Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **26**: 197–207, 1996.

Synthesis and Structures of Nitromethane Complexes of Furanotribenzo-21-Crown-7 and Dibenzo-21-Crown-7

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(Received: 21 December 1995; in final form: 3 May 1996)

Abstract. Single crystal X-ray diffraction analyses of two nitromethane complexes of furanotribenzo-21-crown-7 (**1** and **2**) and the nitromethane complex of dibenzo-21-crown-7 (**3**) are reported. The two nitromethane complexes **1** and **2** are polymorphic in that the macrocyclic ring adopts the 'dentist's chair' conformation in both structures, with a single nitromethane molecule coordinating to either the lower, concave (**1**) or upper, convex (**2**) face of the crown ether. Complex **3** adopts an entirely different conformation with a coplanar arrangement of the crown ether oxygen atoms binding a single nitromethane molecule.

Key words. Crown ether, nitromethane complex, coordination isomers, crystal structure.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. 82209 (31 pages).

1. Introduction

Incorporation of rigid groups into crown ether molecules can be a useful tool for organizing the macrocyclic cavity towards binding of specific guests [1]. Whereas the O—C—C—O dihedral angle has a great deal of flexibility when both carbon atoms are methylene, incorporation of these two carbon atoms into an aromatic ring restricts the O—C$\overset{\cdots}{-}$C—O dihedral angle to values very close to 0°. Likewise, incorporation of the —C—C—O—C— unit into an aromatic subunit (i.e. furan) will restrict a portion of the crown ether ring to planarity. A significant body of work has been reported on the structure and complexation properties of crown ethers bearing multiple aromatic (benzo-, naphthyleno-, and/or 2,6-picolino) substituents

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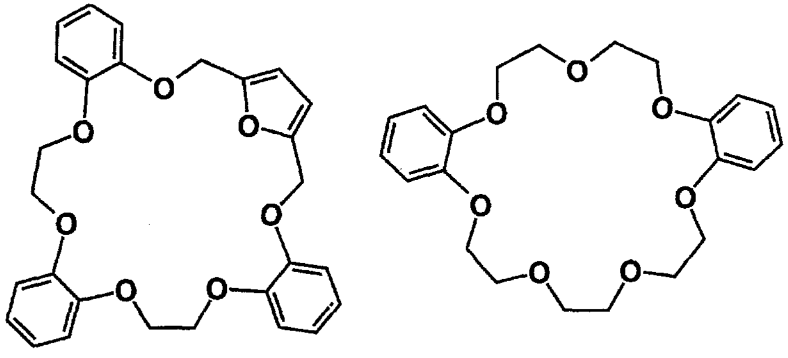

Furanotribenzo-21-crown-7 Dibenzo-21-crown-7

Figure 1. Schematic representations of furanotribenzo-21-crown-7 and dibenzo-21-crown-7.

[1,2]. This work has demonstrated that the particular pattern of substitution can have a significant effect on the structure of the complexes of these crown ethers with ions and with neutral molecules.

As part of our continuing program of studying the effect of conformational constraints on the complexation of cations by crown ethers [3–5], we are investigating the structural effects of adding additional benzene rings and/or a furano group to the intermediate-size (18–24 atom) dibenzo-crown ethers. This paper reports the preparation and two structures of the nitromethane complex of furanotribenzo-21-crown-7 (**1** and **2**) and, for comparison, the structure of the nitromethane complex of dibenzo-21-crown-7 (**3**). These are rare examples of structurally characterized nitomethane-crown inclusion complexes [6–8], and of furano-crown ether molecules [9, 10].

2. Experimental

2.1. SYNTHESIS

2.1.1. *General*

Dibenzo-21-crown-7 (Parrish, see Figure 1), solvents, and reagents were obtained from commercial sources and used as received, unless otherwise specified below. Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of nitromethane solutions of the two crown ethers. Crystals of **1** and **2** grew simultaneously from the same solution, and were separated by hand.

