

## 1,4,7,10,13,16-Hexaoxacyclooctadecane: Crystal Structure at 100 K

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### Abstract

The structure of the title compound (18-crown-6),  $C_{12}H_{24}O_6$ , has been redetermined at 100 K. The crystals are orthorhombic, space group *Pbca*, with  $a = 8.066$  (4),  $b = 20.120$  (10),  $c = 8.437$  (4) Å,  $Z = 4$ . The low-temperature data extend to  $\sin \theta/\lambda = 0.904$  Å<sup>-1</sup>. The structure was refined, starting from the room-temperature coordinates, to  $R = 0.038$ , with 2958 reflections with  $F \geq 3.5\sigma_F$ . The mean C–C length of 1.512 Å is subject to a maximum thermal-motion correction of about 0.007 Å. The molecule does not behave as a rigid body; the effect of internal torsional vibrations on the observed  $U_{ij}$  values is apparent even at 100 K. Difference density maps show peaks along bonding directions and also near the O atoms in expected lone-pair regions.

### Introduction

The crystal structure of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) has already been determined at room temperature (Dunitz & Seiler, 1974). The mean C–C and C–O distances were 1.507 and 1.411 Å respectively, both rather short compared with standard values, but thermal-motion corrections were of uncertain magnitude and were not applied. As part of an attempt to settle the question of the short C–C bonds found in crown ethers and their complexes we have now redetermined the structure of 18-crown-6 at 100 K; the new low-temperature analysis also provides the opportunity to study bonding and lone-pair electron densities in this type of molecule.

### Experimental

Cell dimensions recorded for 18-crown-6 are: 295 K:  $a = 8.295$ ,  $b = 20.230$ ,  $c = 8.490$  Å; 100 K:  $a = 8.066$ ,  $b = 20.120$ ,  $c = 8.437$  Å, with e.s.d.'s of about 0.05%. The contraction on cooling occurs mainly along  $a$ , which is also the direction of largest thermal motion. The space group is taken as *Pbca* at both temperatures. There are a few very weak reflexions that contradict the

systematic absences required by this space group; they have been neglected (see final section).

Cell dimensions and diffracted intensities were measured with an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å) and a slightly modified Nonius low-temperature device. With a  $\theta$  limit of 40° ( $\sin \theta/\lambda = 0.904$  Å<sup>-1</sup>) 4422 unique reflexions were measured, 2958 with  $F > 3.5\sigma_F$  (set A), and 3045 with  $F > 3.0\sigma_F$  (set B).

### Structure refinement

The atomic positions and thermal parameters obtained in the previous room-temperature analysis (Dunitz & Seiler, 1974) served as a starting point for refinement with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The scattering factors were those of Cromer & Mann (1968) for C and O, and of Stewart, Davison & Simpson (1965) for H. Initially the C and O atoms were refined anisotropically, the H atoms isotropically, with modified weights,  $w_F = \sigma_F^{-2} \times \exp(r \sin^2 \theta/\lambda^2)$  (Dunitz & Seiler, 1973), with  $r = 3.5$  Å<sup>2</sup>, leading to  $R = 0.036$  for reflexions of set A. The H atoms were then moved along the C–H vectors to make all C–H distances equal to 1.08 Å and held at their calculated positions during the following cycles, with  $r = 4.5$  Å<sup>2</sup>. Continuation of the refinement led to the positional and vibrational parameters shown in Tables 1 and 2; the final  $R$  was 0.038 (set A).\*

