

- POLONSKI, T. & DAUTER, Z. (1986). *J. Chem. Soc. Perkin Trans. 1*, pp. 1781–1788.
- ROMÁN, L. U., DEL RÍO, R. E., HERNÁNDEZ, J. D., CERDA, C. M., CERVANTES, D., CASTAÑEDA, R. & JOSEPH-NATHAN, P. (1985). *J. Org. Chem.* **50**, 3965–3972.
- ROMÁN, L. U., DEL RÍO, R. E., HERNÁNDEZ, J. D., JOSEPH-NATHAN, P., ZABEL, V. & WATSON, W. H. (1981). *Tetrahedron*, **16**, 2769–2778.
- SALMÓN, M. & BIDAN, G. (1985). *J. Electrochem. Soc.* **132**, 1897–1899.
- SHELDRIK, G. M. (1981). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Revision 3. Univ. of Göttingen, Federal Republic of Germany.
- SOEJARTO, D. D., COMPADRE, C. M., MEDON, P. J., KAMATH, S. K. & KINGHORN, A. D. (1983). *Econ. Bot.* **37**, 71–79.

Acta Cryst. (1988). **C44**, 1644–1646

Bis(2,4-dichlorophenyl) Ether*

BY KARI RISSANEN, JUSSI VALKONEN AND LIISA VIRKKI

Department of Chemistry, University of Jyväskylä, SF-40100 Jyväskylä, Finland

(Received 24 March 1988; accepted 13 May 1988)

Abstract. C₁₂H₆Cl₄O, *M_r* = 308.0, orthorhombic, *Fdd2*, *a* = 21.782 (3), *b* = 11.309 (3), *c* = 10.137 (3) Å, *V* = 2497.1 Å³, *Z* = 8 (one half of the molecule in the asymmetric unit), *D_x* = 1.64 Mg m⁻³, λ(Mo *Kα*) = 0.71073 Å, μ = 0.93 mm⁻¹, *F*(000) = 1232, *T* = 296 K, final *R* = 0.025 for 278 unique observed reflections. The oxygen atom is situated on the twofold axis and the angle (C–O–C) between the symmetry-related phenyl rings is 120.6 (6)°. The molecule has a twist conformation, with a twist angle of 68.4 (8)° between the phenyl rings. The chlorine substituents do not deviate markedly from the least-squares plane formed by the oxygen and the benzene carbon atoms [deviations 0.030 (2) and 0.092 (2) Å].

Introduction. Polychlorinated diphenyl ethers occur, together with related chlorinated aromatics, as impurities in various commercial chlorophenol preparations (Gará, Andersson, Nilsson & Norström, 1981) and are now turning up in environmental samples (Paasivirta, Tarhanen & Soikkeli, 1986). Under photochemical exposure, polychlorinated diphenyl ethers give rise by ring closure to polychlorinated dibenzofurans (Norström, Andersson & Rappe, 1976). Some of these, especially 2,3,7,8-tetrachlorodibenzofuran, are considered acutely toxic. The problem of the preferred conformations of diphenyl ethers and the mechanism of the interconversion between stable conformers have been studied extensively for several years mainly by NMR techniques (Benjamins, Dar & Chandler, 1974; Edlund & Norström, 1977). A major reason for this interest is the structural relationships between diphenyl ethers and thyroid hormones (Lehmann, 1972). Four possible forms have been suggested to be involved in the conformational equilibrium of diphenyl ethers (Edlund & Norström, 1977; Fig. 1). The non-toxicity of the

polychlorinated diphenyl ethers compared to polychlorinated biphenyls has been explained by the non-planarity of the diphenyl ethers. Thus they do not fit into the rectangular (3 × 10 Å) dioxin receptor as do the toxic biphenyls (Singh & McKinney, 1980). The crystal structures of halogenated diphenyl ethers have not been extensively studied; only the crystal structure of bis(3,4-dichlorophenyl) ether has been published (Singh & McKinney, 1980). In this series we will be reporting the crystal and molecular structures of various polychlorinated diphenyl ethers, beginning here with the crystal structure of bis(2,4-dichlorophenyl) ether.

