

## Structure of *rel*-(7*S*,9*S*)-7,9-Dimethyl-6,7,9,10,17,18,20,21,23,24-decahydrodibenzo[*b,k*][1,4,7,10,13,16,19]heptaoxacycloheneicosin (Dimethyldibenzo-21-crown-7)

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**Abstract.**  $C_{24}H_{32}O_7$ ,  $M_r = 432.5$ , monoclinic,  $P2_1/a$ ,  $a = 10.051$  (3),  $b = 20.426$  (8),  $c = 12.129$  (5) Å,  $\beta = 110.10$  (4)°,  $U = 2338.5$  Å<sup>3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $Z = 4$ ,  $D_m = 1.21$ ,  $D_c = 1.23$  g cm<sup>-3</sup>,  $\mu = 0.84$  cm<sup>-1</sup>,  $F(000) = 928$ . The structure was solved by direct methods from observations collected on a two-circle diffractometer. Full-matrix refinement gave a conventional  $R$  factor of 0.057 for 2081 reflections classed as observed. The conformation is similar to those of other methyl derivatives of uncomplexed crowns, indicating that it is determined by intramolecular steric factors.

**Introduction.** The crown ethers (Pedersen, 1967) are a series of flexible compounds which change their shapes when complexed with various metal salts (see, for examples, Bright & Truter, 1970; Bush & Truter, 1972; Dunitz, Dobler, Seiler & Phizackerley, 1974). The conformations of complexed ethers are often different for different salts but, in general, they all feature the O atoms directed towards the cavity of the macrocyclic ring and the C and H atoms on the outside. However, the conformations adopted by the uncomplexed ethers in the crystalline state often contain one or more O atoms directed away from the macrocyclic cavity. This is usually accomplished by rotation about the bonds to give torsion angles which differ markedly from the expected  $\pm 60^\circ$  for C–C bonds, and  $180^\circ$  for C–O bonds. For comparison, we have determined the structure of uncomplexed dimethyldibenzo-21-crown-7 (Fig. 1), prepared and recrystallized from methanol by Dr J. N. Wingfield at Rothamsted.

A crystal of dimensions  $0.35 \times 0.42 \times 0.50$  mm was mounted about the crystallographic  $c$  axis and data were collected on a Stoe Stadi 2 two-circle diffractometer, at Sheffield, in layers of constant  $l$  index up to a maximum of  $l = 12$ . The data were processed to give 3032 planes with  $2\theta \leq 45^\circ$ , of which 2081 had  $I \geq 2\sigma(I)$  and were classed as observed. Systematic

absences were  $h0l$ ,  $h = 2n + 1$ , and  $0k0$ ,  $k = 2n + 1$ , corresponding to space group  $P2_1/a$ . Accurate unit-cell dimensions were obtained from 16 high-order planes on a Nonius CAD-4 diffractometer at Rothamsted. The structure was solved by multiresolution direct methods (Sheldrick, 1976). The numbering scheme is shown in Fig. 1, and the H atoms are numbered according to the C atom to which they are bonded. Thus H(61) and H(62) are bonded to atom C(6). The H atoms were included in positions calculated from the geometry of the molecule, with a C–H bond length of 1.08 Å. A common isotropic temperature factor was used for the non-methyl H atoms, and this refined to a value of  $U = 0.092$  (3) Å<sup>2</sup>. The methyl H atoms were treated in a similar way and the temperature factor refined to  $U = 0.108$  (8) Å<sup>2</sup>. Full-matrix refinement with anisotropic temperature factors for the non-hydrogen atoms gave  $R = 0.057$  and  $R' = 0.080$ . The final atomic parameters are given in Table 1. Scattering factors were calculated using an analytical approximation (*International Tables for X-ray Crystallography*, 1974). The weighting scheme used was  $w = 0.1955/[\sigma^2(F_o) +$

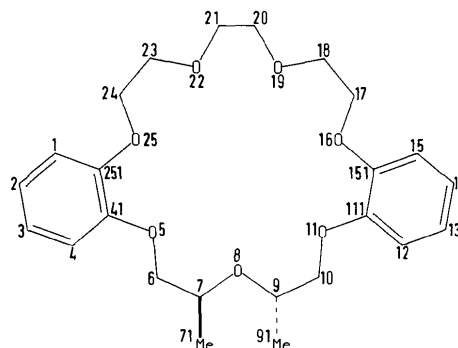


Fig. 1. Numbering scheme for the non-hydrogen atoms.