2.1.2. *Sym-Furanotribenzo-21-crown-7 (see Figure 1)*

A solution of 1,2-bis-(2′-*o*-hydroxy-phenoxy)ethoxybenzene [11] (8.0 g, 21 mmol) and cesium carbonate (8.2 g, 25 mmol) in methanol (100 mL) was heated to reflux under argon for one hour. The methanol was removed *in vacuo* and DMF (100 mL) was added. 2,5-Bischloromethylfuran [12] (3.4 g, 21 mmol) was added and the reaction mixture was heated with stirring, under argon at 50 °C for 4 h. Additional cesium carbonate (3.4 g, 10 mmol) and 2,5- bischloromethylfuran (1.7 g, 10 mmol) were added and stirring at 50 °C was continued overnight ($\sim$18 h). The reaction mixture was dissolved in ether (100 mL) and extracted twice with water (100 mL). The organic phase was dried over sodium sulfate, filtered and evaporated *in vacuo* to give a white crystalline solid. Recrystallization from benzene gave *sym*-furanotribenzo-21-crown-7 (2.25 g, 22.5%). m.p. 143–144 °C (C_6H_6) ^{1}H-NMR: δ_H (400 MHz, $CDCl_3$) 4.30–4.35 (m, 4 H), 4.35–4.40 (m, 4 H), 5.01 (s, 4 H), 6.33 (s, 2H), 6.89-7.04 (m, 12 H); IR (0.1 mm CCl_4 film, NaCl windows, cm^{-1}): 1111, 1068 (C—O—C).

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

The crystal structures of **1**–**3** were determined by X-ray diffraction methods. Intensity data for all compounds were collected on an Enraf-Nonius CAD4 diffractometer. Data collection and treatment of data was the same as previously described [4]. There is disorder in **3** near the mirror plane that relates the two halves of the compound. C(11) is disordered over two sites in a 1 : 1 ratio. The oxygen atoms on nitromethane are disordered over five sites. Two lie on the mirror plane (O(11) and O(12)) and were refined at $\frac{1}{8}$ occupancy each. The other three (O(13), O(14), and O(15)) occupy general positions near the mirror, and were refined at $\frac{1}{4}$ occupancy each. All non-hydrogen atoms, except those involved in disorder, were refined anisotropically. Hydrogen atom positions were given isotropic thermal parameters equivalent to those of the carbon atoms to which they are bonded, and were added to the structure factor calculations without refinement. A summary of data collection parameters is given in Table I. It should be noted that the ratio of data to parameters refined is low for all three structures presented. This is because these crystals are difficult to grow, therefore small, weakly scattering crystals had to be used. Positional and isotropic equivalent thermal parameters are listed in Tables II–IV, selected non-bonded contacts and torsion angles are given in Table V.

3. Results and Discussion

Two single crystals of furanotribenzo-21-crown-7, grown from the same nitromethane solution, were examined by X-ray diffraction. The two structures are illustrated in Figures 2 and 3. They exhibit nearly identical conformation of the crown ether, and are both 1 : 1 nitromethane/crown complexes. As can be seen in Figures 2 and 3, the major difference between these two structures is the relative orientation of the nitromethane to the crown. Examination of space-filling models (not pictured) shows that there is adequate space for the nitromethane to approach from either side of the crown ether. As can be seen in Table V, the average distances

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

Formula	$C_{29}H_{29}NO_9$	$C_{29}H_{29}NO_9$	$C_{23}H_{31}NO_9$
Formula Weight	535.5	535.5	465.5
Temp., °C	24	24	25
Max. crystal dimensions (mm)	0.01 × 0.11 × 0.54	0.08 × 0.35 × 0.39	0.27 × 0.34 × 0.54
Crystal System	monoclinic	monoclinic	orthorhombic
Space Group	$P2_1/c$	$P2_1/n$	$Cmc2_1$
a (Å)	12.274(2)	12.927(5)	20.732(7)
b (Å)	11.024(1)	14.710(3)	13.782(3)
c (Å)	20.582(4)	13.986(5)	8.507(2)
β (deg)	106.99(1)	94.42(2)	
V (Å^3)	2663.3(7)	2651(1)	2430(1)
Z	4	4	4
D_{calc} (g cm^{-3})	1.34	1.34	1.28
μ (cm^{-1})	0.89	0.90	0.92
2θ range (deg)	$2 \leq 2\theta \leq 41$	$2 \leq 2\theta \leq 36$	$2 \leq 2\theta \leq 44$
Reflections measured	2914	2004	937
Reflections observed [$I \leq \sigma(I)$]	1112	1042	603
R	0.079	0.052	0.070
R_w	0.074	0.062	0.089
GOF	1.98	2.13	2.88
Largest feature in final diff. map (e Å^{-3})	0.35	0.18	0.33

