

Neutral Molecule/Crown Ether Interactions 5.* Comparison of the C—H Acidic Interactions of Nitromethane and Acetonitrile with 18-crown-6 and Dibenzo-18-crown-6. Crystal Structures of Dibenzo-18-crown-6·2 CH₃NO₂ and Dibenzo-18-crown-6·2 CH₃CN

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Abstract. Complete structural characterizations of dibenzo-18-crown-6·2 CH₃NO₂ and dibenzo-18-crown-6·2 CH₃CN have been carried out, including location and refinement of the methyl hydrogen atoms. Dibenzo-18-crown-6·2 CH₃NO₂ is monoclinic, $P2_1/c$, with (at -150°C) $a = 9.573(2)$, $b = 14.636(2)$, $c = 33.471(7)$ Å, $\beta = 93.77(2)^\circ$, and $D_{\text{calc}} = 1.37 \text{ g cm}^{-3}$ for $Z = 8$. Interactions between the solvent methyl groups and the crown ethers and other solvent nitro groups associate the 1 : 2 complexes into polymeric chains along b . The acetonitrile adduct exists as discrete 1 : 2 complexes in the solid state with C—H···O interactions exclusively to the ether. This complex is triclinic, $P\bar{1}$, with (at -150°C) $a = 9.458(6)$, $b = 9.570(5)$, $c = 14.404(5)$ Å, $\alpha = 73.18(4)$, $\beta = 79.85(5)$, $\gamma = 66.82(6)^\circ$, and $D_{\text{calc}} = 1.28 \text{ g cm}^{-3}$ for $Z = 2$.

Key words. Dibenzo-18-crown-6, acetonitrile, nitromethane, solvent complex, low temperature crystal structure, C—H acidic hydrogen interactions.

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1. Introduction

In the course of our investigations into f -element/crown ether complexation [2], we have observed the formation and crystallization of a number of neutral solvent/crown ether complexes of nitromethane and acetonitrile, very often in lieu of metal complexation [1, 3–5]. These complexes have all been stabilized by very weak C—H acidic interactions with the crown ether. The number of other complexes which contain these types of interactions is also growing, including: $\{[trans\text{-Ir}(\text{CO})(\text{CH}_3\text{CN})(\text{PPh}_3)_2]_2 \cdot 18\text{-crown-6}\}[\text{PF}_6]_2 \cdot 2 \text{CH}_2\text{Cl}_2$ [6], $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2 \text{CH}_3\text{CN}$ [7], $[(\text{NH}_4)(18\text{-crown-6})]_2[\text{UCl}_6] \cdot 2 \text{CH}_3\text{CN}$ [8], $[(\text{COCPh}_3)_2 \cdot 18\text{-crown-6}] \cdot 2 \text{CH}_3\text{CN}$ [9], and the CH₃NO₂ and CH₃CN complexes of a 21-membered tribenzopyridino crown described in reference [10]. An elegant discussion of interactions like these has appeared which compares acidic C—H crown ether complexes with those containing acidic N—H and O—H functionalities

* For part 4, see reference [1].

[11]. We have begun to study the solvent adducts of the more constrained dibenzo-18-crown-6 and a preliminary report has appeared [5]. Since that first report the low temperature X-ray structures of 18-crown-6·2 CH₃NO₂ [4] and 18-crown-6·2 CH₃CN [1] and the room temperature determination of 18-crown-6·2 CH₃CN [12] have been carried out, giving us this opportunity to directly compare the nitromethane and acetonitrile adducts of both 18-crown-6 and dibenzo-18-crown-6.

2. Experimental

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

The title complexes were crystallized as described in reference [5]. Colorless single crystals of the title complexes were mounted on pins and transferred to the goniometer. The crystals were cooled to -150°C during data collection using a stream of cold nitrogen gas. The space group for the nitromethane adduct was uniquely determined by the systematic absences. The space group for the acetonitrile adduct was determined to be either the centric $P\bar{1}$ or acentric $P1$. Statistical tests indicated that the space group was centric and the subsequent solution and successful refinement of the structure in the space group $P\bar{1}$ confirmed this. A summary of data collection parameters for both complexes is given in Table I.

As observed for their 18-crown-6 analogs the acetonitrile adduct is much less stable than that of nitromethane. This presented several problems in obtaining suitable crystals of the CH₃CN complex for this study. If the crystals were too small they decomposed before they could be placed under the nitrogen stream, but use of larger crystals often resulted in cracking. Two data sets were collected with the better of those two reported here. It appears that the very weak CH₃CN/crown ether interactions immediately start breaking down when the crystals are removed from the solvent. The quick cooling to -150°C thus can and usually does result in either cracking or poor packing. It was not felt that more data sets would yield any better results than reported here.

The crown 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. The methyl hydrogen atoms were located from a difference Fourier map and fully refined for the nitromethane complex and refined with fixed thermal parameters ($B = 3.2 \text{ \AA}^2$) for the acetonitrile complex. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to the final values of R and R_w given in Table I. The final values of the positional parameters are given in Table II for dibenzo-18-crown-6·2 CH₃NO₂ and Table III for dibenzo-18-crown-6·2 CH₃CN.

3. Results and Discussion

Bond distances and angles for the nonhydrogen atoms and for the hydrogen contacts are given in Tables IV and V for dibenzo-18-crown-6·2 CH₃NO₂ and Tables VI and VII for dibenzo-18-crown-6·2 CH₃CN. Both complexes comprise dibenzo-18-crown-6 molecules which interact weakly with two solvent molecules (one above and below the crown ring) *via* weak acidic C—H···O interactions. These weak associations, described below, are sufficient to stabilize the normal conformation of this ether found in all its complexes in the literature but not found for the uncomplexed crown ether [16]. The O—C(alkyl)—C(alkyl)—O torsion angles alternate $\pm g$ ($\pm 60^{\circ}$), the

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

Compound	C ₂₀ H ₂₄ O ₆ ·2 CH ₃ NO ₂	C ₂₀ H ₂₄ O ₆ ·2 CH ₃ CN
Color/Shape	colorless/plate	colorless/parallelepiped
Formula wt.	482.5	442.5
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
Temp., °C	-150	-150
Cell Constants ^a		
<i>a</i> , Å	9.573(2)	9.458(6)
<i>b</i> , Å	14.636(2)	9.570(5)
<i>c</i> , Å	33.471(7)	14.404(5)
<i>α</i> , deg		73.18(4)
<i>β</i> , deg	93.77(2)	79.85(5)
<i>γ</i> , deg		66.82(6)
Cell vol, Å ³	4679	1144
Formula units/unit cell	8	2
<i>D</i> _{calc} , g cm ⁻³	1.37	1.28
<i>μ</i> _{calc} , cm ⁻¹	0.68	0.99
Diffractometer/Scan	Enraf-Nonius CAD-4/θ - 2θ	Enraf-Nonius CAD-4/θ - 2θ
Radiation, graphite monochromator	MoKα(λ = 0.71073)	MoKα(λ = 0.71073)
Max. crystal dimensions, mm	0.15 × 0.45 × 0.50	0.43 × 0.63 × 0.88
Scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
Standard reflections	400; 060; 008	500; 070; 0, 0, 11
Decay of standards	-0.8%	± 1%
Reflections measured	8982	4108
2θ range, deg	2 ≤ 2θ ≤ 50	2 ≤ 2θ ≤ 50
Range of <i>h</i> , <i>k</i> , <i>l</i>	+ 11, + 17, ± 39	+ 11, ± 11, ± 17
Reflections observed [<i>F</i> _o ≥ 5σ(<i>F</i> _o)] ^b	4316	2951
Computer programs ^c	SHELX [13]	SHELX [13]
Structure solution	MULTAN [14]	MULTAN [14]
No. of parameters varied	661	307
Weights	[σ(<i>F</i> _o) ² + 0.00004 <i>F</i> _o ²] ⁻¹	[σ(<i>F</i> _o) ² + 0.00009 <i>F</i> _o ²] ⁻¹
GOF	1.4	2.9
<i>R</i> = Σ <i>F</i> _o - <i>F</i> _c / Σ <i>F</i> _o	0.054	0.105
<i>R</i> _w	0.055	0.110
Largest feature final diff. map	0.3e ⁻ Å ⁻³	0.5e ⁻ Å ⁻³

^a Least-squares refinement of ((sin θ)/λ)² values for 16 reflections θ > 20° (CH₃NO₂) and 25 reflections θ > 10° (CH₃CN).

