

## Structure of the Crown Ether 2,2,7,7,12,12,17,17-Octamethyl-21,22-dioxatricyclo[16.2.1.1<sup>8,11</sup>]docosa-8,10,18,20-tetraene-3,6,13,16-tetrone

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**Abstract.** C<sub>28</sub>H<sub>36</sub>O<sub>6</sub>, *M<sub>r</sub>* = 468.6, tetragonal, *P*4<sub>2</sub>/*mbc*, *a* = 11.823 (1), *c* = 18.823 (5) Å, *V* = 2631.1 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.18 g cm<sup>-3</sup>, Mo *K*α radiation (graphite-crystal monochromator, λ = 0.71069 Å), μ = 0.77 cm<sup>-1</sup>, *F*(000) = 1008, *T* = 293 K, final *R* = 0.041 and *wR* = 0.039 for 1296 observed reflections [*I* > 2σ(*I*)]. The structure of the macrocyclic ring system is interpreted with regard to its complexing abilities. The distance between the furan-ring planes is 7.25 (1) Å. These planes make a dihedral angle of 75° with the plane through the dimethyl-substituted carbons. The C(5)–C(5*D*) bond length is 1.491 (3), C(3)–C(4) is 1.543 (2) Å.

**Introduction.** The ion binding of macrocyclic compounds has drawn attention in both chemistry (Christensen, Eatough & Izatt, 1974) and biology (Newcomb & Cram, 1975). The selective complexation abilities of crown ethers towards various metal ions (Pedersen, 1967) depend on the cavity size of the ring and the ionic diameters of the metal cations. A special class of crown ethers is represented by macrocyclic ligands composed of tetrahydrofuran units (Kobuke, Hanji, Horiguchi, Asada, Nakayama & Furukawa, 1976; Ward & Kung, 1980). We have undertaken a single-crystal X-ray diffraction investigation of the title compound (Fig. 1) to determine the size of the cavity at the center of the compound.

Suitable crystal samples were kindly supplied by Dr Tan Ganzu (Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences).

**Experimental.** White plate-shaped crystals of the title compound were obtained by crystallization from chloroform at room temperature (Tan Ganzu, unpublished results). Initial photographs showed the crystal to belong to the tetragonal system; systematic absences (0*kl*, *k* = 2*n* + 1; *hhl*, *l* = 2*n* + 1) indicated the space group *P*4<sub>2</sub>/*mbc* (No. 135) or *P*4<sub>2</sub>*bc* (No. 106). Subsequently *P*4<sub>2</sub>/*mbc* was shown to be the correct choice.

The crystal used for data collection had an approximate size of 0.1 × 0.26 × 0.35 mm. Accurate cell dimensions were derived from a least-squares refinement of 2θ setting angles for 75 automatically centered reflections (5.3 < θ < 19.5°). Intensity data (*h* 0 → 14, *k* 0 → 14, *l* 0 → 22) were collected at room temperature by ω–2θ scan techniques on an Enraf–Nonius CAD-4 diffractometer equipped with graphite monochromator, using Mo *K*α radiation [λ = 0.71069 Å, max. value of (sinθ)/λ = 0.59 Å<sup>-1</sup>]; they were corrected for Lorentz and polarization effects but not for absorption (μ = 0.77 cm<sup>-1</sup>). Three periodically monitored reflections (800, 080, 0,0,10) showed no significant change in intensity. Within the set of 2363 unique reflections (2627 measured reflections), 1296 reflections were considered observed by the criterion *I* > 2σ(*I*).