As a check, we made two cycles of high-order refinement with only the 572 reflexions with  $F > 3.5\sigma_F$  and  $\sin \theta/\lambda > 0.82$  Å<sup>-1</sup>. Bond distances were within 0.005 Å of those obtained with the previous refinement (C–O bonds shorter, C–C bonds almost unaffected), but their e.s.d.'s were two to three times larger. We concluded that no advantage was to be gained by further sharpening.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34920 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^5$ ) and vibrational parameters ( $\times 10^4$ ) for C and O atoms (e.s.d.'s in parentheses)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
O(1)	-277 (9)	-13445 (2)	-26030 (6)	221 (2)	153 (1)	141 (2)	5 (2)	29 (2)	-11 (1)
C(2)	-404 (10)	-19563 (3)	-17519 (8)	210 (2)	144 (2)	167 (2)	-17 (2)	3 (2)	-20 (2)
C(3)	13290 (10)	-20199 (4)	-5389 (8)	212 (3)	185 (2)	166 (2)	37 (2)	7 (2)	-23 (2)
O(4)	9711 (7)	-16196 (3)	8093 (6)	166 (2)	175 (2)	152 (2)	2 (2)	-0 (1)	-26 (1)
C(5)	24190 (9)	-14278 (3)	16535 (8)	175 (2)	173 (2)	184 (2)	21 (2)	-37 (2)	3 (2)
C(6)	20014 (10)	-8739 (4)	27854 (8)	210 (2)	175 (2)	142 (2)	7 (2)	-39 (2)	18 (2)
O(7)	15293 (8)	-3088 (3)	18877 (6)	266 (2)	152 (2)	128 (2)	25 (2)	-26 (2)	-2 (1)
C(8)	9783 (10)	2268 (3)	28528 (8)	230 (3)	168 (2)	128 (2)	6 (2)	-14 (2)	-9 (2)
C(9)	7574 (9)	8083 (3)	17375 (8)	212 (2)	155 (2)	133 (2)	5 (2)	7 (2)	-11 (2)

Table 2. Fractional coordinates ( $\times 10^3$ ) and isotropic vibrational parameters of H atoms

The H positions were refined, but for the final cycles they were fixed at 1.08 Å from the attached C atom. E.s.d.'s of  $U$  values are 0.004 Å<sup>2</sup>.

	<i>x</i>	<i>y</i>	<i>z</i>	$U$ (Å <sup>2</sup> )
H(2)	-122	-202	-117	0.026
H(22)	15	-234	-263	0.028
H(3)	248	-187	-108	0.027
H(33)	141	-254	-19	0.028
H(5)	335	-126	83	0.022
H(55)	288	-185	233	0.035
H(6)	306	-76	352	0.032
H(66)	101	-102	357	0.027
H(8)	187	34	377	0.026
H(88)	-18	10	342	0.028
H(9)	-1	66	75	0.029
H(99)	194	96	127	0.028

### Molecular structure

Bond distances, bond angles and torsion angles are listed in Table 3 and a drawing of the molecule is shown in Fig. 1. The molecular conformation is essentially the same as that found at room temperature (RT) and is best described as a sequence of (*ap, ap, ap*), (*ap, +sc, ap*), (*ap, -sc, +sc*) partial conformations of the three successive non-equivalent -O-CH<sub>2</sub>-CH<sub>2</sub>-O units. The mean C-O distance (1.423 Å) is markedly longer than at RT (1.411 Å) and is now equal to the C-O distance in gaseous 1,4-dioxane (Davis & Hassel, 1963). The mean C-C distance (1.512 Å) shows a less marked lengthening with respect to the RT value (1.507 Å) and still appears short compared with 1,4-dioxane (1.523 Å). It is certainly short compared with the standard C-C distance of 1.54 Å.

The bond angles at 100 K tend to be slightly but significantly smaller than the RT values (maximum difference 1.2°), probably as a result of the lower thermal motion. There are also small changes in torsion angles (up to 2.3°), but the general pattern is unaltered.

Table 3. Bond distances (Å), bond angles (°) and torsion angles (°) in the centrosymmetric 18-membered ring

E.s.d.'s are 0.001 Å for bond lengths and <0.1° for angles.

<i>W-X-Y-Z</i>	Distance <i>X-Y</i>	Angle <i>W-X-Y</i>	Torsion angle
C(9')-O(1)-C(2)-C(3)	1.425	113.0	-80.3
O(1)-C(2)-C(3)-O(4)	1.511	114.1	74.7
C(2)-C(3)-O(4)-C(5)	1.423	110.2	-154.9
C(3)-O(4)-C(5)-C(6)	1.421	112.8	165.6
O(4)-C(5)-C(6)-O(7)	1.506	109.6	-65.1
C(5)-C(6)-O(7)-C(8)	1.418	108.3	175.2
C(6)-O(7)-C(8)-C(9)	1.422	112.7	172.4
O(7)-C(8)-C(9)-O(1')	1.512	105.5	173.7
C(8)-C(9)-O(1')-C(2')	1.430	108.3	169.2

