Proton-Ionizable Crown Compounds. 10. Preparation and Structural Studies of Macrocyclic Ligands Containing Two Sulfonamide Units and With Seventeen to Twenty-Six Ring Members

Jerald S. Bradshaw*, Hiroyuki Koyama [1], N. Kent Dalley and Reed M. Izatt

Department of Chemistry, Brigham Young University,
Provo, UT 84602, USA

Jan F. Biernat* and Maria Bochenska

Institute of Inorganic Chemistry and Technology, Polytechnical University,
80-952 Gdansk, Poland

Received November 20, 1986

Eight new macrocylic ligands each containing two sulfonamide groups have been prepared. Six of these compounds have both the sulfur and nitrogen atoms of the sulfonamide units substituted with aromatic rings. The nitrogen atoms of the other two compounds have alkyl ring connections. X-ray crystal structure data were obtained for new macrocylic compounds of 20 and 23 ring members. Each crystal structure showed two molecules in the asymmetric unit. Molecule **A** of 5 and both molecules of **7** exist in a compact conformation suggesting that they could wrap around a metal ion during complexation. Some of these compounds will be used as cation carriers in a bulk liquid membrane system.

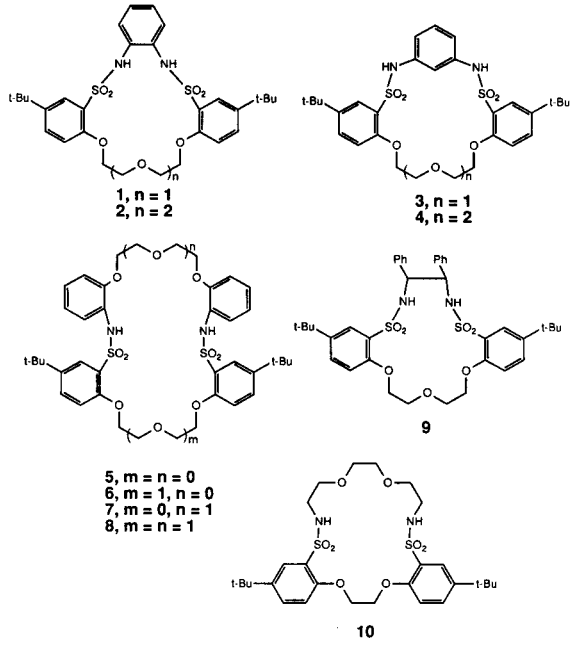
J. Heterocyclic Chem., **24**, 1077 (1987).

Introduction.

Macrocyclic ligands containing proton-ionizable functions are being studied by several research groups. Ligands containing a carboxyl or phenolic group on one or more pendant arms have been used extensively to transport metal cations from aqueous solutions into organic phases [2-6]. Others have used macrocyclic compounds containing phenolic groups wherein the hydroxy function is directed into the ring cavity [7,8].

We have prepared a variety of proton-ionizable compounds which have the ionizable group as part of the macroring cavity. Some of these include crown compounds containing the 4-pyridone [9,10] and triazole [11] subcyclic units. The 4-pyridono-containing crown compounds are excellent transport agents for the alkali metal cations in a water-methylene chloride-water bulk membrane system. Indeed, the crown-6 4-pyridono-containing ligand was found to be selective for potassium ions [12] while the crown-5 analog was selective for lithium ions in the bulk membrane system [13]. A crown containing a dialkylhydrogen phosphate group [14] has also been prepared. We have recently reported two *bis*-sulfonamido crown compounds **1** and **2** (Figure 1) which are excellent alkali metal cation carriers in bulk liquid membranes [15]. We now report the synthesis of additional sulfonamide-containing macrocyclic ligands, compounds **3-10**, (Figure 1), two of which do not have an aromatic group next to the sulfonamide nitrogen atoms. The crystal structures of two of the new compounds are also reported.

Figure 1. Structures of Macrocyclic Compounds

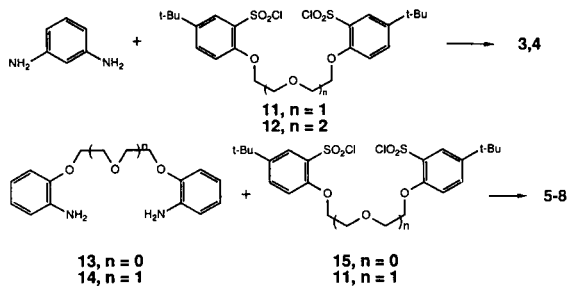


Results and Discussion.

The new sulfonamide-containing crown compounds include six with aromatic groups attached to the sulfonamide nitrogen atoms, **3-8**, and two with aliphatic groups on the nitrogen atom, **9** and **10**. These compounds were prepared by reacting the appropriate *bis*-sulfonyl chloride

and diamine-containing compounds as shown in Scheme I. The yields for these cyclization reactions were generally good and the compounds proved to be high melting solids as one would expect for sulfonamide-containing materials.

Scheme 1. Preparation of Crowns 3-8



The starting *bis*-sulfonyl chlorides **11**, **12**, and **15** (Scheme I) were prepared as reported [15] using the procedure of Bruson [16]. The aromatic amines **13** and **14** were prepared according to the procedure of Biernat and his coworkers [17]. The triethylene glycol diamine needed for the preparation of crown **10** was prepared from triethylene glycol ditosylate and ammonia as reported by King and Krespan [18].

Compound **1** was found to be an excellent carrier for potassium ions in a water-methylene chloride-water bulk liquid membrane system [19] at aqueous source phase *p*H values of 13.5 and higher. No transport was observed at aqueous source phase *p*H values of 10 or 11 even though one of the sulfonamide groups should be ionized. Dauphin and Kergomard reported the pK_a value of *N*-phenylbenzene sulfonamide to be 8.65 [20] so that at source phase *p*H of about 11, one of the protons would be ionized. It is likely that the second sulfonamide must be ionized before complexation takes place because the second proton would probably be hydrogen-bonded into the macrocyclic cavity. The pK_a value for removal of the second proton should be about 11.5 to 12.0. Thus, excellent transport of cations would be expected at *p*H values of 13 and higher which was observed for **1** [15,19].