^b Corrections: Lorentz-polarization.

^c Neutral scattering factors and anomalous dispersion corrections from ref. [15].

O—C(aryl)—C(aryl)—O angles are *syn* (0°), and the C—C—O—C angles are all *anti* (180°). The average bonding parameters in the macrocycles are also relatively unaffected by the weak interactions: O—C(alkyl) = 1.431(6) Å for dibenzo-18-crown-6·2 CH₃NO₂ and 1.42(1) Å for dibenzo-18-crown-6·2 CH₃CN; O—C(aryl) = 1.372(4), 1.36(2) Å; C(alkyl)—C(alkyl) = 1.496(3), 1.49(2) Å; C(aryl)—C(aryl) (in the macrocycle ring) = 1.406(4), 1.40(1) Å; C(aryl)—O—C(alkyl) = 116.2(4), 116.0(8)°; C(alkyl)—O—C(alkyl) = 111.2(5), 112.7(3)°; O—C(alkyl)—C(alkyl) = 108.9(8), 108.8(6)°; O—C(aryl)—C(aryl) (in the macrocycle ring) = 115.6(5), 115(1)°.

The nature of the weak solvent associations in the title complexes has been examined by refining the hydrogen atom positions for the methyl groups and observing the resulting contact geometries. The hydrogen interactions in dibenzo-18-crown-6·2 CH₃NO₂ are not exclusive to the oxygen atoms of a single macrocyclic ring. There are

Table II. Final fractional coordinates for dibenzo-18-crown-6·2 CH₃NO₂.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
O(1)	0.6287(3)	0.4221(2)	0.31098(8)
O(2)	0.8689(3)	0.4816(2)	0.35909(8)
O(3)	0.9016(3)	0.4397(2)	0.44241(8)
O(4)	0.7166(3)	0.3358(2)	0.47180(8)
O(5)	0.4737(3)	0.2722(2)	0.42440(8)
O(6)	0.4430(3)	0.3196(2)	0.34263(8)
O(7)	-0.1395(3)	0.3924(2)	0.09383(8)
O(8)	-0.1110(3)	0.3176(2)	0.17295(8)
O(9)	0.1161(3)	0.3700(2)	0.22423(8)
O(10)	0.3007(3)	0.4836(2)	0.20041(8)
O(11)	0.2839(3)	0.5496(2)	0.12141(8)
O(12)	0.0568(3)	0.4981(2)	0.06785(8)
O(13)	0.9997(4)	0.2556(3)	0.3848(1)
O(14)	0.9014(4)	0.2576(2)	0.3251(1)
O(15)	0.5344(5)	0.5870(3)	0.4548(1)
O(16)	0.3507(4)	0.5542(3)	0.4195(1)
O(17)	-0.1007(5)	0.5774(3)	0.2250(1)
O(18)	-0.2487(4)	0.5352(3)	0.1774(1)
O(19)	0.3883(4)	0.3124(2)	0.0847(1)
O(20)	0.3901(4)	0.2096(2)	0.1300(1)
N(1)	0.8974(4)	0.2634(2)	0.3611(1)
N(2)	0.4727(5)	0.5480(3)	0.4271(1)
N(3)	-0.1304(4)	0.5510(3)	0.1907(1)
N(4)	0.3412(4)	0.2784(2)	0.1139(1)
C(1)	0.7434(5)	0.4691(3)	0.2949(1)
C(2)	0.8088(5)	0.5326(3)	0.3258(1)
C(3)	0.9329(5)	0.5419(3)	0.3887(1)
C(4)	1.0057(4)	0.4879(3)	0.4217(1)
C(5)	0.9494(5)	0.3846(3)	0.4734(1)
C(6)	0.8493(4)	0.3279(3)	0.4895(1)
C(7)	0.6127(4)	0.2763(3)	0.4866(1)
C(8)	0.4745(5)	0.2996(3)	0.4653(1)
C(9)	0.3413(4)	0.2889(3)	0.4040(1)
C(10)	0.3442(5)	0.2619(3)	0.3609(1)
C(11)	0.4588(5)	0.3057(3)	0.3025(1)
C(12)	0.5607(5)	0.3601(3)	0.2858(1)
C(13)	0.5854(5)	0.3509(3)	0.2454(1)
C(14)	0.5080(5)	0.2869(3)	0.2222(1)
C(15)	0.4076(5)	0.2350(3)	0.2384(1)
C(16)	0.3838(5)	0.2431(3)	0.2789(1)
C(17)	1.0870(5)	0.3827(3)	0.4898(1)
C(18)	1.1235(5)	0.3233(3)	0.5211(1)
C(19)	1.0266(5)	0.2670(3)	0.5363(1)
C(20)	0.8873(5)	0.2686(3)	0.5206(1)
C(21)	-0.2475(4)	0.3419(3)	0.1123(1)
C(22)	-0.1782(5)	0.2718(3)	0.1397(1)
C(23)	-0.0446(5)	0.2555(3)	0.2009(1)
C(24)	0.0122(5)	0.3078(3)	0.2365(1)
C(25)	0.1756(4)	0.4266(3)	0.2533(1)
C(26)	0.2753(4)	0.4885(3)	0.2403(1)
C(27)	0.3991(5)	0.5478(3)	0.1868(1)
C(28)	0.4137(4)	0.5308(3)	0.1430(1)
C(29)	0.2952(4)	0.5399(3)	0.0791(1)

