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Macrocycle Complexation Chemistry. 38.* Crystallographic and Ultraviolet/Visible Characterization of Nitrobenzo-15-crown-5, Dinitrobenzo-15-crown-5, and Dinitrodibenzo-18-crown-6·2CH_3CN

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Abstract. The crystal structures of three nitrated benzocrown ethers have been determined. Nitrobenzo-15-crown-5 crystallizes in the orthorhombic space group, $Pca2_1$, with $a = 15.367(2)$, $b = 4.8499(8)$, $c = 19.963(5)$ Å, and $D_{calc} = 1.40$ g cm^{-3} for $Z = 4$. Dinitrobenzo-15-crown-5 crystallizes in the monoclinic space group, $P2_1/n$, with $a = 11.716(2)$, $b = 8.495(3)$, $c = 17.441(5)$ Å, $\beta = 108.40(2)°$ and $D_{calc} = 1.44$ g cm^{-3} for $Z = 4$. Dinitrodibenzo-18-crown-6·2 CH_3CN is monoclinic, $P2_1/n$, with $a = 8.138(2)$, $b = 20.435(9)$, $c = 15.953(9)$ Å, $\beta = 100.55(4)°$ and $D_{calc} = 1.36$ g cm^{-3} for $Z = 4$. The nitro substituents are in the plane of the benzo ring except in the sterically congested dinitrobenzo-15-crown-5. The observed crown ether conformations are similar to their substituted analogs.

Key words. Nitrobenzo-15-crown-5, dinitrobenzo-15-crown-5, dinitrodibenzo-18-crown-6 acetonitrile solvate, X-ray crystal structure.

1. Introduction

The utility of crown ethers as complexing and extraction agents for hard metal cations is well established in the literature [2]. The benzocrowns add some rigidity to the macrocyclic ring and also offer a reactive site for the addition of functional groups. While the chemistry of the aromatic ring is complicated by being attached to a crown ether, it has been shown that typical aromatic reactions such as Friedel–Crafts acylations can still be accomplished [3].

The nitration of the benzocrowns is also possible [3–5]. The nitrated benzocrowns have been shown to be less efficient extractants than their unsubstituted analogs for sodium and potassium [3]; however, complexation chemistry with many other metals has not been investigated. The nitrated benzocrowns show more absorbance in the ultraviolet and visible ranges, which makes them easy to observe spectroscopically. These crowns can also be used as precursors for the addition of other functionalities to the macrocyclic system. This report discusses the solid state characteristics of three of these nitrated crown ethers.

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* For part 37, see reference [1].

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Table I. Crystal data and summary of data collection and structure refinement

Cmpd.	nitrobenzo-15-crown-5	dinitrobenzo-15-crown-5	dinitrodibenzo-18-crown-6·2 CH_3CN
Color/Shape	yellow/parallelepiped	yellow/parallelepiped	amber/parallelepiped
Form. wt.	313.31	358.30	532.51
Space group	$Pca2_1$	$P2_1/n$	$P2_1/n$
Temp., °C	20	22	22
Cell Constants[a]			
a, Å	15.367(2)	11.716(2)	8.138(2)
b, Å	4.8499(8)	8.495(3)	20.435(9)
c, Å	19.963(5)	17.441(5)	15.953(9)
β, deg		108.40(2)	100.55(4)
Cell vol, Å^3	1487.8	1647	2608
Formula units/unit cell	4	4	4
D_{calc}, g cm^{-3}	1.40	1.44	1.36
μ_{calc}, cm^{-1}	1.22	1.31	1.15
Diffractometer/scan	Enraf-Nonius CAD-4/ω-2θ	Enraf-Nonius CAD-4/ω-2θ	Enraf-Nonius CAD-4/ω-2θ
Radiation, graphite monochromator	MoK_α(λ = 0.71073)	MoK_α(λ = 0.71073)	MoK_α(λ = 0.71073)
Max crystal dimensions, mm	0.23 × 0.25 × 0.38	0.20 × 0.30 × 0.30	0.13 × 0.25 × 0.30

Scan width	$0.80+0.35 \tan\theta$	$0.80+0.35 \tan\theta$	$0.80+0.35 \tan\theta$
Standard reflections	10, 0, 0; 020; 006	210; 020; 002	200; 080; 004
Decay of standards	±1%	±2%	±2%
Reflections measured	1586	2432	5059
2θ range, deg	$2 \leqslant 2\theta \leqslant 50$	$2 \leqslant 2\theta \leqslant 50$	$2 \leqslant 2\theta \leqslant 50$
Range of h, k, l	$+18, -5, +23$	$+13, +10, \pm 20$	$+9, +24, \pm 18$
Reflections observed	766 $[F_0 \geqslant 5\sigma(F_0)]^b$	568 $[F_0 \geqslant 2.5\sigma(F_0)]^b$	1057 $[F_0 \geqslant 5\sigma(F_0)]^b$
Computer programs[c]	SHELX [6]	SHELX [6]	SHELX [6]
Structure solution	SHELXS [7]	SHELXS [7]	SHELXS [7]
No. of parameters varied	145	226	344
Weights	$[\sigma(F_0)^2+0.002F_0^2]^{-1}$	$[\sigma(F_0)^2+0.0015F_0^2]^{-1}$	$[\sigma(F_0)^2+0.0005F_0^2]^{-1}$
GOF	0.94	0.92	2.01
$R=\Sigma \lVert F_0\rvert-\lvert Fc\rVert/\Sigma\lvert F_o\rvert$	0.043	0.060	0.089
R_w	0.062	0.061	0.099
R inverse configuration	0.044		
Largest feature final diff. map	$0.3e$ Å^{-3}	$0.2e$ Å^{-3}	$0.4e$ Å^{-3}

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[a] Least squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 9°$.