The structure was solved by direct methods using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined with full-matrix least-squares techniques (Busing, Martin & Levy, 1962); in the refinement procedure all observed reflections were used and their weights were taken as *w* = 1/σ<sup>2</sup>(*F*). After anisotropic refinement, a difference

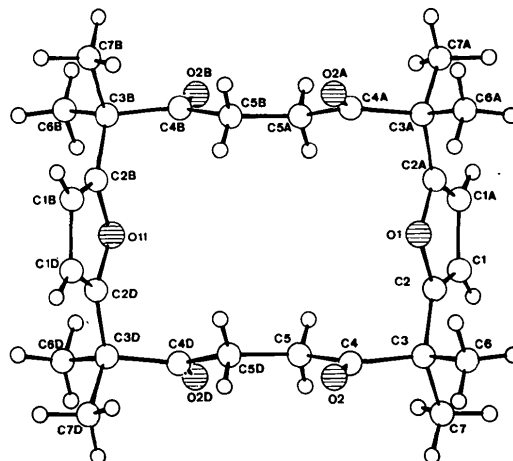


Fig. 1. Perspective drawing of the title compound.

Table 1. Atomic coordinates with *e.s.d.*'s in parentheses and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
O(1)	0.5706 (1)	0.2596 (1)	0.5000	0.036
O(2)	0.6769 (1)	0.1033 (1)	0.3488 (1)	0.067
C(1)	0.4131 (1)	0.3431 (1)	0.4620 (1)	0.043
C(2)	0.5087 (1)	0.2922 (1)	0.4412 (1)	0.034
C(3)	0.5639 (1)	0.2681 (1)	0.3707 (1)	0.035
C(4)	0.5851 (1)	0.1399 (1)	0.3633 (1)	0.038
C(5)	0.4861 (2)	0.0615 (2)	0.3723 (2)	0.062
C(6)	0.6767 (2)	0.3323 (2)	0.3659 (1)	0.048
C(7)	0.4849 (2)	0.3060 (2)	0.3102 (1)	0.050

Table 2. Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ), with *e.s.d.*'s in parentheses, and torsion angles ( $^\circ$ )

O(1)—C(2)	1.383 (2)	C(3)—C(4)	1.543 (2)
C(1)—C(1A)	1.429 (3)	C(3)—C(6)	1.538 (3)
O(2)—C(4)	1.201 (2)	C(3)—C(7)	1.540 (3)
C(1)—C(2)	1.339 (2)	C(4)—C(5)	1.503 (3)
C(2)—C(3)	1.506 (2)	C(5)—C(5D)	1.491 (3)
C(2)—O(1)—C(2A)	106.5 (1)	C(6)—C(3)—C(4)	109.8 (1)
C(1A)—C(1)—C(2)	107.1 (2)	C(6)—C(3)—C(2)	109.6 (1)
O(1)—C(2)—C(3)	115.0 (1)	C(4)—C(3)—C(2)	109.7 (1)
O(1)—C(2)—C(1)	109.7 (1)	C(5)—C(4)—C(3)	118.0 (1)
C(3)—C(2)—C(1)	135.2 (2)	C(5)—C(4)—O(2)	120.5 (2)
C(7)—C(3)—C(6)	109.8 (2)	C(3)—C(4)—O(2)	121.4 (2)
C(7)—C(3)—C(4)	108.5 (1)	C(5D)—C(5)—C(4)	115.4 (2)
C(7)—C(3)—C(2)	109.5 (1)		
C(3)—C(2)—O(1)—C(2A)	−178	O(2)—C(4)—C(5)—C(5D)	8
O(1)—C(2)—C(3)—C(4)	60	C(2)—C(3)—C(4)—O(2)	−127
O(1)—C(2)—C(3)—C(6)	−61	C(2)—C(3)—C(4)—C(5)	55
O(1)—C(2)—C(3)—C(7)	179	C(6)—C(3)—C(4)—O(2)	−7
C(1)—C(2)—C(3)—C(6)	116	C(7)—C(3)—C(4)—O(2)	113
C(1)—C(2)—C(3)—C(4)	−123	C(6)—C(3)—C(4)—C(5)	175

