Conformational Changes of Substituted 14-Crown-4 Ethers upon Complexation

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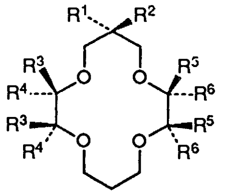
The crystal structures of 6-methylene-2,2,3,3,9,9,10,10-octamethyl-14-crown-4 (**1**), 2,2,3,3,6,9,9,10,10-nonamethyl-14-crown-4 (**2**) and its LiSCN complex (**2**·LiSCN), 6-methylenedibenzo-14-crown-4 (**3**), 6-methyldibenzo-14-crown-4 (**4**), and dibenzo-14-crown-4 (**5**), have been determined by X-ray diffraction. These results, in addition to published literature data, are used to compare the conformational changes of flexible *vs.* rigid 14-crown-4 molecules when each is complexed with LiSCN. In dibenzo-14-crown-4 the oxygen atoms are suitably arranged prior to complexation to form the base of a square pyramidal complex upon complexation with LiSCN, while 2,2,3,3,6,9,9,10,10-nonamethyl-14-crown-4 and other flexible ligands must undergo significant rearrangement of the ring system in order to achieve this configuration.

Interest in the development of lithium-selective ionophores has led to the study of small-ring crown ethers. Thermodynamic investigations on the series of 12–16 member crowns have shown that 13- and 14-member rings containing four crown oxygens form the strongest complexes with the lithium cation.[1–4] Various reports have indicated selective Li^+ complexation by benzo-substituted 13- and 14-member crowns,[5] for 14-crown-4 systems containing olefinic[6] or bulky substituents on the central carbon of the three-carbon bridge,[6b,7] for geminally disubstituted 14-crown-4 ethers,[7] and for a 14-crown-4 containing a small cylindrical cavity.[8] Despite the extensive literature on the effect of substituents on the extraction and/or transport of cations by small-ring crowns, only a limited number of these compounds have been the subject of structural studies.[9,10,11,12]

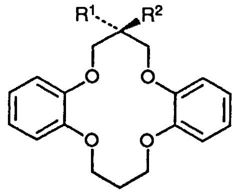
Comparison of the structures of the uncomplexed ligands with those for the complexes can provide insight into the relationship between the orientation of coordinating atoms before and after complexation (that is, the degree of preorganization), the extent of encapsulation of the coordinated ion, the steric influence of substituents and the effect of conformational restraints imposed by substituents. Previous structural studies of 13-crown-4 and 14-crown-4 ligands and their Li^+ complexes include benzo-13-crown-4,[10a] dibenzo-13-crown-4,[11c] dicyclohexano-13-crown-4,[11c] 14-crown-4,[9a] dibenzo-14-crown-4[10b] and dicyclohexano-14-crown-4.[11b] In continuation of our work with substituted 14-crown-4 ethers, and with the aim of comparing the effects of steric and conformational restraints on the preorganization of these ligands, we have recently completed the synthesis of several lipophilic crown ethers, **1**–**4**, containing aliphatic, olefinic and aromatic substituents. Whereas the substituted crowns studied previously by ourselves and others have incorporated either the quite rigid benzo substituent or the flexible, but conformationally-restrained, cyclohexano group, compounds **1** and **2** incorporate a geminal dimethyl moiety, which is expected to provide less conformational restraint, but which may introduce an increased steric factor at the periphery of the crown cavity. We have determined the crystal structures of these crowns and that of the lithium complex of **2**. In addition, we have determined the structure of dibenzo-14-crown-4, **5**,[13] and compared our structural observations with those for related compounds reported in the literature.[9–12]

Results

The structures which the six molecules have in crystals are shown in Figs. 1 and 2. The uncomplexed ligands **1** and **2** adopt similar conformations, which do not form an open macrocyclic cavity. Oxygen atoms O(4) and O(11) are turned outward and C(5) and C(12) point inward, filling the interior of the rings. While O(8) and O(11) are in contact, that is the distance between them is approximately the sum of their van der Waals radii, as are O(1) and O(4), the two pairs are not in contact with each other. The torsion angles are listed in Table 1. The effect of the methylene substituent in **1** is to make the C(5), C(6), C(7), C(19) group planar, but the conformation of the rest of the ring is the same as in **2**. When **2** is complexed with LiSCN, there is a conformational change in the ligand (see Table 1, cols. 2–4). This is achieved by two *anti*-to-*gauche* and two *gauche*-to-*anti* transformations. The resulting complex has the four oxygen atoms in contact in a plane and bonded to the Li^+ ion which lies 0.65 Å from this plane. Two crystallographically independent molecules (A and B) are found, but they have the same conformation and essentially identical dimensions.