[b] Corrections: Lorentz-polarization.

[c] Neutral scattering factors and anomalous dispersion corrections from Ref. [8].

2. Experimental

2.1. SYNTHESIS AND SPECTRAL CHARACTERIZATION

The synthesis of nitrobenzo-15-crown-5, dinitrobenzo-15-crown-5, and dinitrodibenzo-18-crown-6 have been described previously [3–5]. All reagents were obtained commercially and used without further purification. The ultraviolet/visible spectra of the title compounds were measured between 800 and 230 nm on a Varian 2290 spectrometer. All three spectra were measured in ethanol. Nitrobenzo-15-crown-5 exhibits maximum absorbance at 239 nm, a second maximum at 344 nm, and a shoulder at 308 nm. Dinitrobenzo-15-crown-5 exhibits its greatest absorbance at 241 nm. The second greatest absorbance occurred at 330 nm with shoulders at 266 and 300 nm. The maximum absorbance for dinitrodibenzo-18-crown-6 occurred at 272 nm with shoulders at 242 and 330 nm.

2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION, AND REFINEMENT

Yellow transparent crystals of the nitrated crowns were obtained for all three crowns. For nitrobenzo-15-crown-5 and dinitrodibenzo-18-crown-6·2 CH_3CN, crystals were obtained directly from the reaction. In the case of dinitrobenzo-15-crown-5 the reaction produced thin plates which were unsuitable for X-ray studies. Recrystallization from chloroform produced thicker plates. These plates diffracted well but were still inadequate. The crystals that were finally used in the study were recrystallized from acetone. The crystals were sealed in capillary tubes which had been flushed with argon. In all three studies it was extremely difficult to obtain crystals that diffracted at all, much less very strongly. All three studies suffer the effects of too few reflections in the data sets. Fortunately, since the conformational features of these ethers and their packing environments are straightforward enough, the data presented here are adequate for their determination. A summary of data collection parameters is given in Table I.

Least-squares refinement with isotropic thermal parameters led to $R = 0.097$, $R = 0.125$, and $R = 0.135$ for nitrobenzo-15-crown-5, dinitrobenzo-15-crown-5, and dinitrodibenzo-18-crown-6·2 CH_3CN, respectively. Disorder was resolved for one ethylene linkage (C(5)–C(6)) in nitrobenzo-15-crown-5. An initial disorder of 50/50 was assumed and then the occupancy factors were refined. The final values for the occupancy factors were refined to 68% (C(5)–C(6)) and 32% (C(5)′–C(6)′). High thermal motion was noted for the nitro groups and C(3)–C(6) in dinitrobenzo-15-crown-5. Torsion angle analysis did not reveal any unusual conformational features in the C(3)–C(6) portion of the ring and it was not possible to resolve a disorder model. These atoms were therefore given occupancy factors of 1.0. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 $Å^2$ in all three structures. Refinement of nonhydrogen atoms with anisotropic temperature factors (except for C(15) in dinitrodibenzo-18-crown-6·2 CH_3CN which could not be refined anisotropically) led to the final values of R and R_w given in Table I. The final values of the positional parameters for nitrobenzo-15-crown-5, dinitrobenzo-15-crown-5, and dinitrodibenzo-18-crown-6·2 CH_3CN are given in Tables II, III, and IV, respectively.

Table II. Final fractional coordinates for nitrobenzo-15-crown-5

Atom	x/a	y/b	z/c	B(eqv)[a]
O(1)	0.8346(3)	0.096(1)	0.5000	3.37
O(2)	0.8740(3)	−0.069(1)	0.6323(3)	3.50
O(3)	1.0230(4)	0.292(2)	0.6656(4)	7.49
O(4)	1.1037(3)	0.528(2)	0.5095(4)	4.53
O(5)	0.9472(3)	0.372(1)	0.4374(3)	3.22
O(6)	0.6981(4)	−0.533(1)	0.3291(4)	4.72
O(7)	0.7682(4)	−0.444(1)	0.2374(3)	4.51
N	0.7528(4)	−0.405(1)	0.2974(4)	3.45
C(1)	0.7770(4)	−0.071(2)	0.5406(4)	3.53
C(2)	0.7926(6)	0.022(2)	0.6115(4)	3.88
C(3)	0.8987(6)	0.039(2)	0.6972(4)	4.06
C(4)	0.9425(6)	0.305(2)	0.6935(5)	4.50
C(5)	1.0195(8)	0.352(3)	0.5987(6)	4.79
C(6)	1.0835(7)	0.531(3)	0.5776(6)	4.58
C(5)′[b]	1.068(2)	0.456(8)	0.629(2)	5.43
C(6)′	1.030(2)	0.490(8)	0.556(1)	5.38
C(7)	1.0591(5)	0.689(2)	0.4621(5)	4.33
C(8)	1.0194(4)	0.513(2)	0.4079(5)	3.59
C(9)	0.9026(4)	0.191(1)	0.3985(4)	2.77
C(10)	0.8408(4)	0.039(1)	0.4337(4)	2.64
C(11)	0.7911(4)	−0.158(2)	0.4004(4)	2.80
C(12)	0.8044(4)	−0.193(2)	0.3323(4)	2.74
C(13)	0.8668(5)	−0.045(2)	0.2974(4)	3.14
C(14)	0.9151(4)	0.150(2)	0.3304(4)	3.03

[a] $B(\text{eqv}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

[b] Primed atoms were refined with site occupancy factors of 0.32. Unprimed atoms of like number were refined at 68% occupancy.

