organic compounds

1,17-Diphenyl-2,4,6,8,10,12,14,16-octaoxaheptadecane

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The title compound, $C_{21}H_{28}O_8$, crystallizes with two independent molecules, each with a crystallographic twofold axis passing through the central CH_2 group. The two molecules have different orientations of the terminal benzyl groups. The average C—O bond length in the polyoxymethylene helix, corrected for librational motion, is 1.419 Å. The molecules are connected into layers by intermolecular C—H···O and C—H···π(phenyl) interactions.

Comment

The synthesis of polyoxymethylene helices that are terminated at both ends by phenyl groups has been reported by Noe *et al.* (1994). We have previously reported the crystal structure of 1,13-diphenyl-2,4,6,8,10,12-hexaoxatridecane (Noe *et al.*, 1994) and report here the structure of the related title compound, (I).

Crystals of (I) undergo a reversible phase transition at approximately 155 K, accompanied by a splitting of the reflection profiles in the low-temperature phase. The structure determination of (I) was performed at 178 K, which is well above the phase-transition temperature. The crystal structure of (I) is isomorphous with that of 1,13-diphenyl-2,4,6,8,10,12-hexaoxatridecane (Noe *et al.*, 1994).
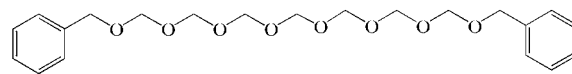
(I)

The molecular structure of compound (I) is shown in Fig. 1. The compound crystallizes with two independent molecules (*A* and *B*), each displaying crystallographic twofold symmetry, with the axis passing through the central CH_2 group. The helical molecule has a chiral axis and both independent molecules have the same chirality. There should be no preference for the molecules to adopt left- or right-handed helices, and thus the bulk material is expected to be a racemate that crystallizes into equal amounts of enantiomorphous crystals.