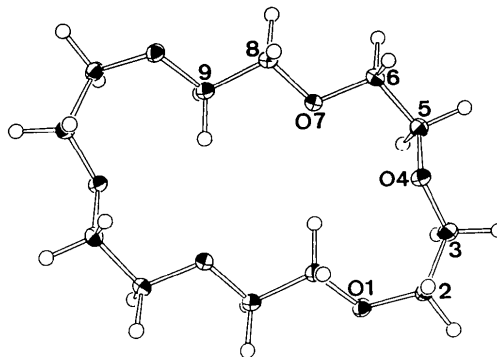


Fig. 1. An ORTEP drawing of the molecule with thermal ellipsoids scaled at the 50% probability level (Johnson, 1965). Hydrogen atoms are represented by circles of radius 0.1 Å.

### Thermal-motion analysis

Atomic mean-square vibrational amplitudes at 100 K (Table 1) are uniformly about 30% of those at RT; the ratio of individual diagonal terms  $U_{ii}(\text{LT})/U_{ii}(\text{RT})$  lies within the range 0.26–0.32. An analysis of the LT atomic vibrational tensors (excluding H atoms) in terms of rigid-body motions was made with THMB (Trueblood, 1978), leading to the following translation-

al and librational tensors (referred to Cartesian crystal axes):

$$\mathbf{T} = \begin{bmatrix} 200 (18) & 20 (7) & -8 (10) \\ & 159 (6) & -13 (5) \\ & & 126 (8) \end{bmatrix} \text{Å}^2 \times 10^{-4}$$

$$\mathbf{L} = \begin{bmatrix} 12 (8) & 25 (12) & -6 (8) \\ & 49 (33) & -10 (8) \\ & & -10 (13) \end{bmatrix} \text{rad}^2 \times 10^{-5}.$$

The agreement between observed and calculated  $U_{ij}$  values is poor considering the low e.s.d.'s of the former:  $\langle (w\Delta U_{ij})^2 \rangle^{1/2} = 13 \times 10^{-4} \text{Å}^2$ ,  $\langle \sigma^2(U_{ij}) \rangle^{1/2} = 2 \times 10^{-4} \text{Å}^2$ ,  $R = [\sum (w\Delta U_{ij})^2 / \sum (wU_{ij})^2]^{1/2} = 0.115$ . This poor agreement suggests either that the quality of the observed  $U_{ij}$ 's is not as good as we think or that the rigid-body model is inappropriate. Since the components of the  $\mathbf{L}$  tensor are not significantly different from zero, the differences among the vibration tensors of the individual atoms cannot be attributed to rigid-body libration, and it is clear that they cannot be attributed to rigid-body translation either because the latter must affect the individual  $\mathbf{U}$  tensors equally. Indeed, as the rigid-body test proposed by Rosenfield, Trueblood & Dunitz (1978) shows, these differences arise mainly from internal molecular motions, which appear to be active even when the librational motion has been frozen out.

This test is based on a comparison of the quantities  $\Delta_{A,B} = z_{A,B}^2 - z_{B,A}^2$  for bonded and non-bonded pairs of atoms  $A, B$  ( $z_{A,B}^2$  is the mean-square vibration amplitude of atom  $A$  in the direction of atom  $B$ ). According to Hirshfeld (1976),  $\Delta_{A,B} \approx 0$  for bonded pairs of atoms of comparable mass; gross violations of this condition would indicate that the  $\mathbf{U}$  tensors are contaminated by errors of various kinds. In our case, the largest value of  $\Delta_{A,B}$  for a bonded pair is  $0.0007 (3) \text{Å}^2$ , so the near equality is satisfied rather well for bonds. If the molecule were rigid, the Hirshfeld (1976) condition should apply just as well to non-bonded pairs as to bonded ones. However, large  $\Delta_{A,B}$  values are found for several non-bonded pairs. The largest (those  $> 30$  in units of  $10^{-4} \text{Å}^2$ ) are:

C(6)—O(4')	-46	C(5)—C(9')	-39
O(7)—O(4')	-45	C(6)—C(9')	-35
C(5)—O(4')	-34	C(5)—O(1)	-35
		C(6)—O(1)	-31

where the negative sign means that the second atom of the pair has a larger vibration amplitude than the first. The internal vibrations of the 18-membered ring are certainly quite complex, but the pattern of large  $\Delta_{A,B}$  values gives the distinct impression that O(1), O(4) and C(9) (all in the *gauche-gauche* corner) suffer relatively

large displacements, while C(5), C(6) and O(7) (all in the *anti-gauche* corner) are least affected by the internal molecular motion. We shall return to this difference later.