3. Results and Discussion

ORTEP illustrations of the title compounds are provided in Figure 1 (nitrobenzo-15-crown-5), Figure 2 (dinitrobenzo-15-crown-5), and Figure 3 (dinitrodibenzo-18-crown-6·2 CH_3CN). The most readily apparent feature of each compound is the similarity between the macrocyclic ring conformation observed here and in the unsubstituted benzo-crown ethers. The torsion angles for dinitrobenzo-15-crown-5 (Table V) are nearly identical to those found for benzo-15-crown-5 [9]. The only difference observed between nitrobenzo-15-crown-5 (Table VII) and benzo-15-crown-5 [9] occurs in the disordered portion of the macrocycle (C(5)–C(6)). (This is likely the result of packing forces introduced in the lattice as a result of the new benzo-environment.) A similar analysis of dinitrodibenzo-18-crown-6·2 CH_3CN (Table VI) reveals that the crown ether adopts the conformation found in the unsubstituted analog [10] and virtually every crystallographically characterized dibenzo-18-crown-6 complex [2]. For all practical purposes, the nitro substituents do not affect the adoption of a specific crown ether conformation.

Table III. Final fractional coordinates for dinitrobenzo-15-crown-5

Atom	x/a	y/b	z/c	B(eqv)[a]
O(1)	0.8975(9)	0.174(1)	0.3196(5)	3.58
O(2)	0.653(1)	0.185(2)	0.3109(6)	4.86
O(3)	0.673(1)	−0.080(2)	0.4170(7)	4.67
O(4)	0.8550(9)	−0.316(1)	0.4239(6)	4.38
O(5)	0.9945(8)	−0.082(1)	0.3715(5)	2.90
O(6)	1.115(1)	0.354(2)	0.1202(9)	6.40
O(7)	1.087(2)	0.128(2)	0.0557(7)	10.59
O(8)	1.2210(9)	−0.211(2)	0.1738(7)	4.60
O(9)	1.294(1)	0.011(2)	0.1670(9)	8.66
N(1)	1.096(2)	0.214(3)	0.117(1)	6.01
N(2)	1.217(2)	−0.069(2)	0.181(1)	4.64
C(1)	0.816(1)	0.306(2)	0.2854(9)	4.58
C(2)	0.730(1)	0.319(2)	0.3347(8)	4.08
C(3)	0.585(2)	0.152(3)	0.366(1)	7.62
C(4)	0.646(2)	0.071(3)	0.437(1)	8.13
C(5)	0.745(2)	−0.149(2)	0.489(1)	7.06
C(6)	0.789(1)	−0.308(3)	0.480(1)	7.43
C(7)	0.977(1)	−0.284(2)	0.4604(8)	3.85
C(8)	1.030(1)	−0.242(2)	0.3955(8)	3.22
C(9)	1.026(1)	−0.019(2)	0.3099(9)	2.58
C(10)	0.974(1)	0.121(2)	0.2830(8)	2.71
C(11)	0.995(1)	0.200(2)	0.2190(9)	3.38
C(12)	1.073(2)	0.136(3)	0.184(1)	4.07
C(13)	1.127(2)	−0.004(3)	0.211(1)	3.44
C(14)	1.108(1)	−0.086(2)	0.2755(9)	2.56

[a] $B(\text{eqv}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

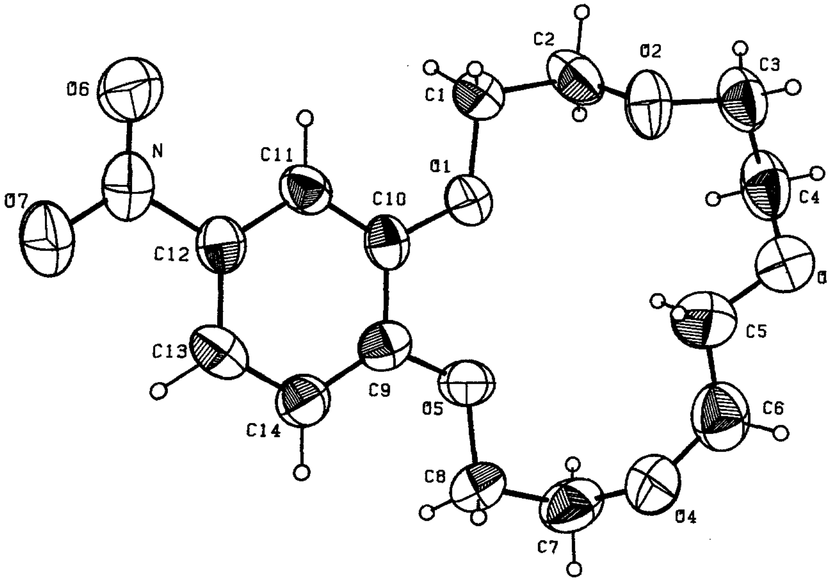

Fig. 1. ORTEP illustration of nitrobenzo-15-crown-5 with 50% probability ellipsoids. The major conformation (68%) of C(5)—C(6) is depicted.