Compounds **3** and **4** have amide nitrogen atoms in *meta*-positions on the benzene ring. In this case, hydrogen bonding of the second proton to the negatively charged amide nitrogen at source phase *p*H values above 11 would be impossible allowing for transport at lower *p*H values than 13.5. Furthermore, the hydrogen atom on the benzene ring between the two nitrogen atoms should provide steric hinderance so that ligands **3** and **4** probably will transport only small metal cations. Compounds **5-8** have the amide nitrogen atoms on separate benzene rings. These latter ligands may transport small cations at a lower aqueous source phase *p*H value since hydrogen bonding of the second proton would be across the macroring. Compounds **9** and **10** have aliphatic groups attached to the amide nitrogen which raises the pK_a value for removal of the proton to about 11.4 [20]. In this case, we do not expect transport until the aqueous source phase has a *p*H value of over 14. Indeed, preliminary results show that **9** does not transport potassium ions at source phase *p*H values of 14. A complete report on the cation transport by these interesting new ligands will be reported when the work is completed.

Computer drawings of x-ray crystal structures of **5** and **7** are shown in Figures 2 and 3, respectively. Atomic labels of the heteroatoms are included in the figures. The asymmetric unit of each structure contained two crystallographically different molecules. The two conformations, **A** and **B**, are designated by the last letter of the atom labels. The crystal structure of **5** also contained a methyl alcohol of solvation. The alcohol molecule does not interact with either macrocycle molecule of **5** and so is omitted from the figure. The atomic parameters of this molecule are included in the Table of atomic parameters of **5**. The atomic parameters of the heavy atoms of **5** and **7** are listed in Tables I and II respectively.

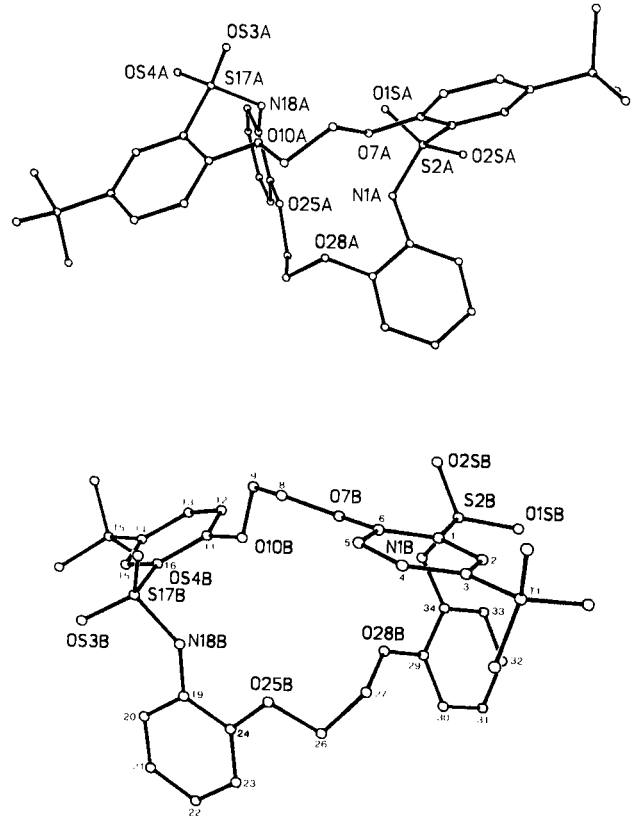


Figure 2. Conformations of the Two Molecules of **5**. The ring heteroatoms are labeled fully, the smaller numbers label the ring carbon atoms.

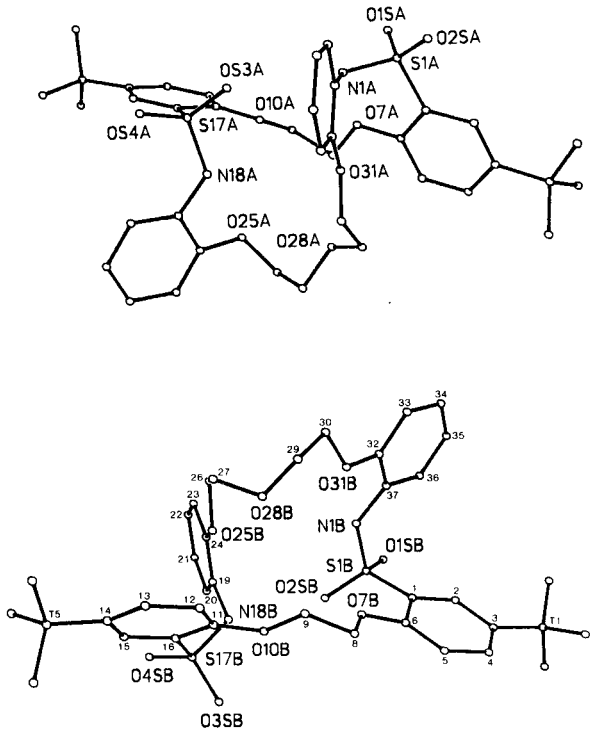


Figure 3. Conformations of the Two Molecules of **7**.

Table I

Positional Parameters (x 10^4) and Thermal Parameters (Å^2 x 10^3) for Atoms of **5** with e. s. d. Values in Parenthesis