between the nitromethane carbon atoms (C_{nm}) and the oxygen atoms (O_{ce}) of the crown ether are nearly identical (3.54 Å in **1** and 3.55 Å in **2**) but are about 0.1 Å longer than reported for other nitromethane/crown complexes [6–8]. Therefore, the coordination of the nitromethane hydrogen atoms by the crown ether is relatively weak, but appears equally accomplished in both **1** and **2**.

The $C_{\text{nm}} \cdots O_{\text{ce}}$ distances vary over several tenths of angstroms in both structures (Table V). This could be due to asymmetric binding of the nitromethane to the crown, possibly brought on by donor/acceptor interactions between the two molecules other than those between the slightly electropositive hydrogen atoms on nitromethane and the crown ether oxygen atoms. For instance, an aryl hydrogen atom makes a close contact (2.33 Å) with one of the nitro oxygen atoms (O(21)) in **1**, and the furano oxygen atom (O(1)) makes a close contact (3.049(7) Å) with the nitromethane nitrogen atom (N) in **2**. In both structures, the nitromethane carbon (C(36)) also makes close contacts with carbon atoms on arene rings. Interactions between the hydrogen atoms on C(36) and the π-clouds may affect the relative orientations of crown and nitromethane. The asymmetric binding of the nitromethane may also be a reflection of the asymmetric (i.e. non-circular) arrangement of the O_{ce} atoms. This is supported by the fact that the $O_{\text{ce}} \cdots O_{\text{ce}}$ distances, across the crown cavity, vary significantly (Table V).

Table II. Atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms in furanotribenzo-21-crown-7·CH_3NO_2 (**1**).

