solution of the structure. Intensity data were obtained using a variable speed (3.91 deg/min to 29.30 deg/min) θ-2θ scan technique to a sin θ/λ limit of 0.59. The hkℓ range was h = 0 to 11, k = −13 to +13 and ℓ = −16 to +16. Backgrounds were collected at the beginning and end of each scan with the total background counting time being equal to the scan time. Three standard reflections, which were measured every 100 reflections, showed no systematic change indicating crystal and electronic stability. A total of 5915 data were measured which included 184 standards and 338 equivalent pairs of 0kℓ data. The data merged to 5393 unique reflections with 2375 data being considered unobserved, I < 2 σ(I). Data were collected at laboratory temperature, 68° ± 2°. Lorentz-polarization corrections and an imperical extinction correction were applied to the data but no absorption correction was made (μ = 2.1 cm^{-1}). A trial model was obtained using direct methods. All non-hydrogen atoms were located in the E map. The hydrogen atoms HN3 and HN10 were located later in a difference map. Postions for the remaining hydrogen atoms were calculated using molecular geometery considerations. The hydrogens of the methyl groups were positioned using a rigid group refinement technique. All non-hydrogen atoms were refined anisotropically using a cascading blocked least-squares procedure. The hydrogen HN3 and HN10 were refined isotropically with the N-H bond distance constrained. The other hydrogen atoms were not refined but allowed to ride on their neighboring carbon atoms. The final residual values were R = 0.065 and Rw = 0.063 with weights based on counting statistics. Atomic scattering factors were obtained from the International Table for X-ray Crystallography [27]. All programs used in data collection and reduction and in the structure solution are contained in the Nicolet R3 system and SHELXTL program package [28].

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