

## Structures of Chlorinated Methoxybiphenyls. I. 2,2',3,4',5'-Pentachloro-4-methoxybiphenyl

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(Received 18 September 1987; accepted 17 November 1987)

**Abstract.**  $C_{13}H_7Cl_5O$ ,  $M_r=356.5$ , triclinic,  $P\bar{1}$  (No. 2),  $a=9.470$  (1),  $b=9.700$  (1),  $c=10.090$  (1) Å,  $\alpha=64.84$  (1),  $\beta=105.86$  (1),  $\gamma=122.31$  (1)°,  $V=707.7$  Å<sup>3</sup>,  $Z=2$ ,  $D_x=1.67$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)=0.7107$  Å,  $\mu=1.02$  mm<sup>-1</sup>,  $F(000)=356$ ,  $T=296$  K, final  $R=0.049$  for 2963 unique observed reflections. The two chlorine substituents occupying the *ortho* positions (2 and 2') in the phenyl rings and the  $\pi$ -electron overlap between adjacent molecules cause a twist angle of 75.35 (9)° between the phenyl rings. The methoxy group is nearly coplanar {deviation of the methoxy carbon [C(7)] from the least-squares plane is  $-0.208$  (4) Å} with the phenyl ring.

**Introduction.** The two rings of biphenyl have the interesting feature of adopting a coplanar (twist angle  $\varphi=0^\circ$ ) arrangement in the crystalline state (Trotter, 1961; Hargreaves & Rivzi, 1962; Charbonneau & Delugeard, 1976, 1977) owing to the  $\pi$ -electron overlap between adjacent molecules, whereas in the gas stage the angle between the rings is 42° (Bastiansen & Trætteberg, 1962). When the *ortho* positions of the phenyl rings are occupied by substituents other than hydrogen, the  $\pi$ -electron overlap, if it occurs, cannot have such a drastic effect on the twist angle as it does in biphenyl. The chlorine substituent in the *ortho* position in 4-acetyl-2'-chlorobiphenyl (Sutherland & Hoy, 1968) causes a twist angle of 49.2°. The two chlorine substituents in *ortho* positions in 2,2'-dichlorobiphenyl (Rømme, Seip & Aanesen Øymo, 1974) and two methoxy substituents in 2,2',4,4',5,5'-hexamethoxybiphenyl (Chattopadhyay, Banerjee, Majumdar, Podder, Kashino & Haisa, 1987) cause twist angles of 66.8 and 81.2 (1)°, respectively. The degree of *ortho* substitution (2, 2', 6 and 6' positions) and the size of the substituents are the main determinants of the size of the twist angle in substituted biphenyls. Methoxy substituents repel each other more than the smaller chlorine substituents and the twist angle increases. In this series we will be reporting the crystal and molecular structures of various polychlorinated methoxybiphenyls, beginning here with the crystal structure of 2,2',3,4',5'-pentachloro-4-methoxybiphenyl.

**Experimental.** Colourless crystals (m.p. 444–446 K) synthesized by known method (Cadogan, 1962),  $0.50 \times 0.30 \times 0.30$  mm, mounted on a glass fibre, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo  $K\alpha$ ,  $\omega$ - $2\theta$  method, lattice parameters from 25 reflections with  $11 < \theta < 18^\circ$ , two standard reflections measured every hour, no loss of intensity, 4115 reflections ( $h: 0 \rightarrow 13, k: -13 \rightarrow 13, l: -14 \rightarrow 14$ ) with  $\theta < 30^\circ$ , 4115 independent, 2963 with  $I > 3\sigma(I)$ , Lp correction, empirical absorption correction (Walker & Stuart, 1983); correction factors: max. = 1.109 and min. = 0.927, direct methods, refinement by full-matrix least-squares method using unit weights and  $F$ 's, all non-H atoms anisotropic, H atoms from difference map and refined with fixed isotropic temperature factor ( $B_{\text{eq}}=5.0$  Å<sup>2</sup>), 201 parameters, max. shift/ $\sigma=0.02$  on final cycle,  $R=0.049$ ,  $wR=0.049$ ,  $S=0.72$ , final difference map with no features greater than  $0.38$  (7) e Å<sup>-3</sup>, scattering factors from *International Tables for X-ray Crystallography* (1974), computer programs MULTAN11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), SDP (Frenz, 1978), PLUTO (Motherwell & Clegg, 1978) and ORTEPII (Johnson, 1976).