atom	x	y	z	U
N1A	11668(6)	1364(3)	6982(8)	60(5)*
S1A	12191(2)	1706(1)	6578(3)	70(2)*
O1SA	11720(5)	1946(3)	5848(7)	86(5)*
O2SA	12849(5)	1534(3)	6171(8)	103(5)*
C1A	12486(4)	1971(2)	7737(5)	44(4)
C2A	13224(4)	2053(2)	7942(5)	62(4)
C3A	13447(4)	2304(2)	8806(5)	75(5)
C4A	12932(4)	2472(2)	9466(5)	67(5)
C5A	12194(4)	2389(2)	9261(5)	63(4)
C6A	11972(4)	2139(2)	8397(5)	53(4)
CT1A	14274(5)	2406(3)	9079(7)	120(7)
CT2A	14479(6)	2312(3)	10313(5)	145(8)
CT3A	14388(8)	2850(3)	8864(11)	172(9)
CT4A	14758(6)	2166(4)	8309(8)	140(7)
O7A	11256(4)	2036(2)	8213(7)	60(4)*
C8A	10735(6)	2197(4)	8900(10)	66(6)*
C9A	10059(6)	1955(4)	8760(10)	64(6)*
O10A	9758(5)	1990(3)	7659(7)	73(4)*
C11A	9049(3)	1874(2)	7452(7)	53(4)
C12A	8661(3)	1658(2)	8200(7)	64(4)
C13A	7955(3)	1535(2)	7904(7)	63(5)
C14A	7636(3)	1628(2)	6861(7)	51(4)
C15A	8025(3)	1844(2)	6113(7)	49(4)
C16A	8731(3)	1967(2)	6408(7)	45(4)
CT5A	6844(4)	1487(2)	6564(7)	80(5)
CT6A	6348(5)	1571(3)	7542(7)	126(7)
CT7A	6867(6)	1034(2)	6347(10)	121(7)
CT8A	6525(5)	1694(3)	5492(6)	89(5)

Table I (continued)

atom	x	y	z	U
S17A	9195(2)	2250(1)	5482(3)	56(2)*
O3SA	9457(5)	2590(2)	6050(7)	70(4)*
O4SA	8724(5)	2286(3)	4495(7)	69(4)*
N18A	9910(5)	2010(3)	5157(8)	48(4)*
C19A	9861(4)	1705(3)	4347(7)	54(4)
C20A	9749(4)	1797(3)	3223(7)	62(4)
C21A	9750(4)	1503(3)	2425(7)	86(5)
C22A	9863(4)	1118(3)	2751(7)	79(5)
C23A	9975(4)	1026(3)	3875(7)	77(5)
C24A	9974(4)	1320(3)	4673(7)	63(4)
O25A	10047(5)	1254(2)	5801(7)	67(4)*
C26A	10099(8)	858(4)	6183(11)	79(7)*
C27A	10007(8)	856(4)	7381(11)	85(7)*
O28A	10555(5)	1073(2)	8002(7)	69(4)*
C29A	11219(4)	899(3)	8161(8)	71(5)
C30A	11302(4)	575(3)	8853(8)	96(6)
C31A	11990(4)	414(3)	9074(8)	101(6)
C32A	12596(4)	576(3)	8603(8)	108(6)
C33A	12513(4)	900(3)	7911(8)	88(5)
C34A	11825(4)	1062(3)	7690(8)	56(4)
N1B	1472(5)	−281(3)	2614(8)	64(5)*
S1B	971(2)	112(1)	2586(3)	64(2)*
O1SB	700(5)	171(3)	1462(7)	77(4)*
O2SB	468(5)	61(3)	3439(8)	91(5)*
C1B	1546(4)	492(2)	2986(6)	49(4)
C2B	1644(4)	801(2)	2259(6)	52(4)
C3B	2071(4)	1118(2)	2603(6)	51(4)
C4B	2400(4)	1127(2)	3674(6)	78(5)
C5B	2303(4)	818(2)	4400(6)	81(5)
C6B	1876(4)	500(2)	4056(6)	79(5)
CT1B	2177(4)	1475(2)	1837(6)	91(5)
CT2B	3005(4)	1534(4)	1687(13)	230(12)
CT3B	1767(8)	1409(4)	685(7)	144(8)
CT4B	1862(8)	1848(3)	2382(11)	143(8)
O7B	1836(6)	158(3)	4671(7)	95(5)*
C8B	2018(9)	182(4)	5810(10)	104(8)*
C9B	1928(8)	−220(4)	6262(11)	98(8)*
O10B	2478(5)	−458(2)	5924(8)	86(5)*
C11B	2564(5)	−805(2)	6493(6)	65(5)
C12B	2036(5)	−1097(2)	6432(6)	75(5)
C13B	2172(5)	−1453(2)	6956(6)	73(5)
C14B	2835(5)	−1518(2)	7542(6)	59(4)
C15B	3363(5)	−1226(2)	7604(6)	58(4)
C16B	3227(5)	−870(2)	7079(6)	63(4)
CT5B	2935(4)	−1914(2)	8149(7)	94(6)
CT6B	2843(8)	−2255(3)	7294(9)	211(11)
CT7B	2333(6)	−1961(4)	9020(9)	230(12)
CT8B	3693(4)	−1936(4)	8776(11)	208(11)
S17B	3867(3)	−504(1)	7233(4)	83(2)*
O3SB	4473(6)	−659(3)	7865(9)	109(6)*
O4SB	3511(6)	−159(3)	7595(8)	117(6)*
N18B	4135(6)	−400(3)	6011(9)	77(5)*
C19B	4643(5)	−585(3)	5398(10)	72(5)
C20B	5083(5)	−889(3)	5810(10)	111(6)
C21B	5595(5)	−1056(3)	5144(10)	135(7)
C22B	5668(5)	−919(3)	4066(10)	136(7)
C23B	5229(5)	−616(3)	3653(10)	119(7)
C24B	4716(5)	−449(3)	4319(10)	94(6)
O25B	4214(5)	−192(3)	4031(7)	87(5)*
C26B	4225(6)	−80(5)	2902(12)	129(10)*
C27B	3548(6)	126(5)	2578(15)	163(11)*
O28B	2884(5)	−103(3)	2525(9)	107(5)*
C29B	2572(7)	−288(3)	1654(8)	96(6)

Table I (continued)

atom	x	y	z	U
C30B	2971(7)	−394(3)	749(8)	147(8)
C31B	2632(7)	−591(3)	−148(8)	104(6)
C32B	1894(7)	−683(3)	−141(8)	132(7)
C33B	1495(7)	−577(3)	764(8)	105(6)
C34B	1834(7)	−380(3)	1662(8)	65(5)
CM	4688(14)	979(8)	9664(21)	222(11)
OM	4784(12)	496(7)	9667(18)	339(11)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table II