Atom	x	y	z	B_{eq} (Å^2)
O(1)	−0.0366(5)	0.3942(5)	0.2416(3)	4.5(2)
O(4)	0.0795(4)	0.3519(6)	0.1320(3)	4.4(2)
O(7)	0.2776(4)	0.2466(5)	0.1659(3)	4.0(2)
O(10)	0.3437(5)	0.0701(5)	0.2751(3)	3.6(2)
O(13)	0.3451(4)	0.0816(5)	0.4027(3)	3.7(2)
O(16)	0.2404(5)	0.2751(6)	0.4585(3)	5.0(2)
O(19)	0.0450(6)	0.3576(6)	0.3967(3)	5.7(2)
O(20)	0.4178(8)	0.4763(9)	0.3857(5)	11.8(3)
O(21)	0.4658(6)	0.3334(8)	0.3375(5)	9.7(3)
N	0.3905(6)	0.3952(8)	0.3450(4)	5.3(2)
C(2)	−0.0381(7)	0.4664(9)	0.1862(5)	4.5(3)
C(3)	−0.0288(8)	0.403(1)	0.1254(5)	5.6(3)
C(5)	0.1709(7)	0.4248(8)	0.1325(4)	3.6(2)
C(6)	0.2739(7)	0.3662(8)	0.1487(4)	3.3(2)
C(8)	0.3869(7)	0.1863(9)	0.1885(4)	3.8(2)
C(9)	0.3622(8)	0.0636(8)	0.2113(5)	4.5(3)
C(11)	0.3335(6)	−0.0412(8)	0.3047(4)	2.8(2)
C(12)	0.3343(7)	−0.0303(8)	0.3720(5)	4.0(2)
C(14)	0.3469(7)	0.0933(9)	0.4736(4)	4.3(3)
C(15)	0.3529(8)	0.223(1)	0.4914(4)	5.0(3)
C(17)	0.2256(7)	0.3923(8)	0.4757(4)	3.9(2)
C(18)	0.1195(8)	0.4358(8)	0.4409(4)	4.3(3)
C(20)	−0.0611(7)	0.3997(9)	0.3545(5)	5.4(3)
C(21)	−0.0487(7)	0.4650(9)	0.2948(5)	4.4(3)
C(22)	−0.0614(8)	0.5806(9)	0.2709(5)	5.1(3)
C(23)	−0.0566(8)	0.5825(9)	0.2029(5)	5.1(3)
C(24)	0.1655(9)	0.5479(8)	0.1177(5)	5.2(3)
C(25)	0.2631(8)	0.6148(8)	0.1208(5)	5.1(3)
C(26)	0.3622(8)	0.5550(8)	0.1349(5)	4.4(3)
C(27)	0.3686(7)	0.4303(8)	0.1499(4)	3.7(2)
C(28)	0.3232(7)	−0.1514(8)	0.2734(5)	4.7(3)
C(29)	0.3154(8)	−0.2551(9)	0.3112(5)	5.2(3)
C(30)	0.3177(8)	−0.247(1)	0.3767(5)	6.0(3)
C(31)	0.3302(9)	−0.1342(9)	0.4125(5)	5.7(3)
C(32)	0.3054(8)	0.4645(9)	0.5180(5)	5.3(3)
C(33)	0.2718(9)	0.585(1)	0.5275(5)	6.0(3)
C(34)	0.1666(9)	0.630(1)	0.4954(5)	5.9(3)
C(35)	0.0862(9)	0.5525(9)	0.4517(5)	5.0(3)
C(36)	0.2757(9)	0.362(1)	0.3144(5)	6.7(3)

$B_{eq} = \frac{4}{3}[a^2 B_{11} + b^2 B_{22} + c^2 B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$

Table III. Atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms in furanotribenzo-21-crown-7·CH$_3$NO$_2$ (**2**).

Atom	x	y	z	B_{eq} (Å^2)
O(1)	0.6453(3)	0.6222(3)	−0.0557(3)	4.0(1)
O(4)	0.7544(4)	0.4489(3)	0.0194(3)	4.0(1)
O(7)	0.8917(3)	0.4269(3)	0.1574(3)	3.6(1)
O(10)	0.9172(4)	0.5460(3)	0.3208(3)	4.6(1)
O(13)	0.8916(4)	0.7226(3)	0.3059(3)	3.8(1)
O(16)	0.8498(3)	0.8357(3)	0.1295(3)	3.8(1)
O(19)	0.7061(4)	0.8158(3)	−0.0033(3)	4.4(1)
O(20)	0.5370(5)	0.6902(4)	0.1357(5)	8.7(2)
O(21)	0.5598(4)	0.5491(4)	0.1528(4)	7.4(2)
N	0.5918(5)	0.6262(4)	0.1528(4)	6.4(2)
C(2)	0.6682(6)	0.5438(5)	−0.1063(5)	4.3(2)
C(3)	0.6652(6)	0.4601(5)	−0.0509(6)	4.7(2)
C(5)	0.8490(5)	0.4205(5)	−0.0091(5)	3.8(2)
C(6)	0.9191(5)	0.4058(5)	0.0673(5)	3.4(2)
C(8)	0.9691(6)	0.4177(5)	0.2363(5)	3.8(2)
C(9)	0.9255(6)	0.4496(5)	0.3252(5)	4.4(2)
C(11)	0.8666(6)	0.5855(5)	0.3939(5)	4.1(2)
C(12)	0.8557(6)	0.6795(5)	0.3835(4)	4.0(2)
C(14)	0.8801(6)	0.8211(5)	0.2995(5)	4.4(2)
C(15)	0.9252(7)	0.8491(5)	0.2071(5)	5.2(2)
C(17)	0.8821(6)	0.8525(5)	0.0392(5)	3.5(2)
C(18)	0.7986(6)	0.8411(5)	−0.0327(5)	3.7(2)
C(20)	0.6252(5)	0.7845(5)	−0.0762(5)	5.1(2)
C(21)	0.6502(5)	0.6936(5)	−0.1157(5)	3.6(2)
C(22)	0.6789(6)	0.6691(6)	−0.2009(5)	5.1(2)
C(23)	0.6911(6)	0.5727(5)	−0.1954(5)	5.3(3)
C(24)	0.8678(6)	0.4025(5)	−0.1028(5)	5.3(2)
C(25)	0.9694(6)	0.3720(5)	−0.1164(5)	5.0(2)
C(26)	1.0469(7)	0.3595(5)	−0.0412(6)	6.0(3)
C(27)	1.0201(7)	0.3770(5)	0.0509(5)	5.1(2)
C(28)	0.8299(6)	0.5440(5)	0.4742(5)	5.3(2)
C(29)	0.7814(7)	0.5942(6)	0.5404(5)	6.3(3)
C(30)	0.7704(7)	0.6859(6)	0.5303(6)	6.6(3)
C(31)	0.8069(6)	0.7294(6)	0.4507(5)	5.5(2)
C(32)	0.9783(6)	0.8808(5)	0.0147(6)	5.0(2)
C(33)	0.9940(6)	0.8927(5)	−0.0811(5)	5.9(2)
C(34)	0.9192(7)	0.8792(6)	−0.1504(5)	6.4(3)
C(35)	0.8177(6)	0.8553(5)	−0.1276(6)	5.1(2)
C(36)	0.7036(6)	0.6403(7)	0.1784(7)	9.0(3)