**Discussion.** The atomic coordinates and equivalent 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 packing scheme is presented in Fig. 2.

Bond distances and angles are normal. The two halves of the molecule are in a planar arrangement [max. deviation from the least-squares plane for Cl(2) is  $0.050$  (1) Å] except for the methoxy group, where oxygen [O(4)] and carbon [C(7)] atoms deviate  $-0.046$  (2) and  $-0.208$  (4) Å, respectively. The angle

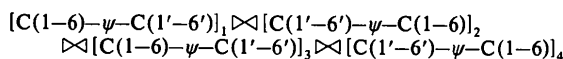
\* Lists of structure factors, anisotropic thermal parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44548 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
Cl(2)	0.2319 (1)	0.1695 (1)	-0.0179 (1)	4.42 (2)
Cl(2')	0.2722 (1)	0.1398 (1)	0.3602 (1)	4.24 (2)
Cl(3)	0.5893 (1)	0.3944 (1)	-0.1384 (1)	4.93 (3)
Cl(4')	-0.3068 (1)	-0.4516 (1)	0.4833 (1)	4.76 (2)
Cl(5')	-0.2066 (1)	-0.5951 (1)	0.3151 (1)	4.49 (2)
O(4)	0.8248 (3)	0.2834 (3)	0.0347 (3)	3.92 (6)
C(1)	0.3555 (3)	-0.0207 (3)	0.2082 (3)	2.82 (6)
C(1')	0.1905 (3)	-0.1255 (3)	0.2734 (3)	2.76 (6)
C(2)	0.3901 (3)	0.1198 (3)	0.0772 (3)	2.85 (6)
C(2')	0.1403 (3)	-0.0647 (3)	0.3462 (3)	3.03 (7)
C(3)	0.5463 (3)	0.2188 (3)	0.0205 (3)	3.00 (7)
C(3')	-0.0116 (4)	-0.1646 (3)	0.4091 (3)	3.35 (7)
C(4)	0.6748 (3)	0.1773 (3)	0.0961 (3)	3.04 (7)
C(4')	-0.1191 (3)	-0.3287 (3)	0.4015 (3)	3.03 (7)
C(5)	0.6403 (4)	0.0356 (4)	0.2240 (4)	3.62 (8)
C(5')	-0.0727 (3)	-0.3928 (3)	0.3296 (3)	2.94 (7)
C(6)	0.4838 (4)	-0.0605 (4)	0.2795 (4)	3.48 (8)
C(6')	0.0804 (3)	-0.2912 (3)	0.2678 (3)	3.03 (7)
C(7)	0.9635 (4)	0.2578 (4)	0.1157 (4)	4.60 (10)
H(3')	-0.051 (4)	-0.117 (4)	0.457 (4)	5.0
H(5)	0.726 (4)	0.014 (4)	0.273 (4)	5.0
H(6)	0.455 (4)	-0.162 (4)	0.371 (4)	5.0
H(6')	0.118 (4)	-0.340 (4)	0.227 (4)	5.0
H(7A)	0.944 (4)	0.143 (4)	0.135 (4)	5.0
H(7B)	1.053 (4)	0.350 (4)	0.049 (4)	5.0
H(7C)	0.977 (4)	0.268 (4)	0.216 (4)	5.0

C(4)—O(4)—C(7), 117.6 (2)°, is very near to values reported for similarly oriented methoxy groups (Chattopadhyay *et al.*, 1987). The distance of 1.485 (4) Å between the phenyl rings [C(1)—C(1')] is slightly shorter than in unsubstituted biphenyl, 1.506 (17) Å (Trotter, 1961), slightly longer than in 4-acetyl-2'-fluorobiphenyl, 1.479 (10) Å (Young, Tollin & Sutherland, 1968), and very similar to the distances in 4-acetyl-2'-chlorobiphenyl (Sutherland & Hoy, 1968), 2,2'-dichlorobiphenyl (Rømming *et al.*, 1974) and 2,2',4,4',5,5'-hexamethoxybiphenyl (Chattopadhyay *et al.*, 1987) [1.490 (10), 1.489 (5) and 1.483 (2) Å, respectively]. A similar narrowing of the endocyclic angle at C(1) and C(1') as in 2,2',4,4',5,5'-hexamethoxybiphenyl (Chattopadhyay *et al.*, 1987) indicates small inter-ring conjugation. Despite the similarity in the C(1)—C(1') distances, the twist angle between the phenyl rings is greater in the title compound [75.35 (9)°] than in 2,2'-dichlorobiphenyl (Rømming *et al.*, 1974) owing to the  $\pi$ -electron overlap between adjacent molecules, and smaller than in 2,2',4,4',5,5'-hexamethoxybiphenyl (Chattopadhyay *et al.*, 1987) owing to the smaller size of the substituents. The molecules of 2,2',3,4',5'-pentachloro-4-methoxybiphenyl are packed in parallel right-handed helices created by the  $\pi$ -electron overlap between adjacent molecules:



where  $\times$  represents the  $\pi$ -electron overlap and  $\psi$  the twist angle between the phenyl rings.

