

# Crystalline Inclusion Compounds of Tetrabenzo-18-crown-6 with Uncharged Organic Molecules. Solid-State Structure of the Nitroethane Complex

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**Abstract.** Tetrabenzo-18-crown-6 (**1**) shows distinct solid-state inclusion properties towards a number of OH-acidic, CH-acidic and low-polar uncharged organic molecules. The single crystal X-ray analysis of the inclusion complex between **1** and EtNO<sub>2</sub> (1 : 1) is reported. Crystals are monoclinic, *P*2<sub>1</sub>/*c*, with *a* = 12.887(1), *b* = 19.365(2), *c* = 10.776(1) Å,  $\beta$  = 96.33(2)°, *D*<sub>c</sub> = 1.321 g cm<sup>-3</sup>, *Z* = 4. The host macrocoring has a conformation similar to a 'dentist's-chair'. The complex is stabilized mainly by C-H...O type interactions involving the methyl group of the EtNO<sub>2</sub> guest molecule which is highly disordered. The nitroethane guests are trapped in channels formed by the host macrocycles.

**Key words:** Inclusion compounds, X-ray crystal structure analysis, tetrabenzo-18-crown-6, nitroethane.

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## 1. Introduction

18-Crown-6, which is the most prominent all-oxygen macrocycle [1], has been shown to form a large number of well-defined crystalline complexes with uncharged organic molecules including protic and dipolar-aprotic compounds [2,3]. One of these complexes (18-crown-6 · MeCN) is useful in the preparation or isolation of the crown [4]. Others have been used to enhance solubility of NH- and OH-acidic reaction components [5].

Compared to 18-crown-6, the complexation chemistry of their benzo-condensed analogs is still in its infancy [6], although benzo- and dibenzo-18-crown-6 are

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TABLE I  
Crystalline inclusion compounds of **1**.

Guest solvent <sup>a</sup>	Stoichiometry (host : guest) <sup>b</sup>
Acetic acid	1 : 1
Propionic acid	2 : 1
Dimethylformamide	1 : 1
Dimethyl sulfoxide	2 : 3
Nitromethane	2 : 3
Nitroethane	1 : 1
Propionic aldehyde	1 : 1
Cyclohexanone	1 : 1
Morpholine	1 : 1
Dioxane	1 : 1
Tetrahydrofuran	1 : 1

<sup>a</sup> Not included: methanol, ethanol, 1-propanol, 1-butyne-3-ol, cyclopentanol, ethylene glycol, diacetone alcohol, pyridine.

<sup>b</sup> Determined by <sup>1</sup>H-NMR integration of the isolated crystals (method of preparation and drying standard, see Experimental Section)

historic compounds [1]. No structure of a crystalline complex comprising a 18-crown-6 host with three or more benzo-condensations [7] and an organic guest molecule is known to date. On the other hand, it is clear that benzo-condensation can improve the host properties of pyridino crowns by means of rigidifying and particular shielding effects [2a,8].

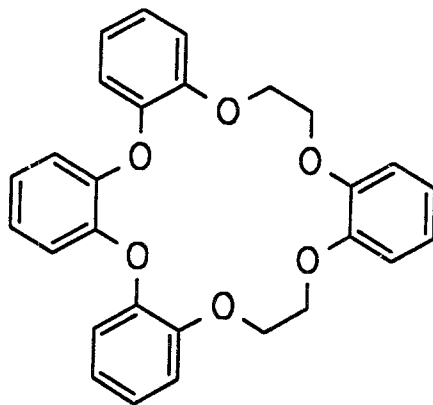
The present study is aimed at shedding light upon the molecular complexation properties of oligobenzo-18-crown-6 hosts such as tetrabenzo-18-crown-6 (**1**). We describe the preparation of crystalline inclusion complexes of **1** and report the X-ray crystal structure of the host-guest complex **1** · EtNO<sub>2</sub> (1 : 1).

## 2. Experimental

### 2.1 SYNTHESIS AND SAMPLE PREPARATION

The method for preparation of compound **1** has been described earlier [7]. Inclusion complexes of **1** (Table I) were obtained by dissolving **1** with heating in a minimum amount of the respective solvent. The solution was allowed to cool slowly. After standing for 12 h at room temperature the crystals which formed were collected by suction filtration, washed with an inert solvent (methanol), and dried (1 h, 15 Torr, room temperature). The host : guest stoichiometry of the crystals was determined by <sup>1</sup>H-NMR integration. Data for each compound are given in Table I. Further

recrystallization of **1** from nitroethane solution was necessary in order to obtain good single crystals of **1** · EtNO<sub>2</sub> (1 : 1) for crystallographic investigations.