$B_{eq} = \frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$

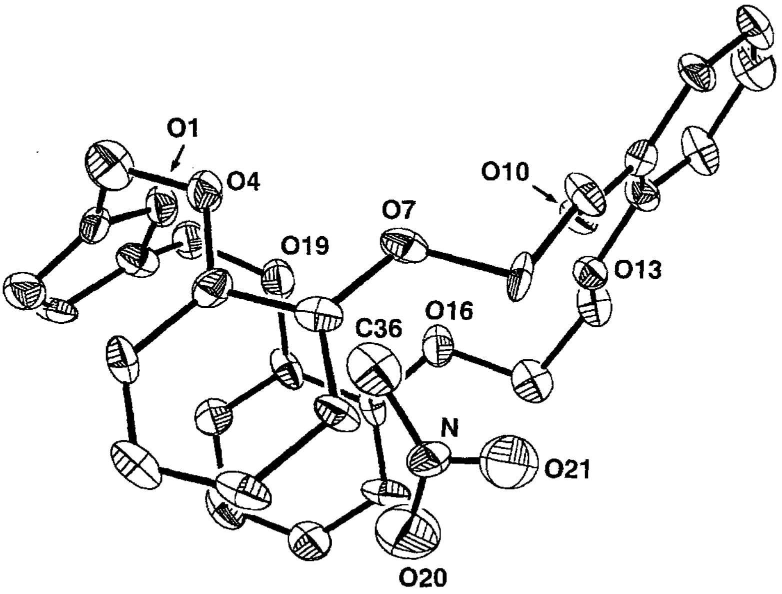

Figure 2. ORTEP representation with 25% probability ellipsoids of the furanotribenzo-21-crown-7 nitromethane complex, isomer 1 (**1**). Unlabelled atoms are carbon. Hydrogen atoms are omitted for clarity.

