with the pseudo symmetry of the subcell. However, all attempts to refine trial structures in the expanded cell led to apparent disorder at one of the two molecular sites. Since it was clear that accurate C–O distances would not be obtainable with this crystal the analysis was not pursued further.

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A 1:2 Host–Guest Complex Formed Between 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) and Phenyl Carbamate

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Abstract

$C_{12}H_{24}O_6 \cdot 2C_7H_7NO_2$, $M_r = 538 \cdot 60$, monoclinic, $P2_1/c$, $a = 10 \cdot 053$ (2), $b = 11 \cdot 893$ (3), $c = 12 \cdot 359$ (3) Å, $\beta = 105 \cdot 51$ (2)°, $V = 1423 \cdot 8$ (5) Å^3, $Z = 2$, $d_c = 1 \cdot 26$ Mg m^{-3}, μ(Cu $K\alpha$) = 0·817 mm^{-1}. Full-matrix least-squares refinement (non-hydrogen atoms anisotropic, H atoms isotropic) based on 1518 reflections led to a final R of 0·040. The 18-crown-6 ether sits on a center of symmetry and exhibits approximate D_{3d} symmetry. The six oxygen atoms are alternately 0·24 (1) Å above and below the mean plane and form a nearly planar hexagon with averaged sides of 2·86 (1) Å. The two guest molecules are related by a center of symmetry and each forms hydrogen bonds with H···O distances of 2·12 (3) and 2·39 (3) Å.

Introduction

The weak interactions between crown ethers and neutral organic molecules are of chemical and biological interest. The study of such interactions may lead to the design of specific host molecules for small neutral biologically active compounds, as well as to a better understanding of secondary interactions that occur at biological receptors or enzyme pockets. These weak interactions may be of importance in stereoselective recognition by receptors and substrates. Although a number of structures of 18-crown-6 ethers with charged species have been described, only the neutral complexes with dimethyl acetylenedicarboxylate (1:1) (Goldberg, 1975), dimethyl sulfone (1:1) (Weber & Vögtle, 1980), urea (1:5) (Harkema, Van Hummel, Daasvatn & Reinhoudt, 1981) and benzenesulfon-amide (1:2) (Knochel, Kopf, Oehler & Rudolph, 1978) have been reported. We would like to describe the

structure of the 1:2 complex formed between 1,4,7,10,13,16-hexaoxacyclooctadecane and phenyl carbamate.

Structure determination and refinement

A crystal of dimensions $0.38 \times 0.25 \times 0.20$ mm was selected for all X-ray measurements. Intensity data were collected on a Syntex $P2_1$ diffractometer system by the $\theta:2\theta$ scanning technique using a variable scan speed, Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å) and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 reflections whose angles were measured by a centering routine associated with the diffractometer. The unit cell was found to be monoclinic, and

Table 1. Atomic positional parameters ($\times 10^4$, $\times 10^3$ for H atoms)

The thermal parameters were not refined for H atoms.

