



## Crown Ether-Dinitrile Interaction: An X-ray Study

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**Abstract.** Formation of the host-guest compounds between isomers of dicyclohexano-18-crown-6 as hosts (DC18C6) and various dinitriles as guests has been observed. The structures of two representative compounds (cis-anti-cis-DC18C6·2(NCCH<sub>2</sub>CH<sub>2</sub>CN) (**I**) and (cis-syn-cis-DC18C6·(NCCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN) (**II**)) were obtained using X-ray diffractometry. Crystal data: (**I**)  $P\bar{1}$ ,  $a = 8.586(3)$ ,  $b = 9.324(3)$ ,  $c = 10.714(4)$  Å,  $\alpha = 72.47(3)^\circ$ ,  $\beta = 73.57(3)^\circ$ ,  $\gamma = 72.37(3)^\circ$ ,  $R_1 = 0.034$ , GooF 1.08,  $Z = 1$ ; (**II**)  $Pbca$ ,  $a = 12.881(5)$ ,  $b = 17.887(8)$ ,  $c = 23.042(13)$  Å,  $R_1 = 0.049$ , GooF 1.02,  $Z = 8$ . Both structures show weak C—H···O interactions between  $\alpha$ -methylene protons of dinitrile guest molecules and oxygen atoms of the macrocyclic host ring.

**Key words:** dicyclohexano-18-crown-6, succinonitrile, glutaronitrile, crystal structure.

**Supplementary Data** related to this article have been deposited with the British Library as Supplementary Publication No. 82249 (24 pages).

### 1. Introduction

The interaction of crown ether molecules with various C—H acids through the formation of C—H···O hydrogen bonds has been discussed in numerous publications (see, for example, [1]). Malononitrile complexes with 18-crown-6 (18C6) [2] and dicyclohexano-18-crown-6 (DC18C6) [3] have been synthesized and their crystal structures studied. The addition of extra methylene groups between the two CN moieties significantly decreases the acidity of  $\alpha$ -methylene hydrogens and, as a result, the stability of crown ether complexes. It has not been possible to isolate succinonitrile and glutaronitrile compounds with DC18C6 from aqueous solutions. Therefore, the very existence of a direct interaction between these dinitriles and DC18C6 has not been established. The possibility of isolating complexes containing 18C6 and various dinitriles (succinonitrile, glutaronitrile, some others) has been shown [4]. Recently, we have detected a dramatic increase in the extraction of  $\text{Sr}^{2+}$  and  $\text{Pb}^{2+}$  complexes with DC18C6 into succinonitrile and glutaronitrile over that observed for common solvents [5]. This observation suggested that it was important to obtain a better understanding of crown ether solvation in dinitrile solvents.

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In this study we report the isolation and crystal structures of two representative compounds (cis-anti-cis-DC18C6·2(NCCH<sub>2</sub>CH<sub>2</sub>CN) (**I**) and cis-syn-cis-DC18C6·(NCCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN) (**II**)).

## 2. Experimental

All reagents were of reagent grade and used without further purification. Single crystals suitable for X-ray studies were grown by slow evaporation of the mixture of corresponding crown ether isomer and dinitrile in diethyl ether solution at 0 °C similar to 18C6 compounds (see [4]).

Crystal data and a summary of relevant experimental parameters for the two crystal structures are reported in Table I. Single crystal intensity measurements were collected at 23 °C with a Siemens R3m/V diffractometer, using Mo K<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with a graphite monochromator. Lattice parameters for **I** and **II** were obtained using least squares refinements of the angles of 22 (**I**) and 26 (**II**) reflections with  $22^\circ < 2\theta < 28^\circ$ . Intensities were collected using  $\theta/2\theta$  scan mode. A detectable decrease of intensities because of the decay of the crystals was observed (−15% (**I**) and −40% (**II**)), therefore corrections were applied to the data using the standard Siemens' software. The structures were solved by the direct methods followed by successive Fourier synthesis [6]. Full-matrix least-squares refinement was performed using SHELXL-97 [7] with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms of both structures were located in the Fourier difference maps. Their parameters were restrained; only hydrogen atoms involved in C—H···A interactions were refined using constant isotropic thermal parameters ( $u = 0.08$ ). Final atomic coordinates of nonhydrogen atoms and  $\alpha$ -methylene hydrogens are listed in Table II. Selected bond distances are listed in Table III with C—H···O contacts data for the two structures contained in Table IV. Full lists of bond lengths and angles, hydrogen atom coordinates, anisotropic thermal parameters and structure factors are in the Supplementary Data.