Positional Parameters (x 10^4) and Thermal Parameters (Å^2 x 10^3) for Atoms of **7** with e. s. d. Values in Parenthesis

atom	x	y	z	U
N1A	6469(8)	2101(5)	2295(7)	44(6)*
S1A	6244(3)	1670(2)	2901(3)	43(2)*
O1SA	5362(7)	1677(5)	2976(7)	57(6)*
O2SA	6661(7)	1240(4)	2652(7)	51(5)*
C1A	6678(5)	1819(3)	3808(4)	31(5)
C2A	7210(5)	1495(3)	4203(4)	44(6)
C3A	7550(5)	1622(3)	4922(4)	38(5)
C4A	7359(5)	2074(3)	5246(4)	33(5)
C5A	6826(5)	2398(3)	4851(4)	45(6)
C6A	6486(5)	2270(3)	4132(4)	42(6)
CT1A	8158(7)	1271(4)	5380(7)	92(8)
CT2A	7801(11)	1176(7)	6196(8)	108(9)
CT3A	8253(12)	780(5)	4943(11)	137(11)
CT4A	9045(8)	1520(7)	5471(11)	121(10)
O7A	5956(7)	2578(4)	3741(7)	49(5)*
C8A	5850(14)	3054(7)	4035(11)	63(9)*
C9A	5096(13)	3297(7)	3605(11)	62(10)*
O10A	5314(8)	3365(5)	2843(7)	56(5)*
C11A	4828(5)	3673(3)	2377(5)	44(5)
C12A	4044(5)	3829(3)	2630(5)	47(6)
C13A	3581(5)	4171(3)	2202(5)	51(6)
C14A	3902(5)	4356(3)	1521(5)	42(6)
C15A	4686(5)	4200(3)	1268(5)	48(6)
C16A	5149(5)	3858(3)	1696(5)	33(5)
CT5A	3396(7)	4760(4)	1072(7)	60(6)
CT6A	2632(10)	4517(7)	637(11)	131(11)
CT7A	3077(12)	5152(6)	1645(10)	130(11)
CT8A	3976(11)	5010(7)	471(10)	125(10)
S17A	6080(3)	3612(2)	1369(3)	44(2)*
O3SA	6076(8)	3087(4)	1396(7)	57(5)*
O4SA	6222(7)	3831(5)	640(6)	53(5)*
N18A	6830(8)	3784(5)	1968(8)	46(6)*
C19A	7083(7)	4282(4)	2082(8)	39(5)
C20A	7282(7)	4584(4)	1465(8)	48(6)
C21A	7620(7)	5047(4)	1601(8)	66(7)
C22A	7759(7)	5208(4)	2354(8)	103(9)
C23A	7560(7)	4907(4)	2971(8)	81(8)
C24A	7222(7)	4444(4)	2835(8)	59(7)
O25A	6941(9)	4138(5)	3384(5)	102(8)*
C26A	7433(16)	4094(9)	4078(10)	150(19)*
C27A	8234(16)	3810(8)	4003(20)	230(29)*
O28A	7913(10)	3330(7)	3929(9)	108(9)*
C29A	8528(14)	2949(9)	3776(12)	101(13)*
C30A	8649(14)	2812(9)	2959(13)	104(13)*
O31A	7881(9)	2597(5)	2761(8)	76(7)*
C32A	7933(9)	2356(4)	2076(6)	56(6)

Table II (continued)

atom	x	y	z	U
C33A	8642(9)	2349(4)	1614(6)	71(7)
C34A	8632(9)	2076(4)	937(6)	93(8)
C35A	7914(9)	1810(4)	720(6)	94(8)
C36A	7206(9)	1818(4)	1182(6)	74(7)
C37A	7215(9)	2091(4)	1860(6)	43(6)
N1B	9159(8)	8642(5)	3140(8)	48(6)*
S1B	8308(3)	8433(2)	3500(3)	48(2)*
O1SB	8287(8)	8585(5)	4286(7)	61(6)*
O2SB	8274(8)	7919(5)	3322(7)	61(6)*
C1B	7500(4)	8741(3)	3014(4)	28(5)
C2B	7027(4)	9079(3)	3423(4)	39(5)
C3B	6312(4)	9291(3)	3081(4)	44(5)
C4B	6069(4)	9165(3)	2331(4)	56(6)
C5B	6542(4)	8827(3)	1922(4)	48(6)
C6B	7257(4)	8615(3)	2264(4)	37(5)
CT1B	5809(8)	9707(4)	3472(8)	86(8)
CT2B	6403(14)	9998(7)	4032(12)	191(15)
CT3B	5069(12)	9482(8)	3933(14)	199(16)
CT4B	5433(15)	10061(7)	2849(12)	195(15)
O7B	7795(7)	8318(5)	1894(7)	55(5)*
C8B	7653(12)	8249(7)	1091(12)	58(9)*
C9B	8374(12)	7988(7)	714(10)	45(9)*
O10B	8453(7)	7509(5)	1055(6)	46(5)*
C11B	8985(5)	7179(3)	702(5)	38(5)
C12B	9340(5)	7273(3)	−10(5)	49(6)
C13B	9811(5)	6914(3)	−373(5)	47(6)
C14B	9928(5)	6460(3)	−23(5)	39(5)
C15B	9574(5)	6365(3)	689(5)	46(6)
C16B	9102(5)	6725(3)	1051(5)	42(5)
CT5B	10369(8)	6051(4)	−496(7)	79(7)
CT6B	11019(13)	6287(7)	−1046(11)	216(17)
CT7B	10837(12)	5682(6)	44(10)	100(9)
CT8B	9685(13)	5770(7)	−986(12)	183(14)
S17B	8644(3)	6595(2)	1927(3)	42(2)*
O1SB	7744(7)	6616(5)	1787(7)	59(5)*
O2SB	9021(7)	6158(4)	2212(7)	52(5)*
N18B	8873(8)	7032(5)	2534(7)	36(6)*
C19B	9584(7)	7015(4)	3059(6)	36(5)
C20B	9499(7)	6789(4)	3773(6)	54(6)
C21B	10171(7)	6791(4)	4304(6)	60(6)
C22B	10929(7)	7018(4)	4122(6)	62(7)
C23B	11014(7)	7243(4)	3409(6)	47(6)
C24B	10342(7)	7242(4)	2877(6)	47(6)
O25B	10362(8)	7441(5)	2163(7)	59(6)*
C26B	11115(11)	7711(7)	1984(9)	55(9)*
C27B	11053(11)	7865(7)	1159(8)	56(9)*
O28B	10380(8)	8203(5)	1001(7)	66(6)*
C29B	10589(15)	8696(7)	842(8)	103(12)*
C30B	10765(14)	8998(7)	1539(8)	88(11)*
O31B	10098(10)	8953(5)	2033(8)	91(7)*
C32B	10009(9)	9260(5)	2623(7)	67(7)
C33B	10387(9)	9719(5)	2654(7)	77(8)
C34B	10223(9)	10034(5)	3264(7)	91(8)
C35B	9682(9)	9889(5)	3842(7)	76(7)
C36B	9304(9)	9429(5)	3811(7)	68(7)
C37B	9467(9)	9115(5)	3202(7)	44(6)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