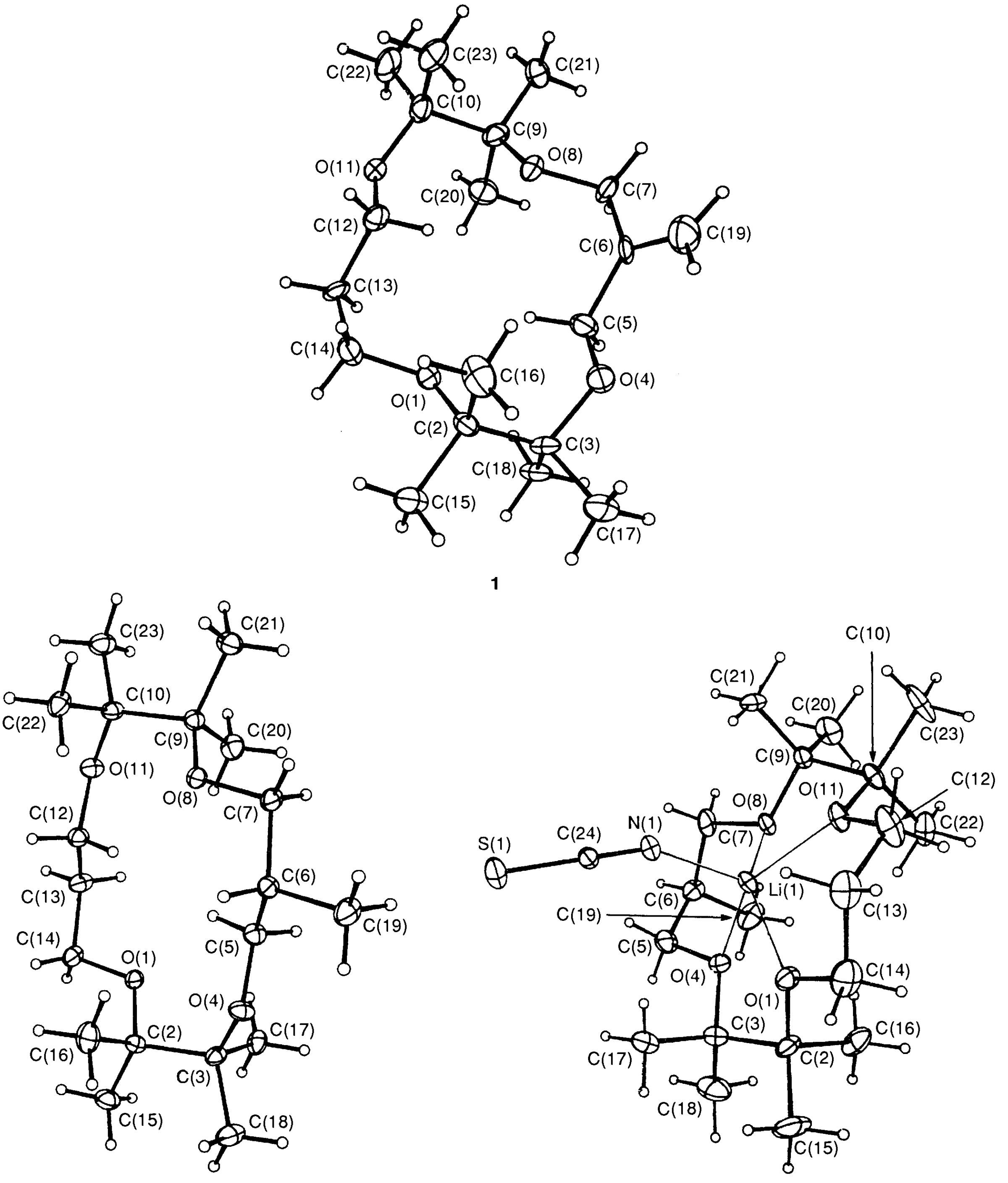


1 $R^1 = R^2 = CH_2$, R^3–$R^6 = CH_3$
2 $R^1 = H$, R^2–$R^6 = CH_3$
7 $R^1,R^2,R^3,R^5 = H$, $R^4,R^6 = —(CH_2)_4—$
8 $R^1,R^2,R^3,R^6 = H$, $R^4,R^5 = —(CH_2)_4—$
9 R^1–$R^6 = H$



3 $R^1 = R^2 = CH_2$
4 $R^1 = H$, $R^2 = CH_3$
5 $R^1 = R^2 = H$
6 $R^1 = H$, $R^2 = OH$

The structures of **3**–**5** are very similar to each other and consist of two planar halves (within ±0.2 Å) intersecting along the C(6)–C(13) line at angles of 120.4° (**3**), 125.7° (**4**) and 122.5° (**5**). Although none of these molecules lies on a crystallographic symmetry element, the molecules have a plane of symmetry through C(6) and C(13) within experimental error. The methyl and methylene substituents have a minor impact on the conformation of the rest of the molecule, evidence of the rigidity of these molecules. All values of the bond lengths and angles are in the deposited material, but a summary is given in Table 2. Averaged values are listed for bonds which are structurally equivalent, except where differences appear to be significant. Bond lengths are all normal by comparison with similar compounds. The shorter lengths for C(2)–C(3) and related bonds in **3**–**5** are due to these bonds being in aromatic rings. The type of bond typified by O(1)–C(2) are also affected by the benzo substituent in **3**–**5**, as has been observed previously in



1

2

2 • LiSCN

Fig. 1 Molecular structure of **1**, **2** and **2**•LiSCN. Non hydrogen atoms are represented by thermal ellipsoids (15% probability for 1 and **2**, and 10% for **2**•LiSCN). Hydrogen atoms are shown as small spheres.

other compounds. The variation in bond angles is much larger in the flexible ligands **1** and **2** than it is in the more rigid ones, **3**–**5**; although the methylene substituent in **3** does induce some distortion in C(5)–C(6)–C(7) compared to its value in **4** and **5**, the impact seems minor with respect to the similarities in the rest of their structures.

Discussion

*Dibenzo-*14*-crown-*4 *Ethers and their Complexes.*—For comparison with **3**, **4** and **5**, the only dibenzo-14-crown-4 for which the structure of the free ligand has been reported is *sym*-hydroxydibenzo-14-crown-4 (**6**).[10d] In the rigid ring systems, **3**, **4**, **5** and **6**, the coordinating atoms are preorganized into the orientation found in the **5**•LiSCN complex. As indicated above, the substitution of a methylene group onto the central carbon of the propylene bridge has only a minor effect on the structure of the free ligand, in contrast to the effect of the double bond of the benzo substituent in the ethylene bridge, which is significant (*vide infra*). The methyl substituent in **5** is found in a pseudo-equatorial position, whereas the hydroxy group in **6** was shown to be in the pseudo-axial position. These results are consistent with the conformations of the sidearms in Li^+ and Na^+ complexes of dibenzo-14-crown-4-acetic[12b] and -oxyacetic acids,[10c] and provide evidence that the presence of an oxygen functionality on the central carbon of the propylene bridge

