

The Structure of bis[(*o*-Hydroxyphenoxy)ethoxy]ethane Monohydrate[★]

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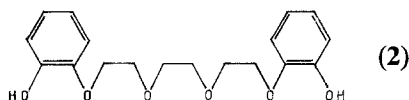
Abstract. The title compound ($C_{18}H_{22}O_6 \cdot H_2O$) crystallizes in space group $P2_12_12_1$ with $a = 25.909(5)$, $b = 8.542(3)$, $c = 8.187(3)$ Å, $Z = 4$. The structure was determined from 1538 X-ray diffractometer data and refined to $R = 8.05\%$. The polyether adopts an annular structure with the water molecule at the center, and is slightly folded like the wings of a butterfly. As usual, all torsion angles about C–O are *trans* and about C–C are *gauche*. This complex displays 3 three-center (bifurcated) and 1 two-center hydrogen bonds, between phenolic hydroxyl and water oxygen. The latter is involved in an infinite homodromic chain $O(1)–H \dots O_w–H \dots O(1)–H \dots$

Key words: Crystal structure, (hydroxyphenoxy) ethoxy ethane hydrate.

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1. Introduction

A series of linear polyethers with good cation binding properties has been synthesized [1,2] and some crystal structures of these polyethers complexed with metal ions have been reported [3,4]. In order to elucidate the molecular conformation and hydrogen bonding scheme of a linear polyether interacting with a water molecule, the crystal structure of bis[(*o*-hydroxyphenoxy) ethoxy]ethane monohydrate (**1**) was determined.



[★] Part XX of the series 'Structures of Polyether Complexes'. For Part XIX, see R. Hilgenfeld, F. Hirayama, V. Bhagwat, W. Saenger, G. Weber, G. M. Sheldrick, H. Sieger, and F. Vögtle, *Isr. J. Chem.*, in press.

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2. Experimental

Thin, lath-shaped crystals of **1** were prepared by slow evaporation of a saturated aqueous solution of **2** in ethyl acetate. A specimen of size $0.1 \times 0.01 \times 0.5 \text{ mm}^3$ was glued onto a glass fiber and used for all X-ray experiments.

Crystals have orthorhombic space group $P2_12_12_1$ with cell constants $a = 25.909(5)$, $b = 8.542(3)$, $c = 8.187(3) \text{ \AA}$ as determined from the angular positions of 20 reflections in the range $30^\circ < 2\theta < 60^\circ$. Other relevant crystal data are: $V = 1811.9 \text{ \AA}^3$, $Z = 4$, $D_c = 1.308 \text{ g cm}^{-3}$, molecular weight = 352.4, chemical formula $\text{C}_{18}\text{H}_{22}\text{O}_6 \cdot \text{H}_2\text{O}$, $\mu_{\text{Cu}} = 7.41 \text{ cm}^{-1}$, $F_{000} = 752$. A total of 1538 integrated X-ray intensities were measured up to $2\theta = 120^\circ$ in the $2\theta/\omega$ scan mode with 30 s for each scan and 15 s for stationary background counts on both sides of each scan using Ni-filtered $\text{CuK}\alpha$ -radiation ($\lambda = 1.54182 \text{ \AA}$). Three standard intensities monitored every 100 reflections were constant with time. Data were corrected for geometrical factors but not for absorption.

The crystal structure was solved by direct methods [5] employing the 175 highest E' s. In several cycles of full-matrix least-squares refinement [6], the nonhydrogen atoms were treated anisotropically, with scattering factors taken from [7], and weights based on counter statistics. Hydrogen atom positions were calculated with C—H distances of 1.08 \AA and those attached to oxygens were located from difference Fourier maps. In refinement cycles, they were treated as 'riding atoms' and their temperature factors were taken as the isotropic equivalent of the bound C and O atoms. The final R -factor of 8.05% could not be reduced further, probably because many reflections were not measured reliably due to the small crystal size and because of the large thermal motion of some atoms of the polyether chain. Table I gives the final positional and thermal parameters of the atoms with their estimated standard deviations.

