

## Crystal Structures of Dibenzo-13-crown-4 and *sym*-(2-Picolyl)oxy)dibenzo-13-crown-4

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**Abstract.** Solid-state structures are determined for two compounds which contain dibenzo-13-crown-4 rings. These include the parent crown ether dibenzo-13-crown-4 and its lariat ether derivative *sym*-(2-picolyl)oxy)dibenzo-13-crown-4. The solid-state structure of dibenzo-13-crown-4 is complicated by disorder of the carbon atoms in the ethylene and propylene bridges. The asymmetric unit of the crystal for the lariat ether derivative consists of two chemically identical, but crystallographically different, molecules.

**Key words.** Small-ring crown ether, lariat ether, solid-state structure

### 1. Introduction

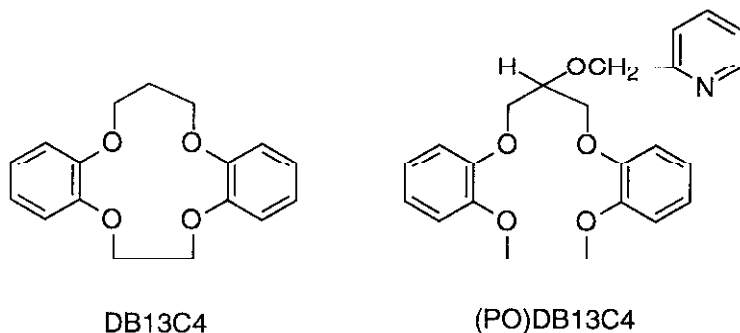
Structural studies of dibenzo-12-crown-4 (DB12C4) [1] and dibenzo-14-crown-4 (DB14C4) [2] have been reported together with the structures of several DB14C4 derivatives [3] and their Li<sup>+</sup> complexes [4]. However, no structure of dibenzo-13-crown-4 (DB13C4), its derivatives, or complexes has been published.

For the 13-crown-4 ring system, structural data have appeared for dicyclohexano-13-crown-4 (DC13C4) and two of its Li<sup>+</sup> complexes [5]. Also, structures of benzo-13-crown-4 (B13C4), and its Li<sup>+</sup> complex [6], and an uncomplexed derivative of B13C4 [7] are available in the literature. It should be noted that the benzo group in the B13C4 compounds is situated opposite to the three-carbon bridge; while in DC13C4 and its complexes and in DB13C4, the two cyclohexano groups and two benzo group substituents, respectively, are adjacent to the three-carbon bridges. In this respect, DB13C4 more closely resembles DC13C4 than it does the B13C4 macrocycle.

Significant rigidity is noted in the 13-crown-4 ring system. This is apparent from comparison of the reported structures for B13C4 and its derivative [7]. This is also noted from a comparison of the structures for B13C4 and its  $\text{Li}^+$  complex.

We have undertaken a structural study of DB13C4 compounds to obtain a better understanding of the stereochemistry in this ring system. It might be anticipated that the DB13C4 macrocycle would possess some structural characteristics of both DB12C4 and DB14C4, for which the conformations differ significantly. DB12C4, which has only two-carbon bridges between the oxygens, contains a center of symmetry. The molecule is somewhat planar with the two oxygens attached to one benzo group pointing above the approximate plane and the two oxygen atoms bonded to the second benzo group directed below. On the other hand, the DB14C4 macrocycle, which has greater flexibility due to the two three-carbon bridges, assumes an inverted V shape [3]. The four oxygen atoms in DB14C4 are in a rectangular arrangement which is preorganized to coordinate with  $\text{Li}^+$ . DB14C4 contains a pseudo mirror plane passing through the central carbon atoms of both three-carbon bridges and many of its derivatives also possess crystallographic mirror planes in the same position [3].

We now report the solid-state structures of DB13C4 and the lariat ether *sym*-(2-picolyloxy)-dibenzo-14-crown-4 [(PO)DB13C4] which reveal the conformation of the DB13C4 ring system.



