The geometry of the four carboxyl groups of the two independent molecules lies within the distribution reported earlier for carboxyl groups with no orientational disorder (Leiserowitz, 1976). From the asymmetry in the carboxyl groups, donor and acceptor atoms can clearly be assigned within the cyclic hydrogen-bonded dimers which form chains in the [$\bar{2}$01] direction. The carbonyl hydroxyl groups within both molecules are on the same side of the aliphatic chain. Chain formation, however, is still possible without inversion centers or twofold axes, because the carboxyl hydroxyl groups of the two independent molecules are on different sides of the polymeric chain. If the two independent molecules are regarded as one supramolecule, the two hydroxyl groups are on different sides of the aliphatic chain and chain formation is then possible by translation, which is the only possible mode in the absence of inversion centers and twofold axes as mentioned by Leiserowitz (1976). It is noteworthy that the carbonyl groups are appreciably rotated away from the α-hydroxyl group, whereas normally a planar situation is preferred (Kroon, 1982).

The chains are connected in the [010] direction by two hydrogen bonds formed by the two aliphatic hydroxyl groups and one carboxyl group, the directionality of which can be inferred from stereochemical considerations (Fig. 2).

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2,2′,3,4,4′,5′-Hexachlorodiphenyl Ether*

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Abstract. $C_{12}H_4Cl_6O$, $M_r = 376{\cdot}9$, triclinic, $P\bar{1}$, $a = 8{\cdot}363\ (2)$, $b = 9{\cdot}306\ (2)$, $c = 10{\cdot}655\ (3)$ Å, $\alpha = 103{\cdot}56\ (2)$, $\beta = 98{\cdot}50\ (2)$, $\gamma = 113{\cdot}81\ (2)°$, $V = 709{\cdot}6\ (8)$ Å^3, $Z = 2$, $D_x = 1{\cdot}76$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}20$ mm^{-1}, $F(000) = 372$, $T = 296$ K, final $R = 0{\cdot}032$ for 1650 unique observed reflections. The angle [C(1)—O(1)—C(1′)] between the phenyl rings is 117·2 (3)°. The molecule has a twist conformation, with a twist angle of 85·46 (8)° between the phenyl rings. The chlorine substituents deviate only slightly from the least-squares plane formed by the O and the benzene C atoms [max. deviations −0·089 (1) and 0·090 (1) Å for Cl(4) and Cl(4′), respectively].

* Structures of Chlorinated Diphenyl Ethers. II. Part I: Rissanen, Valkonen & Virkki (1988).

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Introduction. The relationship between the only moderately toxic or nontoxic polychlorinated diphenyl ethers and the acutely toxic polychlorinated dibenzofurans is attracting considerable interest because polychlorinated diphenyl ethers transform to polychlorinated dibenzofurans under UV light and during pyrolysis (Norström, Andersson & Rappe, 1976; Garå, Andersson, Nilsson & Norström, 1981). The presence of polychlorinated diphenyl ethers in various commercial chlorophenol preparations (Garå, Andersson, Nilsson & Norström, 1981) has forced environmental analysts to focus their attention on polychlorinated diphenyl ethers in the biosphere (Paasivirta, Tarhanen & Soikkeli, 1986; Paasivirta, Mäntykoski, Koistinen, Kuokkanen, Mannila & Rissanen, 1989). Diphenyl ethers have been suggested to have four different conformational

Table 1. *Fractional coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	*y*	*z*	B_{eq}(Å^2)
Cl(2′)	0·4894 (1)	0·9358 (1)	0·3014 (1)	5·78 (3)
Cl(2)	0·2598 (1)	0·4139 (1)	−0·0743 (1)	6·01 (3)
Cl(3)	−0·0559 (1)	0·0484 (1)	−0·2075 (1)	6·29 (3)
Cl(4)	−0·3432 (1)	−0·0907 (1)	−0·0523 (1)	5·56 (3)
Cl(4′)	0·9442 (1)	0·7312 (1)	0·5148 (1)	6·24 (3)
Cl(5′)	0·6352 (1)	0·36115 (9)	0·3911 (1)	4·10 (2)
O(1)	0·2391 (3)	0·5903 (2)	0·1857 (3)	4·28 (6)
C(1′)	0·3991 (4)	0·6132 (4)	0·2634 (3)	3·27 (7)
C(1)	0·1024 (4)	0·4283 (3)	0·1268 (4)	3·52 (8)
C(2′)	0·5322 (4)	0·7763 (3)	0·3237 (4)	3·58 (8)
C(2)	0·0949 (4)	0·3328 (4)	0·0029 (4)	3·79 (8)
C(3)	0·6976 (4)	0·8110 (4)	0·4015 (4)	4·03 (9)
C(3)	−0·0466 (4)	0·1710 (4)	−0·0558 (4)	3·91 (8)
C(4)	−0·1727 (4)	0·1112 (4)	0·0115 (4)	3·75 (8)
C(4′)	0·7324 (4)	0·6845 (4)	0·4214 (3)	3·56 (8)
C(5′)	0·5978 (4)	0·5223 (3)	0·3641 (3)	3·02 (7)
C(5)	−0·1674 (4)	0·2087 (4)	0·1332 (4)	3·99 (9)
C(6′)	0·4317 (4)	0·4861 (3)	0·2849 (3)	3·20 (7)
C(6)	−0·0281 (4)	0·3689 (4)	0·1912 (4)	3·95 (9)
H(3′)	0·790 (5)	0·921 (5)	0·444 (4)	5·0
H(5)	−0·267 (5)	0·157 (5)	0·169 (4)	5·0
H(6)	−0·020 (5)	0·435 (5)	0·268 (4)	5·0
H(6′)	0·343 (5)	0·374 (5)	0·246 (4)	5·0