3. Results and Discussion

Bond distances and angles as well as the atomic numbering scheme are described in Figure 1, and the hydrogen bonding scheme is shown in Figure 2, with some additional data provided in Table II. The molecular packing is shown in the stereoscopic view, Figure 3.

By and large, the C—C and C—O bond distances and associated angles are within the range observed in other polyether crystal structures [3,4]. Therefore, they need not be discussed here in detail, especially since they are not very accurate. They should not deviate too much from normal values because intermolecular forces are only the 'soft' van der Waals and hydrogen bonding interactions.

The torsion angles along the polyether chain are also in agreement with those usually observed in this class of molecules [3,4]. They are *trans* about C—O bonds and + or - *gauche* about C—C, with the angle O(10)—C(11)—C(12)—O(13) being 43° on the lower side, Table IIa. The atoms in the *o*-hydroxyphenoxy ring systems are coplanar, as expected, and the normals to the two rings form an angle of 35.7° , giving the polyether molecule the shape of a butterfly. The polyether oxygen atoms O(1), O(4), O(7), O(13), O(16) are almost coplanar and within $< 0.2 \text{ \AA}$ from the least-squares plane. Atom O(10) is displaced by 0.72 \AA from this plane and the water oxygen atom O_w is displaced by 1.0 \AA , on the same side (see Table IIb) forming the 'apex' of the butterfly structure.

The water oxygen atom is at nearly equal distances from all the polyether oxygens, 2.79 to 3.18 \AA , with the longest separation corresponding to van der Waals contact. The O...O_w...O angles formed between adjacent polyether oxygens are almost constant, from 51.2 to 56.4° . These data suggest that water is an ideal guest for host polyethers consisting

Table I. (left). Fractional atomic coordinates (10^4) and isotropic equivalent (10^3) of anisotropic temperature factors calculated according to $U_{\text{eq}} = 1/3 (U_{11} + U_{22} + U_{33})$, $\sigma = \sqrt{\sigma_{11}^2 + \sigma_{22}^2 + \sigma_{33}^2}$. Estimated standard deviations given in parentheses refer to last digit(s). (right). Fractional atomic coordinates of hydrogen atoms, multiplied by 10^4 .

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}(\text{\AA}^2)$		<i>x</i>	<i>y</i>	<i>z</i>
O _W	4838(2)	6829(7)	1026(8)	84(6)	H(1)	5140	7090	1120
O(1)	5541(2)	9428(7)	2014(7)	84(6)	H(2)	4800	6190	350
O(4)	6001(2)	7077(7)	616(9)	95(7)	H(3)	5380	10200	2920
O(7)	5458(3)	4611(7)	-932(10)	108(8)	H(4)	4370	8460	410
O(10)	4392(4)	4545(11)	-1214(17)	167(17)	H(5)A	6357	5908	-1162
O(13)	3845(3)	7316(7)	-1195(9)	103(7)	H(5)B	6552	5454	588
O(16)	4289(3)	9589(9)	519(11)	114(9)	H(6)A	5751	4302	1119
C(2)	6051(3)	9600(10)	1739(9)	75(8)	H(6)B	6036	3460	-323
C(3)	6307(3)	8360(10)	938(12)	85(9)	H(8)A	5045	3009	99
C(5)	6241(4)	5712(12)	-13(14)	109(12)	H(8)B	5354	2426	-1432
C(6)	5886(6)	4418(14)	67(16)	129(16)	H(9)A	4829	3641	-2998
C(8)	5150(5)	3289(15)	-937(19)	158(20)	H(9)B	4548	2413	-1887
C(9)	4707(6)	3433(19)	-2011(27)	229(37)	H(11)A	4036	4744	-3126
C(11)	3951(5)	4741(13)	-2113(21)	159(22)	H(11)B	3793	3729	-1728
C(12)	3595(4)	5948(12)	-1620(16)	113(13)	H(12)A	3389	5568	-767
C(14)	3553(3)	8624(11)	-892(14)	89(10)	H(12)B	3407	6082	-2604
C(15)	3799(4)	9766(11)	-49(13)	93(10)	H(17)	6152	11772	2712
C(17)	6323(3)	10907(12)	2142(13)	95(10)	H(18)	7053	11955	2049
C(18)	6856(4)	11030(14)	1759(17)	120(14)	H(19)	7439	9902	675
C(19)	7079(3)	9800(17)	939(20)	134(17)	H(20)	6989	7609	-98
C(20)	6814(3)	8434(15)	481(18)	119(14)	H(21)	2894	8013	-2155
C(21)	3057(4)	8828(14)	-1544(18)	123(15)	H(22)	2445	10366	-1488
C(22)	2808(4)	10233(17)	-1155(22)	149(21)	H(23)	2856	12343	-177
C(23)	3046(5)	11382(15)	-323(19)	145(18)	H(24)	3687	11996	833
C(24)	3543(4)	11142(14)	265(15)	110(13)				

