Acta Cryst. (1986). C**42**, 1176–1178

2,2′,4,4′,5,5′-Hexachlorobiphenyl (PCB 153)

By H. J. Geise and A. T. H. Lenstra

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, *B*-2610 *Wilrijk, Belgium*

and C. de Borst and G. W. H. Moes

Prins Maurits Laboratorium TNO, PO Box 45, 2280 *AA Rijswijk, The Netherlands*

(*Received* 1 *November* 1985; *accepted* 7 *February* 1986)

Abstract. $C_{12}H_4Cl_6$, $M_r = 360{\cdot}9$, monoclinic, $P2_1/n$, $a = 12{\cdot}394\,(2)$, $b = 8{\cdot}042\,(1)$, $c = 13{\cdot}383\,(2)$ Å, $\beta = 94{\cdot}48\,(2)^\circ$, $V = 1329{\cdot}8\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}802$ Mg m^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}26$ mm^{-1}, $F(000) = 712$, room temperature, $R = 0{\cdot}045$ for 1924 independent observed reflections. The determination confirms the substitution pattern of the biphenyl moiety by Cl atoms inferred from NMR spectroscopy. The interplanar angle between the phenyl rings is 59(1)°, while the relative disposition of the *ortho*-Cl atoms on both rings is closer to *anti* than to *syn*.

Introduction. Polychlorinated biphenyls (PCB's) form a class of compounds of which some members are a potential threat to the environment. The analysis of the title compound (PCB 153) was undertaken in order to provide unequivocal identification of a sample, prepared as part of a series of high-purity PCB isomers within the reference-materials programme of the Community Bureau of Reference – BCR (Directorate General for Science, Research and Development, Commission of the European Communities, Brussels). The immediate aim of the X-ray analysis was to confirm the substitution pattern of the biphenyl moiety by the six Cl atoms.

Experimental. The title compound was prepared by Inveresk Research International Ltd, Musselburgh EH21 7UB, Scotland. A 100 mg sample of this material was received at the Prins Maurits Laboratorium TNO, where attempts were made to prepare suitable crystals for X-ray diffraction studies.

Samples of approximately 30 mg were dissolved in 2–5 ml ethanol in centrifuge tubes. The tubes were then placed in a beaker, containing a layer of ethanol at the bottom. After covering the beaker with a Petri dish, the beaker was placed in a thermostated cabinet. By means of a time-controlled switch a cooling and heating cycle was maintained over several weeks. During the cooling periods of 4 h a temperature of 278 K was sustained, while during the heating periods of 2 h the temperature was allowed to rise slowly to 288 K.

Several solvents were tested for their usefulness, *i.e.* methanol, ethanol, hexane, ethyl acetate and ethanol–water mixtures, but ethanol seemed to give the best results.

Due to the limited amount of the sample, only a limited number of experiments were possible with this material. Nevertheless, crystals of suitable dimensions could be obtained in this way, and it was decided that enough material remained to allow for an NMR analysis to be carried out.

The solution of PCB 153 in $CDCl_3$, which was used for this analysis, was set aside for several weeks and left unattended. Surprisingly, the optimum conditions for the formation of large crystals were apparently created in this way.

The very slow diffusion of $CDCl_3$ vapour through the plastic stopper of the NMR tube caused a single, large cubic crystal to be formed and this crystal was used for the X-ray diffraction. Unit-cell dimensions deduced from 25 high-order reflections. Enraf–Nonius CAD-4 diffractometer, ω/θ-scan mode, Mo radiation monochromatized by pyrolytic graphite. Max. Bragg angle 27°; 2579 independent measurements of which 1924 reflections considered observed $[I \geq 2\sigma(I)]$, $-14 \leq h \leq 14$, $0 \leq k \leq 9$, $0 \leq l \leq 15$. Intensity control, every 2 h, showed no drift. Space group inferred from systematic extinctions. No absorption correction applied ($\mu = 1{\cdot}26$ mm^{-1}, crystal size $0{\cdot}2 \times 0{\cdot}15 \times 0{\cdot}15$ mm). Structure solved using *MULTAN* (Germain, Main & Woolfson, 1971). H atoms found from

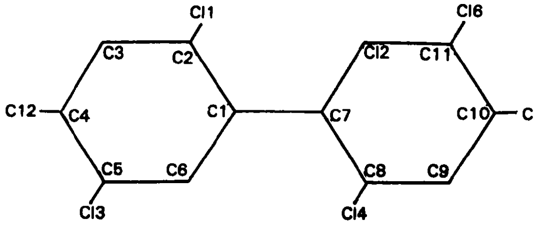

Fig. 1. Structural formula and atomic-numbering scheme of the title compound.