## 2. Experimental

IR spectra were taken with a Perkin Elmer Model 1600 spectrophotometer.  $^1\text{H}$  NMR spectra were recorded with an IBM AF-200 spectrometer and chemical shifts are reported in parts per million ( $\delta$ ) downfield from TMS. Combustion analysis was performed by Desert Analytics Laboratories of Tucson, Arizona. All X-ray data were obtained using a Siemens R3m/V automated diffractometer with Mo,  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Programs used for solving, refining and displaying these structures are contained in the SHELXTL-PLUS program package [8].

## 2.1 MATERIALS

Unless specified otherwise, reagent grade reactants and solvents were used as received from chemical suppliers. Cesium carbonate was obtained from Chemetall GMBH (marketed in the U.S.A. by CM Chemical Products, Inc. of Berkeley Heights, New Jersey).

## 2.2 SYNTHESIS OF DIBENZO-13-CROWN-4 (DB13C4)

Under nitrogen, 4.65 g (19.0 mmol) of bis-1,2-(*o*-hydroxyphenoxy)ethane [9] was dissolved in 100 mL of acetonitrile and pulverized cesium carbonate (15.48 g, 47.5 mmol) was added. The resulting mixture was stirred and refluxed for 3 hours. A solution of 4.40 g. (19.0 mmol) of 1,3-propanediol dimethylsilylate in 50 mL of acetonitrile was added to the refluxing mixture with a syringe pump during an 8-hour period. After an additional 8 hours, the reaction mixture was allowed to cool to room temperature and was filtered through a pad of Celite on a sintered glass funnel. The collected solid was washed with dichloromethane (20 mL) and the combined filtrate and washing were evaporated *in vacuo*. The residue was dissolved in dichloromethane and the solution was washed with water and dried over magnesium sulfate. The solvent was evaporated *in vacuo* and the residue was chromatographed on alumina with ethyl acetate-hexane (1:2) as eluent. The solvent was evaporated *in vacuo* and the residue was recrystallized from dichloromethane-methanol to give 4.02 g (74%) of white solid with mp 134-135 °C (lit [5] mp 134-136 °C). IR (deposit from chloroform solution on a sodium chloride plate): 1116 (C-O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  2.10-2.21 (m, 2H), 4.08-4.34 (m, 8H), 6.86-7.07 (m, 8H).

## 2.3 SYNTHESIS OF *SYM*-(2-PICOLYLOXY)DIBENZO-13-CROWN-4 [(PO)DB13C4]

Under nitrogen, 2-picolyl chloride hydrochloride (0.26 g, 1.58 mmol) and 0.06 g (1.58 mmol) of a 60% dispersion of sodium hydride in mineral oil were added to 80 mL of dry THF and the mixture was stirred for 2 hours at room temperature. The insoluble material was removed by filtration through a bed of Celite on a sintered glass funnel. The filtrate was added dropwise to a solution of *sym*-(hydroxy)dibenzo-13-crown-4 [10] (0.48 g, 1.58 mmol) and 60% dispersion of sodium hydride (0.12 g, 3.16 mmol) in 60 mL of dry THF. The reaction mixture was stirred for 24 hours at room temperature and quenched with 20 mL of water. The THF was removed *in vacuo* and the aqueous residue was extracted with dichloromethane (2 X 50 mL) and dried over magnesium sulfate. The solvent was evaporated *in vacuo* and the crude product was chromatographed on alumina with ethyl acetate as eluent to give 0.21 g (36%) of white solid with mp 72-73 °C. IR (deposit from chloroform solution on a sodium chloride plate): 1114 (C-O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  3.78-3.83 (m, 1H), 4.01-4.45 (m, 8H), 4.84 (s, 2H), 6.85-7.25 (m, 8H), 7.49-7.52 (m, 1H), 7.62-7.69 (m, 2H), 8.51-8.53 (d, 1H). *Anal. Calcd.* for  $\text{C}_{23}\text{H}_{23}\text{NO}_5$ : C, 70.21; H, 5.89. Found: C, 70.06; H, 5.83.

