

### 3,3',4,4'-Tetrachlorophenyl Ether [Bis(3,4-dichlorophenyl) Ether]

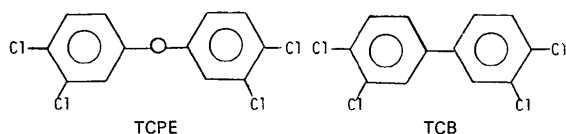
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**Abstract.**  $C_{12}H_6Cl_4O$ ,  $M_r = 307.98$ , triclinic,  $P\bar{1}$ ,  $a = 6.500$  (3),  $b = 12.448$  (5),  $c = 7.807$  (4) Å,  $\alpha = 90.13$ ,  $\beta = 101.73$ ,  $\gamma = 90.62^\circ$ ,  $U = 618.5$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.65$  Mg m<sup>-3</sup>; Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) was used,  $\mu(\text{Mo } K\alpha) = 0.937$  mm<sup>-1</sup>.  $R$  and  $R_w$  are 0.036 and 0.040, respectively, on 1235 reflections. The molecule is non-planar with a dihedral angle of  $73.2^\circ$  between the two benzene rings.

**Introduction.** We are currently investigating the structures of polyhalogenated biphenyls and related compounds, some of which possess high toxicity (Biocca, Moore, Gupta & McKinney, 1975; McKinney, Chae, Gupta, Moore & Goldstein, 1976). One of the more toxic biphenyls is 3,3',4,4'-tetrachlorobiphenyl, TCB. The corresponding ether, 3,3',4,4'-tetrachlorophenyl ether, TCPE, however, is non-toxic (Poland, Glover & Kende, 1976). In order to better understand their structure-activity relationship, we have determined the crystal structure of TCPE. The structure of TCB is still under investigation.



Crystals of TCPE, grown by slow evaporation of a concentrated ethanol solution, were large rhombic plates. One of these plates was mounted along an edge on a glass fiber for preliminary survey by Weissenberg and precession photography. Final cell-constant and intensity data were collected using a crystal fragment,  $0.10 \times 0.25 \times 0.45$  mm, on a Syntex  $P\bar{1}$  diffractometer equipped with an incident-beam graphite monochromator and a Mo X-ray tube ( $\lambda = 0.71069$  Å). 1335 non-equivalent reflections were measured up to  $\sin \theta/\lambda = 0.5$  Å<sup>-1</sup> by the  $\theta/2\theta$  scan technique at a scan rate of  $2^\circ \text{ min}^{-1}$  with stationary background counts of 20 s at the beginning and end of each scan. The data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978)

using 173  $E$ 's  $\geq 1.49$ . The correct solution had an  $R_{\text{Karié}}$  of 27.5 and an absolute FOM of 1.03. All the non-hydrogen atoms were located in the  $E$  map. The H atoms were located in a subsequent difference Fourier synthesis. The structure was refined using 1235 reflections with intensities  $\geq 2\sigma$ . Two of these, 154 and 234, seemed to have instrumental problems since their  $|F_o|$  and  $|F_c|$  values near the end of the refinement were 1.7 and 13.3, and 1.9 and 26.8, respectively. They were, therefore, excluded from the refinement. Full-matrix least-squares refinement was carried out using Ibers's version the *ORFLS* program of Busing, Martin & Levy (1962). H atoms were refined using isotropic and the remainder using anisotropic temperature factors. The function minimized was  $\sum w(|F_o| - |F_c|)^2$ ; the weights,  $w$ , were calculated from the expression  $w = 1/\{1 + [(|F_o| - 34)/31]^2\}$ . The atomic scattering factors for C, O and Cl, including the anomalous-dispersion correction for the last, were taken from *International Tables for X-Ray Crystallography* (1974), and those for H from Stewart, Davidson & Simpson (1965). The final residuals,  $R = \sum |F_o| - |F_c| / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  were 0.036 and 0.040, respectively, for the 1235 data used in the refinement, and 0.043 and 0.070 for all data. No attempt was made to refine the structure in the non-centrosymmetric space group,  $P1$ , since the results of the centrosymmetric refinement were quite satisfactory. The positional parameters derived from the last cycle of refinement with their estimated standard deviations, as derived from the inverse matrix, are given in Table 1.\* The mean shift/ $\sigma$  in the parameters in the final cycle was 0.004, while the maximum was 0.05 [for the  $x$  coordinate of HC(5)]. The standard deviation in an observation of unit weight,  $[\sum w(\Delta F)^2 / (m - n)]^{1/2}$ , was 1.1.