	x	y	z	U_{eq}* or U_{iso} (Å²)
O(1)	−1022 (1)	1922 (1)	817 (1)	51
C(2)	5 (2)	2756 (2)	1183 (2)	61
C(3)	738 (2)	2955 (2)	310 (2)	62
O(4)	1588 (1)	2022 (1)	268 (1)	51
C(5)	2368 (3)	2147 (2)	−519 (2)	61
C(6)	3096 (2)	1081 (2)	−607 (2)	59
O(7)	2128 (1)	238 (1)	−1074 (1)	56
C(8)	2785 (2)	−800 (2)	−1185 (2)	69
C(9)	1704 (3)	−1660 (2)	−1643 (2)	66
O(10)	8383 (1)	5393 (1)	2072 (1)	59
C(11)	8174 (2)	4898 (2)	2859 (2)	43
N(12)	9096 (2)	4391 (2)	3678 (2)	51
O(13)	6871 (1)	4752 (1)	2985 (1)	52
C(14)	5796 (2)	5342 (2)	2250 (1)	43
C(15)	5664 (2)	6475 (2)	2386 (2)	49
C(16)	4533 (2)	7021 (2)	1701 (2)	55
C(17)	3568 (2)	6438 (2)	905 (2)	63
C(18)	3736 (3)	5307 (2)	773 (2)	70
C(19)	4850 (2)	4747 (2)	1454 (2)	58
H(2)	66 (3)	254 (2)	179 (2)	57
H(2')	−40 (3)	341 (2)	127 (2)	57
H(3)	9 (3)	302 (2)	−50 (2)	57
H(3')	123 (3)	360 (2)	43 (2)	57
H(5)	173 (2)	231 (2)	−115 (2)	57
H(5')	296 (3)	271 (2)	−32 (2)	57
H(6)	364 (2)	90 (2)	18 (2)	57
H(6')	376 (3)	113 (2)	−109 (2)	57
H(8)	334 (2)	−100 (2)	−32 (2)	57
H(8')	336 (2)	−69 (2)	−170 (2)	57
H(9)	106 (3)	−139 (2)	−235 (2)	57
H(9')	210 (2)	−238 (2)	−186 (2)	57
H(12)	999 (3)	448 (2)	368 (2)	57
H(12')	882 (3)	415 (2)	415 (2)	57
H(15)	639 (3)	684 (2)	289 (2)	57
H(16)	446 (2)	777 (2)	177 (2)	57
H(17)	281 (2)	692 (2)	38 (2)	57
H(18)	318 (3)	492 (2)	30 (2)	57
H(19)	499 (2)	395 (2)	139 (2)	57

* $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij} a_i^* a_j^* (\mathbf{a}_i . \mathbf{a}_j)]$, e.s.d. = 1 Å² for all U_{eq}.

systematic absences were consistent with space group $P2_1/c$. A periodically monitored reflection showed no significant change in intensity. Of the 2314 independent reflections measured ($2\theta < 130°$) 1518 had intensities greater than $3\sigma(I)$. Lorentz and polarization corrections were applied, but no absorption corrections were made.

The direct-methods program *MULTAN* 78 (Main, Lessinger, Woolfson, Germain & Declercq, 1978) was used to calculate phases for the 350 $|E|$ values greater than 1.45. The phase set with the highest combined figure of merit was selected, and the E map calculated with these phases revealed the positions of all non-hydrogen atoms. After several cycles of refinement difference Fourier maps yielded the coordinates of all hydrogen atoms. After anisotropic refinement of the heavy-atom positions, the data were corrected for extinction through use of the equation $|F_c^*| = k|F_c|(1 + 2r^*|F_c|^2\delta)^{-1/4}$ (Larson, 1970). δ is a dimensionless constant for each reflection and r^* was refined to a value of 5 (1) $\times$ 10^{-3} e^{-2} during the final cycles of least-squares refinement. The refinement was terminated at a final R of 0.040 ($R_w = 0.053$) where R and R_w are defined as $\sum ||F_o| - |F_c||/\sum |F_o|$ and $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The function minimized in the refinement was $\sum w(|F_o| - k|F_c|)^2$, where $w = 1/\sigma(I)$ was determined from counting statistics.

Atomic scattering factors were calculated by the XRAY 76 program (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The largest peak in a final difference Fourier map was 0.25 e Å^{-3}, and the

Table 2. Interatomic distances (Å)

O(1)–C(2)	1.417 (3)	O(10)–C(11)	1.203 (3)
O(1)–C(9)	1.409 (3)	C(11)–N(12)	1.321 (2)
C(2)–C(3)	1.479 (4)	C(11)–O(13)	1.372 (2)
C(3)–O(4)	1.410 (3)	O(13)–C(14)	1.400 (2)
O(4)–C(5)	1.411 (3)	C(14)–C(15)	1.369 (3)
C(5)–C(6)	1.482 (4)	C(14)–C(19)	1.368 (3)
C(6)–O(7)	1.410 (3)	C(15)–C(16)	1.385 (3)
O(7)–C(8)	1.424 (3)	C(16)–C(17)	1.371 (3)
C(8)–C(9)	1.490 (4)	C(17)–C(18)	1.371 (4)
		C(18)–C(19)	1.380 (3)

Table 3. Valence angles (°)