The conformations of the two molecules of **5**, a crown with 20 ring members, differ considerably from one another. Conformer **A** is more compact while **B** has a

more open conformation similar to smaller crown compounds with planar cavities. These differences are apparent in Figure 2. Another indicator of the difference in conformations are the N1-N18 interatomic distances. In conformer **A**, the interatomic distance between nitrogen atoms is 4.412 Å while the similar distance in molecule **B** is 6.225 Å. Conformer **A** appears to have the potential of forming a wrap around coordination of a metal ion similiar to the type of coordination found in the potassium ion-30-crown-10 complex [21].

The two independent conformers of **7** (Figure 3) are considerably more similiar than those of **5** (Figure 2). This molecule is a crown with 23 ring members so that there are three more atoms in the ring than found in the ring of **5**. The added atoms give the molecule an increased flexibility. The two conformers are cup shaped with the nitrogen atoms at the opening of the cup. The nitrogen-nitrogen interatomic distances of conformers **A** and **B** are 4.679 Å and 4.556 Å, respectively. Thus, **7** appears even more likely than **5** to wrap around a metal cation. Both **5** and **7** contain O-C-C-O atomic groups which are found in crown ether molecules. The bond lengths in these groups are similar to those found in the crown compounds. The average bond lengths involving these atoms as well as the other atoms of the macrocyclic ring are found in Table III. There are some short N-O intramolecular interatomic distances which suggest possible hydrogen bonding. However, it was not possible to locate hydrogen atoms in the difference map and also not possible to calculate positions for hydrogen atoms bonded to nitrogen atoms without ambiguity. Thus, we cannot determine if hydrogen bonds are present in these complexes.

Table III

Average Bond Length for Similar Atom Groups for Atoms in the Rings of **5** and **7**. Values in Parenthesis are Standard Deviations

Bond Type	Number of Bonds in Rings	Bond Length (Å)
N-S	8	1.62(1)
$S\text{-}C_{aromatic}$	8	1.736(9)
$O\text{-}C_{aromatic}$	16	1.36(2)
$O\text{-}C_{aliphatic}$ [a]	20	1.42(2)
$C_{aliphatic}\text{-}C_{aliphatic}$ [b]	10	1.50(2)
$N\text{-}C_{aromatic}$	8	1.41(3)

[a] Average includes bonds 025A-C26A and C27A-O28A of **7** which were refined to a bond distance value of 1.42 Å. [b] Average includes bonds C26B-C27B of **5** and C26A-C27A, C29A-C30H, C26B-C27B and C29B-C30A of **7** which were refined to a bond length value of 1.50 Å.

Table IV

Crystal and Experimental Data for **5** and **7**

	5	**7**
Formula	$C_{36}H_{42}N_2O_8S_2 \cdot \frac{1}{2}CH_3OH$	$C_{38}H_{46}N_2O_9S_2$
Mr	711.0	738.9
F(000)	3016	3136
u, cm^{-1}	1.80	1.87
Crystal size, mm	.20 x .30 x .40	.20 x .20 x .15
Space group	$P2_1/c$	$P2_1/a$
a, Å	18.402 (6)	15.854 (4)
b, Å	34.392 (11)	27.386 (4)
c, Å	12.051 (3)	17.388 (4)
β, deg	93.14 (2)	91.26 (2)
V, $Å^3$	7615 (3)	7547 (2)
Z	8	8
dx, g cc^{-1}	1.24	1.30
Sin θ/λ limit	0.48	0.48
Mo Kα, Å	0.71073	0.71073
Unique Reflections	6994	7041
Observed Reflections	3932	2912
R	0.109	0.1081
R_w	0.097	0.116
Max and min peaks in Δ map	0.65, -0.52	0.75, -0.45
ave shift/esd	0.04	0.04

EXPERIMENTAL

Infrared (ir) spectra were obtained on a Beckman Acculab 2 spectrometer. Nuclear magnetic resonance (nmr) spectra were obtained on a JEOL FX-90Q spectrometer using deuteriochloroform as a solvent unless otherwise stated. Molecular weights were carried out on a Perkin-Elmer model 115 molecular weight apparatus. Crystal structure determinations were done on a Nicolet R3 autodiffractometer. Field desorption (fd) mass spectra were obtained on a Varian MAT 711 System. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona. Melting points were carried out on a Thomas-Hoover melting point apparatus and are uncorrected. 1,5-*Bis*(4-*t*-butyl-2-chlorosulfonylphenoxy)-3-oxapentane (**11**) and 1,8-*bis*(4-*t*-butyl-2-chlorosulfonylphenoxy)-3,6-dioxaoctane (**12**) were prepared as reported [15]. 1,2-*Bis*(2-aminophenoxy)ethane (**13**) was prepared by a hydrazine reduction of the corresponding dinitro compound as reported [17,22]. 1,5-*Bis*(2-aminophenoxy)-3-oxapentane (**14**) was prepared as reported by Högberg and Cram [23]. The other starting materials were prepared as outlined below.

1,2-*Bis*(4-*t*-butylphenoxy)ethane.