## 2.4 CRYSTAL GROWTH

Suitable crystals of DB13C4 and (PO)DB13C4 were grown from acetonitrile.

## 2.5 STRUCTURE DETERMINATIONS

The lattice parameters and the orientation matrix of each crystal were obtained using a least-squares procedure with a number of carefully centered reflections (33 for DB13C4 and 31 for (PO)DB13C4). The space group of each crystal was determined uniquely using systematic extinctions since DB13C4 crystallized in space group  $Pbca$  and (PO)DB13C4 crystallized in the space group  $P2_1/n$ . Intensity data for both structures were collected with a variable rate  $2\theta$  scanning procedure in which the scan speed was determined by the peak intensity. Single crystal and experimental data are presented in Table I.

### 2.5.1 Structure of DB13C4

The unit cell parameters and space group of DB13C4 indicated that the crystal is isomorphous with the structure of DB12C4 [2]. DB12C4 lies about a center of symmetry. Since DB13C4 cannot contain a center of symmetry, the only way that isomorphism can exist is if the molecules adopt chiral conformations with each molecular site being occupied by one enantiomer in one half of the units cells and by the other enantiomer in the remaining half. (This arrangement would be favored by the rigidity of the DB13C4 molecule.) If this were the case, the benzo groups would appear to be overlapped in the time-averaged structure. This was the case. In the direct method solution for DB13C4, the atoms of each benzo group were apparent in the E-map along with several peaks which could not be identified. Rather than attempting to resolve the disorder using the E map, the positional coordinates of the atoms of the benzo groups and the attached oxygen atoms of DB12C4 were used as the starting point for the structure determination. The remainder of the structure was developed using difference maps. It was possible to obtain a structure containing all of the atoms of one enantiomer (Figure 1a). These atoms were assigned occupancy factors of 0.5. Because of the disorder, the benzene rings of the benzo groups were refined as rigid bodies and the C-C and C-O bond lengths were constrained to normal values. Positions for hydrogen atoms were calculated. The constrained structure was refined, with the heavy atoms being refined anisotropically, to a R value of 7.97%. Because there were 190 parameters and only 545 observed data, the refinement was accomplished by dividing the parameters into two nearly equal groups which were refined in alternating cycles. The symmetry relationship imposed by the initial atom positions was lost in the refinement, but the molecule does contain a pseudo center of symmetry. A comparison of the structure of DB13C4 (Figure 1a) with the conformation of the crown ether ring portion for molecule A of (PO)DB13C4 (Figure 1b) and also with CPK space-filling models indicates that the structure obtained for DB13C4 is valid. Inaccuracies in the model for the structure of DB13C4 are incorporated into the large anisotropic displacement coefficients for some of

Table I. Crystal data and experimental details

	DB13C4	(PO)DB13C4
Formula	C <sub>17</sub> H <sub>18</sub> O <sub>4</sub>	C <sub>23</sub> H <sub>23</sub> NO <sub>5</sub>
Formula weight	286.3	393.4
F(000)	608	1664
Crystal size, mm	0.18x0.30x0.65	0.30x0.54x0.54
$\mu$ , mm <sup>-1</sup>	0.092	0.092
Crystal system	orthorhombic	monoclinic
Space group	Pbca	P2 <sub>1</sub> /n
a, Å	7.2370(10)	9.423(4)
b, Å	13.586(3)	19.191(10)
c, Å	14.954(3)	22.687(10)
$\beta$ , °	90	101.17(3)
V, Å <sup>3</sup>	1458	4025
Z	4	8
$\rho_x$ , mg/m <sup>3</sup>	1.304	1.298
Max 2 $\theta$ , °	45	45
Total data	1355	5855
Unique data	960(R <sub>int</sub> =2.08%)	5275(R <sub>int</sub> =3.29%)
Observed data	545(F>3.0 $\sigma$ (F))	2699(F>4.0 $\sigma$ (F))
R	7.87%	4.83%
R <sub>w</sub>	6.89%	5.80%
Weighting scheme	w <sup>-1</sup> = $\sigma^2$ (F)+0.0002F <sup>2</sup>	w <sup>-1</sup> = $\sigma^2$ (F)+0.0015F <sup>2</sup>
Data/parameter	block 1 6.9/1 block 2 6.2/1	5.2:1
Goodness of fit	2.83	1.05
Largest peak, $\Delta\mu$ , eÅ <sup>-3</sup>	0.19	0.17
Largest hole, $\Delta\mu$ , eÅ <sup>-3</sup>	-0.23	-0.19
Index range	0≤h≤7 0≤k≤14 -2≤l≤16	0≤h≤10 0≤k≤20 -24≤l≤24

