Crystal Structure of (7*R*,9*R*,18*S*,20*S*)-6,7,9,10,17,18,20,21-Octahydro-7,9,18,20-Tetramethyldibenzo[*b*,*k*][1,4,7,10,13,16]Hexaoxacyclo-octadecin (Tetramethyldibenzo-18-crown-6, Isomer F)

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Crystals of the title compound are triclinic, with a = 8·726(6), b = 8·746(8), c = 9·600(7) Å, α = 107·92(6), β = 117·47(4), γ = 98·35(5)°, Z = 1, space group $P\bar{1}$. The crystal structure has been determined by direct methods and refined by least squares to R 0·057 on 980 diffractometer data. The molecule has crystallographic symmetry $\bar{1}$ with torsion angles differing from the *trans*-C–O and *gauche*-C–C pattern found in complexed polyethers. Mean bond lengths are: C–C(aliphatic) 1·508(8), C–C(aromatic) 1·382(5), $C(sp^3)$–O 1·431(4), and $C(sp)^2$–O 1·364(6) Å. The differences in conformation from dibenzo-18-crown-6 are caused by steric effects of the methyl groups.

It is well established that considerable changes in conformation occur on complex formation by cyclic polyethers with alkali metal salts, from crystal structure comparisons [1-4] of complexed and uncomplexed ethers, including the bicyclic cryptates.[5-6] In the preceding paper it was reported that methyl substitution of (Ia), the ether dibenzo-18-crown-6, to yield (Ib), caused no change in conformation in a complex of one isomer of the ligand, whereas appreciable changes in torsion angles were found in a complex of a different isomer, the comparisons being made with complexes of the unsubstituted ether. To elucidate further the effect

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of substitition on the characteristics of a model compound, this paper makes a similar comparison for the uncomplexed ethers. The four chiral carbon atoms in (Ib) give rise to five stereoisomers, of which the title compound is the first of the two mentioned earlier, and designated isomer F.

EXPERIMENTAL

Crystals of isomer F were prepared by the method of ref. 7.

Crystal Data.—$C_{24}H_{32}O_6$, $M = 416·5$. Triclinic, $a = 8·726(6)$, $b = 8·746(8)$, $c = 9·600(7)$ Å, $\alpha = 107·92(6)$, $\beta = 117·47(4)$, $\gamma = 98·35(5)°$, $U = 582$ Å^3, $D_c = 1·19$, $Z = 1$, $D_m = 1·18$, $F(000) = 224$. Space group $P\bar{1}$ (No. 2). $\mu = 0·763$ cm^{-1} for Mo-$K_{\alpha 1}$ radiation ($\lambda = 0·70926$ Å, 1 Å $\equiv 10^{-10}$ m).

Platy crystals were obtained by recrystallisation from acetic acid. A single crystal of dimensions $0·2 \times 0·1 \times 0·4$ mm was mounted with its longest edge approximately parallel to the fibre. 1912 independent X-ray intensities were measured by 2θ scan from $2\theta_{\alpha 1} - 0·5°$ to $2\theta_{\alpha 2} + 0·5°$ on a Picker four-circle automatic diffractometer by use of zirconium-filtered Mo-K_α radiation. These comprised all possible reflections with $\sin\theta/\lambda \leqslant 0·58$ Å^{-1}. 980 reflections having $I > 2\sigma(I)$ were considered observed (see preceding paper). The intensities of three standard reflections monitored every 50 observations showed no reduction in intensity during data collection. Intensities were corrected [8] for Lorentz and polarisation effects but not for absorption. The unit-cell parameters were determined by least-squares refinement from diffractometer setting angles of 16 reflections.

Computations were carried out as described in the preceding paper with programs used listed in refs. 8 and 9. Atomic scattering factors for hydrogen were taken from ref. 10, and for carbon and oxygen from ref. 11.