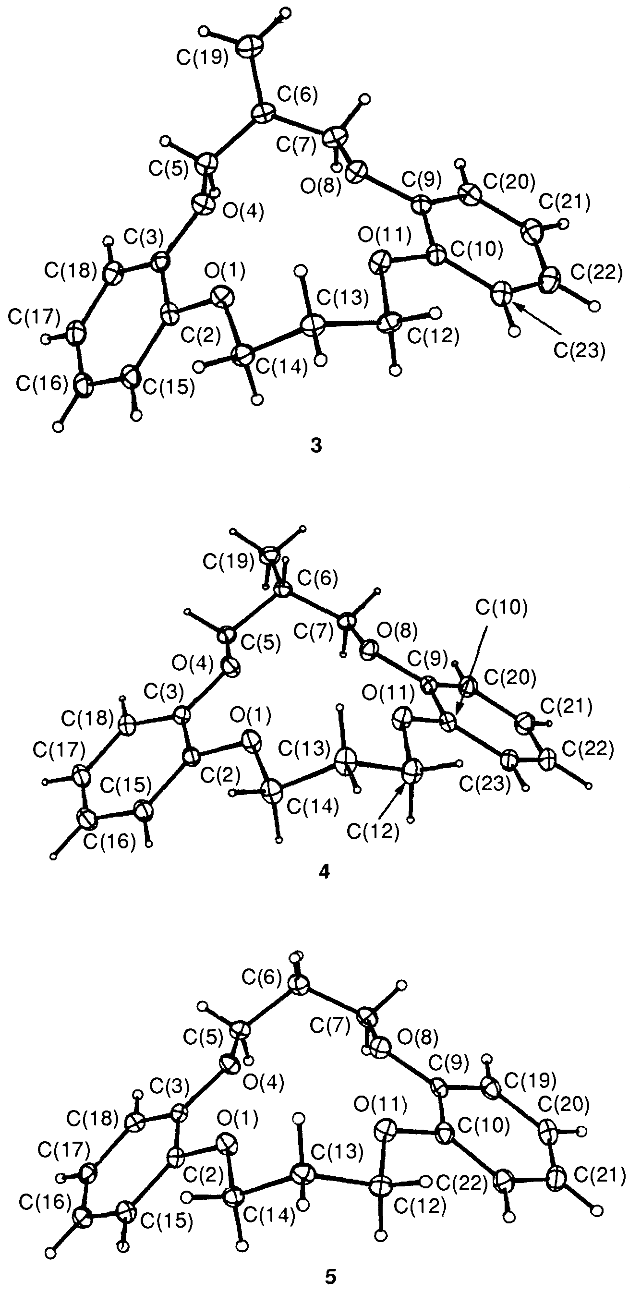
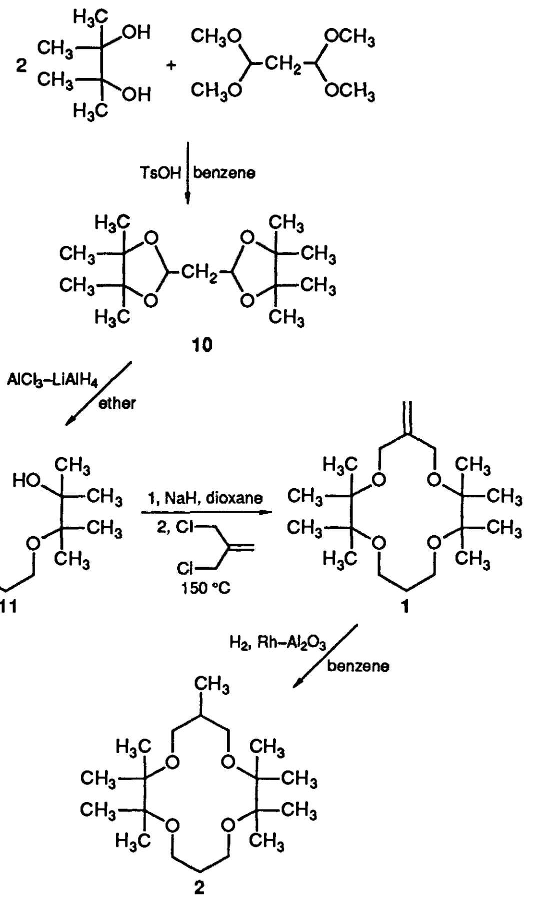


Fig. 2 Molecular structure of **3**, **4** and **5**. Non hydrogen atoms are represented by thermal ellipsoids (15% probability) and hydrogen atoms by small spheres.

appears to influence strongly the orientation that substituent adopts in the free ligands and in their complexes.

Alkyl-substituted 14-*Crown*-4 *Ethers and their Complexes*.—For comparison with **2**, the only other flexible 14-crown-4 derivative for which the structure of the Li^+ complex has been reported is *cis-syn-cis*-dicyclohexano-14-crown-4 (**7**),[11b] although the structures of the uncomplexed ligands *cis-anti-cis*-dicyclohexano-14-crown-4 (**8**),[11b] and the unsubstituted 14-crown-4 (**9**) (at 123 K), have been determined.[9a] The uncomplexed ligand **7** adopts a conformation similar to that of **9**, which is different than the conformation of **8**. Crowns **1** and **2** adopt a conformation, similar to each other, but different from that found in **7** and **9**, or **8**, although the ring conformations of the complexes, **2**·LiSCN and **6**·LiSCN, are the same. In fact, the arrangement of oxygen atoms in all of the Li^+ complexes of 14-crown-4 derivatives is remarkably similar, irrespective of their



Scheme 1

orientations in the free ligands. In complexes, the $O-(CH_2)_2-O$ distance is 2.55 Å and the $O-(CH_2)_3-O$ distance is 2.84 Å, with variations of less than 2%. The Li^+ cation lies 0.55–0.79 Å above the plane formed by the oxygens. In the free dibenzo ligands the distances are 2.57 Å and 2.88 Å, respectively. In the flexible crown the substituents affect the conformations of the uncomplexed ligands, but, in the cases observed, the electrostatic forces between the Li^+ and the crown oxygens overcome these restraints to produce, qualitatively, the same orientations of oxygen atoms in the complexes. In comparison to the four torsion angle changes cited above for the formation of **2**·LiSCN from **2**, the conversion of **7** to **7**·LiSCN requires five torsional angle transformations, plus the inversion of one of the cyclohexyl rings. In the dibenzo crowns, the restraints imposed by the benzo substituents cause the oxygens across the ethylene bridge to be coplanar and the macrocycle adopts a conformation that matches that found for the corresponding complexes.

The orientation of the C(6) methyl substituent in **2** also changes upon complexation with Li^+ cation. In uncomplexed **2**, the C(6) methyl points away from the macrocyclic ring in an orientation roughly coplanar with the four oxygens of the ring. However, in **2**·LiSCN the methyl group is found in a pseudo-axial position *anti* to the thiocyanate ion coordinated to the complexed Li^+. As noted above, in the dibenzo-crowns, substituents attached to the macrocycle through a carbon linkage are found to prefer the pseudo-equatorial position. In addition, unlike the dibenzo crowns where the propylene bridges adopt pseudo-boat conformations with respect to the coordinated Li^+, giving the macrocycle a boat-like conformation, in **2**·LiSCN and **7**·LiSCN, one propylene bridge adopts a pseudo-boat conformation while the other adopts a pseudo-chair conformation, giving the macrocyclic ring a chair-like conformation.