Table IV. Final fractional coordinates for dinitrodibenzo-18-crown-6·2 CH_3CN

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eqv)[a]
O(1)	0.219(1)	0.2476(5)	0.6816(8)	3.27
O(2)	0.250(1)	0.3637(6)	0.5917(6)	3.23
O(3)	0.220(1)	0.4887(6)	0.6650(8)	3.36
O(4)	0.160(2)	0.4952(6)	0.8185(8)	3.56
O(5)	0.133(1)	0.3752(6)	0.9099(7)	3.67
O(6)	0.163(1)	0.2502(6)	0.8336(7)	3.27
O(7)	−0.183(2)	−0.0054(6)	0.737(1)	5.82
O(8)	−0.145(2)	0.0401(7)	0.863(1)	6.24
O(9)	−0.192(2)	0.7435(7)	0.689(1)	6.92
O(10)	−0.156(2)	0.7070(7)	0.819(1)	6.64
N(1)	−0.132(2)	0.037(1)	0.785(1)	4.74
N(2)	−0.138(3)	0.703(1)	0.742(2)	6.10
C(1)	0.236(3)	0.2497(9)	0.592(1)	4.12
C(2)	0.339(2)	0.3077(9)	0.581(1)	3.52
C(3)	0.340(2)	0.4192(9)	0.575(1)	4.05
C(4)	0.241(2)	0.4804(9)	0.577(1)	4.33
C(5)	0.125(2)	0.542(1)	0.681(1)	3.43
C(6)	0.099(2)	0.5446(9)	0.766(1)	3.22
C(7)	0.112(2)	0.4929(9)	0.898(1)	3.83
C(8)	0.191(3)	0.435(1)	0.946(1)	4.33
C(9)	0.206(3)	0.3204(9)	0.958(1)	4.15
C(10)	0.118(2)	0.2575(9)	0.915(1)	4.43
C(11)	0.110(2)	0.1969(8)	0.787(1)	3.05
C(12)	0.134(2)	0.194(1)	0.703(1)	2.98
C(13)	0.062(2)	0.1405(9)	0.650(1)	3.74
C(14)	−0.020(2)	0.088(1)	0.682(1)	4.49
C(15)	−0.038(2)	0.093(1)	0.763(1)	4.0(4)[b]
C(16)	0.020(2)	0.1472(9)	0.820(1)	3.58
C(17)	0.074(2)	0.5936(9)	0.624(1)	4.17
C(18)	−0.020(2)	0.647(1)	0.648(2)	4.70
C(19)	−0.046(2)	0.6431(9)	0.726(2)	3.29
C(20)	0.007(2)	0.5989(9)	0.789(1)	3.81
N(3)	0.678(3)	0.390(1)	0.946(1)	7.31
C(21)	0.586(3)	0.382(1)	0.884(1)	4.29
C(22)	0.474(3)	0.3735(9)	0.806(1)	4.73
N(4)	−0.230(3)	0.373(2)	0.563(1)	9.32
C(23)	−0.154(3)	0.367(1)	0.634(2)	6.99
C(24)	−0.067(2)	0.366(1)	0.716(1)	5.11

[a] $B(\text{eqv}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.
[b] Isotropic refinement.

The bond distances and angles with the macrocycles are also relatively unaffected by the nitro substituents. The average bonding parameters for nitrobenzo-15-crown-5 (Table VIII), dinitrobenzo-15-crown-5 (Table IX), and dinitrodibenzo-18-crown-6·2 CH_3CN (Table X) are as follows: C—O(alkyl) = 1.40(5), 1.43(3), 1.42(3) Å, C—O(aryl) = 1.356(2), 1.34(2), 1.36(2) Å; C—C(alkyl) = 1.48(8), 1.47(4), 1.50(4) Å; C—C(aryl, macrocycle) = 1.39(1), 1.36(2), 1.40(1) Å;

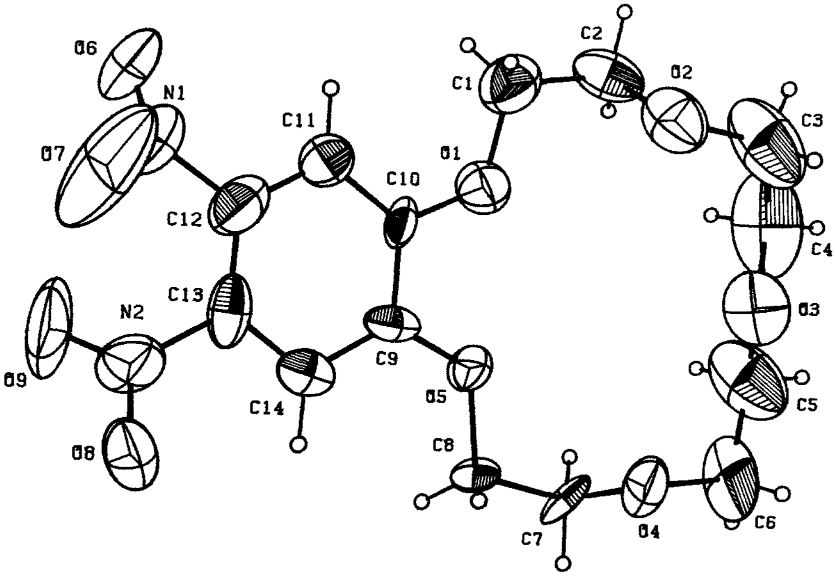

Fig. 2. Dinitrobenzo-15-crown-5.