**1**

## 2.2. CRYSTAL STRUCTURE DETERMINATION OF **1** · EtNO<sub>2</sub> (1 : 1)

### 2.2.1. X-ray data collection and processing

Preliminary photographic studies revealed that the crystals were monoclinic with space group  $P2_1/c$ . Three-dimensional intensity data were collected on a Rigaku four-circle diffractometer using graphite monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) by the  $\omega - 2\theta$  scan technique. A single crystal of approximate dimensions  $0.1 \times 0.2 \times 0.2 \text{ mm}$  was used for intensity data collection. To avoid the decomposition of the crystal, presumably due to the loss of nitroethane, the crystal was mounted on a Lindemann tube of 0.3 mm diameter. Final lattice parameters were determined by least-squares fit of  $2\theta$  values of 25 reflections [ $20 < 2\theta < 40^\circ$ ] widely separated in the reciprocal space and accurately centered on the diffractometer. Crystal stability was monitored by checking the intensity of three standard reflections (231, 240 and 134) which were monitored every hour. This indicated that the crystal was gradually decomposing. The software of the SDP package of CAD4 was used to correct this factor. 1744 Reflections were measured up to max.  $2\theta = 50^\circ$  [ $h: -13$  to  $13$ ;  $k: 0$  to  $20$  and  $l: 0$  to  $10$ ] of which 1487 reflections were above the  $3\sigma$  level after reduction of the data to structure factor amplitudes. The intensities were corrected for Lorentz and polarization effects [9] but not for absorption since  $\mu (\text{MoK}\alpha) = 0.090 \text{ mm}^{-1}$ .

The crystal data are as follows:  $\text{C}_{28}\text{H}_{24}\text{O}_6 \cdot \text{C}_2\text{H}_5\text{NO}_2$ ,  $F_w = 531.6$ , monoclinic,  $P2_1/c$ ,  $a = 12.887(1)$ ,  $b = 19.365(2)$ ,  $c = 10.776(1) \text{ \AA}$ ,  $\beta = 96.33(2)^\circ$ ,  $V =$

2672.8(4) Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.321 \text{ g cm}^{-3}$ ,  $D_m = 1.32(1) \text{ g cm}^{-3}$ ,  $\mu = 0.9 \text{ cm}^{-1}$ ,  $F(000) = 1120$ .

### 2.2.2. Structure determination and refinement

The structure was solved by direct methods using SHELX86 [10]. Eight phase sets were refined out of which set five with the lowest combined figure of merit, 0.258, gave the correct solution. The corresponding point atom  $R$ -value based on  $E$ -values was 0.256. 356 Reflections with  $|E| > 1.2$  were used in the tangent expansion. Most of the non-hydrogen atoms of the host macrocycle, except for four carbon atoms of the phenylene rings were located from the resulting  $E$ -map. Though some peaks were found for the nitroethane guest, they were not interpretable. The structure was refined by a full-matrix least-squares method using SHELX76 [11]. The initial  $R$ -factor for the input scattering matter was 0.32. The non-hydrogen atoms were initially refined with isotropic thermal parameters. The rest of the carbon atoms of the host macrocycle were obtained from the weighted difference Fourier maps without any difficulty after a few cycles of isotropic refinement of the known non-hydrogen atom positions. But the nitroethane guest could not be interpreted since it was highly disordered as revealed by the difference Fourier map. At this stage, a Fourier map was printed and the significant peaks were contoured, which showed a two-fold disorder about the methyl carbon atom, C(1) of the guest (Figure 1). The positions obtained from the above Fourier map and their isotropic thermal parameters ( $0.09 \text{ Å}^2$ ) were kept fixed initially and their occupancies were refined which showed nearly equal occupancies for the disordered atoms. The occupancies of the disordered atoms were then kept fixed at 0.5 and were refined isotropically. During refinement these atoms exhibited large movements and hence they were subjected to constrained least-squares refinement with isotropic thermal parameters throughout the process. After the convergence of the isotropic refinement, the non-hydrogen atoms were allowed anisotropic motion except for the atoms of the guest molecule. Anisotropic refinement of non-hydrogen atoms other than those of the guest gave an  $R$  value of 0.10. All hydrogen atoms of the host molecule were located from the difference Fourier maps and refined isotropically. The hydrogen atoms of the guest were neither located nor fixed geometrically. The final  $R$  and  $R_w$  values were 0.071 and 0.076, respectively, and the goodness of fit,  $S$ , was 2.78 for 343 parameters and 1487 reflections. The weighting scheme used was  $w = k/[\sigma^2(F_o) + g|F_o|]$  where  $k = 1.00$  and  $0.000546$ . The maximum shift per e.s.d. ratio in the final cycle of refinement of non-hydrogen atoms was 0.004 and the ratio of reflections to parameters refined was 4.6. The maximum and the minimum heights in the final difference Fourier map were  $0.43$  and  $-0.17 \text{ e Å}^{-3}$ , respectively, and the maximum peak was near the methyl carbon atom of the disordered guest which may be one of the hydrogen positions. Atomic scattering factors for nonhydrogen and hydrogen atoms were taken from the literature [12,13]. All the computations were done using MICROVAX II and VAX 730 computers.