## 3. Results and Discussion

### 3.1. MOLECULAR STRUCTURE

The views of **I** and **II** are shown in Figures 1 and 2 respectively. The geometrical parameters of the complexes are similar to those found in other crown complexes. Compound **I** contains a crystallographic center of symmetry. The C—O and C—C interatomic distances (Table III) are typical of macrocyclic polyether complexes (average values for crown ethers are 1.43(3) and 1.49(2) Å respectively [8]). The C—O—C and C—C—O bond angles are also normal.

The conformation of the macrocyclic ring in both complexes differs from the pseudo-D<sub>3d</sub> conformation which has been found in most complexes with a 18C6 macrocyclic ring including those with malononitrile and DC18C8[2] and 18C6

Table I. Crystal data and structure refinement parameters.

Compound	I	II
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorhombic, Pbca
Unit cell dimensions:		
$a$ , Å	8.586(3)	12.878(8)
$b$ , Å	9.324(3)	17.878(10)
$c$ , Å	10.714(4)	23.08(3)
$\alpha$ , °	72.47(3)	
$\beta$ , °	73.57(3)	
$\gamma$ , °	72.37(3)	
$V$ , Å <sup>3</sup>	761.9(5)	5314(8)
$Z$	1	8
Crystal size, mm	0.25 × 0.4 × 0.6	0.25 × 0.45 × 0.8
Reflections unique/parameters/ $\theta_{\max}$	1785/184/22.6	2727/304/21.1
Refinement method	Full-matrix least-squares on $F^2$	
Goodness-of-fit on $F^2$	1.079	1.022
Final $R_1$ (wR2) indices [ $I > 2\sigma(I)$ ]	0.034(0.082)	0.049(0.108)
$R_1$ (wR2) indices (all data)	0.045(0.087)	0.087(0.12)
Largest diff. peak/hole (e/Å <sup>3</sup> )	0.14/−0.10	0.34/−0.12

[3]. While all O—C—C—O torsion angles are *gauche* (55–72° for **I**) and 57–75° for **II**), and most of the C—O—C—C torsion angles are *trans* (162–174° (**I**) and 165–179° (**II**)), two of the C—O—C—C torsion angles in each macrocycle have *gauche* torsion angles ( $\pm 63^\circ$  in **I**, 67° and 75° in **II**). The sequence of torsion angles is (tgt)(tgt)(ggt), repeated with inversion because of the center of symmetry in **I**), and (ggt)(tġt)(tgt)(tġġ)(tġt)(tgt) in **II**). These conformations are very similar to those low energy structures calculated for the 18-crown-6 ring (see  $C'_i$  in [9] for **I**), and 4b and 4c [10] respectively for **I**) and **II**). In the free cis-anti-cis-DC18C6 molecule the macrocyclic ring has a different sequence of torsion angles: (ttt)(tgt)(ggġ), also repeated with inversion because of the center of symmetry [11].

The geometry of the oxygen atoms in **I**) is still close to pseudo- $D_{3d}$  with three oxygen atoms above and three below the mean plane with deviations of  $\pm 0.10$ – $0.13$  Å from it. In **II**), the maximum deviation of oxygen donor atoms from their least-squares plane (0.72 Å) is slightly larger than usual, and oxygen atom positions do not follow the  $D_{3d}$  motif. For guests, the succinonitrile molecule possesses a *gauche* (66°) C—CH<sub>2</sub>—CH<sub>2</sub>—C torsion angle, and in glutaronitrile there is a *gauche* and a *trans* conformation.