Table 1. Fractional coordinates ( $\times 10^4$ ) for the non-hydrogen atoms and calculated fractional coordinates ( $\times 10^4$ ) for the H atoms

	x	y	z		x	y	z
C(1)	-4705 (5)	1099 (3)	3792 (4)	H(1)	-5629	851	3846
C(2)	-4523 (6)	1760 (3)	4022 (5)	H(2)	-5314	2028	4255
C(3)	-3363 (6)	2081 (3)	3962 (5)	H(3)	-3235	2599	4141
C(4)	-2340 (5)	1731 (2)	3667 (4)	H(4)	-1423	1983	3608
C(41)	-2488 (4)	1071 (2)	3451 (4)	H(61)	-743	1296	2222
O(5)	-1533 (3)	681 (1)	3191 (3)	H(62)	229	1273	3741
C(6)	-364 (4)	984 (2)	2986 (4)	H(7)	-83	140	2092
C(7)	565 (4)	457 (2)	2781 (4)	H(711)	503	-195	4198
C(71)	1251 (5)	46 (3)	3874 (5)	H(712)	1816	417	4492
O(8)	1670 (3)	764 (1)	2481 (3)	H(713)	1995	-309	3770
C(9)	1303 (4)	920 (2)	1254 (4)	H(9)	186	836	801
C(91)	1653 (7)	1636 (2)	1144 (6)	H(911)	1422	1717	217
C(10)	2126 (5)	495 (2)	722 (4)	H(912)	2775	1698	1605
O(11)	1817 (3)	-171 (1)	886 (3)	H(913)	1072	1985	1472
C(111)	2499 (4)	-642 (2)	485 (4)	H(101)	3246	585	1145
C(12)	3341 (4)	-532 (2)	-186 (4)	H(102)	1827	599	-205
C(13)	3988 (5)	-1047 (3)	-536 (4)	H(12)	3494	-39	-440
C(14)	3817 (6)	-1677 (3)	-227 (4)	H(13)	4641	-951	-1062
C(15)	2960 (5)	-1795 (2)	448 (4)	H(14)	4335	-2077	-501
C(151)	2332 (4)	-1288 (2)	825 (4)	H(15)	2790	-2292	675
O(16)	1541 (3)	-1344 (1)	1534 (3)	H(171)	764	-2287	1335
C(17)	1453 (5)	-1976 (2)	2012 (5)	H(172)	2496	-2192	2350
C(18)	879 (5)	-1902 (3)	2964 (5)	H(181)	1516	-1555	3599
O(19)	-527 (4)	-1674 (2)	2507 (3)	H(182)	900	-2370	3384
C(20)	-1103 (6)	-1571 (3)	3406 (5)	H(201)	-1264	-2034	3771
C(21)	-2496 (5)	-1229 (3)	2844 (5)	H(202)	-400	-1270	4091
O(22)	-3266 (4)	-1251 (2)	3614 (3)	H(211)	-3088	-1472	2033
C(23)	-4659 (5)	-980 (3)	3116 (5)	H(212)	-2311	-726	2666
C(24)	-4752 (5)	-304 (2)	3512 (5)	H(231)	-4953	-980	2172
O(25)	-3816 (3)	101 (2)	3156 (3)	H(232)	-5388	-1284	3367
C(251)	-3699 (4)	760 (2)	3493 (4)	H(241)	-4451	-294	4457
				H(242)	-5825	-127	3121

Table 2. Bond lengths (Å) and bond angles ( $^\circ$ )E.s.d.'s for bond angles are  $\sim 0.4^\circ$ .