Finally, in **7**·LiSCN and **5**·LiSCN, no substituent groups

Table 1 Torsion angles/°

Atoms	Compound[a] 1	2	2LA	2LB	DCH	3	4	5
C(14)–O(1)–C(2)–C(3)	175	178	165	163	−179	−176	−174	−174
C(2)–O(1)–C(14)–C(13)	167	157	173	170	−176	177	180	177
C(5)–O(4)–C(3)–C(2)	−79	−79	179	−178	166	165	171	171
C(3)–O(4)–C(5)–C(6)	163	169	−154	−156	−175	−171	−177	−177
C(9)–O(8)–C(7)–C(6)	−160	−154	159	159	175	175	178	174
C(7)–O(8)–C(9)–C(10)	−173	−178	179	178	−166	−167	−173	−166
C(12)–O(11)–C(10)–C(9)	82	76	−162	−163	179	175	167	174
C(10)–O(11)–C(12)–C(13)	−164	−163	−170	−168	176	−177	−175	−178
O(1)–C(2)–C(3)–O(4)	76	78	50	51	55	2	1	0
O(4)–C(5)–C(6)–C(7)	−172	−172	−69	−69	−69	73	67	73
C(5)–C(6)–C(7)–O(8)	68	69	70	69	69	−73	−68	−76
O(8)–C(9)–C(10)–O(11)	−72	−80	−51	−56	−55	−2	−1	−1
O(11)–C(12)–C(13)–C(14)	171	175	70	76	71	72	75	73
C(12)–C(13)–C(14)–O(1)	−76	−72	−75	−75	−71	−74	−72	−71

[a] 2LA = **2**•LiSCN(A), 2LB = **2**•LiSCN(B), DCH = *cis-syn-cis*-dicyclohexano-14-crown-**4**•LiSCN.

Table 2 Individual and averaged equivalent bond lengths/Å and angles/°

Bond	Compound **1**	**2**	**2**•LiSCN	**3**	**4**	**5**
Bond lengths						
C=CH$_2$	1.250(9)			1.321(7)		
C–CH$_3$	1.53(3)	1.526(5)	1.54(1)		1.531(4)	
C(2)–C(3), *etc.*	1.56(3)	1.566(4)	1.56(1)	1.402(6)	1.395(4)	1.388(9)
C(5)–C(6), *etc.*	1.54(4)	1.519(9)	1.51(1)	1.51(1)	1.519(4)	1.515(4)
O(1)–C(2), *etc.*	1.44(2)	1.445(4)	1.448(9)	1.366(5)	1.366(5)	1.365(5)
O(1)–C(14), *etc.*	1.42(3)	1.427(4)	1.435(9)	1.434(4)	1.429(4)	1.425(7)
C–C (benzo)				1.383(9)	1.38(1)	1.39(1)
C=N			1.14(1)			
C–S			1.642(7)			
Li–N			1.98(2)			
Li–O			2.02(1)			
Bond angles						
C–O–C	119(2)	118.6(4)	117.3(5)	117.4(3)	117.5(3)	118.1(4)
O(1)–C(2)–C(3)	105.5(4)	104.1(3)	103.4(6)	114.2(3)	115.5(3)	115.0(3)
O(4)–C(3)–C(2)	109.3(4)	110.6(2)	103.2(7)	115.5(3)	115.3(2)	115.5(4)
O(8)–C(9)–C(10)	102.6(4)	105.0(2)	102.5(6)	115.3(3)	115.6(3)	115.9(4)
O(11)–C(10)–C(9)	111.8(4)	110.7(2)	103.0(5)	114.9(3)	115.7(3)	115.3(4)
C(13)–C(14)–O(1)	109.7(5)	106.9(3)	109.4(7)	108.2(3)	107.6(3)	108.5(3)
C(13)–C(12)–O(11)	105.0(4)	108.1(3)	109.5(6)	107.3(3)	107.7(3)	107.9(4)
C(6)–C(5)–O(4)	111.6(4)	108.4(3)	110.1(8)	108.6(3)	110.2(2)	107.3(4)
C(6)–C(7)–O(8)	105.6(4)	108.9(3)	110.6(6)	107.8(3)	109.7(2)	108.2(4)
C(5)–C(6)–C(7)	119.3(4)	110.6(3)	112.9(7)	119.0(4)	114.9(3)	115.7(3)
C(12)–C(13)–C(14)	100.8(4)	111.2(3)	114.8(8)	114.7(4)	114.6(3)	114.8(5)

are oriented towards the face of the macrocycle to which the LiSCN is coordinated. In **2**•LiSCN, two methyl substituents are oriented in this direction. To what extent this effects the Li$^+$ binding strengths is not known. We will be investigating these compounds further in order to understand the effects substituents have on the solution and thermodynamic properties of 14-crown-4 ethers.

Experimental

Dibenzo-14-crown-4 (**5**) was obtained as a byproduct from the synthesis of bis(2-hydroxy)phenoxypropane.[10c] 6-Methyldibenzo-14-crown-4 (**4**) was prepared by catalytic hydrogenation of 6-methylenedibenzo-14-crown-4 (**3**).[12b] 6-Methyleneoctamethyl-14-crown-4 (**1**) and nonamethyl-14-crown-4 (**2**) were prepared according to Scheme 1. Crystals suitable for X-ray analysis were obtained by slow evaporation from an appropriate solvent (**1**–**4**, **2**•LiSCN: acetonitrile; **5**: chloroform). All reagents were obtained from commercial sources and used as obtained, unless specified otherwise. 'Ether' refers to diethyl ether throughout. Preparative column chromatography was performed on silica gel 60, 60–200 mesh. IR spectra were recorded on a Biorad/Digilab FTS-60 spectrometer. NMR spectra were recorded on a Bruker MSL400 spectrometer. Chemical shifts are reported in ppm relative to Me$_4$Si and *J* values are reported in Hz. Melting points (uncorrected) were measured on a Hoover Unimelt stirred-bath apparatus. Mass spectra were obtained on a Hewlett Packard 5985A GC/MS using a heated probe inlet and CH$_4$ chemical ionization, by the Organic Spectroscopy Group, Analytical Chemistry Division, Oak Ridge National Laboratory. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Dibenzo-14-*crown*-4 (**5**).—The product of the reaction of sodium catecholate (1 kg, 9 mol) with 1,3-dibromopropane (1 kg, 5 mol),[10c] was triturated twice with boiling water (2 dm^3), then crystallized from benzene (2 dm^3). The mother liquor was