Experimental. Colourless crystals synthesized by known method (Nilsson, Norström, Hansson & Andersson, 1977), 0.20 × 0.20 × 0.20 mm, mounted on a glass fibre, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo *Kα*, ω–2θ method, lattice parameters from 25 reflections with 3 < θ < 12°, two standard reflections measured every hour, no loss of intensity, 629 reflections (*h*: 0→25, *k*: 0→13, *l*: 0→12) with θ < 25°, 629 independent, 278 with *I* > 3σ(*I*), *L_p* correction, empirical absorption correction (Walker & Stuart, 1983); correction factors: max. = 1.352 and min. = 0.572, direct methods, refinement by full-matrix

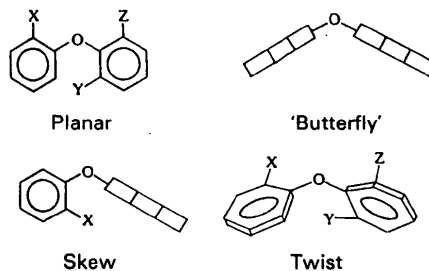


Fig. 1. Possible conformers of diphenyl ether according to Edlund & Norström (1977).

* Structures of Chlorinated Diphenyl Ethers. I.

least-squares method using F^2 s, all non-H atoms anisotropic, H atoms calculated and used as riding atoms in the final refinement with fixed isotropic temperature factor ($B_{\text{eq}} = 5.0 \text{ \AA}^2$), 77 parameters, max. shift/ $\sigma = 0.01$ on final cycle, $R = 0.025$, $wR = 0.035$, $w = 1/[(\sigma F)^2 + (0.032F)^2]$, σF from counting statistics, $S = 0.99$, in final difference map max. and min. peaks 0.13 (4) and -0.13 (4) e \AA^{-3} , scattering factors from *International Tables for X-ray Crystallography* (1974), computer programs *MULTAN11/82* (Main *et al.*, 1982), *SDP* (Frenz, 1978), *PLUTO* (Motherwell, 1978) and *ORTEPII* (Johnson, 1976).

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. 2. A stereoscopic view of the packing is presented in Fig. 3.

Bond distances and angles are normal. The oxygen atom is situated on the twofold axis and the angle between the symmetry-related phenyl rings is 120.6 (6)°. The angle does not deviate markedly from the values observed in the bis(3,4-dichlorophenyl) ether, 119.6 (3)° (Singh & McKinney, 1980) and in a highly substituted diphenyl derivative isolated from the aqueous extract of the brown alga, *Cystophora congesta*, 120.9 (5) and 118.3 (5)° (Gregson & Daly, 1982). In bis(2-bromobenzyl) ether (Berndt, Corey & Glick, 1981) the same angle is 113.9 (10)°. The steric repulsions between the phenyl rings of diphenyl ethers cause the angle to have a larger value than in less sterically hindered ethers. The chlorine-carbon bonds are slightly longer in the title compound than in the bis(3,4-dichlorophenyl) ether (Singh & McKinney, 1980) owing to the *meta* situation of the chlorine atoms. The chlorine substituents are situated on the benzene plane, deviations from the calculated least-squares plane being 0.030 (2) and 0.092 (2) \AA for Cl(2) and Cl(4), respectively, and are comparable to the values observed in bis(3,4-dichlorophenyl) ether (Singh & McKinney, 1980). The title molecule has a twist conformation, with a twist angle of 68.4 (8)°, which is slightly smaller than the same angle (73.2°) in bis(3,4-dichlorophenyl) ether (Singh & McKinney, 1980). The small difference between the twist angles can be explained by the *cis* orientation of the chlorine substituents occupying the *ortho* positions in the title compound. Thus the hydrogen atoms in *ortho* positions are the main determinants for the twist angle observed in both compounds. There may be a weak π -electron

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51027 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (\AA^2)
Cl(2)	0.8514 (1)	0.1516 (2)	0.383	5.25 (4)
Cl(4)	0.9891 (1)	0.3263 (2)	0.7777 (3)	5.74 (5)
O(1)	0.750	0.250	0.5259 (7)	5.1 (2)
C(1)	0.8041 (3)	0.2651 (6)	0.5938 (7)	3.9 (1)
C(2)	0.8560 (3)	0.2234 (6)	0.5341 (7)	3.6 (1)
C(3)	0.9139 (3)	0.2389 (6)	0.5887 (8)	4.2 (1)
C(4)	0.9167 (4)	0.2999 (6)	0.7089 (7)	3.9 (2)
C(5)	0.8658 (3)	0.3454 (7)	0.7690 (8)	4.5 (2)
C(6)	0.8090 (4)	0.3234 (7)	0.7121 (8)	4.7 (2)