Table II. *Continued.*

Atom	x/a	y/b	z/c
C(30)	0.1591(4)	0.5645(3)	0.0579(1)
C(31)	-0.0772(4)	0.5159(3)	0.0536(1)
C(32)	-0.1839(4)	0.4600(3)	0.0676(1)
C(33)	-0.3223(5)	0.4772(3)	0.0554(1)
C(34)	-0.3563(5)	0.5478(3)	0.0284(1)
C(35)	-0.2536(5)	0.5999(3)	0.0140(1)
C(36)	-0.1139(5)	0.5852(3)	0.0268(1)
C(37)	0.1444(5)	0.4261(3)	0.2931(1)
C(38)	0.2129(5)	0.4858(3)	0.3199(1)
C(39)	0.3113(5)	0.5471(3)	0.3074(1)
C(40)	0.3418(5)	0.5486(3)	0.2672(1)
C(41)	0.7599(5)	0.2775(3)	0.3776(1)
C(42)	0.5606(5)	0.4933(3)	0.4020(1)
C(43)	-0.0151(5)	0.5400(3)	0.1637(1)
C(44)	0.2186(5)	0.3222(3)	0.1314(1)
H(1)[C(1)]	0.811	0.426	0.287
H(2)[C(1)]	0.710	0.503	0.272
H(1)[C(2)]	0.739	0.572	0.335
H(2)[C(2)]	0.879	0.568	0.314
H(1)[C(3)]	0.999	0.580	0.377
H(2)[C(3)]	0.862	0.578	0.399
H(1)[C(4)]	1.056	0.528	0.440
H(2)[C(4)]	1.068	0.446	0.411
H(1)[C(7)]	0.636	0.214	0.482
H(2)[C(7)]	0.608	0.285	0.515
H(1)[C(8)]	0.460	0.364	0.466
H(2)[C(8)]	0.402	0.269	0.478
H(1)[C(9)]	0.272	0.254	0.416
H(2)[C(9)]	0.320	0.352	0.406
H(1)[C(10)]	0.254	0.269	0.348
H(2)[C(10)]	0.373	0.200	0.359
H(1)[C(13)]	0.654	0.388	0.234
H(1)[C(14)]	0.525	0.279	0.195
H(1)[C(15)]	0.354	0.193	0.222
H(1)[C(16)]	0.316	0.206	0.290
H(1)[C(17)]	1.155	0.422	0.480
H(1)[C(18)]	1.217	0.322	0.532
H(1)[C(19)]	1.054	0.226	0.558
H(1)[C(20)]	0.802	0.229	0.531
H(1)[C(21)]	-0.302	0.382	0.127
H(2)[C(21)]	-0.306	0.312	0.092
H(1)[C(22)]	-0.111	0.239	0.126
H(2)[C(22)]	-0.247	0.231	0.149
H(1)[C(23)]	-0.110	0.212	0.209
H(2)[C(23)]	0.030	0.225	0.189
H(1)[C(24)]	0.053	0.267	0.256
H(2)[C(24)]	-0.061	0.341	0.248
H(1)[C(27)]	0.365	0.608	0.190
H(2)[C(27)]	0.487	0.541	0.201
H(1)[C(28)]	0.438	0.469	0.139
H(2)[C(28)]	0.485	0.569	0.134
H(1)[C(29)]	0.366	0.580	0.071
H(2)[C(29)]	0.319	0.479	0.073

Table II. *Continued.*

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(1)[C(30)]	0.169	0.564	0.030
H(2)[C(30)]	0.131	0.624	0.066
H(1)[C(33)]	-0.394	0.441	0.065
H(1)[C(34)]	-0.452	0.559	0.020
H(1)[C(35)]	-0.278	0.647	-0.005
H(1)[C(36)]	-0.043	0.623	0.017
H(1)[C(37)]	0.077	0.385	0.302
H(1)[C(38)]	0.192	0.485	0.347
H(1)[C(39)]	0.357	0.588	0.326
H(1)[C(40)]	0.408	0.591	0.258
H(1)[C(41)]	0.721(4)	0.214(3)	0.377(1)
H(2)[C(41)]	0.713(4)	0.322(3)	0.362(1)
H(3)[C(41)]	0.780(4)	0.290(3)	0.405(1)
H(1)[C(42)]	0.514(6)	0.452(4)	0.382(2)
H(2)[C(42)]	0.583(7)	0.535(4)	0.379(2)
H(3)[C(42)]	0.636(7)	0.456(4)	0.414(2)
H(1)[C(43)]	-0.005(4)	0.480(3)	0.160(1)
H(2)[C(43)]	0.069(4)	0.567(3)	0.178(1)
H(3)[C(43)]	-0.039(6)	0.562(4)	0.136(2)
H(1)[C(44)]	0.149(4)	0.280(3)	0.132(1)
H(2)[C(44)]	0.253(5)	0.342(3)	0.158(1)
H(3)[C(44)]	0.189(5)	0.376(3)	0.111(1)

two formula units in the asymmetric unit of this complex (Figure 1), differing mainly in the orientation of the nitromethane groups relative to the ether and the hydrogen atom contacts. H(1)[C(41)] interacts with the alkyl ether O(11) of the second formula unit (H(1)[C(41)] \cdots O(11) = 2.41(4) Å; C(41)—H(1) \cdots O(11) = 159(3) $^\circ$) and H(2)[C(42)] weakly donates to the solvent oxygen atom O(20)(H(2)[C(42)] \cdots O(20) = 2.59(6) Å, C(42)—H(2) \cdots O(20) = 135(2) $^\circ$) to associate both formula units into polymeric chains which propagate along *b* (Figure 2). The remaining weak interactions are between solvent hydrogen and crown oxygen atoms within the same formula unit, two each from all four methyl groups, C(41), C(42), C(43), and C(44). C(41) has one strong interaction with O(1) (H(2)[C(41)] \cdots O(1) = 1.97(4) Å, C(41)—H(2) \cdots O(1) = 166(3) $^\circ$) and has one hydrogen atom with close contacts to O(3) and O(4). C(42) also directs one hydrogen atom (H(3)) between O(3) and O(4) but the distances are quite long, 2.67(7) Å (O(3)) and 2.70(6) Å (O(4)). C(43) and C(44) interact exclusively with O(7)—O(12), again primarily with the less basic aryl ether atoms. The one hydrogen which appears to be directed towards an alkyl ether exhibits a long contact distance, H(1)[C(43)] \cdots O(8) = 2.63(4) Å, C(43)—H(1) \cdots O(8) = 145(3) $^\circ$. C(43) is close enough for some interaction with nitromethane oxygen atoms O(13) and O(14) (C(43) \cdots O(13) = 3.379(6) Å, C(43) \cdots O(14) = 3.555(6) Å), however, the hydrogen atom positions do not indicate such an interaction.

The C—H \cdots O interactions in dibenzo-18-crown-6 \cdot 2 CH₃CN (Figure 3) are confined to a single crown ether unit and thus this structure consists of discreet 1 : 2 complexes. All of the H \cdots O contact distances are quite long, ranging from 2.57(4) to 2.93(5) Å, however, hydrogen atom orientation suggests some interaction. H(2)[C(22)] is directed