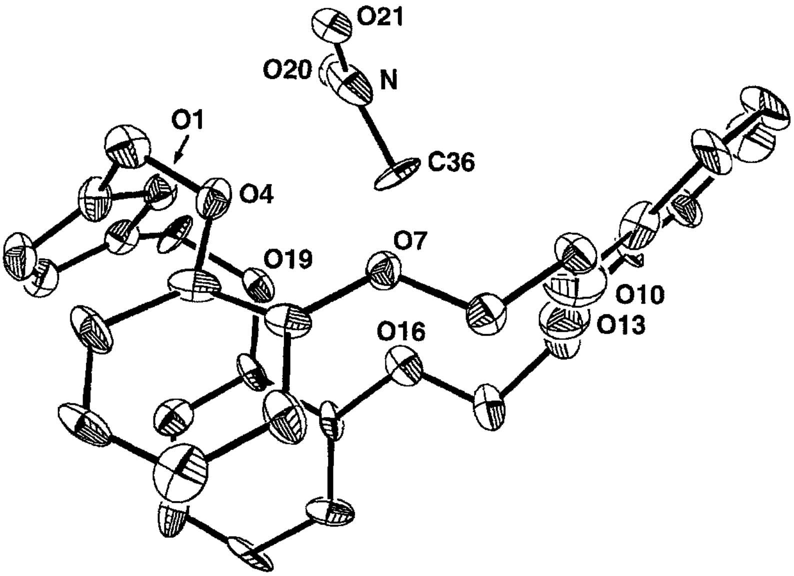

Figure 3. ORTEP representation with 25% probability ellipsoids of the furanotribenzo-21-crown-7 nitromethane complex, isomer 2 (**2**). Unlabelled atoms are carbon. Hydrogen atoms are omitted for clarity.

Table IV. Atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms in dibenzo-21-crown-7·CH_3NO_2 (**3**).

Atom	x	y	z	B_{eq} (Å^2)	pp
O(1)	0.5	0.8004(5)	0.831(0)	5.1(2)	0.5
O(4)	0.6287(2)	0.7372(3)	0.7324(6)	4.6(1)	1.0
O(7)	0.6570(2)	0.6347(3)	0.4889(6)	4.6(1)	1.0
O(10)	0.5696(2)	0.5320(5)	0.2900(6)	7.5(2)	1.0
O(11)	0.5	0.814(2)	0.217(4)	5.0(6)*	0.125
O(12)	0.5	0.899(2)	0.420(4)	5.8(7)*	0.125
O(13)	0.455(1)	0.861(2)	0.320(4)	10.8(8)*	0.25
O(14)	0.534(1)	0.817(2)	0.224(3)	8.0(6)*	0.25
O(15)	0.457(1)	0.895(2)	0.411(2)	6.0(5)*	0.25
N	0.5	0.8211(8)	0.362(1)	8.7(3)	0.5
C(2)	0.5555(3)	0.8591(6)	0.826(1)	6.1(2)	1.0
C(3)	0.6126(3)	0.7997(6)	0.8609(9)	5.7(2)	1.0
C(5)	0.6851(3)	0.6892(4)	0.7388(8)	4.0(1)	1.0
C(6)	0.7013(3)	0.6335(4)	0.6090(8)	3.9(1)	1.0
C(8)	0.6747(3)	0.5842(6)	0.3452(8)	4.9(2)	1.0
C(9)	0.6193(4)	0.5910(6)	0.236(1)	6.3(2)	1.0
C(11A)	0.4728(5)	0.470(1)	0.192(2)	5.2(4)*	0.5
C(11B)	0.4723(6)	0.537(1)	0.145(2)	6.6(4)*	0.5
C(12)	0.7275(3)	0.6930(5)	0.8649(9)	5.0(2)	1.0
C(13)	0.7866(4)	0.6412(5)	0.861(1)	5.4(2)	1.0
C(14)	0.8014(3)	0.5879(5)	0.732(1)	5.5(2)	1.0
C(15)	0.7596(3)	0.5827(5)	0.604(1)	4.9(2)	1.0
C(16)	0.5	0.7379(7)	0.460(1)	5.8(3)	0.5

Starred atoms were refined isotropically. pp = Occupancy factors.
$B_{eq} = \frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$