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

Cl(2)—C(2)	1.729 (3)	C(4)—C(5)	1.380 (4)
Cl(4')—C(4')	1.721 (3)	C(5')—C(6')	1.381 (4)
O(4)—C(7)	1.430 (4)	C(6)—H(6)	0.99 (3)
C(1')—C(2')	1.405 (6)	C(7)—C(7B)	0.98 (3)
C(2)—C(3)	1.384 (4)	Cl(3)—C(3)	1.712 (2)
C(3')—C(4')	1.380 (4)	O(4)—C(4)	1.355 (3)
C(5)—C(6)	1.383 (4)	C(1)—C(2)	1.393 (3)
C(5)—H(5)	0.90 (4)	C(1')—C(6')	1.388 (4)
C(7)—H(7A)	0.96 (4)	C(3)—C(4)	1.407 (5)
Cl(2')—C(2')	1.734 (3)	C(4')—C(5')	1.399 (6)
Cl(5')—C(5')	1.721 (3)	C(3')—H(3')	1.02 (5)
C(1)—C(1')	1.485 (4)	C(6')—H(6')	0.97 (5)
C(1)—C(6)	1.389 (5)	C(7)—H(7C)	1.03 (4)
C(2')—C(3')	1.377 (4)		
Cl(2)—C(2)—C(1)	118.8 (2)	C(1')—C(2')—C(3')	121.6 (3)
Cl(2')—C(2')—C(3')	118.6 (3)	C(2)—C(1)—C(6)	117.4 (3)
Cl(4')—C(4')—C(3')	119.1 (3)	C(2')—C(3')—H(3')	121 (2)
Cl(5')—C(5')—C(6')	120.1 (3)	C(3')—C(4')—C(5')	119.5 (3)
O(4)—C(7)—H(7A)	112 (2)	C(4)—O(4)—C(7)	117.6 (2)
C(1)—C(1')—C(2')	122.1 (2)	C(5')—C(6')—H(6')	123 (2)
C(1)—C(6)—C(5)	121.7 (3)	H(7B)—C(7)—H(7C)	116 (3)
C(1')—C(1)—C(6)	119.8 (2)	Cl(2)—C(2')—C(1')	119.9 (2)
C(1')—C(6')—H(6')	118 (2)	Cl(3)—C(3)—C(4)	118.8 (2)
C(2')—C(3')—C(4')	120.2 (4)	Cl(5')—C(5')—C(4')	120.2 (5)
C(3)—C(4)—C(5)	118.8 (3)	O(4)—C(4)—C(5)	125.5 (3)
C(4')—C(5')—C(6')	119.5 (3)	O(4)—C(7)—H(7C)	108 (3)
C(4)—C(5)—H(5)	117 (2)	C(1)—C(2)—C(3)	121.9 (3)
H(7A)—C(7)—H(7B)	114 (4)	C(1')—C(1)—C(2)	122.9 (3)
Cl(2)—C(2)—C(3)	119.3 (2)	C(1')—C(6')—C(5')	122.1 (4)
Cl(3)—C(3)—C(2)	121.6 (3)	C(2)—C(3)—C(4)	119.6 (2)
Cl(4')—C(4')—C(5')	121.3 (2)	C(2')—C(1')—C(6')	117.1 (3)
O(4)—C(4)—C(3)	115.7 (2)	C(4')—C(3')—H(3')	118 (2)
O(4)—C(7)—H(7B)	100 (2)	C(4)—C(5)—C(6)	120.6 (3)
C(1)—C(1')—C(6')	120.8 (4)	C(6)—C(5)—H(5)	122 (2)
C(1)—C(6)—H(6)	116 (2)	H(7A)—C(7)—H(7C)	106 (3)

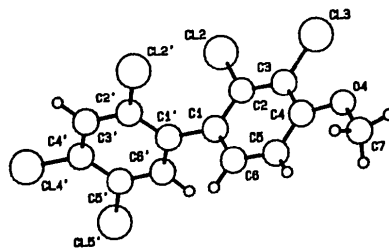


Fig. 1. PLUTO plot (Motherwell &amp; Clegg, 1978) and numbering scheme for 2,2',3,4',5'-pentachloro-4-methoxybiphenyl.