Structure Determination.—Analysis of the X-ray intensity distribution gave the space group $P\bar{1}$, which requires the single molecule in the cell to be centrosymmetric, the asymmetric unit being half the formula unit. Attempts to solve the three-dimensional sharpened Patterson function for either the oxygen positions or the benzene ring failed. The structure was solved by direct methods in conjunction with weighted Fourier syntheses. A molecular fragment consisting of a benzene ring with an oxygen and two carbon atoms in a side chain was located by use of the MULTAN program.[9] The fragment was incorrectly positioned in the unit cell, being too close to a centre of symmetry. The correct position was found by lowering the space-group symmetry to $P1$, in which the origin position is arbitrary. A Fourier synthesis in this space group, phased by the atoms in the recognisable fragment and weighted according to Sim's scheme,[12] revealed the location of second benzene ring and the entire polyether ring, except for two carbon atoms. These and the methyl carbon atoms were located in a second weighted Fourier map. Structure factors calculated for the observed reflections at this stage gave R 0·35, which was reduced to 0·22 after three cycles of refinement of the positional and isotropic thermal parameters of all atoms in space group $P1$. The position of the centre of symmetry was next determined by taking the average of the mean co-ordinates of related pairs of atoms, and subtracting it from all the atomic co-ordinates in the true asymmetric unit to refer them to the centre of symmetry as origin. This increased R to 0·32, but it was reduced to 0·19 after two cycles of refinement of all positional and isotropic thermal parameters. For the anisotropic refinement a weighting scheme was used in which $\sqrt{w} = 1/\sigma$, where $\sigma = \sigma(F_0)\sqrt{-3·85 + 1·6|F_0| + 0·02|F_0|^2}$. This gave similar average values of $w\Delta^2$ for various ranges of $|F_0|$ and of $\sin\theta/\lambda$. After three cycles of block-diagonal anisotropic refinement R was 0·12. A difference synthesis computed at this stage showed all the hydrogen atomic positions. When these were included in the structure factors R was 0·10, and was further reduced to 0·064 after three cycles of anisotropic refinement of carbon and oxygen atoms, with co-ordinates only of the 16 hydrogen atoms. Finally, four cycles of full-matrix refinement of positional parameters of all atoms, with the anisotropic temperature factors of carbon and oxygen and isotropic temperature factors of hydrogen gave R 0·057 for the 980 observed reflections, and R' 0·068 [$R' = (\Sigma w\Delta^2/\Sigma w|F_0|^2)^{\frac{1}{2}}$]. In the final cycle all shifts were $< 0·22\sigma$, and $\Sigma w\Delta^2$ decreased by 0·2%. A difference-Fourier synthesis computed from the final structure factors for the observed reflections, weighted according to the least-squares weights, showed no peaks or holes of magnitude $> 0·1$ eÅ^{-3}.

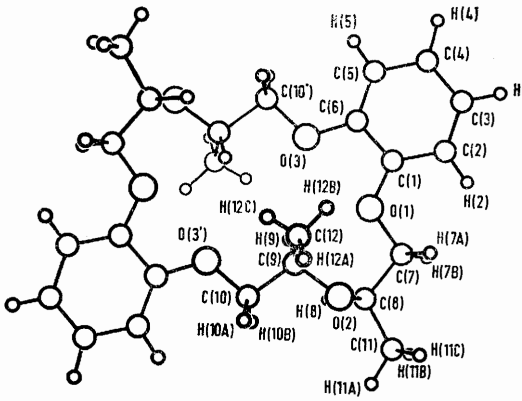

FIGURE 1 The isomer F molecule (Ib)

RESULTS

Atomic co-ordinates and thermal parameters with their estimated standard deviations are given in Tables 1 and 2, mean planes through the atoms in Table 3. Observed and calculated structure factors for the 980 observed reflections are listed in Supplementary Publication No. SUP 21206 (24 pp., 1 microfiche).* The designations of the atoms are shown in Figure 1. Bond lengths and angles in the asymmetric unit are in Figure 2. Standard

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

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Table 1

Fractional atomic co-ordinates ($\times 10^4$, hydrogen co-ordinates $\times 10^3$), with estimated standard deviations in parentheses. Hydrogen atoms are numbered according to the carbon atoms to which they are attached. Isotropic mean square vibration amplitudes ($U \times 10^2$) Å² are given for hydrogen atoms