the atoms (Figure 2) particularly those of the ethylene and propylene bridges which join the oxygens connected to the two benzo groups.

### 2.5.2 Structure of (PO)DB13C4

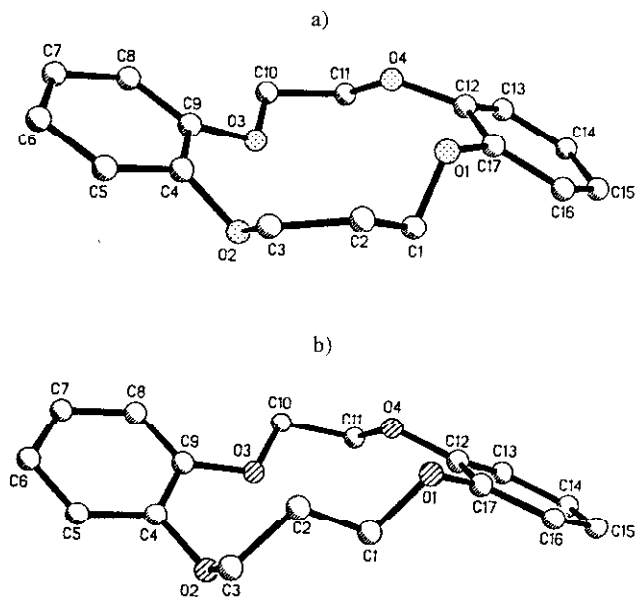


Figure 1. Computer drawings which compare the conformations of a) DB13C4 and b) the crown ether ring portion of molecule A of (PO)DB13C4. Hydrogen atoms are omitted for clarity.

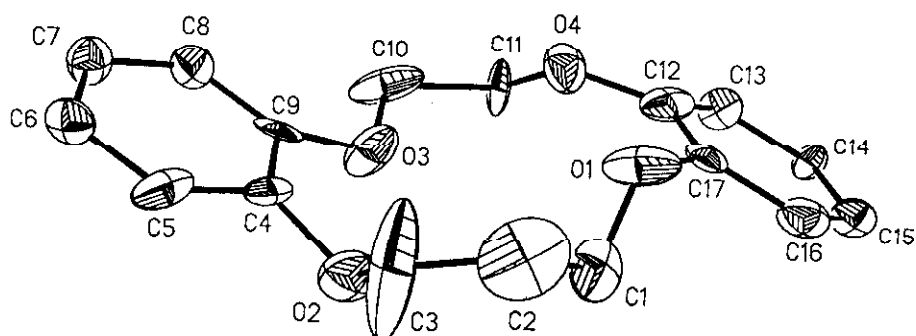


Figure 2. A computer drawing of the crystal structure of DB13C4 with the thermal ellipsoids drawn at the 25% probability level. Hydrogen atoms are omitted for clarity.

The trial structure for (PO)DB13C4 was obtained with direct methods. There are eight molecules in the unit cell. Thus the asymmetric unit of the crystal consists of two chemically similar, but crystallographically different molecules. The atoms of molecule A were assigned atom label numbers from 1 to 23 (Figure 3), while those of molecule B were given atom label numbers ranging from 51 to 73 (Figure 4). It was possible to locate the positions of all non-hydrogen atoms in the E map and succeeding difference maps. Positions for hydrogen atoms were calculated and they were assigned isotropic thermal parameters which were approximately 1.2 times greater than the initial equivalent isotropic thermal parameters of their neighboring carbon atoms. All non-hydrogen atoms were refined anisotropically.