Sodium metal (4.6 g, 0.20 mole) was reacted with 80 ml of ethanol. After the metal had reacted, 30.0 g (0.20 mole) of 4-*t*-butylphenol in 60 ml of ethanol was added slowly. The resulting mixture was stirred for 20 minutes and the ethanol was removed under reduced pressure. The residue was dissolved in 260 ml of dimethylformamide and 33.3 g (0.09 mole) of ethylene glycol ditosylate was added to the solution. The mixture was stirred at 150° for 36 hours. Water (1 *l*) was added to the mixture and the resulting precipitate was filtered and recrystallized from ethanol, 23.4 g (80%), mp 88.5-89°; nmr: δ 1.30 (s, 18H), 4.28 (s, 4H), 6.89 (d, 4H, J = 9.6 Hz), 7.32 (d, 4H, J = 9.6 Hz). Compound **15**, a derivative of this material, gave a satisfactory elemental analysis.

1,2-*Bis*(4-*t*-butyl-2-chlorosulfonylphenoxy)ethane (**15**).

1,2-*Bis*(4-*t*-butylphenoxy)ethane (9.8 g, 0.03 mole) was dissolved in 60 ml of chloroform and the solution was cooled to -5°. Chlorosulfonic acid (28.0 g, 0.24 mole) was added to the stirring solution at a rate so that the temperature of the reaction mixture remained below 0°. After the addition, the mixture was stirred for 30 minutes at -5° to 0° and then poured onto 200 ml of ice which was stirred vigorously. Chloroform (100 ml) was added to the stirring ice solution. The organic layer was separated, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The residue was chromatographed on a short silica gel column using toluene as eluent to give 2.7 g (17%) of **15**, mp 187-188°; ir (potassium bromide): 1365, 1170 and 810 cm^{-1}; nmr: δ 1.32 (s, 18H), 4.66 (s, 4H), 7.24 (d, 2H, J = 8.5 Hz), 7.72 (dd, 2H, J = 8.5 Hz, J = 2.5 Hz), 7.92 (d, 2H, J = 2.5 Hz).

Anal. Calcd. for $C_{22}H_{26}Cl_2S_2O_6$: C, 50.48; H, 5.39; S, 12.25. Found: C, 50.48; H, 5.47; S, 12.13.

1,8-Diamino-3,6-dioxaoctane.

Triethylene glycol ditosylate (22.9 g, 0.05 mole) was stirred in a mixture of 200 ml of 28-30% aqueous ammonium hydroxide and 200 ml of dioxane for 5 days. Potassium hydroxide (6.2 g, 0.11 mole) was added and the resulting mixture was stirred overnight. The solvents were evaporated under reduced pressure and the residue was triturated with dichloromethane. The organic solution was dried over anhydrous magnesium sulfate and the solvent was evaporated to give a brown oil. The oil was distilled to give 1.8 g (25%) of product, bp 83-85°/0.6 mm (lit bp 73-79°/0.1 mm [18]).

Preparation of Macrocyclic Compounds **3-10**.

One of the compounds **11**, **12**, or **15** (0.0025 mole) and 0.005 mole of the appropriate diamine were each dissolved in 200 ml of dichloromethane. The two solutions were simultaneously dripped into 400 ml of vigorously stirring dichloromethane over a period of 4 hours. The reaction mixture was stirred under reflux for 8 days. In the case of **10**, the reaction time was 24 hours. The precipitates were filtered and the filtrate was evaporated to give a solid product. The products were purified as indicated below.

5',4''-Di-*t*-butyl-4,5,13,14-dibenzo-2,16-diaza-6,9,12-trioxa-3,15-dithiabicyclo[15.3.1]henicosa-17,19,21(1)-triene-3,3,15,15-tetraoxide (**3**).

Compound **3** was chromatographed on silica gel using methylene chloride and then chloroform to give 0.18 g (12%) of an oil which crystallized on standing under ethyl ether, mp 230-232°; ir (nujol): 3190 cm^{-1}; nmr: δ 1.2 (s, 18H), 4.15 (m, 4H), 4.4 (m, 4H), 6.7-7.9 (m, 12H).

Anal. Calcd. for $C_{30}H_{38}N_2S_2O_7$: C, 59.78; H, 6.35; S, 10.64; M^+, 602.77. Found: C, 59.87; H, 6.19; S, 10.49; M^+, 602.

5',4''-Di-*t*-butyl-4,5,16,17-dibenzo-2,19-diaza-6,9,12,15-tetraoxa-3,18-dithiabicyclo[18.3.1]tetracosa-20,22,24(1)-triene-3,3,18,18-tetraoxide (**4**).

Compound **4** was purified as above for **3** to give 0.27 g (17%) of a solid material, mp 256-259°; ir (nujol): 3220 cm^{-1}; nmr (dimethylsulfoxide-d_6): δ 1.2 (s, 18H), 3.7 (m, 8H), 4.15 (m, 4H), 6.85-7.7 (m, 10H), 9.18 (s, 2H, disappeared in dideuterium oxide).

Anal. Calcd. for $C_{32}H_{42}N_2S_2O_8$: C, 59.42; H, 6.54; S, 9.91, M^+, 646.82. Found: C, 59.44; H, 6.34; S, 9.66; M^+, 646.

4',5''''-Di-*t*-butyl-5,6,9,10,15,16,19,20-tetrabenzo-8,17-diaza-1,4,11,14-tetraoxa-7,18-dithiacycloicosane-7,7,18,18-tetraoxide (**5**).

Compound **5** was chromatographed on silica gel using dichloromethane/acetone (99:1) as eluant to give 1.21 g (70%) of colorless crystals. The product was recrystallized from ethanol, mp 229-229.5°; ir (potassium bromide): 3330 and 3320 cm^{-1}; nmr: δ 1.25 (s, 18H), 3.99 (s, 4H), 4.59 (s, 4H), 6.87 (m, 6H), 7.01 (d, 2H, J = 9.6 Hz), 7.51 (dd, 2H, J = 9.6 Hz, J = 2.6 Hz), 7.49 (m, 2H), 7.75 (s, 2H, signal disappeared in dideuterium oxide), 7.84 (d, 2H, J = 2.6 Hz).