	x/a	y/b	z/c	U
C(1)	4829(6)	0785(6)	3309(6)	
C(2)	6697(6)	1412(7)	4538(7)	
C(3)	7846(8)	0694(7)	4149(8)	
C(4)	7156(8)	−0581(8)	2540(8)	
C(5)	5269(8)	−1218(8)	1307(8)	
C(6)	4125(6)	−0548(6)	1704(6)	
C(7)	4087(7)	2780(6)	5080(6)	
C(8)	2371(6)	3196(6)	4759(6)	
C(9)	0693(7)	2676(8)	1713(7)	
C(10)	−1304(7)	2462(7)	1026(7)	
C(11)	2741(10)	4565(9)	6422(9)	
C(12)	1402(12)	3296(17)	0759(11)	
O(1)	3537(4)	1347(4)	3516(4)	
O(2)	1788(4)	3887(4)	3495(4)	
O(3)	2270(4)	−1029(4)	0619(4)	
H(2)	710(5)	223(5)	565(5)	5(1)
H(3)	911(6)	111(5)	498(5)	5(1)
H(4)	791(7)	−111(6)	221(6)	9(2)
H(5)	501(6)	−190(6)	036(6)	7(2)
HA(7)	520(5)	386(5)	541(5)	6(1)
HB(7)	472(5)	250(5)	619(5)	5(1)
H(8)	120(6)	197(5)	419(5)	7(1)
H(9)	080(5)	167(5)	166(5)	4(1)
HA(10)	−151(5)	360(5)	098(5)	6(1)
HB(10)	−159(5)	232(5)	191(5)	4(1)
HA(11)	175(6)	488(6)	636(6)	8(2)
HB(11)	319(6)	412(6)	732(7)	8(2)
HC(11)	357(7)	574(7)	661(6)	9(2)
HA(12)	112(10)	431(9)	081(9)	14(4)
HB(12)	255(9)	314(8)	094(8)	12(3)
HC(12)	066(7)	270(7)	−029(7)	8(2)

Table 2

Anisotropic vibration parameters ($\times 10^3$) Å², of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + U_{22}k^2b^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + U_{33}l^2c^{*2})]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	39(3)	50(3)	55(3)	17(2)	24(3)	21(3)
C(2)	44(3)	57(3)	53(4)	14(3)	22(3)	15(3)
C(3)	46(3)	69(4)	76(4)	16(3)	31(3)	28(3)
C(4)	57(4)	91(5)	84(5)	35(3)	47(4)	41(4)
C(5)	60(4)	76(4)	56(4)	30(3)	35(3)	23(3)
C(6)	46(3)	62(3)	45(3)	26(3)	20(3)	19(3)
C(7)	50(3)	44(3)	40(3)	15(2)	18(2)	6(3)
C(8)	53(3)	51(3)	51(3)	20(3)	29(3)	18(3)
C(9)	55(3)	60(4)	47(4)	25(3)	17(3)	6(3)
C(10)	55(3)	61(4)	42(3)	24(3)	21(3)	7(3)
C(11)	87(5)	67(4)	65(4)	36(4)	44(4)	17(3)
C(12)	72(5)	173(10)	60(5)	29(6)	34(5)	18(6)
O(1)	47(2)	67(2)	56(2)	25(2)	22(2)	9(2)
O(2)	67(2)	46(2)	49(2)	22(2)	18(2)	11(2)
O(3)	54(2)	88(3)	55(2)	37(2)	13(2)	−4(2)

Table 3

Deviations (Å) of the atoms from planes. The equations are referred to Cartesian axes *a*, *b′*, and *c′*, where *b′* is in the plane of *a* and *b*

Plane (1): O(1)—(6)

$$0{\cdot}633x + 0{\cdot}684y - 0{\cdot}364z = 0$$

O(1) −0·20, O(2) 0·15, O(3) 0·23, C(1) 0·39, C(2) 0·75, C(3) 1·33, C(4) 1·60, C(5) 1·23, C(6) 0·62, C(7) −0·43, C(8) −0·91, C(9) +0·37, C(10) −0·29, C(11) −1·35, C(12) 1·85, H(8) −1·71, H(9) −0·05