Fourier map revealed the locations of all H atoms, which were subsequently included isotropically in the final cycles of the refinement (115 refined parameters), where the function minimized was  $\sum w(F_o - F_c)^2$ , final  $R = 0.041$  and  $wR = 0.039$ . During the refinement temperature factors of atom O(1) at a special position were constrained. Error of fit = 1.7, final maximum shift/*e.s.d.* = 0.71, maximum residual electron density  $0.29 \text{ e \AA}^{-3}$ . Computer programs used in this investigation were *DATAP* (Coppens, Leiserowitz & Rabinovich, 1965), *DAESD* (Davis & Harris, 1970) and *XANADU* (Roberts & Sheldrick, 1976). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

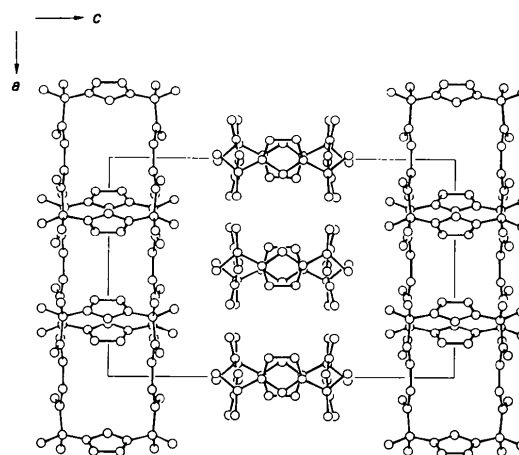
**Discussion.** Atomic coordinates together with  $U_{\text{eq}}$  are given in Table 1 and selected bond distances, angles and torsion angles in Table 2.\*

A molecular plot (Johnson, 1976) of the title compound, together with the atomic labelling, is

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and a table of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44620 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

depicted in Fig. 1. The ring system is characterized by symmetry  $2/m$ , whereby the twofold axis bisects the bonds C(5)—C(5D) and C(5A)—C(5B) and the mirror plane passes through the O atoms of the furan rings and bisects the bonds C(1)—C(1A) and C(1B)—C(1D). The *trans*-1,4-dione units are linked through  $sp^3$ -hybridized C(3) atoms to the 1- and 4-positions of the planar furan rings. The C(3) atoms deviate by  $\pm 0.05$  (1)  $\text{\AA}$  from the furan planes. The torsion angle C(3)—C(2)—O(1)—C(2A) is  $-178^\circ$ . The almost planar dione entity shows torsion angles of  $-166^\circ$  for C(4)—C(5)—C(5D)—C(4D) and  $-174^\circ$  for C(3)—C(4)—C(5)—C(5D). Additional torsion angles are given in Table 2.

In view of the complexing properties of the title compound, some non-bonding intramolecular distances seem to be of interest. The distance between the best planes of both furan rings is 7.25 (1)  $\text{\AA}$ . These rings are tilted such that the atoms O(1) and O(11) point towards the center of the cavity. The dihedral angle between the furan plane and the plane C(3), C(3A), C(3B), C(3D) is  $75^\circ$ . The atoms C(4) and C(5) lie alternately 0.59 (1) and 0.33 (1)  $\text{\AA}$  above and below the latter plane. The ring O atoms O(1) and O(11) are separated by 6.361 (2)  $\text{\AA}$ . The transannular distance between the atoms O(2)...O(2A) of the carbonyl groups is 5.694 (2)  $\text{\AA}$  and the distance between two adjacent atoms O(2)...O(2D) is 4.843 (2)  $\text{\AA}$ . The pairs of atoms C(5)—C(5A) are separated by 4.809 (5)  $\text{\AA}$ , C(3)—C(3A) by 4.866 (2)  $\text{\AA}$  and C(3)—C(3D) by 6.517 (2)  $\text{\AA}$ . The unusually short  $C_{sp^3}$ — $C_{sp^3}$  distance C(5)—C(5D) of 1.491 (3)  $\text{\AA}$  seems to be the result of thermal motion. Similar observations for crown ethers have been reported by Goldberg (1980) and Dunitz, Dobler, Seiler & Phizackerley (1974). The  $C_{sp^2}$ — $C_{sp^3}$  distance C(3)—C(4) of 1.543 (2)  $\text{\AA}$  is longer than normally found, though we have no explanation for this. There are no unusual intermolecular contacts ( $< 3.5 \text{ \AA}$ ) between non-hydrogen atoms within the unit

Fig. 2. Contents of the unit cell projected on the *ac* plane.

cell. Fig. 2 shows the packing of the unit cell projected on the *ac* plane.