The two independent molecules in (I) have different orientations of the terminal benzyl groups. The phenyl group of molecule *A* is synperiplanar with the C7—O1 bond [torsion angle C2—C1—C7—O1 = −29.47 (18)°], while the phenyl group of molecule *B* is almost perpendicular to the C18—O5 bond [torsion angle C17—C12—C18—O5 = −78.76 (18)°]. An almost constant C—O bond length, varying between 1.4067 (17) and 1.4192 (16) Å, with an average of 1.413 Å, is observed in the regions C8—C8(1 − *x*, *y*, −*z*) and C19—C19(1 − *x*, *y*, 1 − *z*). The polyoxymethylene helices (without the benzyl groups) behave as rigid bodies with rather large librational motion along the helix axis [51 (2)$^{\circ 2}$ for molecule *A* and 45 (2)$^{\circ 2}$ for molecule *B*], but with almost no librational motion about axes perpendicular to the molecular axis. The average C—O bond length, corrected for librational motion, is 1.419 Å. A value of 1.420 Å was observed in the structure of the related compound 1,15-diphenylheptaoxapentadecane (Bats *et al.*, 2001). These values are in good agreement with the C—O bond lengths of 1.423 and 1.417 Å obtained from *ab initio* calculations on dimethoxymethane (Jeffrey *et al.*, 1978) and 1,3-dimethoxydimethyl ether (Sawanobori *et al.*, 2001). A major factor stabilizing the helix structure is the stereoelec-
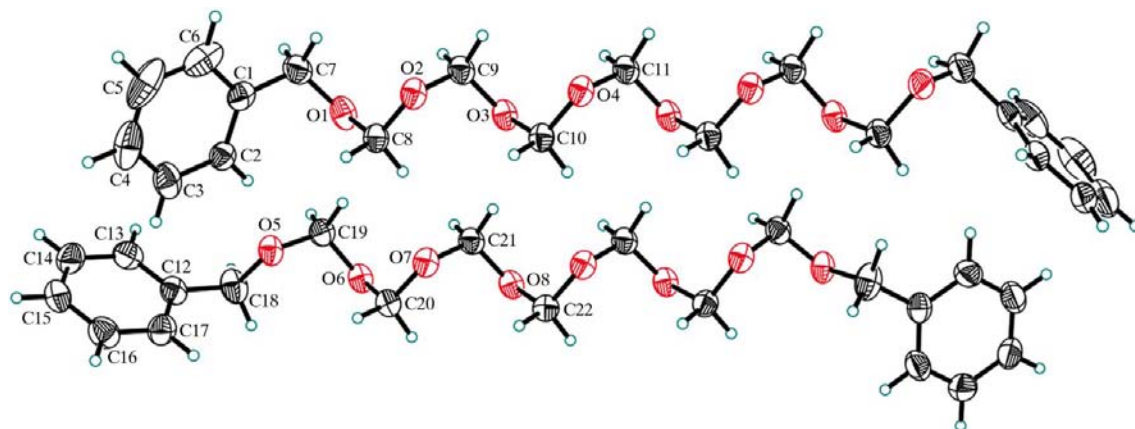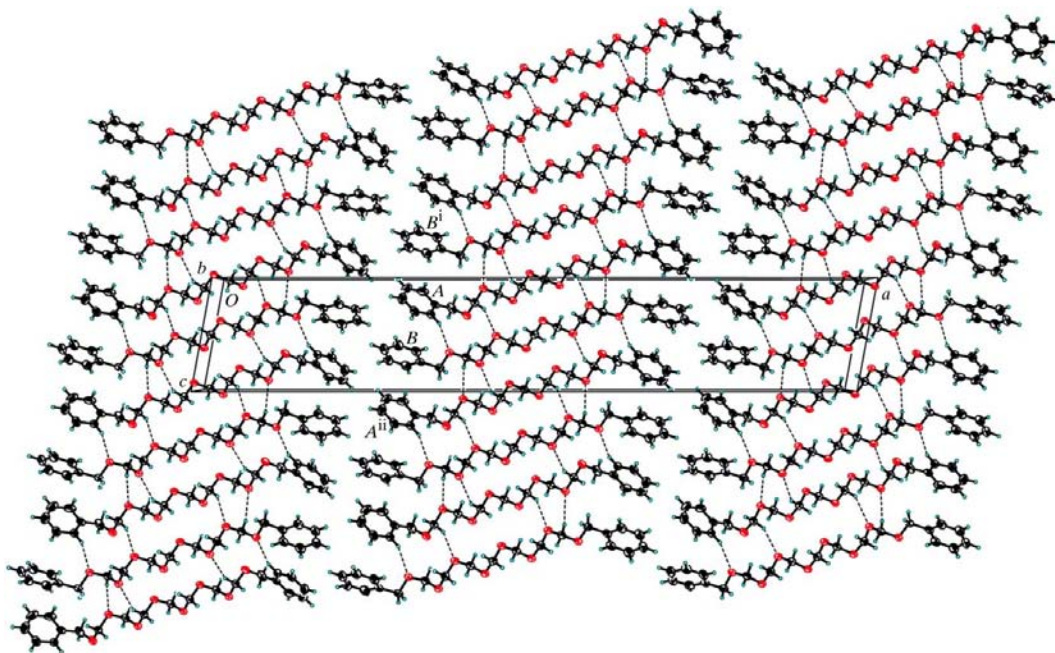

Figure 1
The structures of the two independent molecules of (I), with the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level. Molecule *A* is at the top and molecule *B* at the bottom. Unlabelled atoms are related to labelled atoms by the symmetry operator (1 − *x*, *y*, −*z*) in molecule *A* and by (1 − *x*, *y*, 1 − *z*) in molecule *B*.

Figure 2
The crystal packing of (I), viewed down the b axis. Intermolecular C—H···O contacts with H···O distances shorter than 2.60 Å are shown as broken lines. The positions of molecules A and B are marked by symbols A and B. The molecules are connected into layers parallel to (100) by additional intermolecular interactions along b (not shown). [Symmetry codes: (i) x, y, $z − 1$; (ii) x, y, $z + 1$.]

tronic effect (Kirby, 1983; Deslongchamps, 1984), which results in a preference of *gauche* conformations (all-g^+ or all-g^-) over *trans* conformations for the conjugated C—O bonds. The helix is also stabilized by intramolecular 1→4 C—H···O interactions. The helix of molecule A shows 14 such interactions, with H···O distances between 2.54 and 2.57 Å, while the helix of molecule B shows 12 interactions, with H···O distances between 2.50 and 2.61 Å.