Plane (2): C(1)—(6)

$$0{\cdot}240x + 0{\cdot}906y - 0{\cdot}349z + 0{\cdot}737 = 0$$

C(1) 0·01, C(2) 0·01, C(3) −0·02, C(4) 0·01, C(5) 0·00, C(6) −0·01, O(1) 0·02, O(2) 1·57, O(3) 0·00

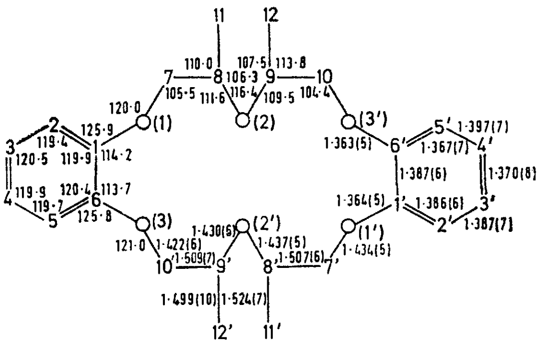

Figure 2 Bond lengths and angles in (Ib). The halves of the molecule are centrosymmetrically related, *e.g.* C(1), C(1′), *etc.* σ for angles 0·4—0·8°. C–H bond lengths 0·82—1·13 Å (σ 0·05 Å); angles involving hydrogen atoms 112—128 (aromatic) and 98—126° (aliphatic), σ 3—10°

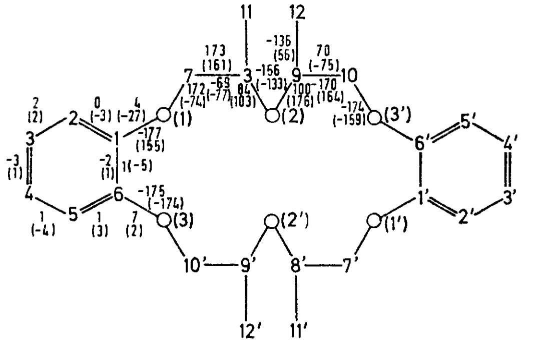

Figure 3 Torsion angles (°) in (Ib). In parentheses are the corresponding values for a dibenzo-18-crown-6 molecule (Ia) viewed with all atoms, except those corresponding to C(8) and C(11), deviating from the oxygen mean plane in the same directions as those in (Ib). Centrosymmetrically-related angles have the same magnitude but opposite sign. The atom labels are those adopted for (Ib); σ 1° for (Ib), 2—3° for (Ia). Some angles for (Ia) were incorrect in ref. 1.

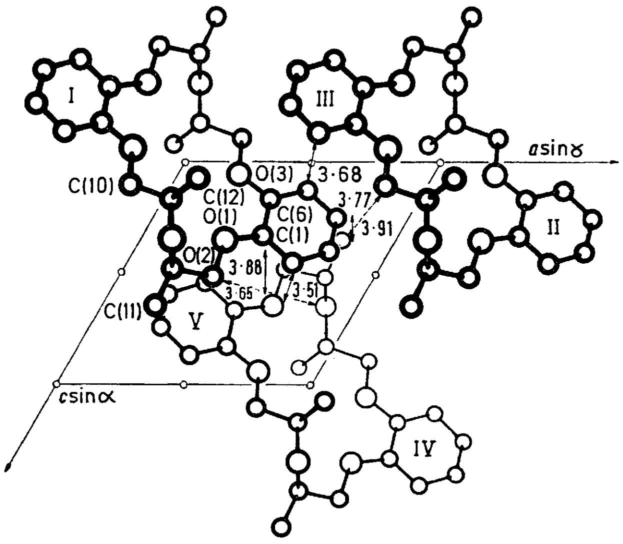

Figure 4 Projection of the structure along [010]. Some distances (Å) between atoms are shown; broken arrows indicate translation ±1 along *b*. Roman numerals refer to the following equivalent positions with respect to the asymmetric unit at *x*, *y*, *z*: I −*x*, −*y*, −*z*; II 1 + *x*, *y*, *z*; III 1 − *x*, −*y*, −*z*; IV 1 + *x*, *y*, 1 + *z*; V 1 − *x*, −*y*, 1 − *z*

deviations were calculated[9] from those in Table 1 with allowance for correlation and for the errors of the cell dimensions. Torsion angles of the ring bonds are in Figure 3. Figure 4 is a projection of the structure along [010].