Table III. Final fractional coordinates for dibenzo-18-crown-6-2 CH₃CN.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
O(1)	0.8850(4)	-0.1293(3)	0.3706(2)
O(2)	0.6686(4)	-0.0708(4)	0.2357(2)
O(3)	0.5923(4)	0.2060(3)	0.0861(2)
O(4)	0.7210(4)	0.4013(3)	0.0752(2)
O(5)	0.9213(4)	0.3545(3)	0.2153(2)
O(6)	1.0020(4)	0.0754(3)	0.3644(2)
C(1)	0.8285(6)	-0.2425(5)	0.3632(3)
C(2)	0.6650(6)	-0.1572(5)	0.3326(3)
C(3)	0.5192(6)	0.0097(5)	0.2003(3)
C(4)	0.5367(6)	0.0833(5)	0.0953(3)
C(5)	0.6311(5)	0.2771(5)	-0.0062(3)
C(6)	0.7012(6)	0.3853(5)	-0.0114(3)
C(7)	0.7994(6)	0.5045(5)	0.0704(3)
C(8)	0.8188(6)	0.5036(5)	0.1703(3)
C(9)	0.9551(6)	0.3468(5)	0.3082(3)
C(10)	1.0699(6)	0.1901(5)	0.3481(3)
C(11)	1.0941(6)	-0.0760(5)	0.3945(3)
C(12)	1.0360(6)	-0.1897(5)	0.3971(3)
C(13)	1.1219(6)	-0.3460(5)	0.4244(3)
C(14)	1.2727(7)	-0.3953(6)	0.4517(3)
C(15)	1.3304(6)	-0.2848(6)	0.4507(3)
C(16)	1.2448(6)	-0.1262(6)	0.4224(3)
C(17)	0.6070(6)	0.2512(5)	-0.0897(3)
C(18)	0.6527(6)	0.3296(6)	-0.1800(3)
C(19)	0.7191(6)	0.4343(6)	-0.1853(3)
C(20)	0.7439(6)	0.4622(5)	-0.1018(3)
N(1)	0.3801(6)	0.2189(5)	0.4166(3)
C(21)	0.4850(7)	0.2326(6)	0.3691(3)
C(22)	0.6221(7)	0.2522(7)	0.3098(4)
N(2)	1.1466(6)	0.1665(5)	0.0263(4)
C(23)	1.0725(7)	0.1027(5)	0.0765(4)
C(24)	0.9770(7)	0.0209(7)	0.1395(4)
H(1)[C(1)]	0.891	-0.297	0.316
H(2)[C(1)]	0.830	-0.315	0.424
H(1)[C(2)]	0.607	-0.088	0.373
H(2)[C(2)]	0.618	-0.231	0.338
H(1)[C(3)]	0.469	-0.062	0.209
H(2)[C(3)]	0.460	0.088	0.234
H(1)[C(4)]	0.440	0.125	0.068
H(2)[C(4)]	0.608	0.008	0.063
H(1)[C(7)]	0.898	0.470	0.037
H(2)[C(7)]	0.740	0.608	0.037
H(1)[C(8)]	0.722	0.526	0.207
H(2)[C(8)]	0.860	0.581	0.168
H(1)[C(9)]	0.996	0.425	0.304
H(2)[C(9)]	0.863	0.364	0.350
H(1)[C(10)]	1.101	0.189	0.408
H(2)[C(10)]	1.157	0.168	0.303
H(1)[C(13)]	1.080	-0.421	0.425
H(1)[C(14)]	1.332	-0.504	0.471
H(1)[C(15)]	1.431	-0.317	0.470
H(1)[C(16)]	1.287	-0.051	0.422
H(1)[C(17)]	0.559	0.179	-0.086

Table III. *Continued.*

Atom	x/a	y/b	z/c
H(1)[C(18)]	0.637	0.310	-0.238
H(1)[C(19)]	0.749	0.489	-0.247
H(1)[C(20)]	0.791	0.535	-0.107
H(1)[C(22)]	0.617(6)	0.353(6)	0.322(3)
H(2)[C(22)]	0.711(6)	0.162(6)	0.338(3)
H(3)[C(22)]	0.609(5)	0.281(5)	0.240(4)
H(1)[C(24)]	0.898(6)	0.064(6)	0.110(4)
H(2)[C(24)]	1.026(6)	-0.091(6)	0.148(3)
H(3)[C(24)]	0.975(6)	0.024(5)	0.204(4)

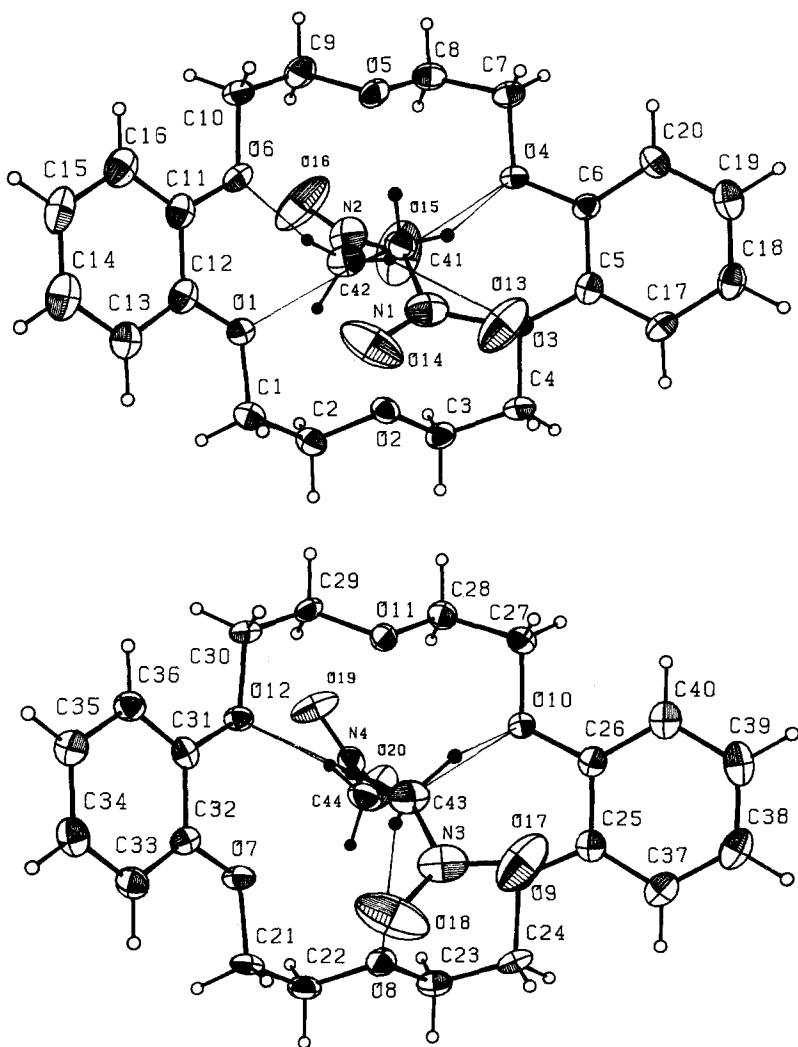


Fig. 1. Top view and atom labeling scheme of the two formula units in the asymmetric unit of dibenzo-18-crown-6-2 CH_3NO_2 . 50% probability ellipsoids for thermal motion; H atoms arbitrarily reduced. Closest H contacts from Tables V and VII are indicated.

Table IV. Bond distances (Å) and angles (deg) for dibenzo-18-crown-6·2 CH₃NO₂.

Atoms	Distance	Atoms	Distance
O(1)—C(1)	1.430(5)	O(1)—C(12)	1.374(5)
O(2)—C(2)	1.430(5)	O(2)—C(3)	1.434(5)
O(3)—C(4)	1.437(5)	O(3)—C(5)	1.368(5)
O(4)—C(6)	1.371(5)	O(4)—C(7)	1.435(5)
O(5)—C(8)	1.425(5)	O(5)—C(9)	1.421(5)
O(6)—C(10)	1.435(5)	O(6)—C(11)	1.376(5)
O(7)—C(21)	1.443(5)	O(7)—C(32)	1.371(5)
O(8)—C(22)	1.416(5)	O(8)—C(23)	1.423(5)
O(9)—C(24)	1.429(5)	O(9)—C(25)	1.372(5)
O(10)—C(26)	1.376(5)	O(10)—C(27)	1.427(5)
O(11)—C(28)	1.423(5)	O(11)—C(29)	1.433(5)
O(12)—C(30)	1.434(5)	O(12)—C(31)	1.364(5)
O(13)—N(1)	1.225(5)	O(14)—N(1)	1.211(5)
O(15)—N(2)	1.210(6)	O(16)—N(2)	1.182(6)
O(17)—N(3)	1.227(6)	O(18)—N(3)	1.212(6)
O(19)—N(4)	1.210(5)	O(20)—N(4)	1.221(5)
N(1)—C(41)	1.475(6)	N(2)—C(42)	1.466(7)
N(3)—C(43)	1.481(7)	N(4)—C(44)	1.491(6)
C(1)—C(2)	1.496(6)	C(3)—C(4)	1.494(6)
C(5)—C(6)	1.402(6)	C(5)—C(17)	1.394(6)
C(6)—C(20)	1.386(6)	C(7)—C(8)	1.500(6)
C(9)—C(10)	1.496(6)	C(11)—C(12)	1.405(6)
C(11)—C(16)	1.380(6)	C(12)—C(13)	1.395(6)
C(13)—C(14)	1.398(6)	C(14)—C(15)	1.366(7)
C(15)—C(16)	1.393(7)	C(17)—C(18)	1.389(6)
C(18)—C(19)	1.364(6)	C(19)—C(20)	1.401(6)
C(21)—C(22)	1.502(6)	C(23)—C(24)	1.489(6)
C(25)—C(26)	1.405(6)	C(25)—C(37)	1.384(6)
C(26)—C(40)	1.382(6)	C(27)—C(28)	1.500(6)
C(29)—C(30)	1.487(6)	C(31)—C(32)	1.412(6)
C(31)—C(36)	1.386(6)	C(32)—C(33)	1.383(6)
C(33)—C(34)	1.398(6)	C(34)—C(35)	1.357(6)
C(35)—C(36)	1.394(6)	C(37)—C(38)	1.386(6)
C(38)—C(39)	1.385(7)	C(39)—C(40)	1.395(6)
C(41)—H(1)	1.00(4)	C(42)—H(1)	1.00(5)
C(43)—H(1)	0.90(4)	C(44)—H(1)	0.91(4)
C(41)—H(2)	0.93(4)	C(42)—H(2)	1.02(6)
C(43)—H(2)	0.99(4)	C(44)—H(2)	0.96(4)
C(41)—H(3)	0.94(4)	C(42)—H(3)	0.97(7)
C(43)—H(3)	1.01(5)	C(44)—H(3)	1.08(4)