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cl(2′)—C(2′)	1·720 (4)	C(2′)—C(3′)	1·371 (5)
Cl(2)—C(2)	1·713 (4)	C(2)—C(3)	1·400 (3)
Cl(3)—C(3)	1·717 (4)	C(3′)—C(4′)	1·375 (6)
Cl(4)—C(4)	1·725 (3)	C(3′)—H(3′)	0·94 (3)
Cl(4′)—C(4′)	1·723 (3)	C(3)—C(4)	1·368 (5)
Cl(5′)—C(5′)	1·727 (4)	C(4)—C(5)	1·381 (5)
O(1)—C(1′)	1·372 (4)	C(4′)—C(5′)	1·382 (3)
C(1′)—C(2′)	1·387 (3)	C(5)—C(6)	1·384 (4)
C(1′)—C(6′)	1·376 (5)	C(5)—H(5)	0·97 (4)
C(1)—C(2)	1·385 (5)	C(6′)—H(6′)	0·94 (3)
C(1)—C(6)	1·371 (5)	C(6)—H(6)	0·88 (4)
O(1)—C(1)	1·388 (3)	C(5′)—C(6′)	1·378 (4)

C(1′)—O(1)—C(1)	117·2 (3)		
O(1)—C(1)—C(2)	120·1 (3)	O(1)—C(1′)—C(2′)	116·1 (3)
O(1)—C(1)—C(6)	118·5 (2)	O(1)—C(1′)—C(6′)	124·1 (2)
C(2)—C(1)—C(6)	121·3 (2)	C(2′)—C(1′)—C(6′)	119·8 (3)
Cl(2)—C(2)—C(1)	119·5 (2)	Cl(2′)—C(2′)—C(1′)	119·9 (2)
Cl(2)—C(2)—C(3)	121·5 (2)	Cl(2′)—C(2′)—C(3′)	119·8 (2)
C(1)—C(2)—C(3)	119·1 (3)	C(1′)—C(2′)—C(3′)	120·2 (3)
Cl(3)—C(3)—C(2)	119·9 (3)	C(2′)—C(3′)—C(4′)	120·3 (2)
Cl(3)—C(3)—C(4)	120·9 (2)	Cl(4′)—C(4′)—C(3′)	119·3 (2)
C(2)—C(3)—C(4)	119·1 (3)	Cl(4′)—C(4′)—C(5′)	121·4 (3)
Cl(4)—C(4)—C(3)	121·0 (3)	C(3′)—C(4′)—C(5′)	119·3 (3)
Cl(4)—C(4)—C(5)	117·5 (3)	C(4′)—C(5′)—C(6′)	120·8 (4)
C(3)—C(4)—C(5)	121·5 (2)	Cl(5′)—C(5′)—C(6′)	118·8 (2)
C(4)—C(5)—C(6)	119·5 (4)	Cl(5′)—C(5′)—C(4′)	120·4 (3)
C(1)—C(6)—C(5)	119·4 (3)	C(1′)—C(6′)—C(5′)	119·5 (2)

forms (Edlund & Norström, 1977): planar, 'butterfly,' skew and twist. Earlier crystal structure studies on bis(3,4-dichlorophenyl) ether (Singh & McKinney, 1980) and bis(2,4-dichlorophenyl) ether (Rissanen, Valkonen & Virkki, 1988) showed that both molecules adopt the twist conformation with almost the same twist angle in the solid state, even though the substitutents are differently positioned. Relative to the non-*ortho*-substituted diphenyl ether there is no change in conformation when positions 2 and 2′ are occupied by Cl atoms. In both compounds the chlorine substituents are on the same side of the molecule and the main determinants of the twist angle are the H atoms occupying the *ortho* positions at the *endo* side of the etheric angle. Supplementing these two earlier studies on polychlorinated diphenyl ethers we report here the crystal and molecular structure of 2,2′,3,4,4′,5′-hexachlorodiphenyl ether.