### 3. Results and Discussion

#### 3.1. SYNTHESIS OF DB13C4 COMPOUNDS

Buchanan *et al.* [5] reported the first synthesis of DB13C4 in 33% yield by the reaction of 1,2-bis(*o*-hydroxyphenoxy)ethane with 1,3-dibromopropane and lithium hydroxide monohydrate in 1-butanol. Our alternative synthesis involves the reaction of 1,2-bis(*o*-hydroxyphenoxy)ethane with cesium carbonate and the dimesylate of 1,3-propanediol in acetonitrile to provide DB13C4 in a markedly enhanced yield of 72% for the cyclization reaction.

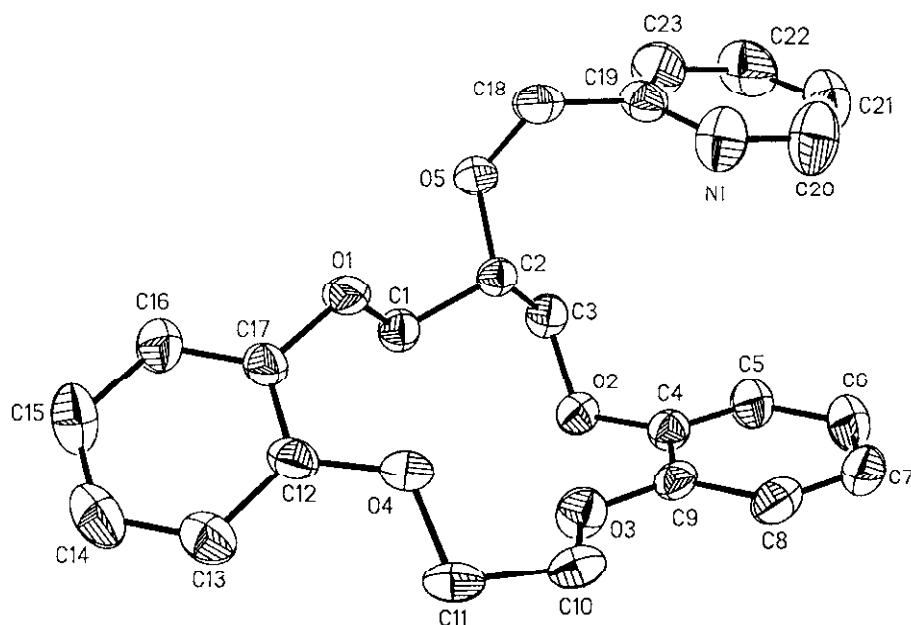


Figure 3. A computer drawing of the crystal structure of molecule A of *sym*-(2-picoloyloxy)dibenzo-13-crown-4 with the thermal ellipsoids drawn at the 25% probability level. Hydrogen atoms are omitted for clarity.