Atoms	Angle	Atoms	Angle
C(1)—O(1)—C(12)	115.5(3)	C(2)—O(2)—C(3)	110.5(3)
C(4)—O(3)—C(5)	116.5(3)	C(6)—O(4)—C(7)	116.4(3)
C(8)—O(5)—C(9)	111.2(3)	C(10)—O(6)—C(11)	116.6(3)
C(21)—O(7)—C(32)	116.3(3)	C(22)—O(8)—C(23)	112.0(3)
C(24)—O(9)—C(25)	116.5(3)	C(26)—O(10)—C(27)	116.1(3)
C(28)—O(11)—C(29)	111.3(3)	C(30)—O(12)—C(31)	115.6(3)
O(13)—N(1)—O(14)	124.2(4)	O(13)—N(1)—C(41)	117.8(4)
O(14)—N(1)—C(41)	118.0(4)	O(15)—N(2)—O(16)	123.6(5)
O(15)—N(2)—C(42)	115.4(5)	O(16)—N(2)—C(42)	121.0(4)
O(17)—N(3)—O(18)	123.9(5)	O(17)—N(3)—C(43)	118.0(4)

Table IV. *Continued.*

Atoms	Angle	Atoms	Angle
O(18)—N(3)—C(43)	118.1(4)	O(19)—N(4)—O(20)	122.9(4)
O(19)—N(4)—C(44)	119.1(4)	O(20)—N(4)—C(44)	118.0(4)
O(1)—C(1)—C(2)	109.6(3)	O(2)—C(2)—C(1)	110.1(3)
O(2)—C(3)—C(4)	110.1(3)	O(3)—C(4)—C(3)	108.1(3)
O(3)—C(5)—C(6)	115.9(4)	O(3)—C(5)—C(17)	124.8(4)
C(6)—C(5)—C(17)	119.3(4)	O(4)—C(6)—C(5)	114.9(3)
O(4)—C(6)—C(20)	124.6(4)	C(5)—C(6)—C(20)	120.5(4)
O(4)—C(7)—C(8)	107.9(3)	O(5)—C(8)—C(7)	109.9(3)
O(5)—C(9)—C(10)	110.2(3)	O(6)—C(10)—C(9)	108.1(3)
O(6)—C(11)—C(12)	115.4(4)	O(6)—C(11)—C(16)	124.9(4)
C(12)—C(11)—C(16)	119.7(4)	O(1)—C(12)—C(11)	116.3(4)
O(1)—C(12)—C(13)	123.8(4)	C(11)—C(12)—C(13)	119.9(4)
C(12)—C(13)—C(14)	119.1(4)	C(13)—C(14)—C(15)	120.8(4)
C(14)—C(15)—C(16)	120.3(4)	C(11)—C(16)—C(15)	120.1(4)
C(5)—C(17)—C(18)	119.6(4)	C(17)—C(18)—C(19)	121.1(4)
C(18)—C(19)—C(20)	120.2(4)	C(6)—C(20)—C(19)	119.3(4)
O(7)—C(21)—C(22)	108.1(3)	O(8)—C(22)—C(21)	108.5(3)
O(8)—C(23)—C(24)	108.8(3)	O(9)—C(24)—C(23)	108.8(3)
O(9)—C(25)—C(26)	115.4(4)	O(9)—C(25)—C(37)	124.9(4)
C(26)—C(25)—C(37)	119.6(4)	O(10)—C(26)—C(25)	115.7(3)
O(10)—C(26)—C(40)	124.2(4)	C(25)—C(26)—C(40)	120.2(4)
O(10)—C(27)—C(28)	108.0(3)	O(11)—C(28)—C(27)	109.2(3)
O(11)—C(29)—C(30)	109.2(3)	O(12)—C(30)—C(29)	108.4(3)
O(12)—C(31)—C(32)	117.3(3)	O(12)—C(31)—C(36)	123.9(4)
C(32)—C(31)—C(36)	118.8(4)	O(7)—C(32)—C(31)	115.4(4)
O(7)—C(32)—C(33)	124.8(4)	C(31)—C(32)—C(33)	119.7(4)
C(32)—C(33)—C(34)	120.2(4)	C(33)—C(34)—C(35)	120.1(4)
C(34)—C(35)—C(36)	120.5(4)	C(31)—C(36)—C(35)	120.6(4)
C(25)—C(37)—C(38)	119.7(4)	C(37)—C(38)—C(39)	121.0(4)
C(38)—C(39)—C(40)	119.4(4)	C(26)—C(40)—C(39)	120.0(4)
N(1)—C(41)—H(1)	102(2)	H(1)—C(41)—H(2)	118(3)
H(1)—C(41)—H(3)	105(3)	N(2)—C(42)—H(1)	118(3)
H(1)—C(42)—H(2)	88(5)	H(1)—C(42)—H(3)	103(5)
N(3)—C(43)—H(1)	107(3)	H(1)—C(43)—H(2)	111(3)
H(1)—C(43)—H(3)	101(4)	N(4)—C(44)—H(1)	108(2)
H(1)—C(44)—H(2)	113(3)	H(1)—C(44)—H(3)	111(3)
N(1)—C(41)—H(2)	107(2)	H(1)—C(41)—H(2)	118(3)
H(2)—C(41)—H(3)	118(3)	N(2)—C(42)—H(2)	105(4)
H(1)—C(42)—H(2)	88(5)	H(2)—C(42)—H(3)	117(5)
N(3)—C(43)—H(2)	106(2)	H(1)—C(43)—H(2)	111(3)
H(2)—C(43)—H(3)	117(4)	N(4)—C(44)—H(2)	104(3)
H(1)—C(44)—H(2)	113(3)	H(2)—C(44)—H(3)	115(4)
N(1)—C(41)—H(3)	105(2)	H(1)—C(41)—H(3)	105(3)
H(2)—C(41)—H(3)	118(3)	N(2)—C(42)—H(3)	121(4)
H(1)—C(42)—H(3)	103(5)	H(2)—C(42)—H(3)	117(5)
N(3)—C(43)—H(3)	114(3)	H(1)—C(43)—H(3)	101(4)
H(2)—C(43)—H(3)	117(4)	N(4)—C(44)—H(3)	104(3)
H(1)—C(44)—H(3)	111(3)	H(2)—C(44)—H(3)	115(4)

Table V. Hydrogen contact geometries (\AA , deg) for dibenzo-18-crown-6-2 CH_3NO_2 .