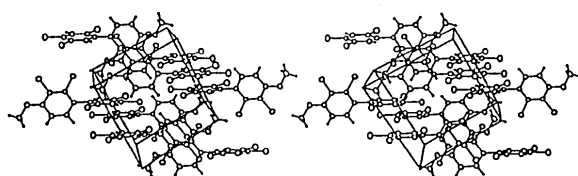


Fig. 2. Stereoscopic view of packing (ORTEPII; Johnson, 1976) for 2,2',3,4',5'-pentachloro-4-methoxybiphenyl.

The turn of one molecule relative to the adjacent one is the same as the twist angle between the phenyl rings, 75.35 (9)°, so that four molecules almost define one complete turn of the helix. The shortest intermolecular distance between chlorine atoms, [Cl(4')—Cl(4')](-*x*, -*y*, -*z*) = 3.334 (2) Å, is noticeably shorter than the sum of the van der Waals

radii (3.6 Å), indicating strong  $\pi$ -electron overlap. All other intermolecular distances are longer than the sums of the van der Waals radii.

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## Structures of Chlorinated Methoxybiphenyls. II. 2,2',4,4',5',6-Hexachloro-3-methoxybiphenyl

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(Received 22 September 1987; accepted 17 November 1987)

**Abstract.**  $C_{13}H_6Cl_6O$ ,  $M_r = 390.9$ , monoclinic,  $P2_1/c$  (No. 14),  $a = 9.821$  (2),  $b = 22.041$  (4),  $c = 7.259$  (1) Å,  $\beta = 102.53$  (2)°,  $V = 1533.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.69$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 1.12$  mm<sup>-1</sup>,  $F(000) = 776$ ,  $T = 296$  K, final  $R = 0.036$  for 1733 unique observed reflections. The three chlorine substituents occupying the *ortho* positions (2, 2' and 6) in the phenyl rings cause a twist angle of 82.72 (11)° between the rings. The methoxy group is perpendicular to the phenyl ring {deviation of the methoxy carbon [C(7)] from the least-squares plane is 1.253 (5) Å} owing to the chlorine substituents occupying the 2- and 4-positions.

**Introduction.** The degree of *ortho* substitution (2, 2', 6 and 6' positions) and the size of the substituents have been identified as the main causes of the twist angle observed in substituted biphenyls (Rissanen, Valkonen & Mannila, 1988; Chattopadhyay, Banerjee, Majumdar, Podder, Kashino & Haisa, 1987). Under some conditions  $\pi$ -electron overlap between adjacent molecules may sometimes contribute a small additional effect (Rissanen, Valkonen & Mannila, 1988). The

orientation of the methoxy group is strongly affected by the substituents occupying the positions on either side of the methoxy-substituted benzene C atom. The methoxy group is coplanar or nearly coplanar with the phenyl ring when there is no or only one substituent present on the adjacent benzene C atoms (Rissanen, Valkonen & Mannila, 1988; Chattopadhyay *et al.*, 1987), but it assumes a perpendicular orientation when there are substituents on both adjacent benzene C atoms (Rissanen, Valkonen & Knuutinen, 1987).

**Experimental.** Colourless crystals synthesized by known method (Cadogan, 1962),  $0.25 \times 0.15 \times 0.05$  mm, mounted on a glass fibre, Enraf-Nonius CAD-4 diffractometer, graphite-monochromatized Mo  $K\alpha$ ,  $\omega$ - $2\theta$  method, lattice parameters from 25 reflections with  $6 < \theta < 14^\circ$ , two standard reflections measured every hour, no loss of intensity, 4459 reflections ( $h: -13 \rightarrow 13$ ,  $k: -30 \rightarrow 0$ ,  $l: 0 \rightarrow 10$ ) with  $\theta < 30^\circ$ , 4459 independent, 1733 with  $I > 3\sigma(I)$ ,  $L_p$  correction, empirical absorption correction (Walker & Stuart, 1983); correction factors: max. = 1.218 and min. = 0.843, direct methods, refinement by full-matrix