In spite of the invalidity of the rigid-body model we can use the observed  $U_{ij}$  values to estimate maximal shrinkage corrections for individual bond lengths (Busing & Levy, 1964). The maximal correction, corresponding to the assumption of completely correlated motion of the two atoms with displacement components perpendicular to the bond and  $180^\circ$  out-of-phase, is given (Johnson, 1970) by

$$\Delta d_{AB} = \frac{\alpha + \beta + 2\gamma}{2d_{AB}},$$

where

$$\alpha = \text{Tr} \mathbf{U}_A - z_{A,B}^2,$$

$$\beta = \text{Tr} \mathbf{U}_B - z_{B,A}^2,$$

$$\gamma = (\alpha\beta)^{1/2}.$$

With the observed  $U_{ij}$  values, we find maximal corrections of the order of  $0.05 \text{Å}$ . This estimate is unrealistically large, however, since it includes contributions from the translational vibration of the molecule, which is certainly in-phase rather than out-of-phase, as assumed in the above treatment. One way of allowing for the in-phase translational-motion contribution would be to subtract  $T_{ii}$  from each  $U_{ii}$  value, but this would make some of the corrected  $U_{ii}$  values negative since  $T_{ii}$  is roughly equal to the average  $U_{ii}$ . Instead, we use a minimal estimate of  $T_{ii}$  equal to the smallest  $U_{ii}$  and subtract it from the remaining  $U_{ii}$ 's to obtain corrected values. With these assumptions we obtain corrections of  $0.006\text{--}0.008 \text{Å}$  for the various bonds. These are still maximal corrections since the treatment assumes that *all* the vibration of a pair of atoms which is not translational is completely anti-phase correlated, an assumption that can hardly be expected to hold for the complex internal molecular motions that actually occur. In any case, even with these maximal corrections, the mean C—C length would only be increased to about  $1.519 \text{Å}$ , close to the dioxane value of  $1.523 \text{Å}$ , but still much shorter than the paraffinic value of  $1.541 \text{Å}$  (Kennard, 1962).

In a previous publication (Dunitz, Dobler, Seiler & Phizackerley, 1974) we argued that the bond shortenings observed in many studies of cyclic ethers and their complexes are largely, if not completely, spurious because of inadequate treatment of thermal motion. In the light of the new results we have to modify the above statement by saying that the bond shortenings in question are largely but not completely spurious.

#### C—H...O interactions

Short H...H and O...H distances are listed in Table 4, with the relevant C—O...H angles for the latter.

Table 4. *Non-bonded interactions: H...H distances* <2.50 Å, *H...O distances (1...5 or greater)* <2.80 Å

H atoms are located along the respective C—H vector at a distance of 1.08 Å.

The equivalent positions for the space group *Pbca* are referred to in the following order:

(II)	$-x, -y, -z$	(VI)	$x, \frac{1}{2} - y, \frac{1}{2} + z$
(III)	$\frac{1}{2} + x, \frac{1}{2} - y, -z$	(VII)	$\frac{1}{2} - x, -y, \frac{1}{2} + z$
(IV)	$\frac{1}{2} - x, \frac{1}{2} + y, z$	(VIII)	$\frac{1}{2} + x, y, \frac{1}{2} - z$
(V)	$-x, \frac{1}{2} + y, \frac{1}{2} - z$		