of about six oxygen atoms. Longer polyethers were less suitable because the end groups would collide. Therefore, considerable distortions are necessary in the polyether chain in order to avoid a steric collision.

The most remarkable feature of the hydrogen bonding scheme is that all except the O(1)—H...O_W interaction are bifurcated, or three-centered [8], as often found in complexes between polyether ligands and H-acid molecules like water [9, 10], thiourea [11, 13] and a hydrazine derivative [14]. The reason for so many three-center bonds is that there are only four hydrogen atoms as donors but seven oxygen atoms with a total of 14 acceptor sites. The four hydrogens do their best to satisfy seven acceptors in 3×2 (three-center) and 1×1 (one-center) bonds, i.e., seven more acceptor sites remain empty, five on each polyether oxygen except phenolic O(16) which accepts no hydrogen bond at all. Only water oxygen satisfies its full hydrogen bonding potential, reflecting the general notion that ether and phenolic oxygens are only weak hydrogen bond acceptors.

Another important aspect of the hydrogen bonding scheme is that an infinite chain extends through the crystal lattice, formed by O(1)—H...O_W—H...O(1)—H...O_W—H... with O(1)—H and O_W—H groups related by the twofold screw axis along *b*. In this chain, all hydrogen bonds point in the same direction (homodromic [15]) as a consequence of the cooperative effect [16].