C(1)–C(2)	1.377 (9)	C(12)–C(13)	1.376 (7)	C(2)–C(3)–C(4)	119.2	C(13)–C(14)–C(15)	118.9
C(2)–C(3)	1.362 (9)	C(13)–C(14)	1.368 (8)	C(3)–C(4)–C(41)	120.7	C(14)–C(15)–C(151)	120.7
C(3)–C(4)	1.395 (8)	C(14)–C(15)	1.399 (7)	C(4)–C(41)–C(251)	118.8	C(15)–C(151)–C(111)	119.7
C(4)–C(41)	1.372 (7)	C(15)–C(151)	1.371 (6)	C(251)–C(41)–O(5)	115.9	C(111)–C(151)–O(16)	114.7
C(41)–C(251)	1.390 (6)	C(151)–C(111)	1.410 (6)	C(4)–C(41)–O(5)	125.4	C(15)–C(151)–O(16)	125.6
C(251)–C(1)	1.374 (7)	C(151)–O(16)	1.363 (5)	C(41)–O(5)–C(6)	118.4	C(151)–O(16)–C(17)	117.5
C(41)–O(5)	1.365 (5)	O(16)–C(17)	1.429 (6)	O(5)–C(6)–C(7)	108.4	O(16)–C(17)–C(18)	108.8
O(5)–C(6)	1.423 (5)	C(17)–C(18)	1.465 (8)	C(6)–C(7)–C(71)	111.9	C(17)–C(18)–O(19)	109.7
C(6)–C(7)	1.502 (6)	C(18)–O(19)	1.409 (6)	C(6)–C(7)–O(8)	108.0	C(18)–O(19)–C(20)	111.5
C(7)–C(71)	1.519 (7)	O(19)–C(20)	1.414 (6)	C(71)–C(7)–O(8)	107.8	O(19)–C(20)–C(21)	106.5
C(7)–O(8)	1.428 (5)	C(20)–C(21)	1.503 (8)	C(7)–O(8)–C(9)	114.5	C(20)–C(21)–O(22)	109.0
O(8)–C(9)	1.440 (5)	C(21)–O(22)	1.403 (6)	O(8)–C(9)–C(10)	108.6	C(21)–O(22)–C(23)	112.9
C(9)–C(91)	1.522 (6)	O(22)–C(23)	1.431 (6)	O(8)–C(9)–C(10)	109.6	O(22)–C(23)–C(24)	112.7
C(9)–C(10)	1.491 (6)	C(23)–C(24)	1.477 (7)	C(91)–C(9)–C(10)	110.0	C(23)–C(24)–O(25)	108.7
C(10)–O(11)	1.424 (5)	C(24)–O(25)	1.427 (6)	C(9)–C(10)–O(11)	108.4	C(24)–O(25)–C(251)	117.8
O(11)–C(111)	1.364 (5)	O(25)–C(251)	1.399 (6)	C(10)–O(11)–C(111)	117.6	O(25)–C(251)–C(1)	124.6
C(111)–C(12)	1.380 (6)			O(11)–C(111)–C(151)	115.5	O(25)–C(251)–C(41)	114.6
C(251)–C(1)–C(2)	119.3	C(111)–C(12)–C(13)	120.5	O(11)–C(111)–C(12)	125.5	C(1)–C(251)–C(41)	120.8
C(1)–C(2)–C(3)	121.2	C(12)–C(13)–C(14)	121.1	C(151)–C(111)–C(12)	118.9		

$0.0586|F_o|^2$ ]. The final difference map showed no peaks greater than  $0.17 \text{ e } \text{Å}^{-3}$ .\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33469 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** Bond lengths and angles and estimated standard deviations are given in Table 2, torsion angles in Table 3, and mean planes in Table 4. The bond lengths and angles are consistent with those found in other crown ethers, both complexed and uncomplexed, and show similar peculiarities. For example, the bonds between  $sp^3$ -hybridized C atoms in the macrocyclic ring

Table 3. Torsion angles ( $^{\circ}$ ) in the macrocyclic ringE.s.d.'s are  $\sim 0.6^{\circ}$ .