Table 3 Crystallographic data for compounds **1**–**5** and **2**·LiSCN

	1	**2**	**2**·LiSCN	**3**	**4**	**5**
Formula	$C_{19}H_{36}O_4$	$C_{19}H_{38}O_4$	$C_{20}H_{38}NO_4SLi$	$C_{19}H_{20}O_4$	$C_{19}H_{22}O_4$	$C_{18}H_{20}O_4$
F.W.	328.50	330.51	395.54	312.37	314.39	300.36
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	7.699(4)	28.048(5)	16.659(6)	13.216(6)	12.915(6)	12.794(2)
b/Å	11.076(3)	8.7115(8)	17.789(3)	5.056(1)	5.290(3)	5.101(1)
c/Å	12.808(5)	16.517(3)	15.828(6)	24.30(1)	24.16(2)	12.792(3)
β/°	111.68(2)	91.65(1)	93.31(2)	100.63(2)	102.01(3)	115.49(2)
V/Å^3	1015(2)	4034(2)	4683(3)	1596(2)	1615(3)	753.6(5)
T/K	293	296	296	294	299	298
Space group	Pc (No. 7)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)
Z	2	8	8	4	4	2
Refl's, angle for cell ls. sq.	24, 9.3–17.9	25, 8.3–12.2	25, 7.4–11.9	25, 8.2–17.7	22, 10.2–17.7	25, 6.9–17.8
d_{calc}/g cm^{-3}	1.08	1.09	1.12	1.30	1.29	1.32
Crystal shape	Prism	Platelet	Prism	Needle	Needle	Needle
Crystal size/mm	0.31 × 0.40 × 0.50	0.13 × 0.28 × 0.38	0.50 × 0.28 × 0.29	0.13 × 0.21 × 0.59	0.11 × 0.18 × 0.63	0.10 × 0.14 × 0.50
Absorption corr'n	0.965–1.0	0.903–1.0	0.916–1.0	0.906–0.997	0.857–0.999	0.948–0.996
Range of 2θ/°	<48	<45	<36	<46	<46	<50
Range of hkl	0, 8; 0, 12; ±14	0, 29; 0, 9, ±17	0, 14; 0, 5; ±26	0, 14; 0, 5; ±26	0, 14; 0, 5; ±26	0, 15; 0, 6; ±15
Unique refl.	1430	2598	2341	2226	2231	1482
Observed, $I > \sigma(I)$	990	1440	1682	1275	1412	879
No. variables	206	208	487	208	208	198
$R(F)$	0.055	0.055	0.051	0.059	0.046	0.045
R_w	0.063	0.061	0.057	0.060	0.053	0.047
GOF	2.05	1.67	1.84	1.48	1.45	1.26
(ρ_o–ρ_c) range	+0.15, −0.16	+0.21, −0.17	+0.17, −0.17	+0.22, −0.24	+0.20, −0.19	+0.17, −0.18

Table 4 Final atomic coordinates for compound **1**

Atom	x	y	z
O(1)	0.251	0.1256(3)	0.104
O(4)	0.0936(5)	0.3711(3)	0.0669(3)
O(8)	0.5509(4)	0.3717(3)	0.3696(3)
O(11)	0.7082(4)	0.1300(3)	0.4069(3)
C(2)	0.1631(6)	0.1791(4)	−0.0044(4)
C(3)	0.0090(6)	0.2603(5)	0.0058(4)
C(5)	0.1728(6)	0.3624(5)	0.1818(4)
C(6)	0.3036(6)	0.4671(4)	0.2326(4)
C(7)	0.4200(7)	0.4658(4)	0.3550(4)
C(9)	0.6394(6)	0.3230(5)	0.4822(4)
C(10)	0.7911(7)	0.2337(5)	0.4688(4)
C(12)	0.6264(6)	0.1306(5)	0.2835(4)
C(13)	0.4996(6)	0.0144(5)	0.2509(5)
C(14)	0.3936(7)	0.0355(5)	0.1212(5)
C(15)	0.0871(7)	0.0757(6)	−0.0960(4)
C(16)	0.3035(8)	0.2497(6)	−0.0406(5)
C(17)	−0.1137(9)	0.3192(6)	−0.1074(5)
C(18)	−0.1136(6)	0.2046(5)	0.0584(4)
C(19)	0.313(1)	0.5608(7)	0.1807(5)
C(20)	0.4913(8)	0.2489(7)	0.5054(6)
C(21)	0.7251(7)	0.4202(5)	0.5633(4)
C(22)	0.9160(9)	0.1913(7)	0.5864(5)
C(23)	0.9106(7)	0.3069(6)	0.4147(6)

Table 5 Final atomic coordinates for compound **2**

Atom	x	y	z
O(1)	0.09143(7)	−0.3345(3)	0.3935(1)
O(4)	0.16391(8)	−0.5410(3)	0.4717(1)
O(8)	0.14945(7)	−0.1782(3)	0.6329(1)
O(11)	0.07607(8)	0.0136(3)	0.5541(1)
C(2)	0.0904(1)	−0.5001(4)	0.3883(2)
C(3)	0.1441(1)	−0.5472(4)	0.3901(2)
C(5)	0.1766(1)	−0.3954(4)	0.5048(2)
C(6)	0.1865(1)	−0.4146(4)	0.5939(2)
C(7)	0.1938(1)	−0.2588(4)	0.6346(2)
C(9)	0.1509(1)	−0.0123(4)	0.6345(2)
C(10)	0.0972(1)	−0.0391(4)	0.6347(2)
C(12)	0.0635(1)	−0.1149(4)	0.5212(2)
C(13)	0.0569(1)	−0.0978(4)	0.4306(2)
C(14)	0.0475(1)	−0.2518(5)	0.3905(2)
C(15)	0.0645(1)	−0.5470(5)	0.3096(2)
C(16)	0.0646(1)	−0.5657(5)	0.4606(2)
C(17)	0.1728(1)	−0.4503(5)	0.3324(2)
C(18)	0.1493(1)	−0.7170(5)	0.3690(2)
C(19)	0.2298(1)	−0.5172(5)	0.6119(2)
C(20)	0.1746(1)	0.0481(5)	0.5594(2)
C(21)	0.1775(1)	0.0410(5)	0.7117(2)
C(22)	0.0681(1)	−0.0549(5)	0.6936(2)
C(23)	0.0928(1)	0.2091(5)	0.6562(2)

concentrated *in vacuo* and triturated with methanol to obtain **5** (33 g, 1.2%). M.p. 148–149 °C (from cyclohexane) (lit.,[1] 150–152 °C). (Found: M$^+$, 300. Calc. for $C_{18}H_{20}O_4$: M, 300).