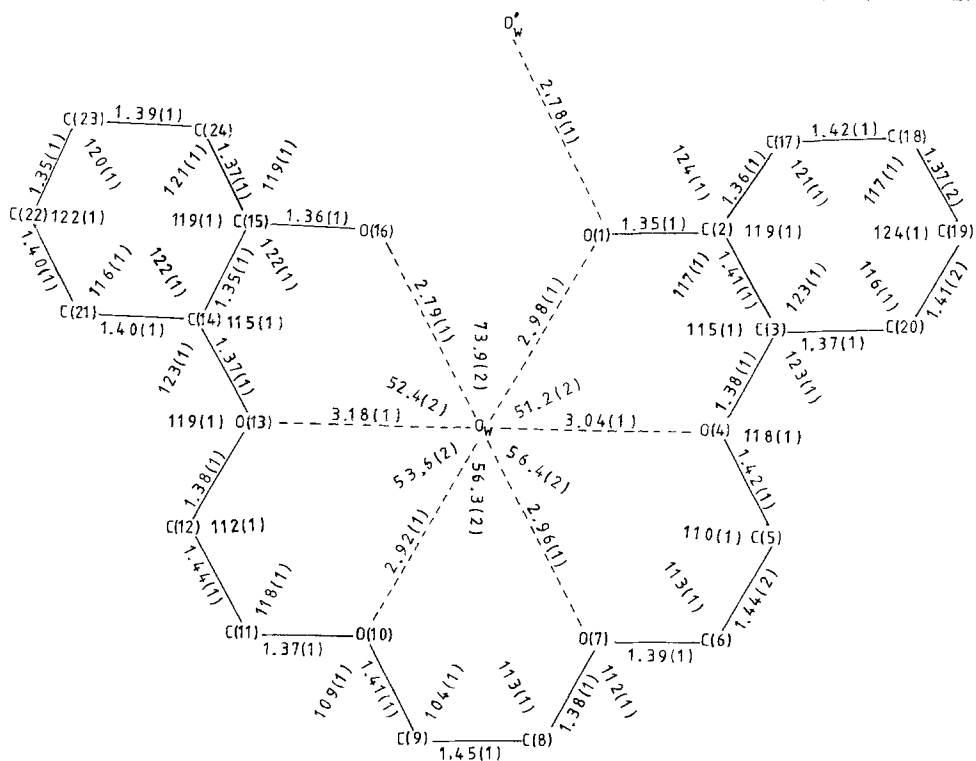


Fig. 1. Description of atom numbering scheme, bond distances (Å) and bond angles (°) in I. Dashed lines indicate hydrogen bonding O...O contacts. Numbers in parentheses refer to estimated standard deviations of the last digit as determined from the least-squares correlation matrix.

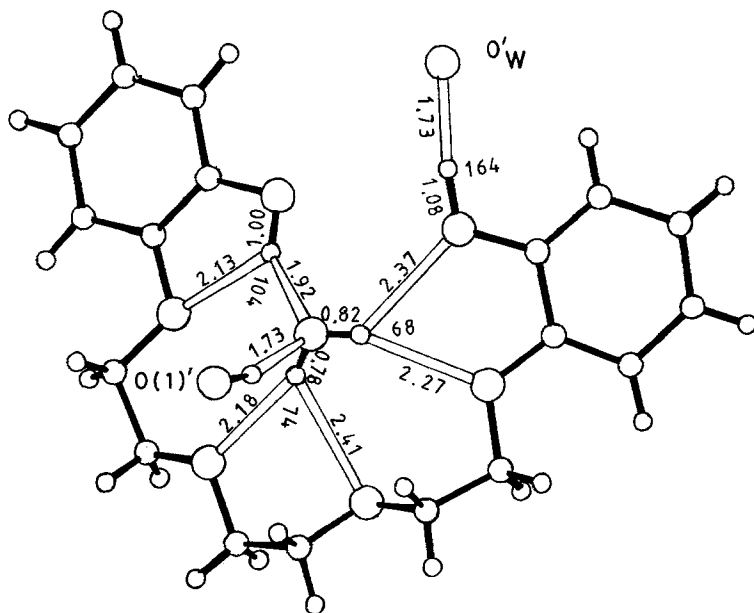


Fig. 2. View of I with hydrogen bonds drawn as open lines and O-H, O...H distances (Å) and O...H...O angles (°) indicated. Atoms marked O(1)' and O_W belong to adjacent asymmetric units and are part of the infinite hydrogen bonding chain. Drawn with ORTEP [17].

Table II. Some geometrical data for I.

(a) Torsion angles (°) in the polyether chain. Standard deviations in parentheses	
O(1)—C(2)—C(3)—O(4)	− 3(1)
C(2)—C(3)—O(4)—C(5)	− 173(1)
C(3)—O(4)—C(5)—C(6)	168(1)
O(4)—C(5)—C(6)—O(7)	65(1)
C(5)—C(6)—O(7)—C(8)	175(1)
C(6)—O(7)—C(8)—C(9)	− 178(1)
O(7)—C(8)—C(9)—O(10)	− 70(2)
C(8)—C(9)—O(10)—C(11)	− 178(1)
C(9)—O(10)—C(11)—C(12)	− 174(1)
O(10)—C(11)—C(12)—O(13)	43(2)
C(11)—C(12)—O(13)—C(14)	172(1)
C(12)—O(13)—C(14)—C(15)	162(1)
O(13)—C(14)—C(15)—O(16)	− 3(2)