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34683 (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 and their *e.s.d.*'s  $\times 10^4$  ( $\times 10^3$  for H),  $U_{eq} \times 10^3$  ( $\times 10^2$  for H)

	x	y	z	$U_{eq}$ ( $\text{Å}^2$ )
Cl(1)	3148 (2)	-1155 (1)	1141 (1)	69 (1)
Cl(2)	7881 (2)	-786 (1)	2969 (1)	75 (1)
Cl(3)	819 (2)	3509 (1)	-3431 (1)	95 (1)
Cl(4)	-3434 (2)	4585 (1)	-3112 (2)	102 (1)
O	1792 (5)	2613 (2)	3029 (3)	76 (2)
C(1)	3213 (6)	1808 (3)	2933 (4)	52 (2)
C(2)	2561 (6)	858 (3)	2107 (5)	51 (2)
C(3)	3983 (5)	51 (3)	2139 (4)	44 (2)
C(4)	6051 (5)	200 (3)	2979 (4)	48 (2)
C(5)	6656 (7)	1153 (3)	3816 (5)	60 (3)
C(6)	5235 (7)	1953 (4)	3800 (5)	59 (2)
C(1')	636 (6)	3036 (3)	1517 (5)	50 (2)
C(2')	1260 (6)	3035 (3)	-48 (5)	50 (2)
C(3')	13 (6)	3516 (3)	-1478 (5)	54 (2)
C(4')	-1844 (6)	3986 (3)	-1331 (6)	59 (3)
C(5')	-2448 (7)	3984 (3)	263 (7)	70 (3)
C(6')	-1216 (7)	3520 (3)	1662 (7)	67 (3)
HC(2)	116 (6)	74 (3)	156 (4)	5 (3)
HC(5)	801 (6)	124 (3)	430 (5)	6 (1)
HC(6)	560 (5)	256 (3)	438 (4)	5 (1)
HC(2')	250 (5)	273 (2)	-20 (4)	4 (1)
HC(5')	-379 (7)	433 (3)	23 (5)	8 (1)
HC(6')	-156 (6)	353 (3)	269 (6)	8 (1)

**Discussion.** The bond lengths and angles involving the C and H atoms in the two benzene rings are normal, Fig. 1. The four C—C—O bond angles, with values of 116.0, 118.2, 120.6 and 124.0° ( $\sigma = 0.4^\circ$ ) are all significantly different from each other. The two smaller ones, however, are similar to the external C—C—O bond angles (117.7°) and the two larger ones to the internal C—C—O bond angles (122.0°) in dioxins (Singh & McKinney, 1978; Boer, van Remoortere, North & Newman, 1972). The C—O—C angle (119.6°) is approximately 4° larger than that observed in dioxins (116.0°), which is to be expected since the present molecule does not have the constraints of a six-membered dioxin ring. The mean C—O bond length (1.379 Å) compares very well with that observed in dioxins (1.380 Å; Singh & McKinney, 1978), and in

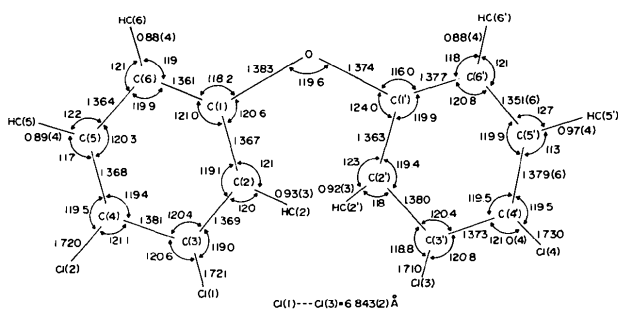
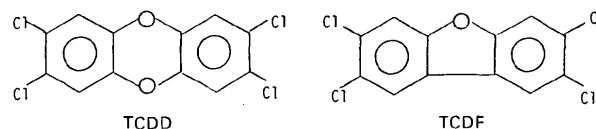


Fig. 1. Bond lengths ( $\text{Å}$ ) and bond angles ( $^\circ$ ) and their *e.s.d.*'s. The *e.s.d.*'s, if not shown, are as follows: 0.005 Å for C—C, 0.004 Å for C—Cl and C—O, 0.03 Å for C—H, 0.4° for C—C—C and C—C—O, 0.3° for C—C—Cl and C—O—C, and 2° for C—C—H.

2,3,7,8-tetrachlorodibenzofuran (TCDF) (1.385 Å; Hubbard, Mighell & Pomerantz, 1978).

The four C—Cl bond lengths have values of 1.710, 1.720, 1.721 and 1.730 Å ( $\sigma = 0.004$  Å), with a mean of 1.720 Å. Since the difference between the minimum and maximum C—Cl bond length is greater than  $3\sigma$ , it is quite likely that our  $\sigma$ 's are underestimated, resulting in part from a neglect of absorption correction.\* The mean C—Cl bond length, however, is quite comparable to those observed in 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) (1.728 Å; Boer *et al.*, 1972), TCDF (1.729 Å; Hubbard *et al.*, 1978) and 2,2',4,4',6,6'-hexachlorobiphenyl (1.730 Å; Singh & McKinney, 1979).



A view of the molecule is shown in Fig. 2. The two benzene rings are planar within experimental error (Table 2), although that containing atoms C(1) to C(6) with a  $\chi^2$  value of 22.8 is less so than that containing atoms C(1') to C(6') with  $\chi^2 = 4.4$ . The molecule itself is non-planar, the dihedral angle between the two benzene rings being 73.2°. The non-planarity of TCPE seems primarily to be due to steric interactions between HC(2) and HC(2') for, if the molecule were forced into a planar conformation, the non-bonded

\* Another reason, suggested by a referee, could be the high thermal anisotropy of the Cl atoms not being adequately described in the refinement by ellipsoidal representation.