6-*Methyldibenzo*-14-*crown*-4 (**4**).—A solution of 6-methylenedibenzo-14-crown-4 (0.511 g, 1.6 mmol) in benzene (10 cm^3) was hydrogenated (1 atm. H_2, 5% rhodium on alumina) for 5 h. Activated charcoal was added, the suspension filtered through Celite and evaporated *in vacuo* to obtain **4** (0.49 g, 95%), m.p. 123 °C (from acetonitrile) (Found: C, 72.1; H, 6.4. $C_{19}H_{22}O_4$ requires C, 72.6; H, 7.0%); δ_H(400 MHz; $CDCl_3$) 1.14 (3 H, d, J 7, CH_3), 2.20 (1 H, m, $-CH_2HC\mathit{H}CH_2-$), 2.31 (1 H, m, $-CH_2\mathit{H}CHCH_2-$), 2.48 [1 H, m, $-CH_2(CH_3)C\mathit{H}CH_2-$], 4.08 (2 H, m, $-OCH_2R$), 4.25 (6 H, m, $-OCH_2R$), 6.92 (8 H, m, Ar–); ν_{max}/cm^{-1} 1253 (Ar–O–C); m/z 314 (100%, M$^+$).

1,3-*Bis*(4′,4′,5′,5′-*tetramethyl*-1,3-*dioxolan*-2-*yl*)*methane* (**10**).—A solution of pinacol (54.6 g, 0.462 mol), 1,1,3,3-tetramethoxypropane (36 cm^3, 0.23 mol) and *p*-toluenesulfonic acid (0.1 g, 0.5 mmol) in benzene (150 cm^3) was refluxed through a soxhlet extractor containing 4Å molecular sieves for 1 h. The solution was cooled, filtered through a bed of silica gel (*ca.* 15 g), eluted with benzene (100 cm^3) and evaporated *in vacuo* to obtain **10** (57 g, 95%), m.p. 79–80 °C (from acetonitrile) (Found: C, 66.4; H, 10.3. $C_{15}H_{28}O_4$ requires C, 66.1; H, 10.4%); δ_H(400 MHz; $CDCl_3$) 1.19 (24 H, s, CH_3), 1.91 (2 H, t, J 5.5, $-CHC\mathit{H}_2CH-$), 5.19 (2 H, t, J 5.5, $-C\mathit{H}CH_2CH-$); ν_{max}/cm^{-1} 1161 and 1120 (C–O–C); m/z 273 (2%, M$^+$ + H), 271 (2, M$^+$ − H), 171 (4), 129 (100), 101 (7) (CH_4 chemical ionization).

Table 6 Final atomic coordinates for **2**•LiSCN

Atom	*x*	*y*	*z*
S(A)	−0.0946(2)	−0.2296(1)	0.5278(1)
O(1A)	0.1416(3)	−0.1695(3)	0.7612(3)
O(4A)	0.1672(3)	−0.1012(3)	0.6253(3)
O(8A)	0.0839(3)	0.0264(2)	0.6777(2)
O(11A)	0.0515(3)	−0.0383(2)	0.8138(2)
N(A)	−0.0205(4)	−0.1304(3)	0.6437(3)
C(2A)	0.2196(4)	−0.1845(4)	0.7306(5)
C(3A)	0.2067(5)	−0.1735(5)	0.6332(5)
C(5A)	0.1472(5)	−0.0740(5)	0.5413(4)
C(6A)	0.1433(4)	0.0105(5)	0.5428(4)
C(7A)	0.0731(5)	0.0399(4)	0.5877(4)
C(9A)	0.0379(4)	0.0724(4)	0.7312(4)
C(10A)	0.0635(4)	0.0423(4)	0.8219(4)
C(12A)	0.0458(6)	−0.0806(5)	0.8901(4)
C(13A)	0.0485(5)	−0.1641(5)	0.8697(4)
C(14A)	0.1288(6)	−0.1929(5)	0.8449(5)
C(15A)	0.2504(6)	−0.2639(5)	0.7533(7)
C(16A)	0.2783(5)	−0.1250(5)	0.7670(6)
C(17A)	0.1485(5)	−0.2352(5)	0.5958(6)
C(18A)	0.2857(6)	−0.1734(6)	0.5884(6)
C(19A)	0.2237(4)	0.0474(5)	0.5738(5)
C(20A)	−0.0521(4)	0.0603(5)	0.7113(5)
C(21A)	0.0603(5)	0.1562(4)	0.7236(5)
C(22A)	0.1515(5)	0.0568(5)	0.8451(5)
C(23A)	0.0104(6)	0.0750(5)	0.8898(5)
C(24A)	−0.0513(4)	−0.1712(4)	0.5959(4)
Li(A)	0.0769(7)	−0.0853(7)	0.7039(7)
S(B)	0.5927(2)	0.2243(1)	0.0465(1)
O(1B)	0.3704(3)	0.1460(3)	0.2882(3)
O(4B)	0.3156(3)	0.0863(3)	0.1512(3)
O(8B)	0.4268(3)	−0.0334(2)	0.1727(2)
O(11B)	0.4879(3)	0.0231(2)	0.3088(3)
N(B)	0.5000(3)	0.1343(3)	0.1464(4)
C(2B)	0.2849(5)	0.1533(4)	0.2746(5)
C(3B)	0.2710(4)	0.1533(4)	0.1764(6)
C(5B)	0.3198(5)	0.0699(5)	0.0630(5)
C(6B)	0.3350(5)	−0.0134(5)	0.0498(5)
C(7B)	0.4193(5)	−0.0369(4)	0.0815(5)
C(9B)	0.4901(4)	−0.0776(4)	0.2146(4)
C(10B)	0.4815(4)	−0.0584(4)	0.3083(4)
C(12B)	0.5041(6)	0.0589(4)	0.3883(5)
C(13B)	0.4918(5)	0.1417(4)	0.3787(5)
C(14B)	0.4047(6)	0.1652(5)	0.3716(5)
C(15B)	0.2543(6)	0.2276(5)	0.3105(7)
C(16B)	0.2431(5)	0.0864(5)	0.3121(6)
C(17B)	0.3107(6)	0.2221(5)	0.1341(6)
C(18B)	0.1807(6)	0.1456(6)	0.1477(8)
C(19B)	0.2692(5)	−0.0636(5)	0.0833(6)
C(20B)	0.5724(4)	−0.0552(5)	0.1825(5)
C(21B)	0.4725(5)	−0.1631(4)	0.1990(5)
C(22B)	0.4005(5)	−0.0800(4)	0.3402(4)
C(23B)	0.5480(5)	−0.0928(4)	0.3648(5)
C(24B)	0.5397(4)	0.1702(4)	0.1060(4)
Li(B)	0.4254(8)	0.0754(7)	0.2115(7)