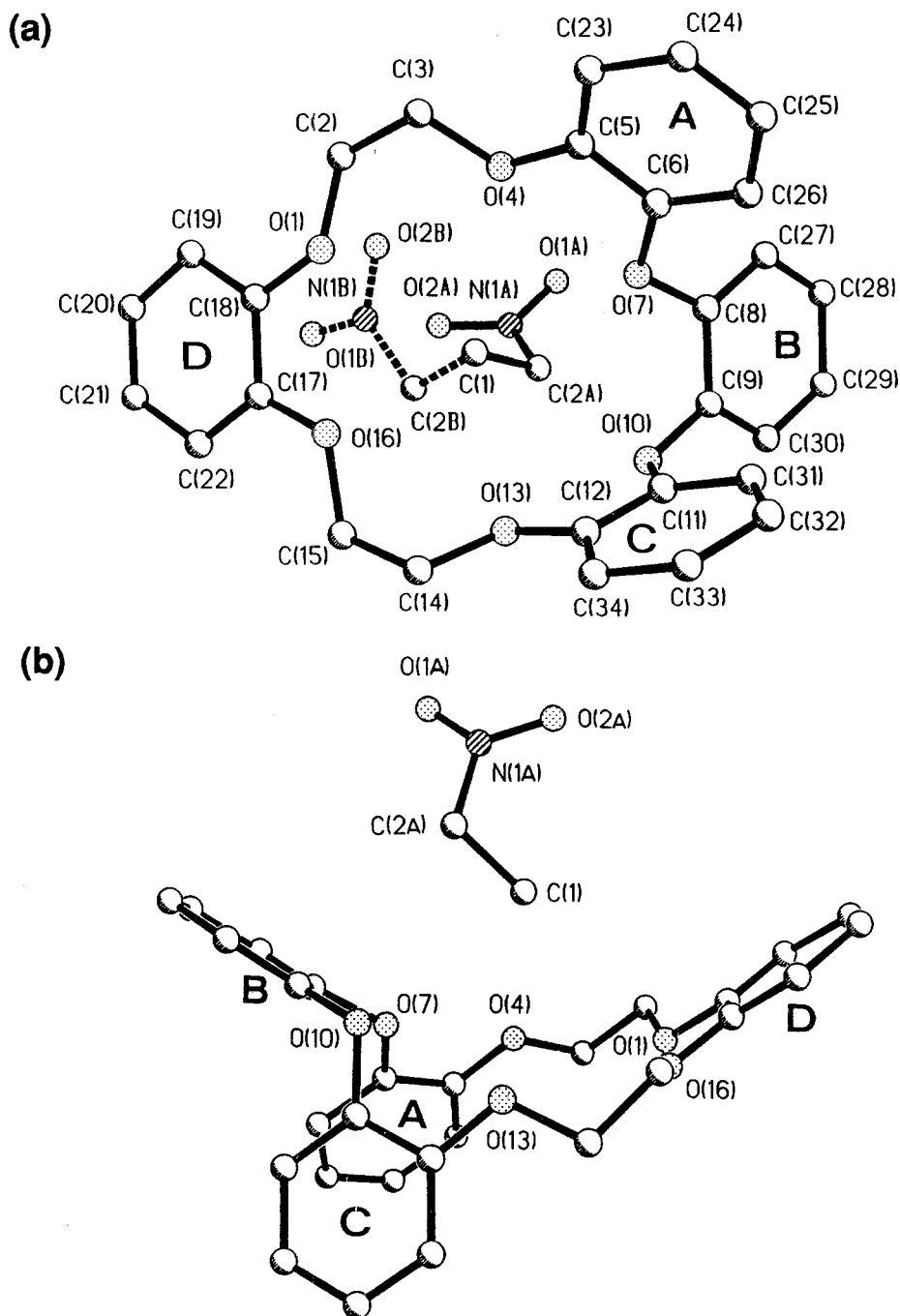


Fig. 1. Molecular structure of the 1 · EtNO<sub>2</sub> (1 : 1) inclusion complex: (a) top view giving indication of the numbering scheme for the atoms; (b) side view showing the 'dentist's chair' conformation. Only one of the two disordered sites of EtNO<sub>2</sub> (A) is indicated in (b). Heteroatoms are shaded.

### 3. Results and Discussion

#### 3.1 INCLUSION PROPERTIES OF **1**

The solvents tested and inclusion compounds formed are specified in Table I. Host **1** shows solid-state inclusion properties towards a few CH-acidic substrates typical of 18-crown-6 [2]. They include dimethyl sulfoxide and nitromethane, while the complex between **1** and nitroethane, which is of the same class of compounds, has no analogue with 18-crown-6. Nevertheless, the mentioned correspondence between **1** and 18-crown-6 in the formation of the complexes with dimethyl sulfoxide and nitromethane is not complete since the stoichiometric ratios are different in both cases (2 : 3 for **1** vs. 1 : 2 for 18-crown-6 [2]). There are two other potentially CH-acidic guest molecules given in Table I (propionic aldehyde and cyclohexanone) which form complexes with **1** but do not form complexes with 18-crown-6.

Moreover, strong proton donors, like acetic acid or propionic acid, also form solid complexes with **1**. One may ask, how do these highly molecules match with the rather lipophilic environment of the host? A solid-state structure analogous to a clathrate [14] with interstitial space formed by the host molecules, incorporating dimers of carboxylic acids [15], seems likely.

Most of the other inclusion compounds of **1** might also be of the clathrate (lattice inclusion) type [16], and this would be in keeping with the heavy bulk of **1** as compared with 18-crown-6 (cf. Refs. 8b and 8d). In this context it is important to notice that dimethylformamide, morpholine, dioxane and tetrahydrofuran, which are not accommodated by 18-crown-6 and lower benzo-condensed analogues of 18-crown-6 [2], are included by **1**.