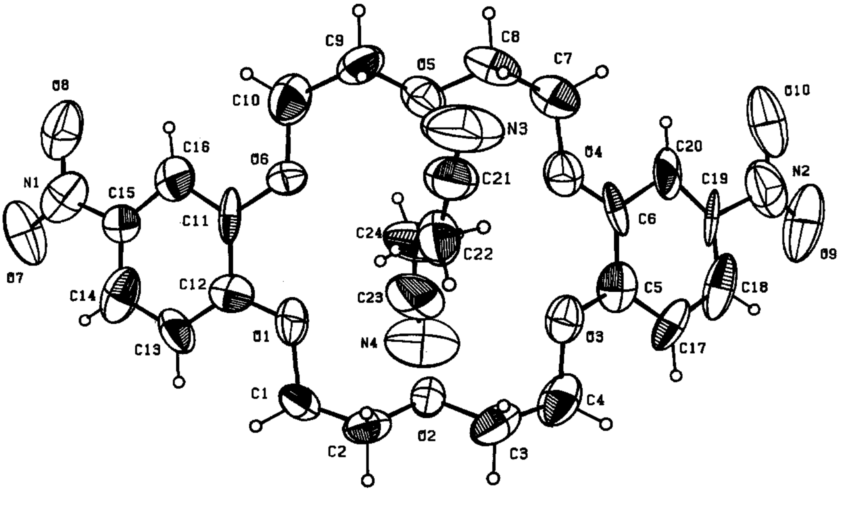

Fig. 3. Dinitrodibenzo-18-crown-6·2 CH_3CN.

C—O—C(alkyl) = 116(12), 110(3), 112(2)°; C—O—C(aryl-alkyl) = 118.0(4), 120(2), 116(1)°, O—C—C(alkyl) = 111(4), 110(4), 109(2)°; O—C—C(aryl, macrocycle) = 115(1), 115(1), 115(3)°.

The nitro-substituents in the two complexes with only one per benzo ring are in the aromatic plane (Figures 4, 5). In the sterically more congested dinitrobenzo-15-

Table V. Torsion angles (deg) for dinitrobenzo-15-crown-5

Atoms	Angle
O(1)—C(1)—C(2)—O(2)	−72.3
C(1)—C(2)—O(2)—C(3)	164.4
C(2)—O(2)—C(3)—C(4)	−79.5
O(2)—C(3)—C(4)—O(3)	−65.9
C(3)—C(4)—O(3)—C(5)	174.1
C(4)—O(3)—C(5)—C(6)	−177.0
O(3)—C(5)—C(6)—O(4)	56.4
C(5)—C(6)—O(4)—C(7)	87.5
C(6)—O(4)—C(7)—C(8)	−161.5
O(4)—C(7)—C(8)—O(5)	77.4
C(7)—C(8)—O(5)—C(9)	−176.9
C(8)—O(5)—C(9)—C(10)	169.7
O(5)—C(9)—C(10)—O(1)	−0.8
C(9)—C(10)—O(1)—C(1)	−167.1
C(10)—O(1)—C(1)—C(2)	171.7

Table VI. Torsion angles (deg) for dinitrodibenzo-18-crown-6·2 CH_3CN

Atoms	Angle
O(1)—C(1)—C(2)—O(2)	−67.9
C(1)—C(2)—O(2)—C(3)	−175.8
C(2)—O(2)—C(3)—C(4)	174.0
O(2)—C(3)—C(4)—O(3)	67.5
C(3)—C(4)—O(3)—C(5)	−177.6
C(4)—O(3)—C(5)—C(6)	175.2
O(3)—C(5)—C(6)—O(4)	−3.0
C(5)—C(6)—O(4)—C(7)	−170.7
C(6)—O(4)—C(7)—C(8)	179.8
O(4)—C(7)—C(8)—O(5)	−66.2
C(7)—C(8)—O(5)—C(9)	−178.2
C(8)—O(5)—C(9)—C(10)	175.1
O(5)—C(9)—C(10)—O(6)	67.1
C(9)—C(10)—O(6)—C(11)	175.8
C(10)—O(6)—C(11)—C(12)	171.2
O(6)—C(11)—C(12)—O(1)	3.1
C(11)—C(12)—O(1)—C(1)	−175.5
C(12)—O(1)—C(1)—C(2)	−176.5

crown-5 (Figure 6), the nitro groups are forced out of the benzo plane. In this compound the nitro groups are twisted 48° relative to each other and 48° (N(1)) and 41° (N(2)) out of the C(9)—C(14) plane. We have recently crystallographically characterized this crown ether in the hydronium ion complex, $[(H_5O_2)((NO_2)_2\text{benzo-15-crown-5})_2]_2[(UO_2(NO_3)_2)_2C_2O_4]$ [11]. In this complex the nitro groups are twisted an average of 45° out of the benzene ring planes.