Table 7 Final atomic coordinates for compound **3**

Atom	*x*	*y*	*z*
O(1)	0.3083(2)	0.7452(6)	0.6330(1)
O(4)	0.4043(2)	0.4181(6)	0.5814(1)
O(8)	0.5735(2)	0.4151(6)	0.6793(1)
O(11)	0.4731(2)	0.7523(6)	0.7269(1)
C(2)	0.2463(3)	0.5722(9)	0.5991(2)
C(3)	0.2994(3)	0.3956(9)	0.5702(2)
C(5)	0.4625(3)	0.2033(9)	0.5642(2)
C(6)	0.5739(3)	0.2448(9)	0.5885(2)
C(7)	0.6102(3)	0.1994(9)	0.6496(2)
C(9)	0.5908(3)	0.4036(9)	0.7364(2)
C(10)	0.5349(3)	0.5858(9)	0.7625(2)
C(12)	0.4082(3)	0.9274(9)	0.7509(2)
C(13)	0.3439(3)	1.0797(9)	0.7033(2)
C(14)	0.2603(3)	0.919(1)	0.6670(2)
C(15)	0.1411(3)	0.563(1)	0.5925(2)
C(16)	0.0861(3)	0.375(1)	0.5567(2)
C(17)	0.1369(3)	0.206(1)	0.5272(2)
C(18)	0.2436(3)	0.212(1)	0.5339(2)
C(19)	0.6404(3)	0.297(1)	0.5556(2)
C(20)	0.6568(3)	0.2257(9)	0.7688(2)
C(21)	0.6666(3)	0.232(1)	0.8266(2)
C(22)	0.6110(3)	0.407(1)	0.8519(2)
C(23)	0.5450(3)	0.5838(9)	0.8200(2)

Table 8 Final atomic coordinates for compound **4**

Atom	*x*	*y*	*z*
O(1)	0.6480(1)	−0.2788(4)	0.20592(8)
O(4)	0.6052(1)	0.0594(4)	0.12841(8)
O(8)	0.8178(1)	0.0428(4)	0.11480(8)
O(11)	0.8649(1)	−0.2828(4)	0.19550(8)
C(2)	0.5460(2)	−0.2770(6)	0.1760(1)
C(3)	0.5224(2)	−0.0921(6)	0.1341(1)
C(5)	0.5893(2)	0.2252(6)	0.0810(1)
C(6)	0.6903(2)	0.3689(6)	0.0796(1)
C(7)	0.7804(2)	0.2086(6)	0.0678(1)
C(9)	0.8976(2)	−0.1227(6)	0.1108(1)
C(10)	0.9223(2)	−0.2995(6)	0.1544(1)
C(12)	0.8721(2)	−0.4903(7)	0.2342(1)
C(13)	0.7950(2)	−0.4401(7)	0.2727(1)
C(14)	0.6790(2)	−0.4802(7)	0.2451(1)
C(15)	0.4685(2)	−0.4433(7)	0.1847(1)
C(16)	0.3664(2)	−0.4211(7)	0.1516(1)
C(17)	0.3429(2)	−0.2393(7)	0.1112(1)
C(18)	0.4208(2)	−0.0721(7)	0.1020(1)
C(19)	0.6634(3)	0.5644(7)	0.0321(1)
C(20)	0.9514(2)	−0.1258(7)	0.0668(1)
C(21)	1.0293(2)	−0.3060(7)	0.0662(1)
C(22)	1.0542(2)	−0.4773(7)	0.1087(1)
C(23)	1.0009(2)	−0.4748(6)	0.1536(1)

1,1,2,2,8,8,9,9-*Octamethyl*-3,7-*dioxanonan*-1,9-*diol* (**11**).—Lithium aluminium hydride (6.30 g, 0.165 mol) was added portionwise, with stirring, to an ice-cold solution of aluminium chloride (73 g, 0.54 mol) in anhydrous ether (500 cm^3).[14] After 30 min, a solution of **10** (57.1 g, 21.0 mmol) in anhydrous ether (250 cm^3) was added. The cooling bath was removed and the reaction mixture stirred for 8 h. Excess hydride was destroyed by addition of water (30 cm^3) followed by sulfuric acid (500 cm^3; 2 mol dm^{-3}). The organic phase was separated, washed once with saturated aqueous sodium chloride and once with saturated aqueous sodium hydrogencarbonate. The solution was concentrated *in vacuo*, dissolved in hexanes (500 cm^3), and washed twice with water (200 cm^3). The organic phase was dried and concentrated *in vacuo* to obtain **11** (48 g, 82%) as an oil (Found: C, 64.9; H, 11.7. $C_{15}H_{32}O_4$ requires C, 65.2; H, 11.7%); δ_H(400 MHz; $CDCl_3$) 1.15 (12 H, s, CH_3), 1.18 (12 H, s, CH_3), 1.77 (2 H, pent, *J* 6.0, $-CH_2CH_2CH_2-$), 2.60–2.90 (2 H, br, OH), 3.45 (4 H, tr, *J* 6.0, $-CH_2CH_2CH_2-$); ν_{max}/cm^{-1} 3415 br (O–H), 1157 and 1120 (C–O–C), 1069 (C–OH); *m*/*z* 277 (100%, M$^+$ + H), 177 (81), 159 (56), 101 (59), (CH_4 chemical ionization).