No stereoelectronic effects are expected for the terminal O—C_{benzyl} bonds. Those bond lengths are 1.4276 (19) and 1.4360 (16) Å, respectively, and thus are significantly longer than the remaining C—O bonds. The O1—C8 and O5—C19 bonds in (I) are surprisingly short [1.3985 (16) and 1.3981 (16) Å, respectively]. This bond shortening at the ends of the helices is significant, but its origin is not clearly understood. However, this bond-length variation is reproduced in the *ab initio* calculation of 1,3-dimethoxydimethyl ether (Sawanobori *et al.*, 2001).

The C—O—C bond angles in (I) range between 113.47 (10) and 114.40 (9)°, and are almost constant, with an average value of 114.20°. The O—C—O angles range between 112.17 (17) and 113.18 (12)°, and these values are also almost constant, with an average value of 112.62°. The C—O—C—O torsion angles vary between −61.37 (14) and −68.85 (13)°, with an average value of −65.50°. Almost constant torsion angles, corresponding to an undisturbed helix, are found in molecule A. The helix of molecule B is slightly bent, resulting in deviations of the C—O—C—O torsion angles by up to 4° from their average value.

The crystal packing in (I), shown in Fig. 2, is stabilized by a number of intermolecular C—H···O and C—H···π(phenyl) interactions. Each A molecule is connected to four symmetry-related B molecules, and each B molecule is connected to four symmetry-related A molecules. There are no contacts between A molecules or between B molecules. The molecules are arranged by these intermolecular interactions to form layers parallel to (100). C—H···O contacts with H···O distances of less than 2.61 Å are reported in Table 1. This cut-off value was chosen arbitrarily and there are several additional contacts with still longer distances. The molecules in the layers are also connected by weak intermolecular C(phenyl)—H···π(phenyl) interactions, which have been included in Table 1. The C—H donor groups do not point to the mid-point of the acceptor phenyl groups, but instead are closer to individual C atoms of the acceptor rings. The shortest H···C distances for the four contacts are 2.92, 2.84, 2.94 and 2.86 Å. There are no short intermolecular contacts between the layers along the a direction.

Experimental

Compound (I) was prepared as described by Noe *et al.* (1994). Thin plates were obtained by crystallization from chloroform–hexane (1:1) at low temperature.

Crystal data

$C_{21}H_{28}O_8$	$Z = 4$
$M_r = 408.43$	$D_x = 1.299$ Mg m^{-3}
Monoclinic, $C2$	Cu $K\alpha$ radiation
$a = 47.506$ (8) Å	$\mu = 0.83$ mm^{-1}
$b = 5.392$ (2) Å	$T = 178$ (2) K
$c = 8.288$ (2) Å	Thin plate, colourless
$\beta = 100.38$ (2)°	$0.55 \times 0.55 \times 0.04$ mm
$V = 2088.3$ (10) Å^3	

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Table 1
Hydrogen-bond geometry (Å, °).

$Cg1$ and $Cg2$ are the centroids of the phenyl rings of molecules A and B, respectively.

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
C2—H2$\cdots$O5	0.95	2.45	3.345 (2)	158
C8—H8$A \cdots$O7	0.99	2.59	3.510 (2)	155
C10—H10$A \cdots$O6^{i}	0.99	2.60	3.474 (2)	148
C19—H19$B \cdots$O2^{ii}	0.99	2.58	3.524 (2)	159
C22—H22$A \cdots$O3^{iii}	0.99	2.61	3.497 (2)	149
C3—H3$\cdots Cg2$	0.95	2.90	3.702	143
C6—H6$\cdots Cg2^{iv}$	0.95	3.00	3.745	137
C13—H13$\cdots Cg1^{ii}$	0.95	3.19	3.905	134
C16—H16$\cdots Cg1^{iii}$	0.95	3.06	3.705	126

Symmetry codes: (i) $x, y, z - 1$; (ii) $x, y, z + 1$; (iii) $x, y + 1, z$; (iv) $x, y - 1, z - 1$.

H atoms were located in a difference Fourier map and refined as riding, with Csp^2—H = 0.95 Å and secondary C—H = 0.99 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$. Friedel opposites were not merged. The absolute structure was determined from the anomalous scattering contribution of the O atoms, using 1511 Friedel pairs. The thermal motion analysis was performed using the *WinGX* program package (Farrugia, 1999).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL97*.

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