	Atoms	Distance	Atoms	Distance
C(41)	H(1)—O(11) ^a	2.41(4)	H(2)—O(1)	1.97(4)
	H(3)—O(4)	2.45(4)	H(3)—O(3)	2.74(4)
C(42)	H(1)—O(6)	2.41(5)	H(2)—O(20) ^b	2.59(6)
	H(3)—O(3)	2.67(7)	H(3)—O(4)	2.70(6)
C(43)	H(1)—O(8)	2.63(4)	H(1)—O(7)	2.79(4)
	H(2)—O(10)	2.60(4)	H(3)—O(12)	2.67(5)
C(44)	H(1)—O(8)	2.97(4)	H(2)—O(10)	2.55(4)
	H(2)—O(9)	2.69(4)	H(3)—O(12)	2.57(4)
	H(3)—O(11)	2.71(5)		
	C(41)—O(1)	3.264(5)	C(41)—O(2)	3.237(5)
	C(41)—O(3)	3.434(5)	C(41)—O(4)	3.319(5)
	C(41)—O(5)	3.245(5)	C(41)—O(6)	3.237(5)
	C(41)—O(11) ^a	3.363(5)		
	C(42)—O(1)	3.323(5)	C(42)—O(2)	3.369(6)
	C(42)—O(3)	3.538(5)	C(42)—O(4)	3.542(5)
	C(42)—O(5)	3.437(6)	C(42)—O(6)	3.374(5)
	C(42)—O(20) ^b	3.385(6)		
	C(43)—O(7)	3.343(5)	C(43)—O(8)	3.402(5)
	C(43)—O(9)	3.397(5)	C(43)—O(10)	3.293(5)
	C(43)—O(11)	3.278(6)	C(43)—O(12)	3.380(5)
	C(43)—O(13) ^b	3.379(6)	C(43)—O(14) ^b	3.555(6)
	C(44)—O(7)	3.718(5)	C(44)—O(8)	3.530(6)
	C(44)—O(9)	3.391(5)	C(44)—O(10)	3.360(5)
	C(44)—O(11)	3.406(5)	C(44)—O(12)	3.623(5)
Atoms	Angle	Atoms	Angle	
C(41)—H(1)—O(11) ^a	159(3)	C(41)—H(2)—O(1)	166(3)	
C(41)—H(3)—O(4)	153(3)	C(41)—H(3)—O(3)	131(3)	
C(42)—H(1)—O(6)	164(4)	C(42)—H(2)—O(20) ^b	135(2)	
C(42)—H(3)—O(3)	150(5)	C(42)—H(3)—O(4)	146(5)	
C(43)—H(1)—O(8)	145(3)	C(43)—H(1)—O(7)	121(3)	
C(43)—H(2)—O(10)	128(3)	C(43)—H(3)—O(12)	128(4)	
C(44)—H(1)—O(8)	121(3)	C(44)—H(2)—O(10)	142(3)	
C(44)—H(2)—O(9)	130(3)	C(44)—H(3)—O(12)	165(4)	
C(44)—H(3)—O(11)	122(3)			

^a Atoms related to those in Table II by $1-x, y-0.5, 0.5-z$.

^b $1-x, 0.5+y, 0.5-z$.

between aryl ether O(1) and O(6), H(3)[C(22)] between the other two aryl ethers O(3) and O(4). Similarly, two hydrogen atoms from C(24) are directed between these same two pairs of oxygen atoms, H(1)[C(24)] between O(3) and O(4) and H(3)[C(24)] between O(1) and O(6).

In both of the title complexes all of the methyl groups, except for C(43) of the nitromethane adduct, have the same relative orientation to the macrocyclic ring: two hydrogens of each methyl group generally toward pairs of aryl ethers, with the third hydrogen directed over the center and away from the polyether. These latter hydrogen

Table VI. Bond distances (Å) and angles (deg) for dibenzo-18-crown-6·2 CH₃CN.

Atoms	Distance	Atoms	Distance
O(1)—C(1)	1.419(6)	O(1)—C(12)	1.391(6)
O(2)—C(2)	1.405(5)	O(2)—C(3)	1.421(5)
O(3)—C(4)	1.429(5)	O(3)—C(5)	1.366(5)
O(4)—C(6)	1.353(5)	O(4)—C(7)	1.431(6)
O(5)—C(8)	1.412(5)	O(5)—C(9)	1.404(5)
O(6)—C(10)	1.423(6)	O(6)—C(11)	1.349(5)
C(1)—C(2)	1.513(6)	C(3)—C(4)	1.483(6)
C(5)—C(6)	1.412(7)	C(5)—C(17)	1.369(6)
C(6)—C(20)	1.376(6)	C(7)—C(8)	1.480(6)
C(9)—C(10)	1.482(6)	C(11)—C(12)	1.388(7)
C(11)—C(16)	1.405(7)	C(12)—C(13)	1.366(6)
C(13)—C(14)	1.405(7)	C(14)—C(15)	1.362(7)
C(15)—C(16)	1.384(6)	C(17)—C(18)	1.390(6)
C(18)—C(19)	1.356(7)	C(19)—C(20)	1.381(7)
N(1)—C(21)	1.131(6)	C(21)—C(22)	1.468(8)
C(22)—H(1)	1.01(5)	C(22)—H(2)	0.98(5)
C(22)—H(3)	0.98(5)	N(2)—C(23)	1.134(6)
C(23)—C(24)	1.453(8)	C(24)—H(1)	0.82(5)
C(24)—H(2)	0.96(5)	C(24)—H(3)	0.94(5)
Atoms	Angle	Atoms	Angle
C(1)—O(1)—C(12)	114.9(3)	C(2)—O(2)—C(3)	112.4(3)
C(4)—O(3)—C(5)	116.5(3)	C(6)—O(4)—C(7)	115.6(4)
C(8)—O(5)—C(9)	113.0(3)	C(10)—O(6)—C(11)	117.1(4)
O(1)—C(1)—C(2)	107.9(4)	O(2)—C(2)—C(1)	108.9(4)
O(2)—C(3)—C(4)	108.2(4)	O(3)—C(4)—C(3)	107.9(4)
O(3)—C(5)—C(6)	114.6(4)	O(3)—C(5)—C(17)	125.4(5)
C(6)—C(5)—C(17)	120.0(4)	O(4)—C(6)—C(5)	115.4(4)
O(4)—C(6)—C(20)	126.3(5)	C(5)—C(6)—C(20)	118.3(4)
O(4)—C(7)—C(8)	109.2(4)	O(5)—C(8)—C(7)	109.3(4)
O(5)—C(9)—C(10)	109.7(4)	O(6)—C(10)—C(9)	109.1(4)
O(6)—C(11)—C(12)	117.5(4)	O(6)—C(11)—C(16)	124.6(5)
C(12)—C(11)—C(16)	117.9(4)	O(1)—C(12)—C(11)	113.9(4)
O(1)—C(12)—C(13)	124.3(5)	C(11)—C(12)—C(13)	121.8(5)
C(12)—C(13)—C(14)	119.9(5)	C(13)—C(14)—C(15)	118.8(5)
C(14)—C(15)—C(16)	121.7(5)	C(11)—C(16)—C(15)	119.9(5)
C(5)—C(17)—C(18)	120.4(5)	C(17)—C(18)—C(19)	119.7(5)
C(18)—C(19)—C(20)	120.7(5)	C(6)—C(20)—C(19)	120.0(5)
N(1)—C(21)—C(22)	178.2(6)	C(21)—C(22)—H(1)	100(3)
C(21)—C(22)—H(2)	106(3)	H(1)—C(22)—H(2)	112(4)
C(21)—C(22)—H(3)	112(3)	H(1)—C(22)—H(3)	103(4)
H(2)—C(22)—H(3)	121(4)	N(2)—C(23)—C(24)	179.1(6)
C(23)—C(24)—H(1)	100(4)	C(23)—C(24)—H(2)	111(3)
H(1)—C(24)—H(2)	117(5)	C(23)—C(24)—H(3)	111(3)
H(1)—C(24)—H(3)	120(5)	H(2)—C(24)—H(3)	98(4)