Table VII. Torsion angles (deg) for nitrobenzo-15-crown-5

Atoms	Angle	Atoms	Angle
O(1)—C(1)—C(2)—O(2)	−71.3	C(7)—C(8)—O(5)—C(9)	−177.6
C(1)—C(2)—O(2)—C(3)	173.2	C(8)—O(5)—C(9)—C(10)	172.3
C(2)—O(2)—C(3)—C(4)	−87.7	O(5)—C(9)—C(10)—O(1)	0.4
O(2)—C(3)—C(4)—O(3)	−68.8	C(9)—C(10)—O(1)—C(1)	−174.8
C(3)—C(4)—O(3)—C(5)	94.9	C(10)—O(1)—C(1)—C(2)	173.8
C(4)—O(3)—C(5)—C(6)	134.7	C(3)—C(4)—O(3)—C(5)′	146.9
O(3)—C(5)—C(6)—O(4)	158.5	C(4)—O(3)—C(5)′—C(6)′	−69.3
C(5)—C(6)—O(4)—C(7)	87.3	O(3)—C(5)′—C(6)′—O(4)	−146.5
C(6)—O(4)—C(7)—C(8)	−122.1	C(5)′—C(6)′—O(4)—C(7)	−150.8
O(4)—C(7)—C(8)—O(5)	72.3	C(6)′—O(4)—C(7)—C(8)	−91.4

Table VIII. Bond distances (Å) and angles (deg) for nitrobenzo-15-crown-5

Atoms	Distance	Atoms	Distance
O(1)—C(1)	1.447(9)	O(1)—C(10)	1.355(7)
O(2)—C(2)	1.39(1)	O(2)—C(3)	1.45(1)
O(3)—C(4)	1.36(1)	O(3)—C(5)	1.37(1)
O(3)—C(5)′	1.28(3)	O(4)—C(6)	1.40(1)
O(4)—C(6)′	1.48(3)	O(4)—C(7)	1.40(1)
O(5)—C(8)	1.429(9)	O(5)—C(9)	1.358(9)
O(6)—N	1.22(1)	O(7)—N	1.23(1)
N—C(12)	1.48(1)	C(1)—C(2)	1.51(1)
C(3)—C(4)	1.46(1)	C(5)—C(6)	1.38(2)
C(5)′—C(6)′	1.59(4)	C(7)—C(8)	1.51(1)
C(9)—C(10)	1.39(1)	C(9)—C(14)	1.39(1)
C(10)—C(11)	1.39(1)	C(11)—C(12)	1.38(1)
C(12)—C(13)	1.38(1)	C(13)—C(14)	1.37(1)
Atoms	Angle	Atoms	Angle
C(1)—O(1)—C(10)	118.5(5)	C(2)—O(2)—C(3)	112.9(6)
C(4)—O(3)—C(5)	110.9(8)	C(4)—O(3)—C(5)′	134(2)
C(6)—O(4)—C(7)	122.9(8)	C(6)′—O(4)—C(7)	97(1)
C(8)—O(5)—C(9)	117.6(7)	O(6)—N—O(7)	124.0(7)
C(6)—N—C(12)	118.6(7)	O(7)—N—C(12)	117.4(7)
O(1)—C(1)—C(2)	105.2(6)	O(2)—C(2)—C(1)	109.2(7)
O(2)—C(3)—C(4)	113.3(7)	O(3)—C(4)—C(3)	113.6(8)
O(3)—C(5)—C(6)	114(1)	O(4)—C(6)—C(5)	117(1)
O(3)—C(5)′—C(6)′	113(2)	O(4)—C(6)′—C(5)′	108(2)
O(4)—C(7)—C(8)	111.5(7)	O(5)—C(8)—C(7)	106.8(7)
O(5)—C(9)—C(10)	113.4(7)	O(5)—C(9)—C(14)	125.8(6)
C(10)—C(9)—C(14)	120.8(6)	O(1)—C(10)—C(9)	115.7(6)
O(1)—C(10)—C(11)	124.6(6)	C(9)—C(10)—C(11)	119.7(7)
C(10)—C(11)—C(12)	118.2(6)	N—C(12)—C(11)	118.0(6)
N—C(12)—C(13)	119.8(7)	C(11)—C(12)—C(13)	122.2(7)
C(12)—C(13)—C(14)	119.4(7)	C(9)—C(14)—C(13)	119.8(7)

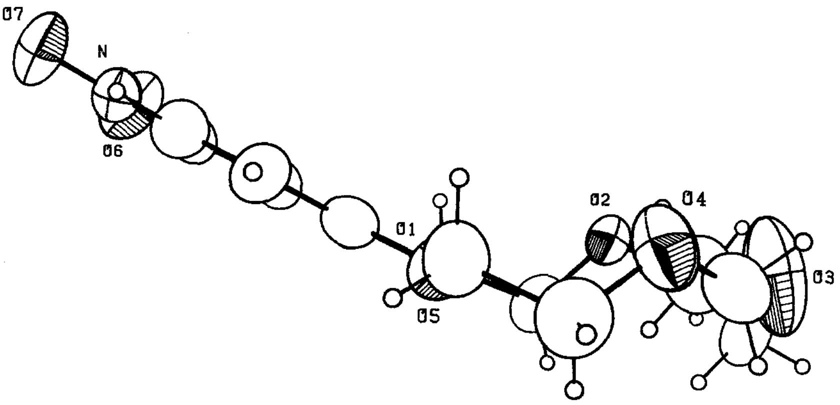

Fig. 4. Side view of nitrobenzo-15-crown-5.