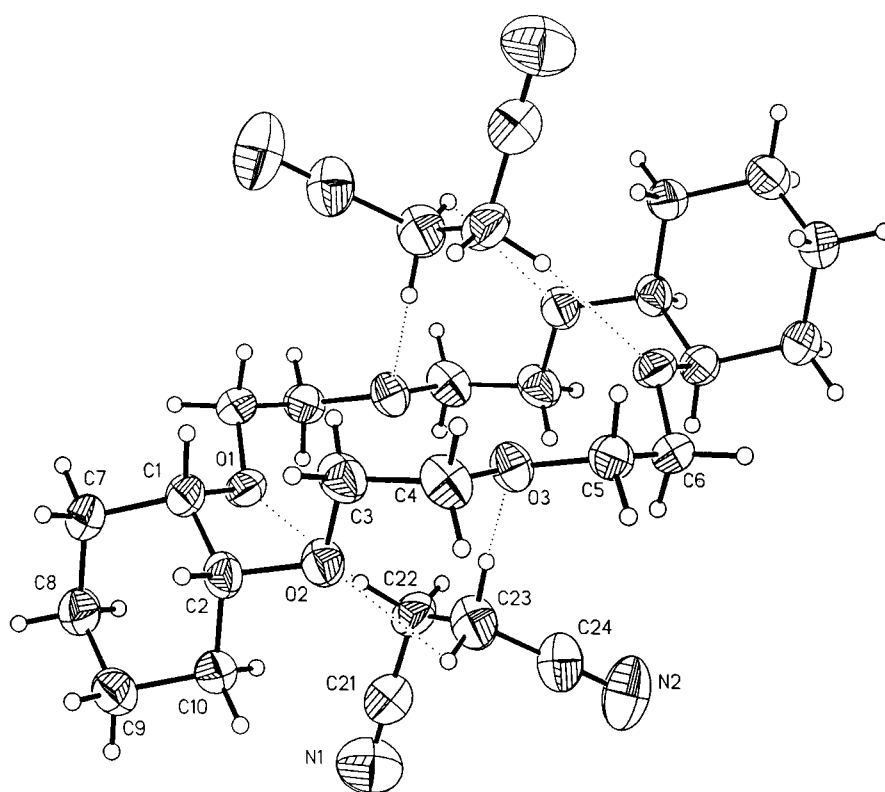


Figure 1. ORTEP view of compound **I** with atomic numbering scheme; thermal ellipsoids drawn at 50% probability level.

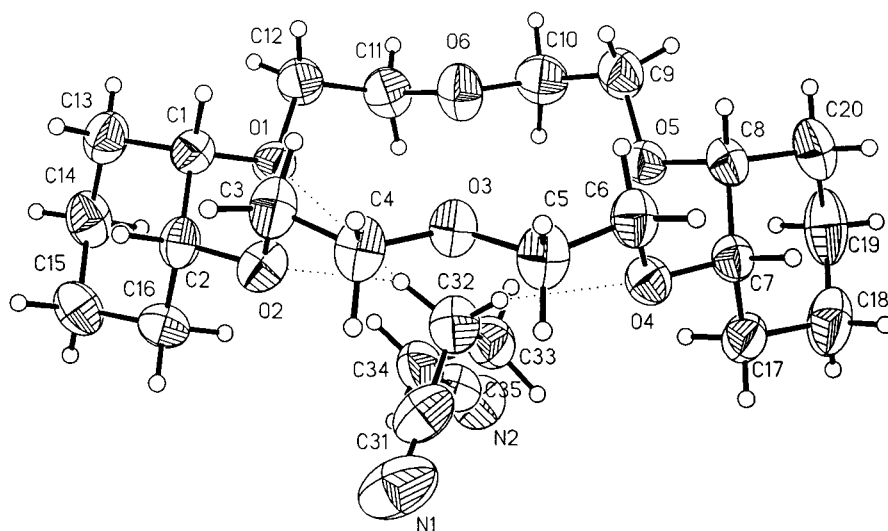


Figure 2. ORTEP view of compound **II** with atomic numbering scheme; thermal ellipsoids drawn at 50% probability level.