In order to elucidate potential H-bond host-guest relationships of this particular crown type (**1**), we have carried out an X-ray structural study of the **1** · nitroethane (1 : 1) inclusion complex.

#### 3.2 CRYSTAL STRUCTURE OF **1** · EtNO<sub>2</sub> (1 : 1)

The crystals of the title compound (**1** · EtNO<sub>2</sub>) are highly unstable and decompose very quickly when removed from the solvent in air. Nitromethane complexes of 18-crown-6 and dibenzo-18-crown-6 were also reported to be very unstable on removal from the solvent [17]. Boer and coworkers have noted a decrease in intensity during the intensity data collection of the 1 : 2 complex of 18-crown-6 with nitromethane, which they attribute to the loss of nitromethane guest molecule [17a]. Due to the inaccuracy indicated in the intensity data collection section, namely, the decrease in intensity during data collection, no detailed information on the interaction between the host and the nitroethane guest could be obtained in the present complex, but some conclusions can be drawn. The standard deviations of the positional and bond parameters are generally high due to the poor quality of the data. Nevertheless, comparison of the bond parameters, conformation and the nature of interactions can be made with similar compounds.

TABLE II

Final fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for non-hydrogens of **1** · EtNO<sub>2</sub> (1 : 1) (e.s.ds are in parentheses).

Atom	$x/a$	$y/b$	$z/c$	$U_{eq}$
O(1)	0.3143(5)	-0.0376(4)	0.4018(7)	0.072(3)
C(2)	0.3129(9)	0.0155(7)	0.4910(11)	0.075(5)
C(3)	0.3895(8)	0.0706(6)	0.4644(10)	0.071(5)
O(4)	0.3511(5)	0.1033(4)	0.3496(6)	0.060(3)
C(5)	0.4187(9)	0.1481(6)	0.3039(11)	0.058(5)
C(6)	0.3873(8)	0.1749(6)	0.1864(11)	0.064(5)
O(7)	0.2925(6)	0.1504(4)	0.1308(7)	0.089(3)
C(8)	0.2345(8)	0.1895(7)	0.0404(11)	0.064(5)
C(9)	0.1935(8)	0.1530(6)	-0.0674(11)	0.058(5)
O(10)	0.2119(5)	0.0837(4)	-0.0784(6)	0.068(4)
C(11)	0.3069(8)	0.0650(6)	-0.1143(10)	0.055(4)
C(12)	0.3358(9)	-0.0032(6)	-0.0980(9)	0.056(5)
O(13)	0.2677(5)	-0.0429(4)	-0.0382(7)	0.070(3)
C(14)	0.2965(8)	-0.1138(6)	-0.0128(10)	0.068(5)
C(15)	0.2308(9)	-0.1399(5)	0.0831(14)	0.077(5)
O(16)	0.2680(5)	-0.1094(4)	0.2010(9)	0.076(3)
C(17)	0.2246(9)	-0.1308(7)	0.2996(17)	0.074(6)
C(18)	0.2469(8)	-0.0922(7)	0.4091(15)	0.072(6)
C(19)	0.2058(9)	-0.1097(7)	0.5188(13)	0.085(6)
C(20)	0.1384(10)	-0.1670(9)	0.5164(15)	0.097(7)
C(21)	0.1152(11)	-0.2037(8)	0.4127(19)	0.108(7)
C(22)	0.1583(9)	-0.1857(7)	0.3001(13)	0.084(6)
C(23)	0.5158(9)	0.1663(5)	0.3619(10)	0.068(5)
C(24)	0.5800(8)	0.2105(6)	0.2998(13)	0.077(6)
C(25)	0.5483(9)	0.2365(6)	0.1854(13)	0.078(5)
C(26)	0.4492(9)	0.2198(5)	0.1250(11)	0.070(5)
C(27)	0.2136(9)	0.2583(7)	0.0526(11)	0.075(6)
C(28)	0.1492(9)	0.2925(6)	-0.0387(14)	0.079(6)
C(29)	0.1064(8)	0.2566(8)	-0.1450(12)	0.082(6)
C(30)	0.1286(8)	0.1857(7)	-0.1563(9)	0.068(5)
C(31)	0.3723(9)	0.1106(6)	-0.1682(9)	0.062(5)
C(32)	0.4664(8)	0.0880(6)	-0.2056(10)	0.065(5)
C(33)	0.4923(8)	0.0185(7)	-0.1922(11)	0.072(6)
C(34)	0.4263(9)	-0.0275(6)	-0.1403(10)	0.065(5)
C(1) <sup>a</sup>	0.1021(12)	0.0397(10)	0.1870(15)	0.189(8)
C(2A) <sup>a</sup>	0.0204(18)	0.0862(14)	0.1195(15)	0.130(11)
N(1A) <sup>a</sup>	-0.0602(15)	0.1004(12)	0.2015(20)	0.144(11)
O(1A) <sup>a</sup>	-0.0868(21)	0.1616(15)	0.2174(18)	0.251(7)
O(2A) <sup>a</sup>	-0.0896(16)	0.0537(18)	0.2676(24)	0.277(20)
C(2B) <sup>a</sup>	0.0117(16)	-0.0079(10)	0.2031(13)	0.077(17)
N(1B) <sup>a</sup>	-0.0116(12)	-0.0044(8)	0.3326(14)	0.164(12)
O(1B) <sup>a</sup>	-0.0729(21)	-0.0428(14)	0.3685(22)	0.271(18)
O(2B) <sup>a</sup>	0.0370(19)	0.0337(13)	0.4068(13)	0.234(14)

<sup>a</sup> These atoms were refined with isotropic thermal parameters.