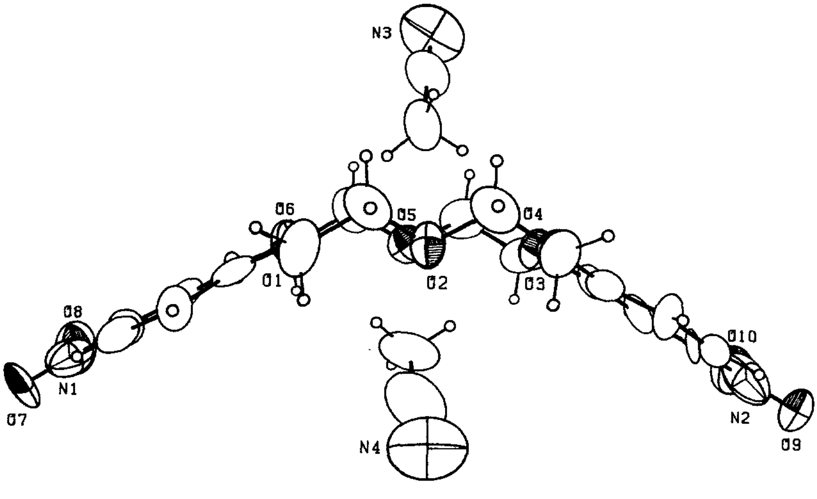

Fig. 5. Side view of dinitrodibenzo-18-crown-6·2 CH_3CN.

Acknowledgement

We wish to thank the NSF Chemical Instrumentation Program for funds used to purchase the diffractometer.

Table IX. Bond distances (Å) and angles (deg) for dinitrobenzo-15-crown-5

Atoms	Distance	Atoms	Distance
O(1)—C(1)	1.47(2)	O(1)—C(10)	1.33(1)
O(2)—C(2)	1.43(2)	O(2)—C(3)	1.46(2)
O(3)—C(4)	1.39(2)	O(3)—C(5)	1.40(2)
O(4)—C(6)	1.43(2)	O(4)—C(7)	1.39(1)
O(5)—C(8)	1.45(1)	O(5)—C(9)	1.36(1)
O(6)—N(1)	1.21(2)	O(7)—N(1)	1.27(2)
O(8)—N(2)	1.22(1)	O(9)—N(2)	1.20(2)
N(1)—C(12)	1.45(2)	N(2)—C(13)	1.44(2)
C(1)—C(2)	1.51(2)	C(3)—C(4)	1.40(2)
C(5)—C(6)	1.47(2)	C(7)—C(8)	1.49(2)
C(9)—C(10)	1.36(2)	C(9)—C(14)	1.39(2)
C(10)—C(11)	1.39(2)	C(11)—C(12)	1.36(2)
C(12)—C(13)	1.37(2)	C(13)—C(14)	1.39(2)

Atoms	Angle	Atoms	Angle
C(1)—O(1)—C(10)	121(1)	C(2)—O(2)—C(3)	113(1)
C(4)—O(3)—C(5)	106(2)	C(6)—O(4)—C(7)	112(1)
C(8)—O(5)—C(9)	118(1)	O(6)—N(1)—O(7)	125(2)
O(6)—N(1)—C(12)	120(2)	O(7)—N(1)—C(12)	115(2)
O(8)—N(2)—O(9)	120(2)	O(8)—N(2)—C(13)	118(2)
O(9)—N(2)—C(13)	123(2)	O(1)—C(1)—C(2)	107(1)
O(2)—C(2)—C(1)	105(1)	O(2)—C(3)—C(4)	117(2)
O(3)—C(4)—C(3)	108(2)	O(3)—C(5)—C(6)	115(2)
O(4)—C(6)—C(5)	114(2)	O(4)—C(7)—C(8)	108(1)
O(5)—C(8)—C(7)	107(1)	O(5)—C(9)—C(10)	114(1)
O(5)—C(9)—C(14)	126(2)	C(10)—C(9)—C(14)	121(2)
O(1)—C(10)—C(9)	116(1)	O(1)—C(10)—C(11)	123(2)
C(9)—C(10)—C(11)	121(2)	C(10)—C(11)—C(12)	119(2)
N(1)—C(12)—C(11)	120(2)	N(1)—C(12)—C(13)	120(2)
C(11)—C(12)—C(13)	120(2)	N(2)—C(13)—C(12)	121(2)
N(2)—C(13)—C(14)	116(2)	C(12)—C(13)—C(14)	123(2)
C(9)—C(14)—C(13)	117(2)		

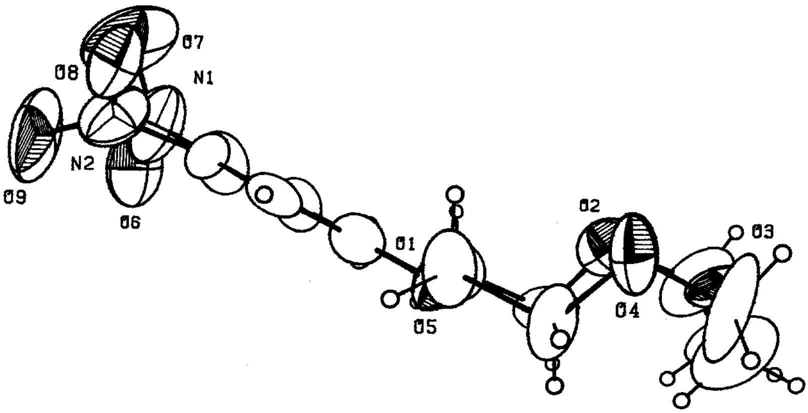

Fig. 6. Side view of dinitrobenzo-15-crown-5.