Table 2. Bond distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

Cl(2)—C(2)	1.738 (7)	C(1)—C(2)	1.366 (10)	C(3)—C(4)	1.402 (10)
Cl(4)—C(4)	1.749 (8)	C(1)—C(6)	1.372 (10)	C(4)—C(5)	1.366 (11)
O(1)—C(1)	1.376 (8)	C(2)—C(3)	1.389 (10)	C(5)—C(6)	1.389 (11)
Cl(2)—C(2)—C(1)	120.2 (6)	Cl(2)—C(2)—C(3)	117.6 (6)		
Cl(4)—C(4)—C(3)	118.0 (6)	Cl(4)—C(4)—C(5)	119.3 (6)		
O(1)—C(1)—C(2)	116.4 (6)	O(1)—C(1)—C(6)	124.2 (6)		
C(1)—O(1)—C(1)	120.0 (6)	C(1)—C(2)—C(3)	122.1 (7)		
C(1)—C(6)—C(5)	121.2 (7)	C(2)—C(1)—C(6)	119.3 (7)		
C(2)—C(3)—C(4)	116.6 (7)	C(3)—C(4)—C(5)	122.5 (7)		
C(4)—C(5)—C(6)	118.1 (7)				

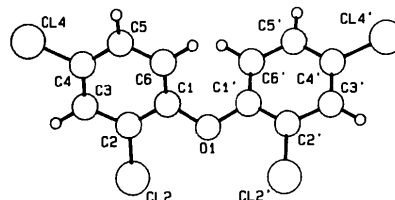


Fig. 2. *PLUTO* plot (Motherwell, 1978) and the numbering scheme for bis(2,4-dichlorophenyl) ether.

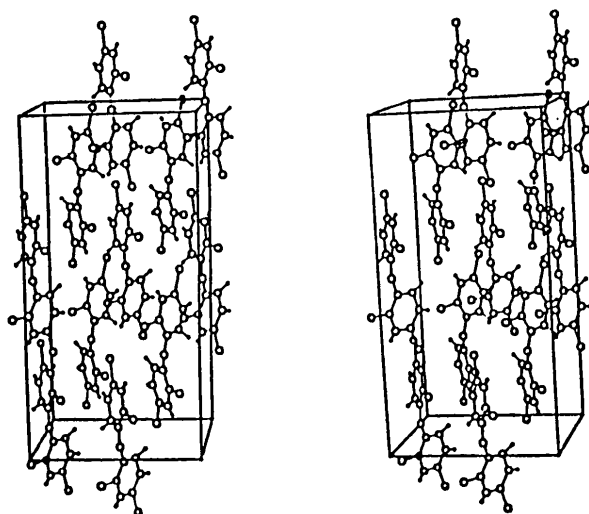


Fig. 3. A stereoscopic view (*ORTEPII*; Johnson, 1976) of packing for bis(2,4-dichlorophenyl) ether. The *a* axis is vertical and the *b* axis horizontal.

overlap between the adjacent molecules, which can also have some effect on the twist angle between the phenyl rings, as in 2,2',3,4',5'-pentachloro-4-methoxybiphenyl (Rissanen, Valkonen & Mannila, 1988). There are no intermolecular contacts shorter than the sums of the van der Waals radii.

The authors thank Dr Tarmo Humpi for synthesizing the compound.