TABLE III

Bond distances (Å) and bond angles (°) involving non-hydrogen atoms of  $1 \cdot \text{EtNO}_2$  (1 : 1) (e.s.d.s are in parentheses).

Atoms	Distance	Atoms	Distance
O(1)—C(2)	1.41(2)	O(1)—C(18)	1.38(2)
C(2)—C(3)	1.50(2)	C(3)—O(4)	1.43(1)
O(4)—C(5)	1.36(1)	C(5)—C(6)	1.39(2)
C(5)—C(23)	1.38(2)	C(6)—O(7)	1.38(1)
C(6)—C(26)	1.40(2)	O(7)—C(8)	1.39(1)
C(8)—C(9)	1.41(2)	C(8)—C(27)	1.37(2)
C(9)—O(10)	1.37(1)	C(9)—C(30)	1.36(2)
O(10)—C(11)	1.37(1)	C(11)—C(12)	1.38(2)
C(11)—C(31)	1.39(2)	C(12)—O(13)	1.38(1)
C(12)—C(34)	1.38(2)	O(13)—C(14)	1.44(1)
C(14)—C(15)	1.49(2)	C(15)—O(16)	1.44(2)
O(16)—C(17)	1.32(2)	C(17)—C(18)	1.40(2)
C(17)—C(22)	1.36(2)	C(18)—C(19)	1.39(2)
C(19)—C(20)	1.41(2)	C(20)—C(21)	1.33(3)
C(21)—C(22)	1.43(2)	C(23)—C(24)	1.41(2)
C(24)—C(25)	1.35(2)	C(25)—C(26)	1.41(2)
C(27)—C(28)	1.38(2)	C(28)—C(29)	1.40(2)
C(29)—C(30)	1.41(2)	C(31)—C(32)	1.40(2)
C(32)—C(33)	1.40(2)	C(33)—C(34)	1.39(2)
C(1)—C(2A)	1.51(3)	C(1)—C(2B)	1.51(3)
C(2A)—N(1A)	1.46(3)	N(1A)—O(1A)	1.25(4)
N(1A)—O(2A)	1.24(4)	C(2B)—N(1B)	1.46(2)
N(1B)—O(1B)	1.18(3)	N(1B)—O(2B)	1.21(3)

The final atomic coordinates of the non-hydrogen atoms are listed in Table II; atom labelling is in accordance with Figure 1. Table III shows bond distances and angles, Table IV gives a selection of torsion angles, and Table V gives significant short intermolecular contacts. Lists of final atomic coordinates for the hydrogen atoms, bond distances and bond angles involving hydrogen atoms, selected least-squares planes, and anisotropic thermal parameters as well as structure factors have been deposited. The molecular structure of the complex is shown in Figure 1 and the packing diagram is illustrated in Figure 2.

### 3.2.1. Molecular structure

*Bond parameters.* Chemically equivalent bond lengths and bond angles in the



Table III (continued)

Atoms	Angle	Atoms	Angle
C(2)—C(1) —C(18)	117.8(9)	C(1)—C(2) —C(3)	109.3(9)
C(2)—C(3) —O(4)	107.9(9)	C(3)—O(4) —C(5)	114.9(8)
O(4)—C(5) —C(23)	125.7(10)	O(4)—C(5) —C(6)	115.8(10)
C(6)—C(5) —C(23)	118.4(10)	C(5)—C(6) —C(26)	122.8(11)
C(5)—C(6) —O(7)	115.0(10)	O(7)—C(6) —C(26)	122.1(10)
C(6)—O(7) —C(8)	119.9(9)	O(7)—C(8) —C(27)	124.1(10)
O(7)—C(8) —C(9)	115.4(10)	C(9)—C(8) —C(27)	120.5(11)
C(8)—C(9) —C(30)	119.5(11)	C(8)—C(9) —O(10)	120.6(10)
O(10)—C(9) —C(30)	119.7(10)	C(9)—O(10) —C(11)	116.8(8)
O(10)—C(11) —C(31)	123.4(10)	O(10)—C(11) —C(12)	117.0(9)
C(12)—C(11) —C(31)	119.6(10)	C(11)—C(12) —C(34)	120.7(10)
C(11)—C(12) —O(13)	114.6(10)	O(13)—C(12) —C(34)	124.7(10)
C(12)—O(13) —C(14)	117.2(8)	O(13)—C(14) —C(15)	107.5(9)
C(14)—C(15) —O(16)	108.3(9)	C(15)—O(16) —C(17)	117.0(9)
O(16)—C(17) —C(22)	124.7(15)	O(16)—C(17) —C(18)	116.4(11)
C(18)—C(17) —C(22)	118.9(15)	O(1)—C(18) —C(17)	115.8(11)
C(17)—C(18) —C(19)	121.7(12)	O(1)—C(18) —C(19)	122.6(12)
C(18)—C(19) —C(20)	118.0(13)	C(19)—C(20) —C(21)	121.2(15)
C(20)—C(21) —C(22)	120.6(14)	C(17)—C(22) —C(21)	119.6(14)
C(5)—C(23) —C(24)	119.3(11)	C(23)—C(24) —C(25)	121.7(10)
C(24)—C(25) —C(26)	120.3(11)	C(6)—C(26) —C(25)	117.5(10)
C(8)—C(27) —C(28)	120.4(12)	C(27)—C(28) —C(29)	119.7(12)
C(28)—C(29) —C(30)	119.3(11)	C(9)—C(30) —C(29)	120.6(10)
C(11)—C(31) —C(32)	120.6(11)	C(31)—C(32) —C(33)	118.8(10)
C(32)—C(33) —C(34)	120.8(11)	C(12)—C(34) —C(33)	119.4(11)
C(1)—C(2A)—N(1A)	109.0(16)	C(2A)—N(1A)—O(2A)	119.6(24)
C(2A)—N(1A)—O(1A)	119.0(25)	O(1A)—N(1A)—O(2A)	120.5(32)
C(1)—C(2B)—N(1B)	108.9(15)	C(2B)—N(1B)—O(2B)	120.9(17)
C(2B)—N(1B)—O(1B)	119.9(19)	O(1B)—N(1B)—O(2B)	118.9(18)