atoms in dibenzo-18-crown-6·2 CH₃NO₂ are responsible for connecting the formula units into polymeric chains. Interestingly, the hydrogen atoms bonded to C(43) have a relative orientation to the other methyl groups rotated by 180°. Thus for this methyl group, one hydrogen is directed toward alkyl ether O(8) and the remaining two are directed between one aryl ether each and one solvent oxygen of another formula unit each. H(2)[C(43)]

Table VII. Hydrogen contact geometries (Å, deg) for dibenzo-18-crown-6·2 CH₃CN.

Atoms		Distance	Atoms		Distance
C(22)	H(2)—O(1)	2.57(4)	H(2)—O(6)		2.61(5)
	H(3)—O(3)	2.57(6)	H(3)—O(4)		2.56(5)
C(24)	H(1)—O(3)	2.71(5)	H(1)—O(4)		2.93(5)
	H(3)—O(1)	2.62(5)	H(3)—O(6)		2.57(6)
	C(22)—O(1)	3.472(6)	C(22)—O(6)		3.441(7)
	C(22)—O(3)	3.449(7)	C(22)—O(4)		3.388(6)
	C(22)—O(2)	3.400(8)	C(22)—O(5)		3.270(8)
	C(24)—O(1)	3.332(6)	C(24)—O(6)		3.488(7)
	C(24)—O(3)	3.478(7)	C(24)—O(4)		3.446(6)
	C(24)—O(2)	3.330(8)	C(24)—O(5)		3.486(8)
Atoms		Angle	Atoms		Angle
	C(22)—H(2)—O(1)	153(5)	C(22)—H(2)—O(6)		143(5)
	C(22)—H(3)—O(3)	150(4)	C(22)—H(3)—O(4)		142(5)
	C(24)—H(1)—O(3)	158(4)	C(24)—H(1)—O(4)		123(6)
	C(24)—H(3)—O(1)	134(5)	C(24)—H(3)—O(6)		167(5)

resides between O(10) (aryl ether) and O(14) (solvent) and H(3)[C(43)] between O(12) and O(13).

As seen in Tables V and VII and from the above discussion, the C—H acidic interactions with the crown ethers are very weak, many of the distances greater than the van der Waals contact distance of 2.60 Å. We have previously observed that the relative orientations of the hydrogen atoms in complexes of this type are subject to the temperature of data collection and possibly the method of crystallization [3, 4]. We will therefore discuss the title complexes and their 18-crown-6 analogs in terms of solvent molecule orientation and methyl···O contact geometry.

18-Crown-6 is more flexible than its dibenzo analog, yet in the acetonitrile and nitromethane adducts, it is the most common complexed form of 18-crown-6, its D_{3d} conformation, which is observed. The formula units in 18-crown-6·2 CH₃NO₂ and 18-crown-6·2 CH₃CN reside around crystallographic centers of inversion and the orientation of the methyl groups match that found for all but one (C(43)) of the methyl groups in the title complexes: two hydrogen atoms directed towards oxygen atoms in the ring and one directed over the cavity and up and away with no interaction. The relative orientations of the solvent groups themselves, however, do show some differences. The planes defined by the nonhydrogen atoms of the nitromethane groups are parallel by symmetry in 18-crown-6·2 CH₃NO₂ while they are twisted by 33° (N(1)/N(2)) and 72° (N(3)/N(4)) in dibenzo-18-crown-6·2 CH₃NO₂. Similarly, the N—C—C acetonitrile solvent axes are parallel by symmetry in 18-crown-6·2 CH₃CN but not in its dibenzo-18-crown-6 complex (the solvent axes intersect at an angle of 13°).

The methyl···O contact distances are much closer in the 18-crown-6 complexes. In D_{3d} 18-crown-6, the oxygen atoms alternate up and down from a mean plane of all six. Thus every other oxygen is directed toward one methyl group, the remainder toward the other. In both 18-crown-6·2 CH₃CN and 18-crown-6·2 CH₃NO₂, the methyl···O contacts to the three closest oxygen atoms average 3.25 Å and to the three farthest oxygen atoms 3.51 Å.

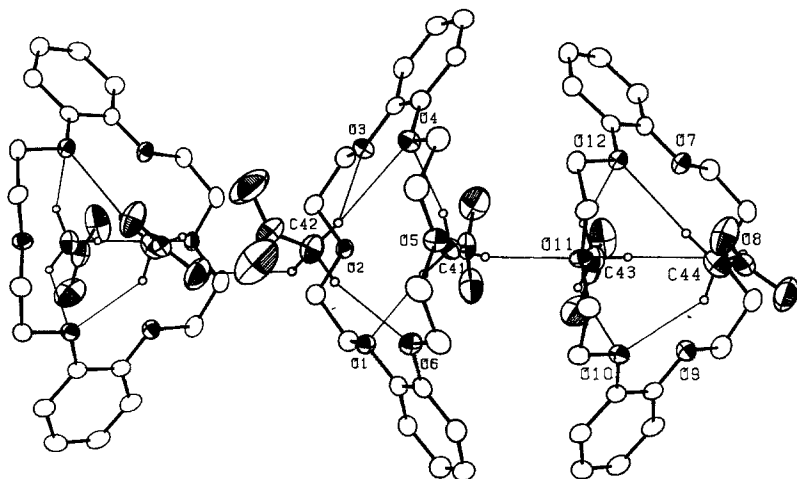


Fig. 2. Association of the dibenzo-18-crown-6-2 CH_3NO_2 units into polymeric chains. The two crown ethers shown containing O(7)—O(12) are related by a unit translation along b .

Also indicative of the closer approach of the methyl groups are the $\text{Me}\cdots\text{Me}$ through the ring contact distances of 3.676(5) Å for 18-crown-6-2 CH_3NO_2 and 3.66(1) Å for 18-crown-6-2 CH_3CN .