6-*Methylene*-2,2,3,3,9,9,10,10-*octamethyl*-14-*crown*-4 (**1**).—A mixture of **11** (5.5 g, 20 mmol) and sodium hydride (1.5 g, 60 mmol) in anhydrous dioxane (250 cm^3; freshly distilled from sodium) was stirred overnight (*ca.* 14 h) at 50 °C in a stainless steel pressure vessel. The vessel was cooled to room temperature, vented, and 3-chloro-2-chloromethylprop-1-ene (3.44 cm^3, 30 mmol) was added. The vessel was sealed and heated with stirring to 200 °C for 9 h. After cooling to room temperature, excess pressure was vented and 50 cm^3 of water was added. The mixture was concentrated *in vacuo*, dissolved in ether, extracted with saturated aqueous sodium chloride, dried and evaporated *in vacuo*. Chromatography on silica gel with

Table 9 Final atomic coordinates for compound **5**

Atom	x	y	z
O(1)	0.2492(2)	0.164	0.5375(2)
O(4)	0.4098(2)	−0.1790(8)	0.6248(2)
O(8)	0.3780(2)	−0.1796(9)	0.8372(2)
O(11)	0.2139(2)	0.1579(8)	0.7433(2)
C(2)	0.2614(3)	0.002(1)	0.4593(3)
C(3)	0.3489(3)	−0.186(1)	0.5067(3)
C(5)	0.4878(3)	−0.390(1)	0.6794(3)
C(6)	0.5386(3)	−0.343(1)	0.8091(3)
C(7)	0.4576(4)	−0.393(1)	0.8651(3)
C(9)	0.2898(3)	−0.195(1)	0.8700(3)
C(10)	0.2003(3)	−0.013(1)	0.8188(3)
C(12)	0.1204(3)	0.330(1)	0.6790(3)
C(13)	0.1547(3)	0.490(1)	0.5990(3)
C(14)	0.1544(3)	0.342(1)	0.4967(3)
C(15)	0.1924(3)	0.007(1)	0.3409(3)
C(16)	0.2129(3)	−0.171(1)	0.2701(3)
C(17)	0.2989(3)	−0.355(1)	0.3151(3)
C(18)	0.3680(3)	−0.364(1)	0.4345(3)
C(19)	0.2845(4)	−0.375(1)	0.9477(3)
C(20)	0.1889(4)	−0.380(1)	0.9740(4)
C(21)	0.1008(4)	−0.206(1)	0.9228(3)
C(22)	0.1053(4)	−0.018(1)	0.8440(4)

ether–hexanes (0–30% gradient) gave **1** (3.9 g, 60%), m.p. 64–67 °C (from acetonitrile) (Found: C, 68.9; H, 10.7. $C_{19}H_{36}O_4$ requires C, 69.5; H, 11.0%); δ_H(400 MHz; $CDCl_3$) 1.11 (12 H, s, CH_3), 1.21 (12 H, s, CH_3), 1.72 (2 H, pent, J 6, $-CH_2CH_2CH_2-$), 3.62 (4 H, t, J 6, $-CH_2CH_2CH_2-$), 4.15 (4 H, s, $-OCH_2C$), 5.08 (2 H, s, $=CH_2$); ν_{max}/cm^{-1} 3095 and 3079 ($=CH_2$), 1152, 1094, 1085, 1071 and 1051 (C–O–C); m/z 329 (2%, $M^+ + H$), 327 (2, $M^+ - H$), 313 (2, $M^+ - CH_3$), 171 (100), 159 (50), 101 (62) (CH_4 chemical ionization).

2,2,3,3,6,9,9,10,10-*Nonamethyl*-14-*crown*-4 (**2**).—A solution of **1** (1.000 g, 3.0 mmol) in benzene (20 cm³) was hydrogenated (1 atm., 5% rhodium on alumina) for 5 h. Norite was added, the suspension filtered through Celite and evaporated *in vacuo* to obtain **2** (0.970 g, 96%), m.p. 52 °C (from acetonitrile) (Found: C, 68.5; H, 11.2. $C_{19}H_{38}O_4$ requires C, 69.0; H, 12.4%); δ_H(400 MHz; $CDCl_3$) 0.88 (3 H, d, J 7, 6-CH_3), 1.13, 1.14, 1.16 and 1.17 (each 6 H, s, $-CH_3$), 1.69 (2 H, p, J 6, $-CH_2CH_2CH_2-$), 1.80 (1 H, m, 6-H), 3.36 [2 H, d/d, J 4/8, $CH_2C(CH_3)HCH_2-$], 3.56 [2 H, t, J 8, $CH_2C(CH_3)HCH_2-$], 3.63 (4 H, tr, J 6, $-CH_2CH_2CH_2-$); ν_{max}/cm^{-1} 1156 and 1073 (C–O–C); m/z 331 (63%, $M^+ + H$), 315 (6, $M^+ - CH_3$), 249 (57), 173 (65), 159 (100) (CH_4 chemical ionization).

X-Ray Diffraction.—Single crystal samples of **1**–**5** and **2**·LiSCN were studied by use of an Enraf Nonius CAD4 diffractometer employing Mo-Kα radiation (λ = 0.710 69 Å). Many of the experimental conditions are given in Table 3 along with the crystal data obtained. Unit-cell dimensions were determined from the angle settings of up to 25 reflections and refined by least squares. Intensities were measured by the ω–2θ scan method with background measured on each side of the peaks. Lorentz and polarization corrections were applied to the intensities as well as empirical absorption corrections based on psi scans. The crystal structures were all determined by use of MULTAN-82 and difference Fourier syntheses, and were refined by full-matrix least squares using the Enraf Nonius Structure Determination Package. Hydrogen atoms in calculated positions (C–H = 0.95 Å) were included in the structures and given isotropic thermal parameters equivalent to those of the atoms to which they are attached. Observations, F_o, were assigned weights, w, as $w = 4F_o^2/\{[\sigma(I)]^2 + [0.05F_o^2]^2\}$, where I = scaled, observed intensity. Final values of the atomic coordinates for all six structures are given in Tables 4–9.*

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