The structure of the nitromethane complex of dibenzo-21-crown-7 (**3**) is pictured in Figure 4. In contrast to the furanotribenzo-21-crown-7 complexes discussed above, the crown ether oxygen atoms in **3** are all coplanar (rms deviation from plane is 0.07 Å). While there seems to be no pattern to the distribution of $C_{nm}\cdots O_{ce}$ distances in **1** and **2**, those observed in **3** seem to vary with the basicity of the oxygen atom. The more basic oxygen atoms (O(1) and O(10)), attached solely to aliphatic carbons exhibit significantly shorter $C_{nm}\cdots O_{ce}$ distances (3.272(3) and 3.497(10) Å respectively) than the less basic oxygen atoms (O(4): 3.534(5) Å and O(6): 3.561(6) Å) associated with the arene group. As a result, the average $C_{nm}\cdots O_{ce}$ distance (3.45 Å) is about 0.1 Å smaller than those observed for **1** and **2**, while the average $O_{ce}\cdots O_{ce}$ distance is about 0.1 Å greater than in **1** and **2**. The larger $O_{ce}\cdots O_{ce}$ distances indicate that the crown cavity is slightly larger, and the smaller $C_{nm}\cdots O_{ce}$ distances indicate that binding of nitromethane is stronger, for

Table V. Selected non-bonded contacts (Å) and torsion angles (deg)[a].

Contacts	**1**	**2**	**3**
C_{nm}[b] ···O(1)	3.702(13)	3.313(11)	3.272(3)
C_{nm}···O(4)	3.824(12)	3.678(11)	3.534(5)
C_{nm}···O(7)	3.317(12)	3.995(10)	3.561(6)
C_{nm}···O(10)	3.479(12)	3.559(10)	3.497(10)
C_{nm}···O(13)	3.561(12)	3.144(10)	
C_{nm}···O(16)	3.264(12)	3.536(11)	
C_{nm}···O(19)	3.700(13)	3.624(11)	
Average C_{nm}···O_{ce}[c]	3.55	3.55	3.47
Range O_{ce}···O_{ce}[d]	5.93–6.48	5.95–6.53	6.08–6.51
Average O_{ce}···O_{ce}	6.21	6.20	6.32
Torsion Angles			
O—C$\overset{\cdots}{-}$C—O	0, 2, −3	−1, 1, −5	0
O—C$\overset{\cdots}{-}$O$\overset{\cdots}{-}$C	174, −179	178, −180	
O—C—C—O	73, −77	82, −72	73, −72, 82

[a] Errors for some of the values reported in this table were not determined. Sigma values average approximately 0.01 Å for bond distances, and about 1° for bond angles in all three structures.

[b] C_{nm} represents the carbon atom in nitromethane (i.e. C(36) in **1** and **2**, and C(16) in **3**). C_{nm}···O_{ce} distances and their sigma values were calculated using PLATON, A. L. Spek: *Acta Crystallogr.* **A46**, C34 (1990).

[c] O_{ce} represents the crown ether oxygen atoms.

[d] O_{ce}···O_{ce} represents the longest distance from each crown ether oxygen atom to another across the ring (e.g. O(7)···O(16) in **1**).

the less substituted, and more basic dibenzo-21-crown-7. Structurally, the major difference is the degree of flexibility in the macrocyclic ring. This can be observed in the torsion angles of complexes **1**–**3**. Torsion angles for O—CH_2—CH_2—O, and CH_2—CH_2—O—CH_2 units in crown ether molecules are observed to vary over a range of roughly 20 degrees [13]. However, replacement of these units by benzo O—C$\overset{\cdots}{-}$C—O and furano C—C$\overset{\cdots}{-}$O$\overset{\cdots}{-}$C restricts their torsion angles to values very close to 0° and 180° respectively. This is well illustrated in Table V. The absolute values of the benzo (O—C$\overset{\cdots}{-}$C—O) torsion angles for all three complexes vary from 0° to 5°, averaging less than 2°; and the furano (C—C$\overset{\cdots}{-}$O$\overset{\cdots}{-}$C) angles range from 180° to 174°, averaging 178°. On the other hand, the ethyleno (O—C—C—O) torsion angles vary from their optimal value of 72° [13] to as much as 82°.