References

- BENJAMINS, H., DAR, H. F. & CHANDLER, W. D. (1974). *Can. J. Chem.* **52**, 3297–3302.
- BERNDT, A. F., COREY, E. R. & GLICK, M. D. (1981). *Acta Cryst.* **B37**, 1294–1296.
- EDLUND, U. & NORSTRÖM, Å. (1977). *Org. Magn. Reson.* **9**, 196–202.
- FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution*. In *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64–71. Delft Univ. Press.
- GARÅ, A., ANDERSSON, K., NILSSON, C.-A. & NORSTRÖM, Å. (1981). *Chemosphere*, **10**, 365–390.
- GREGSON, R. P. & DALY, J. J. (1982). *Aust. J. Chem.* **35**, 649–657.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LEHMANN, P. A. (1972). *J. Med. Chem.* **15**, 404.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MOTHERWELL, W. D. S. (1978). *PLUTO78*. Program for plotting crystal and molecular structures. Univ. of Cambridge, England.
- NILSSON, C.-A., NORSTRÖM, Å., HANSSON, M. & ANDERSSON, K. (1977). *Chemosphere*, **9**, 599–607.
- NORSTRÖM, Å., ANDERSSON, K. & RAPPE, C. (1976). *Chemosphere*, **1**, 21–24.
- PAASIVIRTA, J., TARHANEN, J. & SOIKKELI, J. (1986). *Chemosphere*, **15**, 1429–1433.
- RISSANEN, K., VALKONEN, J. & MANNILA, B. (1988). *Acta Cryst.* **C44**, 682–684.
- SINGH, P. & MCKINNEY, J. D. (1980). *Acta Cryst.* **B36**, 210–212.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1988). **C44**, 1646–1648

Functionalized Hydrocarbons with Condensed Ring Skeletons. I. Tricyclo[7.4.0.0^{2,6}]tridecane Skeleton

BY ANDRÉ G. MICHEL,* MARTIN PROULX AND NADINE MICHEL-DEWEZ

Laboratoire de Chimie Structurale, Université de Sherbrooke, Sherbrooke (Québec), Canada J1K 2R1

(Received 9 September 1987; accepted 17 May 1988)

Abstract. Dimethyl 1,2-*cis*-1,9-*trans*-11-benzyl-oxy-methyl-2-methoxymethoxy-1-methyltricyclo[7.4.0.0^{2,6}]tridec-7-ene-4,4-dicarboxylate, C₂₈H₃₈O₇, *M_r* = 486.57, triclinic, *P* $\bar{1}$, *a* = 12.822 (2), *b* = 15.560 (1), *c* = 6.5851 (7) Å, α = 85.73 (1), β = 96.42 (1), γ = 98.26 (1)°, *V* = 1289.71 Å³, *D_x* = 1.253 Mg m⁻³, *Z* = 2, $\lambda(\text{Mo } K\alpha)$ = 0.71069 Å, μ = 0.0924 mm⁻¹, *F*(000) = 524, room temperature, final *R* = 0.043 for 4285 observed reflexions. The title compound possesses a condensed ring skeleton closely related to the *B*, *C*, and *D* rings of steroid-like molecules. Ring *B* adopts a chair conformation with the methyl group axial at C(1), ring *C* has a boat conformation owing to the double bond between C(7)–C(8) and ring *D* has a β -envelope conformation, with the benzyloxymethyl group equatorial at C(11). The relative stereochemistry is *trans* for the *BC* junction, *syn* for the orientation of the methyl and

methoxymethyl groups, and *trans* for the *CD* junction (*T*–*S*–*T*).

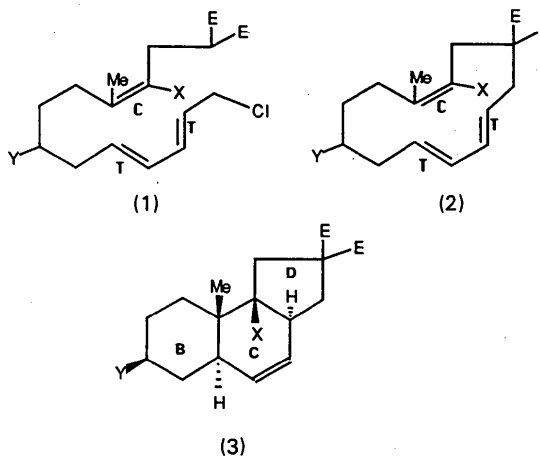


Fig. 1. Molecular schemes (*X* = OCH₂OCH₃, *Y* = CH₂OCH₂C₆H₅, *E* = COOCH₃).

* To whom correspondence should be addressed.