Table X. Bond distances (Å) and angles (deg) for dinitrodibenzo-18-crown-6·2 CH_3CN

Atoms	Distance	Atoms	Distance
O(1)—C(1)	1.46(2)	O(1)—C(12)	1.36(2)
O(2)—C(2)	1.38(2)	O(2)—C(3)	1.40(2)
O(3)—C(4)	1.45(2)	O(3)—C(5)	1.39(2)
O(4)—C(6)	1.35(2)	O(4)—C(7)	1.40(2)
O(5)—C(8)	1.41(2)	O(5)—C(9)	1.43(2)
O(6)—C(10)	1.42(2)	O(6)—C(11)	1.34(2)
O(7)—N(1)	1.18(2)	O(8)—N(1)	1.27(2)
O(9)—N(2)	1.20(2)	O(10)—N(2)	1.27(2)
N(1)—C(15)	1.45(2)	N(2)—C(19)	1.48(3)
C(1)—C(2)	1.48(2)	C(3)—C(4)	1.49(2)
C(5)—C(6)	1.41(2)	C(5)—C(17)	1.40(2)
C(6)—C(20)	1.42(2)	C(7)—C(8)	1.48(2)
C(9)—C(10)	1.57(2)	C(11)—C(12)	1.40(2)
C(11)—C(16)	1.41(2)	C(12)—C(13)	1.44(2)
C(13)—C(14)	1.40(2)	C(14)—C(15)	1.34(2)
C(15)—C(16)	1.45(2)	C(17)—C(18)	1.42(3)
C(18)—C(19)	1.30(2)	C(19)—C(20)	1.36(2)
N(3)—C(21)	1.13(2)	C(21)—C(22)	1.41(2)
N(4)—C(23)	1.20(3)	C(23)—C(24)	1.37(3)

Atoms	Angle	Atoms	Angle
C(1)—O(1)—C(12)	114(1)	C(2)—O(2)—C(3)	110(1)
C(4)—O(3)—C(5)	116(1)	C(6)—O(4)—C(7)	117(2)
C(8)—O(5)—C(9)	113(1)	C(10)—O(6)—C(11)	118(1)
O(7)—N(1)—O(8)	125(2)	O(7)—N(1)—C(15)	125(2)
O(8)—N(1)—C(15)	110(2)	O(9)—N(2)—O(10)	123(3)
O(9)—N(2)—C(19)	125(2)	O(10)—N(2)—C(19)	111(3)
O(1)—C(1)—C(2)	107(1)	O(2)—C(2)—C(1)	109(1)
O(2)—C(3)—C(4)	112(2)	O(3)—C(4)—C(3)	106(1)
O(3)—C(5)—C(6)	113(2)	O(3)—C(5)—C(17)	126(2)
C(6)—C(5)—C(17)	121(2)	O(4)—C(6)—C(5)	118(2)
O(4)—C(6)—C(20)	125(2)	C(5)—C(6)—C(20)	117(2)
O(4)—C(7)—C(8)	109(2)	O(5)—C(8)—C(7)	113(2)
O(5)—C(9)—C(10)	107(2)	O(6)—C(10)—C(9)	108(1)
O(6)—C(11)—C(12)	118(2)	O(6)—C(11)—C(16)	121(2)
C(12)—C(11)—C(16)	120(2)	O(1)—C(12)—C(11)	112(2)
O(1)—C(12)—C(13)	129(2)	C(11)—C(12)—C(13)	119(2)
C(12)—C(13)—C(14)	123(2)	C(13)—C(14)—C(15)	116(2)
N(1)—C(15)—C(14)	109(2)	N(1)—C(15)—C(16)	125(2)
C(14)—C(15)—C(16)	126(2)	C(11)—C(16)—C(15)	117(2)
C(5)—C(17)—C(18)	121(2)	C(17)—C(18)—C(19)	113(2)
N(2)—C(19)—C(18)	107(2)	N(2)—C(19)—C(20)	122(2)
C(18)—C(19)—C(20)	131(2)	C(6)—C(20)—C(19)	116(2)
N(3)—C(21)—C(22)	178(2)	N(4)—C(23)—C(24)	175(4)

References

1. R. D. Rogers and M. M. Benning: *J. Incl. Phenom.* **11,** 121 (1991).
2. L. F. Lindoy: *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge (1989).

3. R. Ungaro, B. El Haj, and J. Smid: *J. Am. Chem. Soc.* **98**, 5198 (1976).
4. V. S. Kalishevich, O. S. Timofeev, K. S. Zakharov, and A. I. Gren: *Zh. Org. Khim.* **24**, 396 (1988).
5. B. Rieckemann, K.-B. Ebhardt, and F. Umland: *Z. Naturforsch.* **39b**, 542 (1984).
6. G. M. Sheldrick: *SHELX76, A System of Computer Programs for X-ray Structure Determination* as locally modified (1976).
7. G. M. Sheldrick, 'SHELXS', in *Crystallographic Computing* 3, Eds. G. M. Sheldrick, C. Kruger, and R. Goddard, Oxford University Press, pp. 175–189 (1985).
8. *International Tables for X-ray Crystallography*, Vol IV., pp. 72, 99, 149, Kynoch Press, Birmingham, England (Distr: Kluwer Academic Publishers, Dordrecht and Boston).
9. I. R. Hanson: *Acta Crystallogr.* **B34**, 1026 (1978).
10. R. D. Rogers: *J. Incl. Phenom.* **6**, 629 (1988).
11. R. D. Rogers, A. H. Bond, W. G. Hipple, A. N. Rollins, and R. F. Henry: *Inorg. Chem.* **30**, 2671 (1990).