These observations are in contrast to what is found for the title complexes. First, the solvent molecules are not presented with identical faces when complexing dibenzo-18-crown-6. Even though all six oxygen atoms are planar, the benzo groups fold towards one of the solvent molecules (C(24) in the acetonitrile adduct and C(41) and C(43) for the nitromethane complex; see Figures 4 and 5). As a result of the axial hydrogen (crown ether) steric interactions outside the crown 'envelope', the solvent molecule on the side of

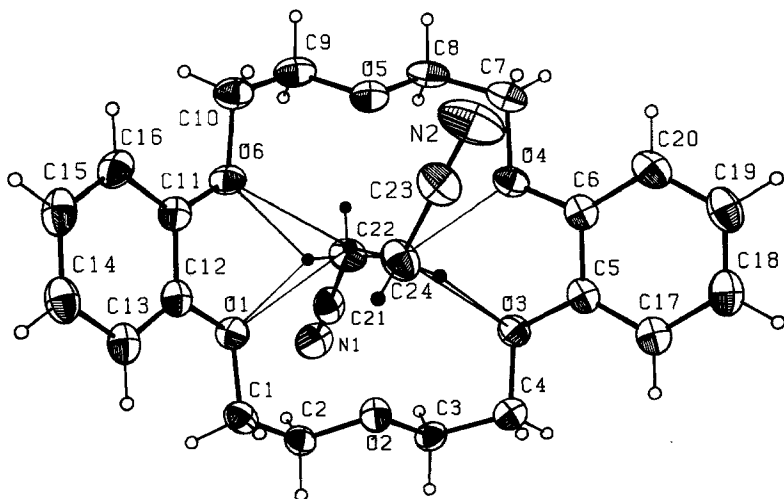


Fig. 3. Dibenzo-18-crown-6-2 CH_3CN .

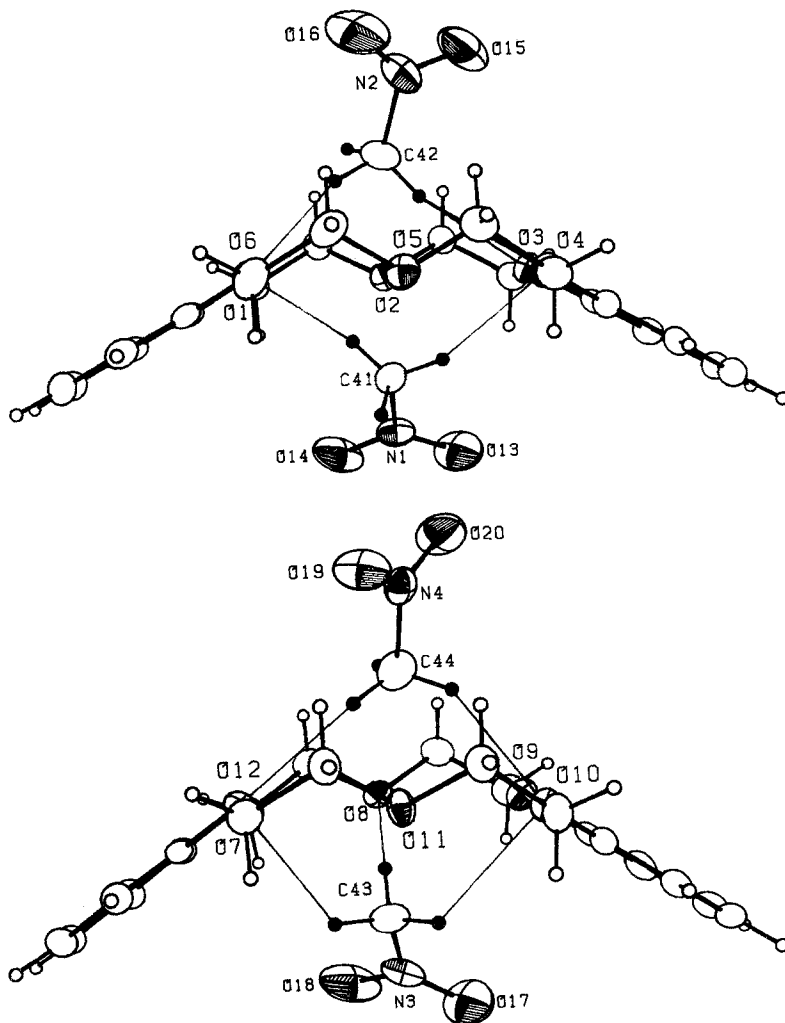


Fig. 4. Side view of the two formula units in dibenzo-18-crown-6·2 CH₃NO₂. The planes formed by the benzo groups intersect the plane of the six ether atoms at an average angle of 146°.

the benzo group folding can actually make the closest approach. This is clearly seen in the distances of the nitromethane methyl group from the plane of the oxygen atoms in the ring: 1.77 Å (C(41)) and 1.91 Å (C(43)) for those on the side of the fold versus 2.03 Å (C(42)) and 2.16 Å (C(44)) for the other two. Similarly the average Me···O contacts are shorter: C(41)···O = 3.29(7) Å, C(43)···O = 3.35(5) Å, C(42)···O = 3.43(8) Å, and C(44)···O = 3.5(1) Å. Interestingly, there is little statistical difference in the contacts observed for the essentially linear acetonitrile molecule: C(22)···O = 3.40(7) Å average, C(24)···O = 3.43(7) Å average, and C(22) resides 2.02 Å, C(24) 2.05 Å from the mean oxygen atom plane.

One final feature of the dibenzo-18-crown-6·2 CH₃NO₂ complex deserves mention, focusing on the differences in the formula units. The planes defined by the four nonhydrogen atoms in each solvent group intersect at angles of 33° for N(1)/N(2) versus

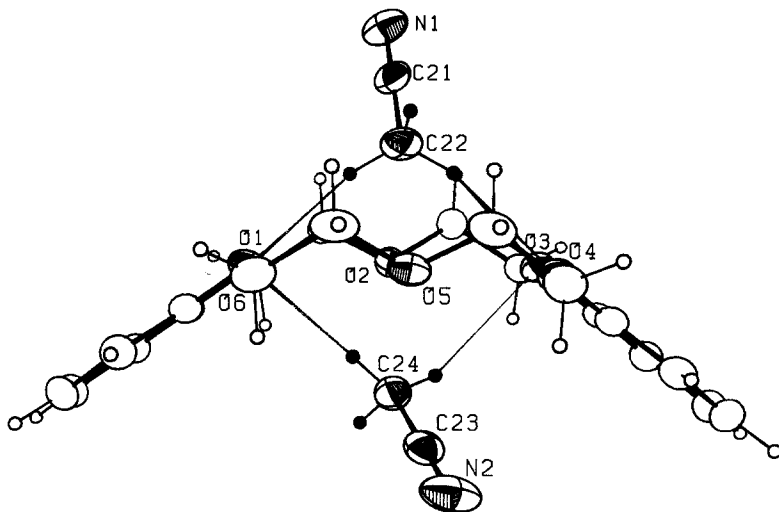


Fig. 5. Side view of dibenzo-18-crown-6-2 CH_3CN . The benzo group fold averages 143° .

72° for N(3)/N(4) and are parallel in 18-crown-6-2 CH_3NO_2 . C(41) and C(42) make closer approaches to the macrocyclic cavity than C(43) and C(44), and C(41) exhibits the shortest C—H \cdots O contact ($1.97(4)$ Å). This is reflected in the Me \cdots Me through the ring contacts of C(41) \cdots C(42) = $3.805(6)$ Å and C(43) \cdots C(44) = $4.079(7)$ Å. The latter is very close to the value observed in dibenzo-18-crown-6-2 CH_3CN ($4.071(8)$ Å).

In conclusion the above discussion points towards several key items. First, the interaction of acetonitrile and nitromethane with dibenzo-18-crown-6 are much weaker than observed with the more flexible 18-crown-6, perhaps a clue to the difficulty in isolating the dibenzo-18-crown-6 adducts [5, 17]. Second, the H \cdots O contacts observed for the title complexes, for the most part just under or at the van der Waals contact distance, are perhaps at the upper limit of what we can call 'hydrogen bonds' [18]. Finally, different orientations of the solvent molecules themselves and of the methyl groups, do not seem to greatly affect the overall energy levels of these complexes and, therefore, it would not be surprising if other forms of these complexes were isolated.

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