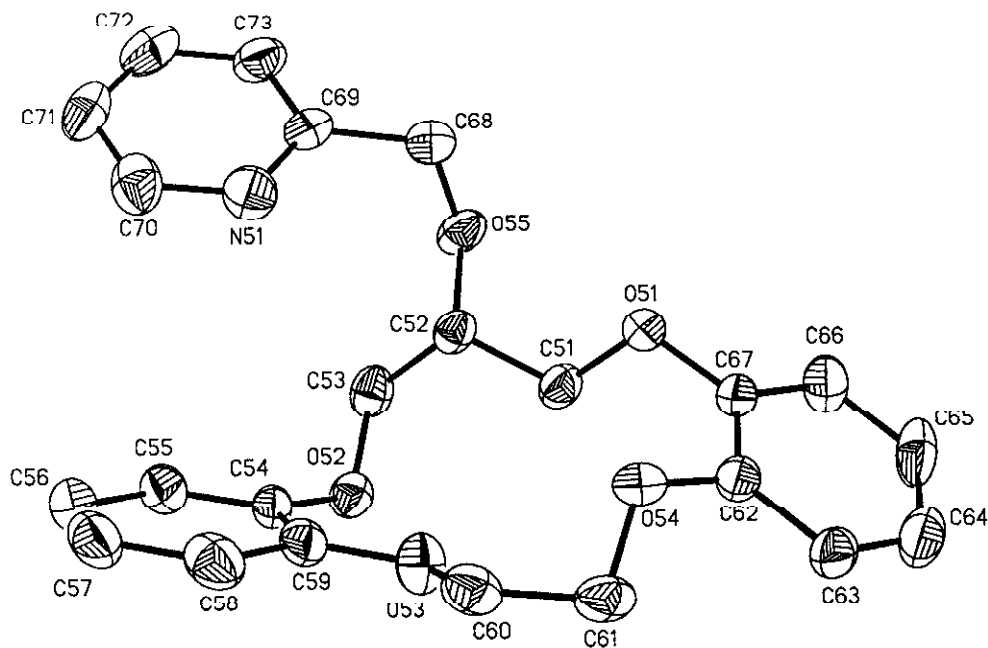


Figure 4. A computer drawing of the crystal structure of molecule B of *sym*-(2-picolyl)oxydibenzo-13-crown-4 with the thermal ellipsoids drawn at the 25% probability level. Hydrogen atoms are omitted for clarity.

Reaction of *sym*-(hydroxy)dibenzo-13-crown-4 with sodium hydride and 2-picolyl chloride in THF gave a 36% yield of lariat ether (PO)DB13C4

### 3.2 STRUCTURE DETERMINATIONS

Positional parameters and equivalent isotropic displacement coefficients of the non-hydrogen atoms of DB13C4 are given in Table II and are listed in Tables III and IV, respectively, for molecules A and B of (PO)DB13C4. A computer drawing of DB13C4 is shown in Figure 2. Computer drawings of the two crystallographically different molecules of (PO)DB13C4 are presented in Figures 3 and 4.

Because DB13C4 is found to be isomorphous with DB12C4, it resembles that ring system, but does not have any characteristics of the DB14C4 ring system. The solid-state structure of DB13C4 is complicated by the presence of disorder, primarily in the carbon atoms of the ethylene and propylene bridges. The molecule is somewhat planar with the average deviation of an atom from the least-square plane of 0.34 Å. Because the molecule possesses a pseudo-center of symmetry (see Experimental), the donor atom geometry is similar to that reported for DB12C4 with O1 and O4 being directed in one direction relative to the least-square plane of the molecule and O2 and O3 pointing in the opposite direction.



Table II. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for the non-hydrogen atoms of DB13C4.

	x	y	z	U(eq) <sup>a</sup>
O1	2791(1)	5632(1)	5192(1)	115(1)
C1	2551(1)	5804(1)	4289(1)	103(1)
C2	3259(1)	4924(1)	3801(1)	172(1)
C3	1762(1)	4338(1)	3373(1)	266(1)
O2	-109(1)	4510(1)	3458(1)	112(1)
C4	-751(1)	3596(1)	3716(1)	65(1)
C5	-681	2769	3163	92(1)
C6	-1814	1961	3340	70(1)
C7	-3016	1980	4069	80(1)
C8	-3085	2807	4621	86(1)
C9	-1953	3615	4444	68(1)
O3	-2083(1)	4521(1)	4857(1)	109(1)
C10	-2992(1)	4517(1)	5660(1)	120(1)
C11	-2179(1)	5356(1)	6181(1)	67(1)
O4	-270(1)	5345(1)	6254(1)	94(1)
C12	800(1)	6180(1)	6374(1)	82(1)
C13	145	6940	6915	74(1)
C14	981	7865	6883	69(1)
C15	2470	8029	6310	70(1)
C16	3125	7269	5769	85(1)
C17	2289	6344	5801	58(1)

<sup>a</sup>Equivalent isotropic U defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