Interaction	Equivalent position and translation	Distance (Å)
H(2)...H(33)	(III), -1, -1, 0	2.40
H(22)...H(33)	(VI), 0, -1, -1	2.41
H(22)...H(55)	(III), -1, -1, 0	2.47
H(5)...H(66)	(VIII), 0, 0, 0	2.25
H(6)...H(99)	(VII), 0, 0, 0	2.35
H(6)...H(9)	(VII), 0, 0, 0	2.46
O(1)...H(3)	(VIII), -1, 0, -1	2.53
O(1)...H(99)	(VII), 0, 0, -1	2.77
O(4)...H(9)	(II), 0, 0, 0 (intramolecular)	2.46
O(4)...H(22)	(VI), 0, -1, 0	2.56
O(7)...H(9)	(II), 0, 0, 0 (intramolecular)	2.64
O(7)...H(88)	(VIII), 0, 0, 0	2.79

Angles pertaining to short O...H distances (°)

C(2)—O(1)...H(3)	82	C(3)—O(4)...H(22)	90
C(9')—O(1)...H(3)	102	C(5)—O(4)...H(22)	100
C(2)—O(1)...H(99)	115	C(6)—O(7)...H(9)	111
C(9')—O(1)...H(99)	110	C(8)—O(7)...H(9)	123
C(3)—O(4)...H(9)	95	C(6)—O(7)...H(88)	92
C(5)—O(4)...H(9)	108	C(8)—O(7)...H(88)	97

Although Fig. 1 gives the impression that the intramolecular H of C(9) points directly at the opposite O(7), the O(7)...H distance of 2.64 Å is actually 0.18 Å longer than the O(4)...H distance in the *gauche-gauche* corner of the molecule. From Fig. 1 it is also apparent that the H atom concerned lies approximately in the bisecting planes of the two relevant C—O—C fragments; the same approximate relationship holds also for the two intermolecular contacts made by O(1) and O(4), as shown by the approximate equality of the two C—O...H angles involved in each such contact.

### Force-field calculations

In order to test the notion that these short CH...O contacts correspond to weak hydrogen bonds we have made some calculations with the consistent-force-field program *CFE* (Niketic & Rasmussen, 1977) and the FF3 set of energy parameters developed by Kildeby, Melberg & Rasmussen (1977) for carbohydrates. This force field includes terms for bond stretching, angle bending and torsion-angle deformations, as well as for non-bonded interactions between atoms separated by at

least three bonds, but it excludes Coulombic or other terms that allow specifically for hydrogen-bonded interactions.

The same minimum-energy conformation with an overall strain energy of about 16 kJ mol<sup>-1</sup> was reached from two starting points: (a) the centrosymmetric structure observed in the crystal; (b) a hypothetical structure, lacking an exact centre of symmetry, obtained by ring-closing a folded chain with ideal bond lengths, bond angles and torsion angles. The minimum-energy structure has mean C—C and C—O distances of 1.526 and 1.427 Å, respectively, and has the same general pattern of bond angles and torsion angles as the observed structure. However, the calculated structural parameters do not vary as much from their equilibrium values as the observed ones. For example, although the largest O—C—C angle occurs at C(2) in both structures, the calculated value is 112.0°, observed 114.1°. Similarly, the largest torsion-angle differences are all in such a sense that the calculated angle is closer to 60 or 180° than the observed one:

C(9')—O(1)—C(2)—C(3)	-80° (obs.)	-67° (calc.)
C(2)—C(3)—O(4)—C(5)	-155	-173
O(4)—C(5)—C(6)—O(7)	-65	-59.

Exact agreement between calculated and observed conformations is hardly to be expected since the former refers to an isolated molecule at 0 K while the latter pertains to a molecule subject to crystal-packing forces at 100 K. Nevertheless, the systematic nature of the differences suggests that the energy functions we used to describe bond-angle and torsion-angle deformations are a little too stiff, or else that non-bonded repulsions are not adequately represented.

The defect may lie partly in the use of spherical atom-atom functions to build up the non-bonded interaction energies. According to *ab initio* studies (Popkie, Kistenmacher & Clementi, 1973; Maverick, 1979) O...O interaction energies have a strong directional dependence for O...O distances of 3 Å or less. Pertinent distances in the present structure are:

O(1)...O(4)	3.04 Å (obs.)	2.86 Å (calc.)
O(4)...O(7)	2.83	2.77.

The *ab initio* studies suggest that optimal spherical potentials for O...O interactions could be in error by as much as 4 kJ mol<sup>-1</sup> for such distances.