present macrocycle **1** (Table III) compare very well with the mean values of those observed in the complexes of similar crown compounds [17–19] or are normal [20]. The nitroethane guest is highly disordered and hence it is not worth comparing its bond parameters.

*Host conformation.* The macrocyclic host adopts a distorted ‘dentist’s-chair’ conformation [2a,21] as shown in Figure 1(b). Starting from the O(1)–C(2) bond, the macrocycle has the conformation  $ag^+ aasaxsxaag^- aasa$  where the values of  $x$  are  $134(1)^\circ$  and  $-80(1)^\circ$ , respectively (Table IV). The conformation of the macro-

TABLE IV

Selected torsion angles ( $^{\circ}$ ) involving non-hydrogen atoms of **1** · EtNO<sub>2</sub> (1 : 1) (e.s.ds are in parentheses).

Atoms	Angle
C(18)—O(1) —C(2) —C(3)	-178(1)
O(1)—C(2) —C(3) —O(4)	68(1)
C(2)—C(3) —O(4) —C(5)	-171(1)
C(3)—O(4) —C(5) —C(6)	174(1)
O(4)—C(5) —C(6) —O(7)	-2(2)
C(5)—C(6) —O(7) —C(8)	156(1)
C(6)—O(7) —C(8) —C(9)	134(1)
O(7)—C(8) —C(9) —O(10)	-0(2)
C(8)—C(9) —O(10) —C(11)	-80(1)
O(10)—C(11) —C(12) —O(13)	-5(1)
C(11)—C(12) —O(13) —C(14)	-177(1)
C(12)—O(13) —C(14) —C(15)	163(1)
O(13)—C(14) —C(15) —O(16)	-73(1)
C(14)—C(15) —O(16) —C(17)	-175(1)
C(15)—O(16) —C(17) —C(18)	-169(1)
O(16)—C(17) —C(18) —O(1)	-2(2)
C(17)—C(18) —O(1) —C(2)	159(1)
C(1)—C(2A)—N(1A)—O(1A)	130(3)
C(1)—C(2A)—N(1A)—O(2A)	-40(3)
C(1)—C(2B)—N(1B)—O(1B)	-172(2)
C(1)—C(2B)—N(1B)—O(2B)	2(2)

ring is thus roughly  $D_{3d}$  as observed in many complexed 18-crown-6 macrocycles [2, 22–24]. However, two of the endocyclic torsion angles about the C–O bonds in **1** deviate from the usual *anti* conformation [2, 22–24] [O(7)–C(8) = 134(1) and C(9)–O(10) = -80(1) $^{\circ}$ ]. Nevertheless, similar deviations of the torsion angles about C–O bonds have previously been observed in benzo crowns [21, 25]. The torsion angles about C(6)–O(7) [156(1) $^{\circ}$ ] and O(7)–C(11) [165(1) $^{\circ}$ ] of **1** also adjust accordingly. The deviation of these torsion angles probably ensures the favourable disposition of the oxygen atoms O(7) and O(10) towards the methyl group of the guest. These two oxygen atoms participate in probable C–H ··· O type interactions [26] with the methyl carbon atom C(1) of the nitroethane guest molecule.

The nonbonded interaction distances for the oxygen atoms of the macrocycle are: 2.84(1) Å for O(1) ··· O(4), 2.56(1) Å for O(4) ··· O(7), 2.70(1) Å for O(7) ··· O(10), 2.58(1) Å for O(10) ··· O(13), 2.88(1) Å for O(13) ··· O(16) and 2.59(1) Å for O(1) ··· O(16). The values of 2.56(1), 2.58(1) and 2.59(1) Å are short

TABLE V

Significant short intermolecular contacts (Å) observed in the crystal structure of **1** · EtNO<sub>2</sub> (1 : 1) (e.s.ds are in parentheses).