C(2)–O(1)–C(9)	112.2 (2)	O(10)–C(11)–N(12)	127.2 (2)
O(1)–C(2)–C(3)	109.9 (2)	O(10)–C(11)–O(13)	122.2 (1)
C(2)–C(3)–O(4)	109.0 (2)	N(12)–C(11)–O(13)	110.5 (2)
C(3)–O(4)–C(5)	113.3 (2)	C(11)–O(13)–C(14)	117.2 (1)
O(4)–C(5)–C(6)	109.7 (2)	O(13)–C(14)–C(15)	119.8 (1)
C(5)–C(6)–O(7)	109.7 (2)	O(13)–C(14)–C(19)	118.3 (2)
C(6)–O(7)–C(8)	111.7 (2)	C(15)–C(14)–C(19)	121.8 (2)
O(7)–C(8)–C(9)	108.8 (2)	C(14)–C(15)–C(16)	118.5 (2)
C(8)–C(9)–O(1)	108.8 (2)	C(15)–C(16)–C(17)	120.7 (2)
		C(16)–C(17)–C(18)	119.7 (2)
		C(17)–C(18)–C(19)	120.4 (2)
		C(14)–C(19)–C(18)	118.9 (2)

Table 4. *Torsion angles* (°) *for the centrosymmetric*
18-crown-6 ether

	Phenyl carbamate	Benzene-sulfonamide*
C(9')O(1)C(2)C(3)	177·0 (2)	176·7
O(1)C(2)C(3)O(4)	−71·8 (2)	−65·8
C(2)C(3)O(4)C(5)	−178·1 (2)	−157·6
C(3)O(4)C(5)C(6)	−173·2 (2)	180·0
O(4)C(5)C(6)O(7)	66·3 (2)	−66·6
C(5)C(6)O(7)C(8)	179·4 (2)	180·0
C(6)O(7)C(8)C(9)	178·0 (2)	−72·5
O(7)C(8)C(9)O(1')	−69·7 (2)	−68·4
C(8)C(9)O(1')C(2')	−178·7 (2)	+172·9

* Knochel, Kopf, Oehler & Rudolph (1978). Several values have been recalculated.

average shift/error during the final cycle of refinement was 0·09. Atomic positional parameters and U_{eq} values are presented in Table 1 while interatomic distances, valence angles and torsion angles are given in Tables 2, 3 and 4.*

Discussion

Fig. 1 is an *ORTEP* drawing (Johnson, 1971) of the title compound with three phenyl carbon atoms omitted for clarity. Fig. 2 shows the stacking of the molecules. Parallel sheets of phenyl rings and 18-crown-6 ether moieties are oriented approximately 90° relative to each other. The hexaether lies at an inversion cente· and exhibits approximate D_{3d} symmetry. The torsion angles about the C—C bonds average 69 (1)°, corresponding to a *gauche* conformation of the ethyleneoxy units. The torsion angles about the C—O bonds average 177 (1)° indicating the planarity of these segments. As shown by the torsion angles in Table 4, the conformation of the 18-crown-6 ether is not identical to that in the 1:2 benzenesulfonamide complex which is also described as having D_{3d} symmetry (Knochel, Kopf, Oehler & Rudolph, 1978) although significant deviations from this symmetry are apparent. The C—O and C—C distances average 1·414 (4) and 1·484 (4) Å while the C—O—C and O—C—C angles are 112·4 (2) and 109·3 (2)°, respectively. The shortening of the bonds is consistent with reported values for other 18-crown-6 complexes (Dunitz, Dobler, Seiler & Phizackerley, 1974). The six oxygen atoms of the hexaether are alternately about 0·24 (1) Å above and below the mean plane and form a nearly planar hexagon with average O···O separation
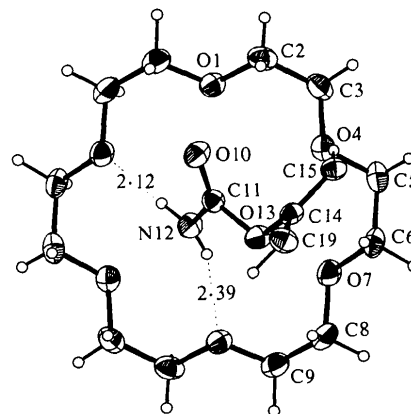
Fig. 1. *ORTEP* drawing of the 1:2 complex between 18-crown-6 ether and phenyl carbamate. Three phenyl carbon atoms have been omitted for clarity. (Distances shown are in Å.)
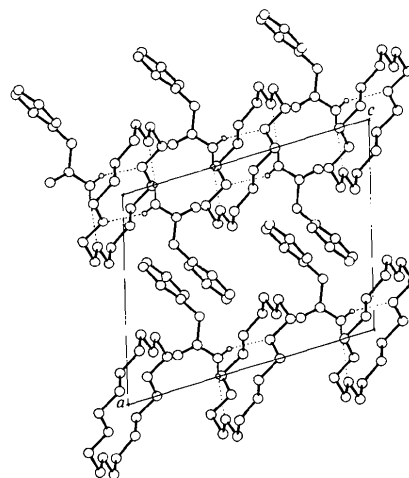