Anal. Calcd. for $C_{36}H_{42}N_2S_2O_8$: C, 62.23; H, 6.09; S, 9.23; mol wt, 694.87. Found: C, 62.11; H, 6.22; S, 9.40, mol wt, 738.

4',5''''-Di-*t*-butyl-8,9,12,13,18,19,22,23-tetrabenzo-11,20-diaza-1,4,7,14,-17-pentaoxa-10,21-dithiacyclotricosane-10,10,21,21-tetraoxide (**6**).

Compound **6** was purified as above for **3** to give 0.12 g (6%) of white crystals, mp 277-279°; ir (nujol): 3250 cm^{-1}; nmr: δ 1.23 (s, 18H), 3.77 (m, 4H), 4.05 (m, 8H), 6.5-7.9 (m, 14H), 8.0 (s, 2H, disappeared in dideuterium oxide).

Anal. Calcd. for $C_{38}H_{46}N_2S_2O_9$: C, 61.77; H, 6.28; S, 8.68; M^+, 738.92. Found: C, 61.59; H, 6.23; S, 8.43; M^+, 738.

4',5''''-Di-*t*-5,6,9,10,18,19,22,23-tetrabenzo-8,20-diaza-1,4,11,14,17-pentaoxa-7,21-dithiacyclotricosane-7,7,21,21-tetraoxide (**7**).

Compound **7** was purified as above for **5** to give 1.68 g (91%) of **7**. The product was recrystallized from ethanol, mp 183-183.5°; ir (potassium bromide): 3290 and 3250 cm^{-1}; nmr: δ 1.23 (s, 18H), 3.73 (m, 4H), 4.13 (m, 4H), 4.57 (s, 4H), 6.88 (m, 6H), 6.90 (d, 2H, J = 8.5 Hz), 7.42 (dd, 2H, J = 8.5 Hz, J = 2.6 Hz), 7.51 (m, 2H), 7.82 (d, 2H, J = 2.6 Hz), 7.88 (s, 2H, signal disappeared in dideuterium oxide).

Anal. Calcd. for $C_{38}H_{46}N_2S_2O_9$: C, 61.77; H, 6.28; S, 8.68; mol wt, 738.92. Found: C, 61.69; H, 6.16; S, 8.50; mol wt 789.

4',5''''-Di-*t*-butyl-8,9,12,13,21,22,25,26-tetrabenzo-14,23-diaza-1,4,7,14,-17,20-hexaoxa-13,24-dithiacyclohexacosane-13,13,24,24-tetraoxide (**8**).

Compound **8** was purified as above for **3** to give 0.24 g (10%) of a white powder, mp 164-165°; ir (nujol): 3240 cm^{-1}; nmr: δ 1.26 (s, 18H), 3.72 (m, 4H), 4.24 (s, 8H), 4.32 (m, 4H), 6.91 (m, 8H), 7.45 (m, 2H), 7.88 (d, 1H), 8.12 (s, 2H, signal disappeared in dideuterium oxide).

Anal. Calcd. for $C_{40}H_{50}N_2S_2O_{10}$: C, 61.36; H, 6.44; S, 8.19; M^+, 782.93. Found: C, 61.50; H, 6.52; S, 8.40; M^+, 783.

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

Compound **9** was purified as above for **3** to give an 8.8% yield of white crystals, mp 183-186°; ir (nujol): 3310 cm^{-1}; nmr: δ 1.25 (s, 18H), 3.8-4.7 (m, 10H), 6.0 (d, 2H, J = 8 Hz), 6.6-7.9 (m, 16H).

Anal. Calcd. for $C_{38}H_{46}N_2S_2O_7$: C, 64.46; H, 6.56; M^+, 706.92. Found: C, 64.64; H, 6.66; M^+, 706.

4',5''-Di-*t*-butyl-5,6,19,20-dibenzo-8,17-diaza-1,4,11,14-tetraoxa-7,18-dithiacycloeicosane-7,7,18,18-tetraoxide (**10**).

Compound **10** was chromatographed on silica gel using dichloromethane/acetone (49:1) as eluant to give 1.07 g (72%) of colorless crystals. The product was recrystallized from ethanol, mp 251.5-252°; ir (potassium bromide): 3340 and 3290 cm^{-1}; nmr: δ 1.32 (s, 18H), 3.30 (m, 12H), 4.52 (s, 4H), 5.73 (t, 2H, signal disappeared in dideuterium oxide), 7.08 (d, 2H, J = 8.5 Hz), 7.57 (dd, 2H, J = 8.5 Hz, J = 2.6 Hz), 7.92 (d, 2H, J = 2.6 Hz).

Anal. Calcd. for $C_{28}H_{42}N_2S_2O_6$: C, 56.17; H, 7.07; S, 10.71; mol wt, 598.78. Found: C, 56.30; H, 7.17; S, 10.46; mol wt, 597.

X-Ray Determination.

Suitable crystals of **5** and **7** were obtained by a carefully recrystallization from ethanol. The crystals were not dried. Crystal and intensity data were obtained using a Nicolet R3 automated diffractometer which used graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Lattice parameters and the orientation matrix for each crystal were obtained using a least-squares procedure involving 23 centered reflections ($8.5 < 2\theta < 21.5$) for 5 and 25 reflections ($8.1 < 2\theta < 22.3$) for **7**. Crystal data and experimental conditions for both compounds are listed in Table IV. Intensity data for the two studies were obtained using a variable scan rate (3.9 deg/min to 29.3 deg/min) θ-2θ scan procedure. Backgrounds were collected at the beginning and end of each scan with the scan time equal to the total background counting time. Both cells were large as there are 8 molecules in the unit cell for each structure. Some of the reflections were not resolved particularly in the case of **5**, with the b axis of about 34 Å. For this reason many of the data with small h and ℓ values were omitted from the refinement. Data were collected to a 2θ limit of 40° as there were relatively few observable reflections beyond that limit. This did not allow a favorable variable to parameter ratio, and for this reason many of the atoms of the molecules were refined isotropically. Both structures were solved using direct methods. A later difference map of **5** revealed a molecule of methanol in the crystal structure. The structures were refined using a cascading blocked least-squares refinement procedure. During the refinement process, the benzo groups and the *t*-butyl groups were refined as rigid idealized groups. These same atoms along with the methanol molecule in **5** were refined isotropically. The other non-hydrogen atoms were refined anisotropically. Positions for hydrogen atoms bonded to ring carbons were calculated based on sp^2 and sp^2 geometry. It was not possible to calculate positions of hydrogen atoms bonded to nitrogens because of the non-bonding electrons on the nitrogen atoms. Parameters of these atoms were not refined. Hydrogen