Atoms	Symmetry	Distance
C(2)...O(2B)	$x, y, z$	3.58(3)
O(7)...C(1)	$x, y, z$	3.35(2)
O(8)...C(2A)	$x, y, z$	3.56(3)
C(9)...C(2A)	$x, y, z$	3.42(3)
O(1)...C(1)	$x, y, z$	3.42(2)
O(10)...C(2A)	$x, y, z$	3.43(2)
O(16)...C(1)	$x, y, z$	3.59(2)
C(1)...O(1A)	$x, y, z$	3.43(4)
C(1)...O(1B)	$x, y, z$	3.53(3)
C(1)...O(10)	$x, y, z$	3.44(2)
O(10)...C(2B)	$-x, -y, -z$	3.38(2)
O(10)...O(1B)	$-x, -y, -z$	3.52(2)
O(13)...N(1A)	$-x, -y, -z$	3.23(2)
O(13)...O(2A)	$-x, -y, -z$	3.19(3)
C(14)...N(1A)	$-x, -y, -z$	3.48(2)
O(16)...C(32)	$-x + 1, -y, -z$	3.44(1)
C(19)...O(1A)	$-x, -y, -z + 1$	3.52(4)
C(19)...O(2A)	$-x, -y, -z + 1$	3.08(4)
C(20)...N(1A)	$-x, -y, -z + 1$	3.55(3)
C(20)...O(2A)	$-x, -y, -z + 1$	3.31(4)
C(22)...O(1A)	$-x, +y - 1/2, -z + 1/2$	3.10(3)

when compared with the van der Waals O...O nonbonded contact distance of 2.80 Å [27] and it reflects the conformational strain in the macrocycle, particularly in the O(4) to O(13) section of the molecule. These unfavourable dipolar interactions of O(4)...O(7), O(10)...O(13) and O(1)...O(16) in the present conformation are reduced by the electron-accepting methyl groups of the guest molecule through C-H...O type interactions (see below).

All the benzo groups are approximately planar with the maximum deviation from planarity being -0.01(1) Å for ring *A*, 0.02(1) Å for *B*, -0.02(1) Å for *C* and -0.01(1) Å for *D*. The oxygen atoms attached to the benzo groups are nearly coplanar with the respective benzene ring least-squares planes (supplementary material).

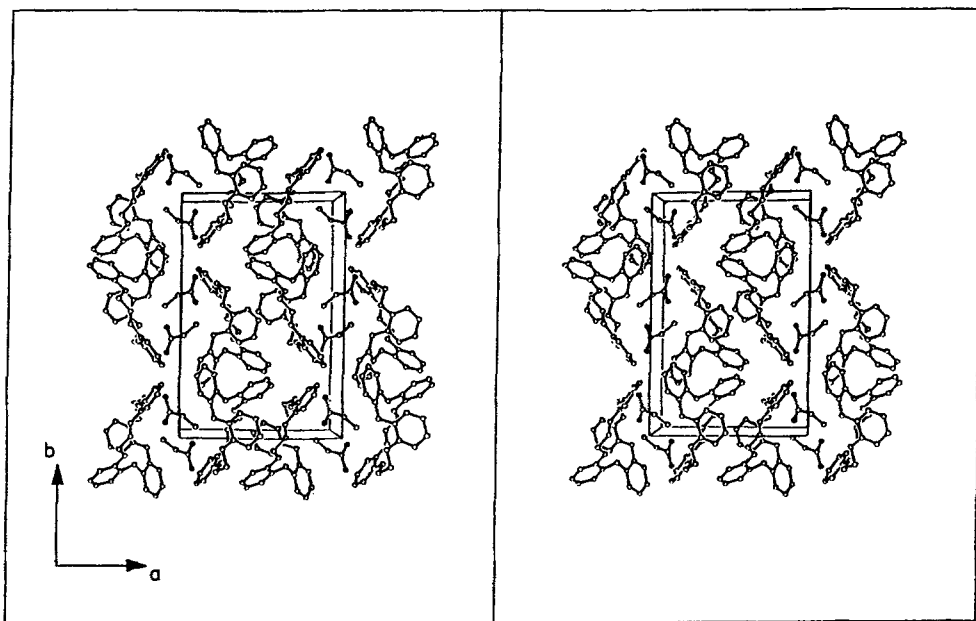


Fig. 2. Crystal packing of the **1** · EtNO<sub>2</sub> (1 : 1) inclusion complex in the unit cell (stereo view down the *c*-axis). The oxygen atoms of the EtNO<sub>2</sub> guest are represented by filled circles.