Experimental. Colourless crystals synthesized by known method (Nilsson, Norström, Hansson & Andersson, 1977), 0·20 × 0·14 × 0·18 mm, mounted on a glass fibre, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, ω–2θ method, lattice parameters from 25 reflections with $7 < \theta < 15°$, two standard reflections measured every hour, no loss of intensity, 4337 reflections (h −11→11, k −13→12, l 0→14) with $\theta < 30°$, 4337 independent, 1650 with $I > 3\sigma(I)$, Lp correction, empirical absorption correction (Walker & Stuart, 1983); correction factors: max. = 1·053 and min. = 0·862. The structure was solved with direct methods and refined by full-matrix least-squares method using F's, all non-H atoms anisotropic, H atoms with fixed isotropic temperature factor (B_{eq} = 5·0 Å^2), 184 parameters, max. shift/σ = 0·02 on final cycle, R = 0·032, wR = 0·045, $w = 1/[(\sigma F)^2 + (0{\cdot}032F)^2]$, σF from counting statistics, S = 1·08, in final difference map max. and min. peaks 0·27 (5) and −0·32 (5) e Å^{-3}, scattering factors from *International Tables for X-ray Crystallography* (1974), computer programs *MULTAN*11/82 (Main *et al.*, 1982), *SDP* (Frenz, 1978), *PLUTO* (Motherwell, 1978).

Discussion. The atomic coordinates and isotropic temperature factors are listed in Table 1, and the bond distances and angles are given in Table 2.* A view of the molecule and the numbering scheme are shown in Fig. 1. A stereoscopic view of the packing is presented in Fig. 2.

Bond distances and angles are normal. The angle between the phenyl rings [C(1)—O(1)—C(1′)] is 117·2 (3)°. Though slightly smaller than the values of 119·6 (3)° and 120·6 (6)° observed for bis(3,4-dichlorophenyl) ether (Singh & McKinney, 1980) and for bis(2,4-dichlorophenyl) ether (Rissanen, Valkonen & Virkki, 1988), the angle can be regarded as

* Lists of structure factors, bond angles involving H atoms, least-squares planes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51897 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

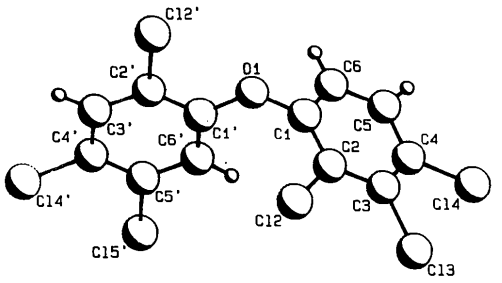

Fig. 1. *PLUTO* plot (Motherwell, 1978) and the numbering scheme for 2,2′,3,4,4′,5′-hexachlorodiphenyl ether.

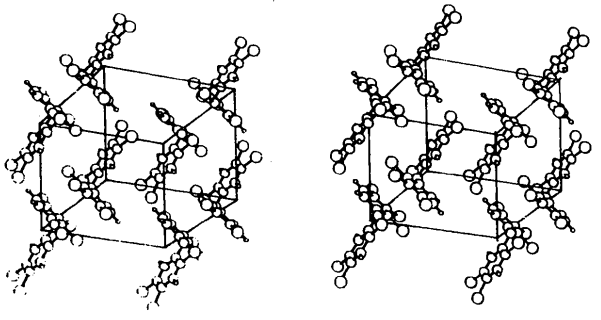

Fig. 2. A stereoscopic view of the packing for 2,2′,3,4,-4′,5′-hexachlorodiphenyl ether. The *a* axis is vertical; and the *c* axis horizontal.

normal for diphenyl ethers. The C—Cl bond distances are almost equal. They are comparable to the values found in bis(3,4-dichlorophenyl) ether and a little shorter than those in bis(2,4-dichlorophenyl) ether. The C—Cl bond distances tend to shorten when the Cl atoms are located on adjacent C atoms and with increasing substitution of the benzene ring by Cl atoms. The Cl substituents lie in the benzene plane, deviations from the calculated least-squares plane being −0·089 (1) and 0·090 (1) Å for Cl(4) and Cl(4′), respectively. The deviations are comparable to those for bis(3,4-dichlorophenyl) ether and bis(2,4-dichlorophenyl) ether. The title compound has a twist conformation, with a twist angle of 85·46 (8)°, which is considerably larger than found in the two earlier-studied polychlorinated diphenyl ethers where it was 73·2° [bis(3,4-dichlorophenyl) ether] and 68·4 (8)° [bis(2,4-dichlorophenyl) ether]. At first there would seem to be no obvious reason for such a large change in the twist angle; however, the closing of the C—O—C angle from about 120° in bis(3,4-dichlorophenyl) ether to 117° in the title compound and the corresponding increase in intramolecular *ortho*-hydrogen distance [H(6)—H(6′)] from 3·04 to 3·34 (7) Å are associated with the large value observed. These two changes in turn may be caused by the packing forces. The molecules are packed along the unit-cell diagonal, with the corresponding phenyl rings of adjacent molecules parallel to each other and are held together by the weak π-electron overlap and van der Waals forces. As a result of the packing there is one intermolecular Cl—Cl distance [Cl(2′)—Cl(5′), 3·471 (1) Å] shorter than the sum of the van der Waals radii.

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