Fig. 2. Packing diagram showing hydrogen bonding.

of 2·86 (1) Å [2·83 (1) to 2·88 (1) Å]. The distance is close to the van der Waals contact distance for oxygen atoms.

Phenyl carbamate molecules are located about the center of symmetry on both sides of the ether moiety. The NH₂ groups are oriented toward the cavity and are hydrogen bonded to two oxygen atoms unrelated by symmetry. The conformation of the 18-crown-6 ether is not the same as that in the benzenesulfonamide complex, where hydrogen bonds involve oxygen atoms related by the center of symmetry. The distances and

Table 5. *Hydrogen-bond distances* (Å) *and angles* (°)

	N–H	N···O	H···O	N–H···O
N(12)–H(12)···O(7ⁱ)	0·90 (3)	3·013 (2)	2·12 (3)	172 (2)
N(12)–H(12')···O(1ⁱ)	0·77 (3)	3·099 (2)	2·39 (3)	154 (2)

(i) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$.

angles describing the hydrogen bonding in the phenyl carbamate complex are presented in Table 5. There are no intermolecular contacts, other than the hydrogen bonding, which are shorter than 3·6 Å.

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1,1',8,8'-Tetrahydroxy-10,10'-bi-9(10H)-anthrone

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Abstract

$C_{28}H_{18}O_6$, $M_r = 450.4$, $F(000) = 840$, is monoclinic, $C2/c$, with $a = 17.751$ (3), $b = 7.581$ (2), $c = 16.316$ (3) Å, $\beta = 106.64$ (3)°, $V = 2103.7$ Å^3, $Z = 4$, $D_{calc} = 1.420$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·06 mm^{-1}. The structure was solved by direct methods. The final R and R_w values were 0·066 and 0·061 respectively for 846 unique observed reflections, $I > 3\sigma(I)$. There is a crystallographic twofold symmetry axis perpendicular to the C(10)–C(10') bond which links the two halves of the molecule, and each half is markedly less planar than the monomeric precursor, 1,8-dihydroxy-9(10H)-anthrone. The C(10)–C(10') bond is long (1·62 Å) and probably weaker than a normal bond.

Introduction

Since it was first synthesized in 1915 (Bayer & Co., 1915) and used clinically (Unna, 1916), dithranol

(1) has remained the most widely prescribed preparation used exclusively for the treatment of psoriasis (Weigand & Everett, 1967). Its mode of action involves its ability to oxidize readily within the epidermal tissues which, by enzymatic inhibition, results in a slowing down of cellular proliferation (Fisher & Maibach, 1975), with subsequent clinical clearance.

(1)
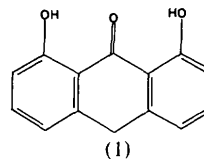
Spectroscopic (Avdovitch & Neville, 1980) and crystallographic (Ahmed, 1980) examination of dithranol has recently shown that it exists as the keto tautomer, 1,8-dihydroxy-9(10H)anthrone (1). When (1) was dissolved in acetone, Segal, Katz & van Duuren (1971) were able to obtain a dimeric species to