O(25)—C(251)—C(41)—O(5)	-5.5
C(251)—C(41)—O(5)—C(6)	172.0
C(41)—O(5)—C(6)—C(7)	177.1
O(5)—C(6)—C(7)—O(8)	175.3
C(6)—C(7)—O(8)—C(9)	-85.3
C(7)—O(8)—C(9)—C(10)	-111.4
O(8)—C(9)—C(10)—O(11)	58.3
C(9)—C(10)—O(11)—C(111)	-178.3
C(10)—O(11)—C(111)—C(151)	170.5
O(11)—C(111)—C(151)—O(16)	-1.7
C(111)—C(151)—O(16)—C(17)	-173.6
C(151)—O(16)—C(17)—C(18)	165.7
O(16)—C(17)—C(18)—O(19)	65.2
C(17)—C(18)—O(19)—C(20)	-177.7
C(18)—O(19)—C(20)—C(21)	171.0
O(19)—C(20)—C(21)—O(22)	166.3
C(20)—C(21)—O(22)—C(23)	-175.4
C(21)—O(22)—C(23)—C(24)	-100.0
O(22)—C(23)—C(24)—O(25)	60.9
C(23)—C(24)—O(25)—C(251)	-177.2
C(24)—O(25)—C(251)—C(41)	160.8

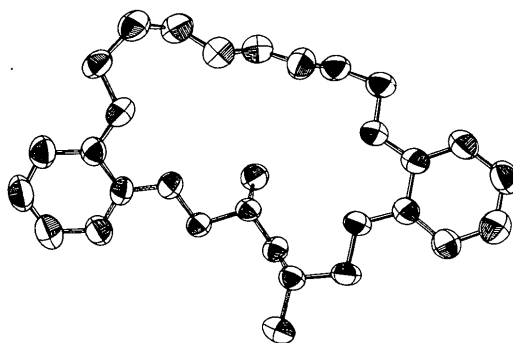


Fig. 2. The conformation of dimethyldibenzo-21-crown-7 in the crystal.

torsion angles for C(6)—C(7)—O(8)—C(9)  $-85.3^{\circ}$  and C(7)—O(8)—C(9)—C(10)  $-111.4^{\circ}$ .

The conformation of this section of the molecule is similar to that found in the *F* isomer of tetramethyldibenzo-18-crown-6, which has the same relative configuration of the methyl groups (Mallinson, 1975). This supports the supposition that intramolecular steric effects involving the methyl groups decide the conformation of this section of the molecule.

Notable values are also found for torsion angles for bonds on the other side of the ring [e.g. torsion angles for O(19)—C(20)—C(21)—O(22)  $166.3^{\circ}$  and C(21)—O(22)—C(23)—C(24)  $-100.0^{\circ}$ ].

The intermolecular distances are unremarkable and there are no strong interactions present in the crystal. Left- and right-handed forms of the molecule (*7S,9S* and *7R,9R*) are present in equal numbers, giving the racemic crystals.

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Table 4. Mean planes through groups of atoms and deviations ( $\text{\AA}$ ) of atoms from these planes

Designations in italics are of atoms excluded from the calculations of the planes.

#### Plane A: benzene ring

C(1)	-0.003 (5)	C(2)	-0.004 (6)	C(3)	0.003 (6)
C(4)	0.006 (5)	C(41)	-0.013 (4)	C(251)	0.011 (5)
O(5)	-0.051 (3)	O(25)	0.114 (3)		

#### Plane B: benzene ring

C(111)	0.008 (4)	C(12)	0.001 (5)	C(13)	-0.003 (5)
C(14)	-0.003 (5)	C(15)	0.011 (5)	C(151)	-0.014 (4)
O(11)	0.003 (3)	O(16)	-0.073 (3)		

#### Plane C: O atoms

O(5)	-0.165 (3)	O(8)	-0.614 (3)	O(11)	0.668 (3)
O(16)	-0.005 (3)	O(19)	-0.229 (4)	O(22)	-0.234 (3)
O(25)	0.577 (3)				

#### Angles between planes ( $^{\circ}$ )

Plane A/Plane B	29.5
Plane A/Plane C	13.1
Plane B/Plane C	16.4

are shorter than the standard, and several bond angles are different from the ideal values. It is notable that the bonds to the methyl C atoms are much closer to the value expected for the C—C single-bond length.

The conformation is such as to direct atom C(7) to the centre of the macrocyclic cavity (Fig. 2) and torsion angles involving this atom reflect this (Table 3) [*viz*