(b) Deviations of oxygen atoms from least-squares plane defined by atoms marked*

Atom	Deviation (Å)
O(1)*	0.124
O(4)*	− 0.187
O(7)*	0.145
O(10)	0.722
O(13)*	− 0.087
O(16)*	− 0.015
O _w	1.003

(c) Hydrogen bond angles and bond lengths

O—H...O	O...O (Å)	O—H (Å)	H...O (Å)	O—H...O (°)
O _w —H(1)...O(1)	2.98(1)	0.82	2.37	133
O _w —H(1)...O(4)	3.04(1)		2.27	157
O _w —H(2)...O(7)	2.96(1)	0.78	2.41	127
O _w —H(2)...O(10)	2.92(1)		2.18	158
O(1)—H(3)...O _w ^a	2.78(1)	1.08	1.73	164
O(16)—H(4)...O _w	2.79(1)	1.00	1.92	145
O(16)—H(4)...O(13)	2.66(1)		2.13	112

^a Symmetry code 1 − *x*, 1/2 + *y*, 1/2 − *z*.

Concerning O—H and H...O distances in the hydrogen bonds, the covalent links with water, 0.82 and 0.78 Å are too short compared with 0.97 Å determined from neutron data, whereas the phenolic O—H with 1.00 and 1.08 Å are too long. This could be due to the higher acidity of the latter which is also reflected in short H...O contacts, 1.73 Å and 1.92 Å for H...O_w whereas all other H...O_{ether} and H...O_{phenol} hydrogen bonds are longer, 2.13 Å to 2.41 Å, and in a range commonly observed for three-center bonds. These distances are shorter in reality because the corresponding covalent O—H bonds are determined as being too short from electron density maps, as discussed above. This misplacement also influences the O—H...O angles, which are all in a range acceptable for good two- and three-center hydrogen bonds with values from 112 to 157° (Table IIc).

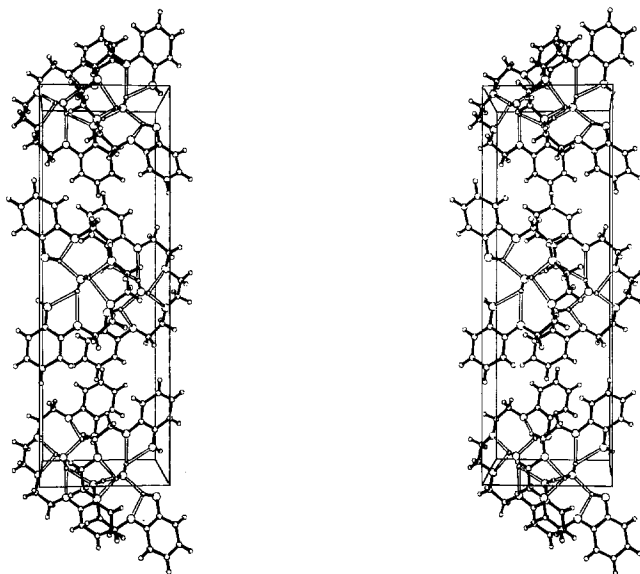


Fig. 3. Stereoplot of a unit cell of **1**, with a vertical, b horizontal and c toward the viewer. All intermolecular contacts are of the van der Waals type except the infinite hydrogen bond chain running parallel to b . Drawn with ORTEP [17].

We can assume that **1** also occurs in aqueous ethyl acetate solutions. If suitable metal ions are added which form complexes with the polyether ligand **2**, the bound water has to be expelled if traces of water are present. The ligand then changes conformation so that its shape is adjusted to the size of the metal ion for optimum coordination with the polyether oxygens.

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