In the calculated structure the C(9')—H...O(7) distance is approximately equal to the observed distance, and the C(9)—H...O(4) distance is even shorter (by 0.10 Å) than observed. The need to invoke C—H...O hydrogen bonding as an important factor in holding the molecule in its observed conformation is thus seen to be superfluous, at least for this force field, since no interaction terms corresponding to hydrogen bonds are specifically included in it.

The *CFF* program provides for diagonalization of the second-derivative matrix and hence for calculation of normal vibrational modes and frequencies. The four lowest vibrational modes with calculated frequencies of 31, 52, 55 and 73  $\text{cm}^{-1}$  ( $kT \sim 70 \text{ cm}^{-1}$  at 100 K) involve mainly changes in torsion angles, chiefly those about C(6)–O(7) and O(4)–C(5). The reliability of this result is hard to assess, but it may not be coincidental that C(5), C(6) and O(7) are the very atoms which appear to be least affected by the internal molecular motion, as judged by the  $\Delta_{A,B}$  test mentioned earlier.

### Difference electron density maps

Although our analysis was not begun with the intention of carrying out deformation density studies, the low *R* encouraged us to believe that the deformation density

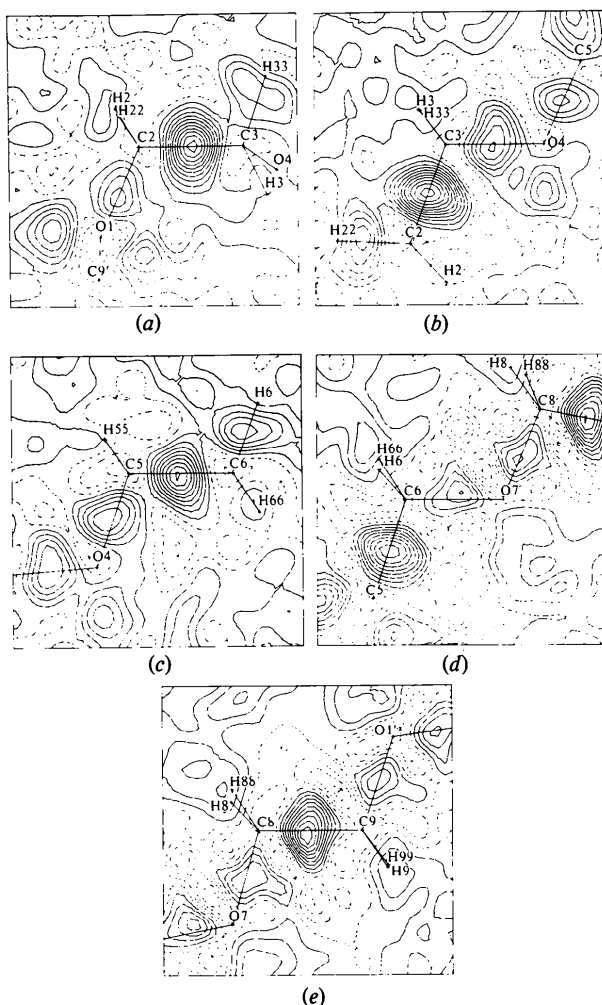


Fig. 2. Sections through the deformation density maps. The planes (a), (b), (c), (d) and (e) are defined by O(1)–C(2)–C(3), C(2)–C(3)–O(4), O(4)–C(5)–C(6), C(6)–O(7)–C(8), and C(8)–C(9)–O(1'), respectively. Contours are drawn at intervals of  $0.05 \text{ e } \text{\AA}^{-3}$ ; dashed lines represent negative contours.