For (PO)DB13C4, the asymmetric unit of the crystal contains two chemically identical, but crystallographically different molecules. The major difference in the conformations of molecules A and B is the twist of the pyridine ring in the side arm with respect to the benzo groups of the crown ether ring (see Figures 3 and 4, respectively). The distances between the centers of the pyridine and benzene rings in both molecules are greater than 4 Å which suggests very weak or non-existent  $\pi$ - $\pi$  interactions between the aromatic rings of the polyether unit and the side arm. However in molecule A, the aromatic rings of one benzo group substituent of the crown ether ring and the pyridine ring in the side arm are nearly parallel with a dihedral angle between the planes of the rings of 12.1°. In contrast, for molecule B this dihedral angle is 39.1°.

Conformations of the polyether ring systems in DB13C4 and (PO)DB13C4 are similar. Values of the torsion angles are listed in Table V.

Table III. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for the non-hydrogen atoms of molecule A of (PO)DB13C4.

	x	y	z	U(eq) <sup>a</sup>
O1	11588(3)	-135(2)	1403(2)	63(1)
C1	11474(5)	349(2)	910(2)	54(2)
C2	10028(5)	701(2)	809(2)	50(2)
C3	9918(5)	1247(2)	321(2)	58(2)
O2	10918(3)	1817(2)	494(1)	60(1)
C4	10465(5)	2327(3)	846(2)	54(2)
C5	9382(6)	2782(3)	620(3)	76(2)
C6	8964(7)	3306(3)	977(4)	92(3)
C7	9651(7)	3352(3)	1565(3)	82(3)
C8	10740(6)	2903(3)	1794(3)	68(2)
C9	11170(5)	2387(2)	1437(2)	54(2)
O3	12310(4)	1941(2)	1615(2)	68(1)
C10	13024(6)	1940(3)	2228(2)	67(2)
C11	14058(5)	1343(3)	2309(2)	66(2)
O4	13209(3)	723(2)	2184(2)	69(1)
C12	13866(5)	131(3)	2030(2)	58(2)
C13	15294(6)	-41(3)	2254(2)	68(2)
C14	15850(6)	-653(4)	2081(3)	88(3)
C15	14995(7)	-1102(3)	1701(3)	92(3)
C16	13558(6)	-923(3)	1472(3)	78(3)
C17	13008(5)	-314(3)	1634(2)	58(2)
O5	8926(3)	192(2)	620(2)	63(1)
C18	7756(6)	214(3)	937(3)	73(2)
C19	6761(5)	824(3)	758(3)	65(2)
N1	6819(6)	1336(3)	1152(2)	88(2)
C20	5960(9)	1890(4)	992(3)	105(4)
C21	5019(8)	1947(4)	462(4)	107(4)
C22	5005(7)	1441(4)	38(4)	106(3)
C23	5891(6)	870(3)	198(3)	95(3)

<sup>a</sup>Equivalent isotropic U defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

As would be expected, there is little difference in the absolute values of the torsion angles for molecules A and B of (PO)DB13C4. The major differences between the absolute values of the torsion angles of the (PO)DB13C4 molecules and those of DB13C4 involve the central carbon of the propylene bridges, C2 (C52 in molecule B of (PO)DB13C4) to which the side arm oxygen is attached. It is interesting to note that C2 and C3 are in a nearly

Table IV. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for the non-hydrogen atoms of molecule B of (PO)DB13C4.