Table IIIa. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **I**.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
O(1)	4523(2)	6608(1)	2051(1)	50(1)
O(2)	1648(2)	6850(1)	4140(1)	53(1)
O(3)	2830(2)	5452(1)	6656(1)	51(1)
C(1)	3287(3)	8050(2)	1975(2)	51(1)
C(2)	1625(2)	7700(2)	2783(2)	49(1)
C(3)	1987(3)	7651(2)	4927(2)	63(1)
C(4)	1613(3)	6859(2)	6377(2)	60(1)
C(5)	2631(2)	4770(2)	8046(2)	54(1)
C(6)	3815(3)	3215(2)	8299(2)	57(1)
C(7)	3145(3)	8886(2)	535(2)	61(1)
C(8)	2515(3)	7986(2)	-109(2)	64(1)
C(9)	862(3)	7636(2)	712(2)	64(1)
C(10)	990(3)	6791(2)	2155(2)	51(1)
N(1)	2727(3)	2004(3)	2033(2)	105(1)
N(2)	2831(3)	434(2)	6249(2)	102(1)
C(21)	3361(3)	2440(2)	2592(2)	66(1)
C(22)	4115(3)	3013(2)	3333(2)	63(1)
C(23)	3051(4)	3127(2)	4709(2)	70(1)
C(24)	2920(3)	1616(3)	5587(2)	70(1)
H(22A)	4260(3)	4020(3)	2820(2)	80
H(22B)	5190(3)	2320(2)	3380(2)	80
H(23A)	1920(3)	3740(3)	4680(2)	80
H(23B)	3580(3)	3560(2)	5110(2)	80

### 3.2. C—H···O INTERACTIONS

The parameters of the possible C—H···O interactions in compounds (**I**) and (**II**) are listed in Table IV. All C—H bond lengths are close to the normal values of approximately 0.96 Å. All hydrogen atoms of the succinonitrile guest are involved in the C—H···A (A = O or N) interaction network involving also all oxygen atoms of the macrocyclic host. C···O distances are quite similar ( $3.30 \pm 0.06$  Å) while C···N is slightly longer (3.48 Å). In all cases the H···A distances of each  $\angle\text{C—H}\cdots\text{A}$  angle are slightly shorter than the van der Waals separations (see [12], Figure 5.7). This may be explained as a confirmation of weak hydrogen bonding. Distances in **II** are significantly longer, especially for the three center C(32)—H(32A)···O(1),O(3) bond, but they are still within the range of observed

*Table IIIb.* Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **II**.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
O(1)	2149(2)	3193(1)	4745(1)	56(1)
O(2)	2254(2)	1898(1)	5445(1)	59(1)
O(3)	1131(2)	2255(1)	6512(1)	60(1)
O(4)	1673(2)	3407(1)	7362(1)	57(1)
O(5)	1377(2)	4722(1)	6707(1)	59(1)
O(6)	1283(2)	4422(1)	5437(1)	76(1)
C(1)	1865(3)	2492(2)	4504(1)	56(1)
C(2)	2444(3)	1888(2)	4836(1)	56(1)
C(3)	1284(3)	1620(2)	5611(2)	71(1)
C(4)	1213(3)	1547(2)	6255(2)	68(1)
C(5)	957(4)	2224(2)	7121(2)	71(1)
C(6)	743(3)	2995(2)	7339(2)	66(1)
C(7)	1571(3)	4128(2)	7621(2)	54(1)
C(8)	917(3)	4663(2)	7270(2)	59(1)
C(9)	704(4)	5046(2)	6292(2)	77(1)
C(10)	1209(4)	5104(2)	5717(2)	82(1)
C(11)	1723(3)	4485(2)	4870(2)	72(1)
C(12)	1519(3)	3789(2)	4538(2)	71(1)
C(13)	2133(3)	2428(2)	3860(2)	72(1)
C(14)	3292(4)	2478(2)	3758(2)	79(1)
C(15)	3876(3)	1895(2)	4107(2)	76(1)
C(16)	3605(3)	1953(2)	4746(2)	64(1)
C(17)	2647(3)	4423(2)	7723(2)	69(1)
C(18)	2615(4)	5178(3)	8023(2)	98(2)
C(19)	1940(5)	5719(2)	7689(2)	103(2)
C(20)	873(4)	5414(2)	7577(2)	83(1)
N(1)	4250(4)	2140(3)	6493(2)	130(2)
N(2)	5710(3)	5130(2)	5693(2)	94(1)
C(31)	3735(4)	2626(3)	6366(2)	84(2)
C(32)	3116(4)	3268(3)	6194(2)	74(1)
C(33)	3766(3)	3978(2)	6174(2)	82(1)
C(34)	4512(4)	3967(2)	5694(2)	85(1)
C(35)	5196(4)	4636(3)	5702(2)	73(1)
H(32A)	2790(3)	3150(2)	5828(16)	80
H(32B)	2610(3)	3310(2)	6457(16)	80