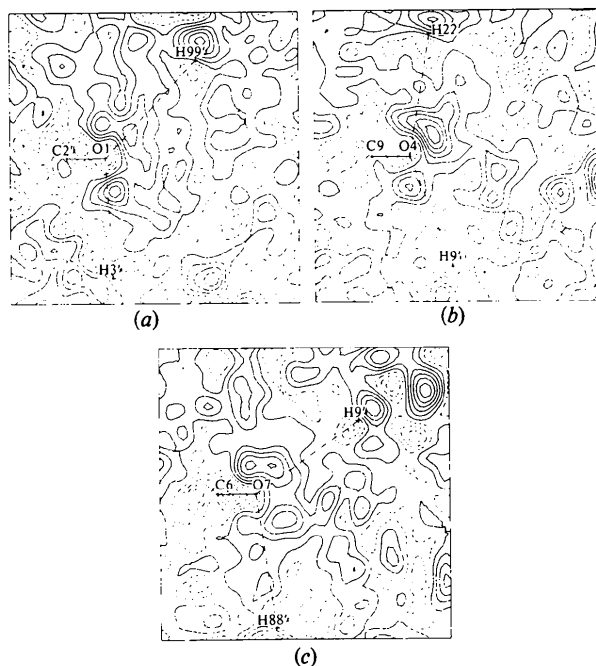


Fig. 3. Sections through the deformation density maps. The planes (a), (b), and (c) are defined by the bisectors of the C–O–C fragments at O(1), O(4) and O(7) respectively. For the identification of the H atoms see Table 4; they are 0.1 and 0.5  $\text{\AA}$  out of the plane in (a), 0.3  $\text{\AA}$  out of the plane in (b) and 0.2 and 0.3  $\text{\AA}$  out of the plane in (c). Contours are drawn at intervals of  $0.05 \text{ e } \text{\AA}^{-3}$ ; dashed lines represent negative contours.

might be of interest, particularly in view of the lack of information about O atom lone-pair densities in crown ethers.

Difference syntheses computed with the *F* values of set *B* show peaks along all C–C, C–H and C–O bonds (Fig. 2). The highest of these peaks [C(2)–C(3)] reaches  $0.50 \text{ e } \text{\AA}^{-3}$ . The e.s.d. of the difference density was estimated by summing over 125 points in the featureless background of the map: mean value  $0.004 \text{ e } \text{\AA}^{-3}$ , r.m.s. value  $0.03 \text{ e } \text{\AA}^{-3}$ . In addition to the bonding density peaks, we find indications of lone-pair density near each of the O atoms (Fig. 3). In the bisecting plane of each C–O–C fragment there are two peaks of  $0.15\text{--}0.3 \text{ e } \text{\AA}^{-3}$  lying at distances of about  $0.7 \text{ \AA}$  from the respective O atoms. Although these peaks are diffuse, their spatial distribution corresponds roughly to what we would expect for  $sp^3$  lone pairs rather than to  $sp^2$ , *p* lone pairs. We also find H atoms at distances of  $2.46\text{--}2.79 \text{ \AA}$  roughly along the extensions of the  $sp^3$  directions.

Particularly at O(4), there is a significant difference in the height of the two peaks; the weaker lies approximately along the intramolecular O(4)–H(9') vector and the stronger approximately along the intermolecular O(4)–H(22) vector (see Table 4).

Although the deformation densities obtained so far are little more than indicative, we are confident that they can be improved by inclusion of more extensive high-order data, and we intend to investigate this possibility.

### The space-group problem

As mentioned in the *Experimental* section, there are a few weak reflections that contradict the systematic absences required by the assumed space group *Pbca*. At 100 K, contradictions occur for all three glide planes. They are most serious for the *0kl* zone, where about a dozen reflexions with *k* odd were measured to have statistically significant non-zero intensities. The strongest, the 0,19,0 reflexion, gave several thousand counts compared with a background of a few hundred counts. The *F* values for the strongest, formally absent reflexions are about 5 [ $F(000) = 576$ ].

These anomalous reflexions do not result from double reflection (Renninger effect) and they occur with comparable relative intensities from several crystal specimens. On warming the crystals the intensities of the anomalous reflexions become weaker, but they are still observable above background at room temperature. A similar situation was encountered in the analysis of low-temperature ferrocene (Seiler & Dunitz, 1979).

Our discussion of the present crystal structure has been based on the assumption that the space group is *Pbca*. If this assumption is incorrect, the *Pbca* description applies only to a kind of space-averaged structure and what we have interpreted as atomic vibrations could be partly the expression of the deviation of the actual structure from the *Pbca* idealized one. This difficulty should not seriously invalidate the main conclusions, apart from minor matters of wording.

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