### 3.2.2. Host–guest interaction and crystal packing

*Host–guest interaction.* Crystallographic studies of complexes between 18-crown-6 and polar C–H-acidic organic guest molecules have revealed that C–H···O interactions [26] play an important role in stabilizing the conformation of the host macrocycle [2, 22–24]. 18-Crown-6 has two equal sides and hence it forms complexes with identical substrate molecules bound to both ring faces. On the other hand, the presence of aromatic building blocks in the specified positions of macrocycle **1** produces a concave and rigid conformation of the host molecule which is similar to a ‘dentist’s chair’ [2a, 21] as shown in Figure 1(b). In this conformation the six donor oxygen atoms of the macrocycle do not lie in a plane, but the oxygen atoms O(1), O(4), O(13), O(16) and O(4), O(7), O(10), O(13) are individually planar with the maximum deviation from planarity being  $-0.022(7)$  and  $0.204(8)$  Å, respectively. These two planes are folded about the oxygen atoms O(4) and O(13) with a folding angle of  $24.9(2)^\circ$ , thus forming a rigid concave structure (Figure 1).

The methyl group of the nitroethane guest is in a perching position with respect to the crown ring; the methyl carbon atom C(1) being displaced by about  $-2.69(2)$  and  $-2.66(2)$  Å from the mean planes specified by O(1), O(4), O(13), O(16) and O(4), O(7), O(10), O(13), respectively. Since the nitroethane guest is highly disordered, the hydrogen atoms of the guest molecule could not be located from

the difference Fourier maps and hence the precise nature of C–H···O interactions could not be established. Nevertheless, C–H···O interactions between the methyl carbon atom of the guest and two oxygen atoms of the host are very likely in the complex, namely C(1)···O(7) = 3.35(2) Å and C(1)···O(10) = 3.44(2) Å. These C–H···O interactions contribute substantially to the stability of the complex, which is confirmed by the fact that the complex loses its crystalline nature as soon as it is removed from the solvent due to the loss of EtNO<sub>2</sub>. Similar observations have been noted for the MeNO<sub>2</sub> complexes of 18-crown-6 [17]. The methyl and methylene groups of the EtNO<sub>2</sub> guest are activated because of their proximity to the electron-withdrawing NO<sub>2</sub> group and hence their interaction could perhaps be regarded as weak hydrogen bonds [26]. Similar C–H···O type interactions were observed in low and room temperature studies of 1 : 2 complexes of 18-crown-6 with MeNO<sub>2</sub> [17a, 17c] where each of the methyl hydrogen atoms participate in a C–H···O type interaction. On the other hand, in the complex with dimethyl acetylenedicarboxylate only two of the hydrogen atoms of the methyl group are involved in C–H···O type interactions [28]. Also in the present complex, a weak C···O interaction involving the methylene carbon atom C(2A) of the nitroethane guest and the oxygen atom O(10) of the host macrocycle has been found [C(2A)···O(10) = 3.43(2) Å]. Coordination of an organic guest molecule to a crown ether host via a methylene entity was previously observed in the structure of the 2 : 1 complex between malononitrile and 18-crown-6 [29].

The studies of thermodynamic constants in solution indicated that MeNO<sub>2</sub> forms both 1 : 1 and 2 : 1 complexes with 18-crown-6. The former appears to be considerably more important in solution while only the latter has been observed in the solid state [17]. It is significant that EtNO<sub>2</sub> forms a 1 : 1 complex with the present macrocycle which may be due to the modification of the 18-crown-6 macroring.

*Crystal packing.* As seen from Figure 2, the nitroethane guest molecules are trapped in extramolecular channels by the host macrocycles. These channels are along the *bc*-plane running through the crystal lattice with the interior of the channels being hydrophilic, such that the oxygen atoms of the host macrocycle are pointing inwards while the exterior of the channels is hydrophobic with the methylene and aromatic groups pointing outwards. The centrosymmetrically related concave hosts are similar to a sandwich complex where the guest molecules are encapsulated between the two macrocyclic hosts, and where the methyl and the methylene constituents of the nitroethane guest interact with their respective macrocycles while the oxygen atoms of the nitro group interact with the C–H-groups of the aromatic ring *D*. The crystal structure is stabilized by intermolecular C–H···O type interactions [26], partial stacking interactions and van der Waals interactions. Table V lists the significant short intermolecular contacts observed in the crystal structure.

Similar channel-type inclusion behaviour has been found for different clathrate host macrocycles such as tri-*o*-thymotide [30], the trianthranilides [31], and deoxycholic acid [32]. Some of the linear peptides including gramicidins A, B and C or

almethicin [33] form transmembrane channels across which alkali metal ions can migrate. Similar to the carrier cavities, these channels provided by the mentioned examples display a hydrophilic interior and a lipophilic exterior.

#### 4. Conclusion

Tetrabenzo condensation to 18-crown-6, as in **1**, significantly alters the solid state inclusion properties towards uncharged organic molecules. Due to the heavy bulk of the host framework, **1** is close to a typical clathrate former, creating extramolecular channels into which small guests, in the present case molecules of EtNO<sub>2</sub> are trapped. On the other hand, as revealed by the structural results, **1** has retained part of the complexation behaviour of uncondensed 18-crown-6 with reference to the C-H...O type interaction involving the C-H-acidic guest molecule EtNO<sub>2</sub>. Thus, crown compound **1** not only shows properties superior to uncondensed 18-crown-6 in the solvent extraction of cations [34], due to the increased lipophilicity, but is also a versatile host molecule for the inclusion of uncharged organic guests by amalgamating properties from the typical crown complexation [2] and clathrate inclusion [14] fields.

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