The crown conformation adopted in structures **1** and **2** bears a striking resemblance to the 'dentist's chair' conformation reported for the structure of benzodinaphthopyridino-21-crown-7·potassium thiocyanate [14]. Remarkably, the direct-

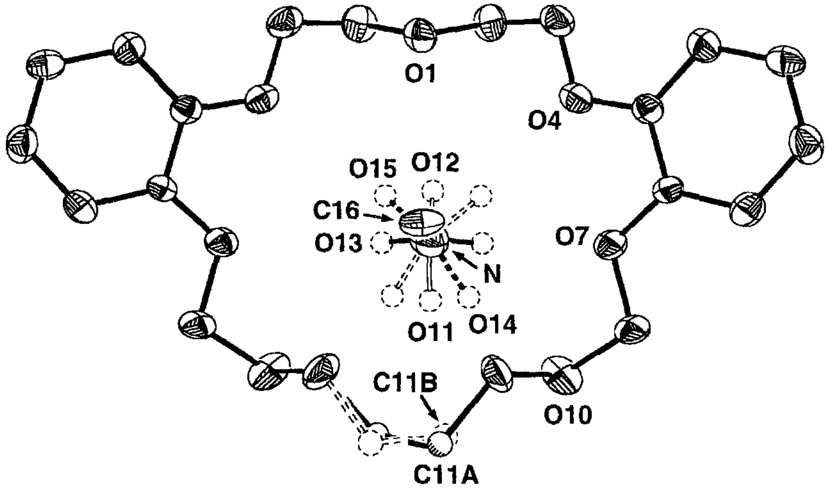

Figure 4. ORTEP representation with 25% probability ellipsoids of the dibenzo-21-crown-7 nitromethane complex (**3**). Aartially occupied atoms were refined isotropically, and are represented as shaded or dotted circles. Unlabelled atoms are carbon. Hydrogen atoms are omitted for clarity.

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analogous tribenzopyridino-21-crown-7 adopts somewhat different conformations both as the free ligand and as the methanol complex [15]. In these structures, the pyridino group is the 'back' of the dentist's chair, whereas the furano group in **1** and **2** is the 'footstool'. Thus, despite the appearance of 'rigidity' imposed by the incorporation of multiple aromatic substituents in these 21-crown-7 ethers, there may be significant flexibility in the remaining ethylene bridges to allow these molecules to undergo structural reorganization and thereby adopt a variety of conformations in these complexes and in the uncomplexed state [2].

The formation of two different nitromethane complexes from the same solution represents an interesting example of polymorphism in the complexation of a neutral organic guest by a crown ether host. This can be contrasted to the face differentiation observed for tribenzopyridino-21-crown-7 (where the three benzene rings are connected directly by ether linkages rather than the more typical and synthetically-accessible ethylenedioxy bridges) which forms crystalline complexes with both nitromethane [8] and acetonitrile [15], but where the two molecules coordinate to opposite faces of the molecule. In this latter case, facial differentiation was rationalized in terms of electronic effects: H-bonding of the stronger acid (nitromethane) to the more basic face (as a result of the orientation of the pyridine nitrogen), while the more polar guest (acetonitrile) binds to the face containing the highest electron density (due to the orientation of the aliphatic ethers of the macrocycle). In the present case, no facial differentiation for the guest, nitromethane, is observed despite significant differences in the topography of the two faces (one open, convex face and one concave face possessing a cleft formed by the three benzo groups, *vide supra*). It appears that the guest molecule finds a similar electronic environment (with regards to the oxygen polarities) on both faces of the host. It may seem surprising that the furan substituent does not influence the preferred orientation of the guest more strongly. Thus, steric factors appear to play a relatively minor role, if any, in the orientation of the guest molecule in these types of inclusion complexes.

Acknowledgments

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. The participation of MCD was made possible through the U.S. Department of Energy, Science and Engineering Research Semester Program.

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