DISCUSSION

The macrocyclic ether (Ib) has crystallographic symmetry $\bar{1}$, whereas in the CsNCS complex $\cdot$ (II)[13] it has an approximate plane of symmetry. Dibenzo-18-crown-6 (Ia), the unsubstituted analogue of (Ib) is present in both complexed and uncomplexed forms in in the crystals of $[Rb/NaNCS]_2[\text{dibenzo-18-crown-6}]_3$;[1] the ether of crystallisation is crystallographically centrosymmetric, identical in its molecular symmetry to uncomplexed isomer F. Figure 1 shows the isomer F molecule. The oxygen atoms deviate from coplanarity by as much as 0·227(4) Å (Table 3), compared with deviations up to 0·184 Å from the oxygen mean plane in (Ia).[1] There are no significant deviations from coplanarity of the catechol group atoms. The normal to the catechol plane is inclined at 26° to the oxygen plane normal, compared with 56° in (Ia).

Torsion angles in the substituted and unsubstituted ethers in their uncomplexed forms are compared in Figure 3. The bonds O(1)–C(7) and O(2)–C(9) show the greatest differences in torsion angles between the two molecules. This is caused by C(8) and the corresponding atom in (Ia) being on opposite sides of the oxygen mean plane. There is also a difference in configuration at C(8); in isomer F, H(8) is in the axial position −1·71 Å from the plane, whereas the corresponding axial hydrogen atom in (Ia) is 1·6 Å from the plane (an estimated position as the hydrogen atoms in the latter structure were not refined). In both molecules some torsion angles have magnitudes in the range 80—160°, intermediate between *gauche* and *trans* conformations, and in either case there is at least one C–O bond in the *gauche* conformation and one *trans* C–C bond. These characteristics of C–C and C–O bonds are the opposite of those usually found in complexed polyethers.[2]

The bond lengths and angles (Figure 2) are similar to those in other uncomplexed and complexed macrocyclic ethers derived from catechol,[1,2,13-16] including short aliphatic C–C bonds[4] [mean 1·508(8) Å], $C(sp^2)$–O bonds [mean 1·364(6) Å] shorter than the $C(sp^3)$–O bonds [mean 1·431(4) Å], and distorted C–C–O angles involving the aromatic carbon atoms [mean 113·9(4)° endocyclic to the polyether ring, 125·9(3)° exocyclic]. The mean aromatic C–C bond length [1·382(5) Å] is not significantly different from that in benzene.

The standard deviation of an aromatic C–C bond length calculated from the spread of values is 0·011 Å, rather greater than the value obtained from the variance–covariance matrix. The standard deviation 0·005 Å of the mean bond length is given by $\left[\sum_{i=1}^{n}\sigma_i^2\right]^{\frac{1}{2}}/n$, where $n = 6$ for a benzene ring and each σ value is taken as 0·011 Å. The standard deviations of the mean aliphatic C–C (0·008), aliphatic C–O (0·004), and aromatic C–O (0·006) bond lengths are similarly obtained by taking the individual σ as 0·011 for C–C and 0·008 Å for C–O. The bond lengths have not been corrected for the effects of thermal motion of the atoms.

Inter- and Intra-molecular Contacts.—The shortest distances (Figure 4) between atoms in different molecules are: C $\cdots$ C 3·81, C $\cdots$ C(H) 3·74, C $\cdots$ O 3·88, C(H) $\cdots$ C(H) 3·68, C(H) $\cdots$ $C(H_2)$ 3·70, C(H) $\cdots$ Me 3·91, C(H) $\cdots\cdot$ C(HMe) 3·86, C(H) $\cdots$ O 3·51, $C(H_2)$ $\cdots$ Me 3·77, and $C(H_2)$ $\cdots$ O 3·64 Å. These are typical van der Waals distances. There are some short intramolecular contacts, *viz.*: O(1) $\cdots$ O(3) 2·49, C(9) $\cdots$ C(7) 3·18, C(9) $\cdots$ O(1) 2·94, C(12) $\cdots$ C(8) 3·56, and C(12) $\cdots$ O(3′) 2·93 Å. The approach of the aliphatic carbon atoms C(7) and C(9) is very close, and must be a determining factor in the conformation. Two of the other short contacts involve a methyl group, so steric interactions resulting from the methyl substitution are probably responsible for the change in conformation from that in (Ia), forcing C(8) to the opposite side of the plane of the oxygen atoms. There is no such hindrance in the altered conformation of (II),[13] which shows no change from the [Rb/NaNCS] [dibenzo-18-crown-6] complex.[1] Hence the conformation of isomer F in the free state is more sensitive to the effects of substitution than in the complex. All other contacts (not involving hydrogen) are >4 Å.

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