atoms bonded to ring atoms were allowed to ride on their neighboring atom. The thermal parameters were set to approximately 1.2 times the U_{iso} or U_{eq} of the heavy atom to which they were bonded. An emperical extinction correction was applied to both data sets. Weights were based on counting statistics. Several of the atoms had very large thermal motion (See Tables I and II), especially some terminal carbon atoms of the tertiary butyl groups and the atoms in the vicinity of C26 and C27 in both molecules. The large U_{iso} or U_{eq} value probably indicates some disorder, but it was not possible to resolve the disorder in difference Fourier maps. Because of the probable disorder, a restraint was imposed upon the C-C bond lengths of the butyl groups and interatomic distances in the vicinity of the disorder in the ring, and these distances were refined to about 1.54 Å for a C-C bond in the butyl group, 1.50 Å for a C-C bond in the ring and 1.42 Å for a C-O bond in the ring. Atomic scattering factors were obtained from Volume IV of the International Tables for X-ray Crystallography [24]. All programs used in solving, refining and displaying these structures are contained in the SHELXTL [25] computer package.

Acknowledgement.

Financial support by the U. S. Department of Energy, Office of Basic Energy Sciences Grant No. DE-AC02-78ER05016 and by Polish Project No. CPBP 0.1.15.3.05 is gratefully acknowledged.

REFERENCES AND NOTES

[1] Permanent address for H. K.: College of General Education, Kyushu University, Roppanmatsu, Fukuoka, 810 Japan.

[2] B. Czech, S. I. Kang and R. A. Bartsch, *Tetrahedron Letters*, 457 (1983).

[3] R. A. Bartsch, B. P. Czech, S. I. Kang, L. E. Stewart, W. Walkowiak, G. S. Heo and B. Son, *J. Am. Chem. Soc.*, **107**, 4997 (1985).

[4] R. C. Helgeson, J. M. Timko and D. J. Cram, *J. Am. Chem. Soc.*, **95**, 3023 (1973).

[5] L. M. Dulyea, T. M. Fyles and D. M. Whitfield, *Can. J. Chem.*, **62**, 498 (1984).

[6] C. Thomas, C. Sauterey, M. Castaing, C. M. Gary-Bobo, J. M. Lehn and P. Plumere, *Biophys. Res. Commun.*, **116**, 981 (1983).

[7] C. M. Browne, G. Ferguson, M. A. McKervey, D. L. Mulholland, T. O'Connor and M. Parvez, *J. Am. Chem. Soc.*, **107**, 2703 (1985).

[8] S. R. Izatt, R. T. Hawkins, J. J. Christensen and R. M. Izatt, *J. Am. Chem. Soc.*, **107**, 63 (1985).

[9] J. S. Bradshaw, Y. Nakatsuji, P. Huszthy, B. E. Wilson, N. K. Dalley and R. M. Izatt, *J. Heterocyclic Chem.*, **23**, 353 (1986).

[10] J. S. Bradshaw, P. Huszthy, H. Koyama, S. G. Wood, S. A. Strobel, R. B. Davidson, R. M. Izatt, N. K. Dalley, J. D. Lamb and J. J. Christensen, *J. Heterocyclic Chem.*, **23**, 1837 (1986).

[11] J. S. Bradshaw, R. B. Nielsen, P. K. Tse, G. Arena, B. E. Wilson, N. K. Dalley, J. D. Lamb, J. J. Christensen and R. M. Izatt, *J. Heterocyclic Chem.*, **23**, 361 (1986).

[12] R. M. Izatt, G. C. LindH, G. A. Clark, Y. Nakatsuji, J. S. Bradshaw, J. D. Lamb and J. J. Christensen, *J. Membrane Sci.*, **31**, 1 (1987).

[13] R. M. Izatt, G. C. LindH, P. Huszthy, J. D. Lamb, J. S. Bradshaw and J. J. Christensen, *J. Incl. Phenom.*, submitted.

[14] J. S. Bradshaw, P. Huszthy and R. M. Izatt, *J. Heterocyclic Chem.*, **23**, 1673 (1986).

[15] J. F. Biernat, J. S. Bradshaw, B. E. Wilson, N. K. Dalley and R. M. Izatt, *J. Heterocyclic Chem.*, **23**, 1667 (1986).

[16] H. A. Bruson, U. S. Patent 2,171,498 (1937); *Chem. Abstr.*, **34**, 1100 (1940).

[17] J. F. Biernat, E. Jerecsek and A. Bujewski, *Pol. J. Chem.*, **53**, 2367 (1979).

[18] A. P. King and C. G. Krespan, *J. Org. Chem.*, **39**, 1315 (1974).

[19] R. M. Izatt, G. LindH and J. S. Bradshaw, unpublished observations.

[20] G. Dauphin and A. Kergomard, *Bull. Soc. Chim. France*, 486 (1961).

[21] D. Bright and M. R. Truter, *J. Chem. Soc., Perkin Trans.* **2**, 345 (1972).

[22] E. Wagner, *J. Pract. Chem.*, **2**, 201 (1927); *Beilstein*, **13**, 360.

[23] S. A. G. Högberg and D. J. Cram, *J. Org. Chem.*, **40**, 151 (1975).

[24] International Tables for X-ray Crystallography, Vol **4**, J. A. Ibers and W. C. Hamilton, eds, Kynock Press, Birmingham, England 1974, p 99.

[25] G. M. Sheldrick, "SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data," 4th revision, University of Göttingen, Federal Republic of Germany, 1983.