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## Structure of 2-Amino-4-methylphenol

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**Abstract.** C<sub>7</sub>H<sub>9</sub>NO, *M<sub>r</sub>* = 123.15, orthorhombic, *Pbca*, *a* = 7.7803 (7), *b* = 22.901 (2), *c* = 7.5962 (6) Å, *V* = 1353.5 (2) Å<sup>3</sup>, *Z* = 8, *D<sub>m</sub>* = 1.20, *D<sub>x</sub>* = 1.206 Mg m<sup>-3</sup>, λ(Cu *Kα*) = 1.5418 Å, μ = 0.62 mm<sup>-1</sup>, m.p. 410–413 K, *F*(000) = 528, *T* = 293 K, final *R* = 0.061 for 999 non-zero reflections. The molecules are held together by N–H...O and O–H...N hydrogen bonds to form a sheet parallel to (010). The sheets are stacked along *b* by weak van der Waals interactions. The *sp*<sup>3</sup> character of the amino group is evidenced by the C–N length, 1.417 (3) Å, the N-atom deviation from the benzene ring plane, 0.110 (3) Å, and the sum of the angles about N, 333 (1)°. The crystal and molecular structures are comparable with those of 2-aminophenol.

**Introduction.** Morphotropism in the crystal structures of the derivatives of 2-aminophenol is of particular interest, because the structure of 2-aminophenol shows remarkable correspondence to that of benzene (*Pbca*) (Haisa, Kashino & Kawashima, 1980). Among the derivatives of 2-aminophenol, the structure of 2-amino-4-chlorophenol (*P2<sub>1</sub>/c*, maximal subgroup of *Pbca*) has already been determined (Ashfaquzzaman & Pant, 1979). In the present work the structure of 2-amino-4-methylphenol has been determined in order to obtain

information on the effect of the 4-methyl group, which is similar in size to the 4-Cl atom, on the crystal structure of 2-aminophenol (Ashfaquzzaman & Pant, 1979).

**Experimental.** Crystals grown by slow evaporation from ethanol, brown plates with developed faces {010}. *D<sub>m</sub>* by flotation in aqueous KI. Systematic absences *0kl* for *k* odd, *h0l* for *l* odd, *hk0* for *h* odd, space group *Pbca*. Crystal 0.24 × 0.12 × 0.20 mm. Rigaku AFC-5 four-circle diffractometer. Lattice parameters determined with 20 reflections in the range 15 < 2θ < 48° by least-squares method; intensities measured up to (sinθ)/λ 0.5753 Å<sup>-1</sup>, ω–2θ scan method [scan speed 4° min<sup>-1</sup> in ω, scan range (2θ): 1.2° + 0.15° tanθ], Ni-filtered Cu *Kα*, 40 kV, 200 mA (rotating anode), background measured for 4 s on either side of the peak. Three standard reflections measured for every 57 reflections, fluctuation within 2.2% in *F*. Lorentz and polarization corrections; no absorption correction. All 1076 unique reflections (ranging over *h* = 0 to 8, *k* = 0 to 26, *l* = 0 to 8) used for refinement; 936 reflections with *F<sub>o</sub>* > 1.0σ(*F<sub>o</sub>*). Structure solved by Patterson method, and refined (anisotropically for non-H atoms) by block-diagonal least squares; ∑w(|*F<sub>o</sub>*| – |*F<sub>c</sub>*|)<sup>2</sup> minimized, with *w* = 1.0/(σ(*F<sub>o</sub>*))<sup>2</sup> – 0.0552|*F<sub>o</sub>*| +