Table 2. Displacements, and their *e.s.d.*'s ( $\times 10^3$  for C, Cl and O, and  $\times 10^2$  for H) from least-squares planes of atoms in the phenyl rings

Plane I ( $\chi^2 = 22.8$ )				Plane II ( $\chi^2 = 4.4$ )			
C(1)*	9 (4)	Cl(1)	-58 (1)	C(1')*	4 (3)	Cl(3)	-11 (1)
C(2)*	-1 (4)	Cl(2)	60 (1)	C(2')*	0 (4)	Cl(4)	8 (1)
C(3)*	-8 (3)	O	-76 (3)	C(3')*	-4 (4)	O	-37 (3)
C(4)*	9 (3)	HC(2)	-4 (3)	C(4')*	3 (4)	HC(2')	-1 (3)
C(5)*	-1 (4)	HC(5)	5 (4)	C(5')*	1 (4)	HC(5')	2 (4)
C(6)*	-8 (4)	HC(6)	-5 (3)	C(6')*	-5 (4)	HC(6')	-4 (4)

Dihedral angle between planes I and II = 73.2°

\* Atoms included in the least-squares plane calculation.

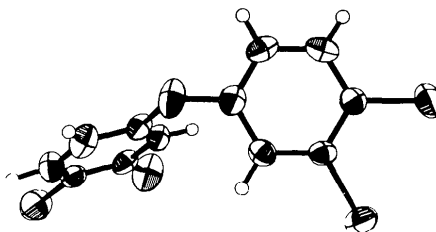


Fig. 2. A view (Johnson, 1976) of the molecule (50% probability thermal ellipsoids) approximately normal to the benzene ring containing atoms C(1') to C(6').

distance between HC(2) and HC(2') of 1.80 Å (1.61 Å assuming a normal C–H distance of 1.08 Å) would become prohibitively small compared to the normal van der Waals distance of 2.40 Å between two H atoms (Pauling, 1960). The observed distance between HC(2) and HC(2') is 3.04 Å.

It has been postulated that a planar or approximately planar polyhalogenated biphenyl would be more toxic than a non-planar one and that the most toxic should be able to fit into a rectangle of approximate dimensions  $3 \times 10$  Å with at least three of the four corners occupied by halogens (Poland & Glover, 1977). In TCPE the distance between the halogen atoms, Cl(2) and Cl(4), which are attached to C(4) and C(4'), respectively, is 10.41 Å. This is very close to the distance, approximately 10.50 Å, between the Cl atoms attached to C(4) and C(4') in toxic TCB. TCPE, however, is not only non-planar in the solid state but, as

shown above, a planar conformation for it would be highly energetic and very unlikely to be observed under any conditions. The molecule would, therefore, be expected to be relatively non-toxic. The same is true if the two halogens at positions 3 and 3' were at positions 5 and 5' instead, since the non-planarity is due to the H at the 2 and 2' positions.

Short intermolecular contacts in the crystal lattice are given in Table 3 and a stereoscopic packing diagram is shown in Fig. 3. Interestingly, three of the four contacts involve at least one Cl atom.

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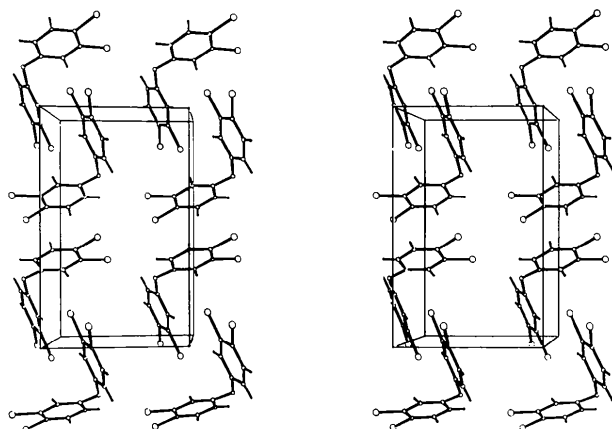


Fig. 3. A stereoscopic view (Johnson, 1976) of the packing of molecules in the unit cell, approximately in the *bc* plane, with the origin in the upper left-hand corner, *b* down the page and *c* to the right.

Table 3. Short intermolecular distances

Atom 1*	Atom 2	Position of atom 2	Distance	vdW†
Cl(2)	Cl(3)	$1 - x, -y, -z$	3.504 (2) Å	3.60 Å
Cl(4)	Cl(4)	$-1 - x, 1 - y, -1 - z$	3.394 (2)	3.60
Cl(3)	O	$x, y, -1 + z$	3.161 (3)	3.20
HC(5')	HC(5')	$-1 - x, 1 - y, -z$	2.29 (9)	2.40

\* Atom 1 refers to an atom in the reference molecule whose coordinates are given in Table 1.

† vdW is the sum of the van der Waals radii given by Pauling (1960).