Table III. Selected bond lengths (Å) in macrocyclic host molecules.

I		II			
C—O bonds					
O(1)—C(6)# 1	1.417(2)	O(1)—C(12)	1.421(4)	O(4)—C(6)	1.408(4)
O(1)—C(1)	1.435(2)	O(1)—C(1)	1.419(4)	O(4)—C(7)	1.426(4)
O(2)—C(3)	1.415(2)	O(2)—C(2)	1.428(4)	O(5)—C(9)	1.417(4)
O(2)—C(2)	1.433(2)	O(2)—C(3)	1.397(4)	O(5)—C(8)	1.432(4)
O(3)—C(5)	1.415(2)	O(3)—C(5)	1.425(4)	O(6)—C(10)	1.385(4)
O(3)—C(4)	1.419(2)	O(3)—C(4)	1.402(4)	O(6)—C(11)	1.434(4)
C—C bonds					
C(1)—C(2)	1.518(3)	C(1)—C(2)	1.519(5)	C(7)—C(8)	1.510(5)
C(3)—C(4)	1.494(3)	C(3)—C(4)	1.495(5)	C(9)—C(10)	1.482(5)
C(5)—C(6)	1.495(3)	C(5)—C(6)	1.492(5)	C(11)—C(12)	1.484(5)

Table IV. Parameters of C—H···A interactions.

C—H···A	r(C···A), Å	r(C—H), Å	r(H···A), Å	∠C—H···A, °
<b>I</b>				
C(22)—H(22a)···O(1)	3.30(1)	0.96(1)	2.36(1)	167
C(22)—H(22b)···N(2) (1 - x, 1 - y, 1 - z)	3.48(1)	0.96(1)	2.60(1)	152
C(23)—H(23a)···O(2)	3.24(1)	0.97(1)	2.73(1)	113
C(23)—H(23b)···O(3)	3.37(1)	0.94(1)	2.59(1)	140
<b>II</b>				
C(32)—H(32a)···O(1)	3.57(1)	0.97(2)	2.64(2)	163*
C(32)—H(32a)···O(2)	3.20(1)	0.97(2)	2.50(2)	129*
C(32)—H(32b)···O(4)	3.28(1)	0.90(2)	2.42(2)	163

\* ∠O(1)···H(32a)···O(2) = 67°.

parameters [12–14]. The sum of the three angles about H(32A) is 359° which is close to the expected 360°. In both cases C···O distances are shorter than those observed for malononitrile complexes [3] with cis-syn-cis-DC18C6 (average 3.334 Å) and cis-anti-cis-DC18C6 (average 3.41 Å).

#### 4. Conclusions

Complexation of succinonitrile and glutaronitrile molecules with DC18C6 provides the information about solvation of crown ether molecules in dinitrile solutions. Despite the decrease of acidity of α-methylene hydrogens, hydrogen bond

formation between guest C—H groups and host oxygen atoms could be observed. The formation of host-guest compounds changes the stereochemistry of the host macrocyclic molecules making it closer to the pseudo- $D_{3d}$  geometry of metal ion complexes. This reorganization likely enhances the overall stability of the metal ion complexes with crown ethers in dinitrile solvents.

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