	x	y	z	U(eq) <sup>a</sup>
O51	17944(3)	-161(2)	3769(2)	67(1)
C51	18218(5)	440(2)	4150(2)	56(2)
C52	16849(5)	817(2)	4177(2)	51(2)
C53	17142(5)	1472(3)	4565(2)	61(2)
O52	18011(3)	1972(2)	4330(1)	57(1)
C54	17262(5)	2419(2)	3897(3)	53(2)
C55	16394(6)	2928(3)	4054(3)	71(2)
C56	15691(6)	3392(3)	3627(4)	90(3)
C57	15859(6)	3327(3)	3044(4)	84(3)
C58	16744(6)	2817(3)	2877(3)	73(2)
C59	17460(5)	2361(3)	3316(3)	55(2)
O53	18397(3)	1854(2)	3210(1)	63(1)
C60	18507(6)	1699(3)	2615(2)	67(2)
C61	19501(6)	1095(3)	2642(2)	67(2)
O54	18810(3)	525(2)	2876(2)	63(1)
C62	19662(5)	-23(3)	3125(2)	55(2)
C63	20919(6)	-220(3)	2944(3)	67(2)
C64	21677(6)	-785(4)	3209(3)	86(3)
C65	21188(7)	-1164(3)	3639(3)	86(3)
C66	19921(6)	-962(3)	3825(3)	74(2)
C67	19179(5)	-387(3)	3579(3)	58(2)
O55	15922(3)	379(2)	4442(2)	67(1)
C68	14514(6)	263(3)	4089(3)	75(2)
C69	13502(5)	870(3)	4106(2)	58(2)
N51	13670(5)	1425(3)	3774(2)	72(2)
C70	12808(7)	1975(3)	3805(3)	77(3)
C71	11756(6)	1983(4)	4139(3)	79(3)
C72	11598(6)	1418(4)	4480(3)	85(3)
C73	12490(5)	853(3)	4466(3)	71(2)

<sup>a</sup>Equivalent isotropic U defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

eclipsed conformation in DB13C4. (A similar conformation was indicated by CPK space-filling models.) This is not the case for the two molecules of (PO)DB13C4.

These structural studies suggest an arrangement of donor atoms in the DB13C4 ring system which will not form strong complexes with metal cations. Rigidity in the molecule will make it difficult to achieve a confor-

Table V. Torsion angles of the DB13C4 ring system.<sup>a</sup>

atoms <sup>b</sup>	torsion angle (°)		
	DB13C4	(PO)DB13C4	
		molecule A	molecule B
C17-O1-C1-C2	178.5	-161.6	160.3
O1-C1-C2-C3	110.3	176.5	-178.1
C1-C2-C3-O2	-5.1	-65.6	62.8
C2-C3-O2-C4	-127.8	-82.2	84.6
C3-O2-C4-C5	-65.7	-71.1	71.4
C3-O2-C4-C9	132.5	111.3	-111.6
O2-C4-C5-C6	-160.8	-178.2	177.4
O2-C4-C9-C8	162.4	179.1	-178.4
O2-C4-C9-O3	-9.8	2.3	0.3
C5-C4-C9-O3	-172.2	-175.4	177.3
C7-C8-C9-O3	171.1	175.5	-177.7
C4-C9-O3-C10	-170.4	-175.6	171.3
C8-C9-O3-C10	18.0	7.8	-10.0
C9-O3-C10-C11	153.4	171.8	-175.3
O3-C10-C11-O4	-52.4	-62.9	64.1
C10-C11-O4-C12	153.4	158.7	-159.5
C11-O4-C12-C13	37.1	33.6	-29.9
C11-O4-C12-C17	-128.3	-147.8	150.8
O4-C12-C12-C14	-165.3	178.8	-178.3
C1-O1-C17-C12	112.2	80.2	-76.6
C1-O1-C17-C16	-60.1	-99.7	103.9
O4-C12-C17-O1	-6.8	2.5	-3.2
O4-C12-C17-C16	165.4	-177.6	176.3
C13-C12-C17-O1	-172.2	-178.8	177.4
C15-C16-C7-O1	172.2	179.0	-177.8

<sup>a</sup>Or corresponding atom numbers for molecule B of (PO)DB13C4.

<sup>b</sup>Torsion angles for the benzene ring carbons are omitted.

mation in which more than two oxygen atoms of the crown ether ring can interact with a metal cation simultaneously. This is not the case when only one benzo group [6] or two cyclohexano groups [5] are attached to the 13C4 ring for which complexation of Li<sup>+</sup> involves all four oxygen atoms. Although <sup>1</sup>H NMR spectral shifts suggest that DB13C4 does form a complex with Li<sup>+</sup> [5], the nature of this complex remains unknown.

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