0108-2701/86/091176-03$01.50

Table 1. *Distances* (Å) *of substituent atoms to the corresponding phenyl planes, with e.s.d.'s in parentheses*

Plane *A*: C(1), C(2), C(3), C(4), C(5), C(6)
Plane *B*: C(7), C(8), C(9), C(10), C(11), C(12)

	Distance to plane *A*		Distance to plane *B*
Cl(1)	0·031 (2)	Cl(4)	−0·041 (2)
Cl(2)	−0·061 (2)	Cl(5)	0·009 (2)
Cl(3)	0·012 (2)	Cl(6)	−0·028 (2)
C(7)	−0·141 (5)	C(1)	0·072 (5)

subsequent difference Fourier map. Least-squares refinements (on *F*'s) on all positional and thermal parameters: anisotropic for C and Cl, isotropic for H. Reflections given individual weights based on counting statistics. Extinction correction (Zachariasen, 1963) applied; refined to an extinction coefficient of 0·28 × 10^{-6} mm. Convergence reached at $R = 0{\cdot}045$, $wR = 0{\cdot}052$, $S = 5{\cdot}15$, $(\Delta/\sigma)_{\max} = 0{\cdot}02$, 180 variables.* Max. noise level in final difference Fourier map 0·25 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius *SDP* (Frenz, 1978) employed.

^{1}H NMR (in $CDCl_3$ with Me_4Si as reference) showed two singlets at $\delta = 7{\cdot}34$ and $7{\cdot}60$, tentatively assigned to H(3) and H(6), respectively. ^{13}C NMR (in $CDCl_3$ with $CDCl_3$ as reference) gave six signals at $\delta = 130{\cdot}9$, 131·0, 131·7, 131·8, 133·9 and 135·9, tentatively assigned to C(6), C(2), C(3), C(5), C(4) and C(1), respectively. Even though the assignments are provisional, the spectra indicate that, on both rings, the H atoms are in *para* positions to each other.

Discussion. The atomic-numbering scheme is presented in Fig. 1. The analysis identified the compound unequivocally as 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB 153), confirming the spectroscopic conclusion.

Both phenyl rings are individually planar, none of the C atoms being more than 2σ outside the corresponding least-squares plane. Substituents on the phenyl fragments are not located in these planes. Table 1 lists their distances.

A schematic view of the molecule along the central C(1)—C(7) bond, given in Fig. 2, shows that the disposition of both *ortho*-Cl atoms, Cl(1) and Cl(4), with respect to the C(1)—C(7) axis is closer to *anti* than to *syn*. This is remarkable because in all *ortho,ortho*′-dihalobiphenyls the prevailing conformer is the one with the halogens in *syn* rather than *anti* position (Bastiansen, Kveseth & Møllendal, 1979). The angle between the least-squares planes through the phenyl rings is 59 (1)°. This is lower than the value, 67°, found in crystalline 2,2′-dichlorobiphenyl (Rømming, Seip & Aanesen Øymo, 1974), and agrees well with the value, 63°, obtained by Stølevik & Thingstad (1984) from molecular-mechanics calculations on the free molecule 2,2′-dichlorobiphenyl. Interestingly, the latter authors state that the shallow potential curve for rotation around C(1)—C(7), calculated with excess charges on the Cl atoms, shows a slight preference for the *anti* position of the *ortho*-Cl atoms.

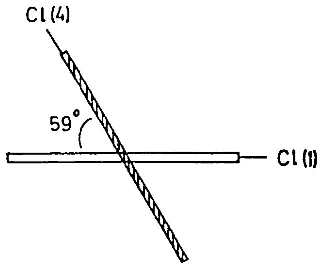

Fig. 2. Schematic view of the molecule as seen along the central C(1)—C(7) bond.

Table 2. *Bond lengths* (Å) *and valence angles* (°) *in the title compound*

E.s.d.'s are in parentheses.

Cl(1)—C(2)	1·721 (2)	Cl(4)—C(8)	1·727 (2)
Cl(2)—C(4)	1·735 (2)	Cl(5)—C(10)	1·738 (2)
Cl(3)—C(5)	1·718 (2)	Cl(6)—C(11)	1·713 (2)
C(1)—C(2)	1·406 (3)	C(7)—C(8)	1·402 (3)
C(2)—C(3)	1·389 (3)	C(8)—C(9)	1·382 (3)
C(3)—C(4)	1·354 (3)	C(9)—C(10)	1·363 (3)
C(4)—C(5)	1·392 (3)	C(10)—C(11)	1·395 (3)
C(5)—C(6)	1·390 (3)	C(11)—C(12)	1·384 (3)
C(6)—C(1)	1·366 (3)	C(12)—C(7)	1·374 (3)
C(1)—C(7)	1·502 (3)	C(7)—C(1)	1·502 (3)
C(3)—H(3)	0·94 (2)	C(9)—H(9)	0·96 (2)
C(6)—H(6)	0·95 (2)	C(12)—H(12)	1·01 (2)
Cl(1)—C(2)—C(1)	121·6 (2)	Cl(4)—C(8)—C(7)	122·1 (2)
Cl(1)—C(2)—C(3)	118·3 (2)	Cl(4)—C(8)—C(9)	117·0 (2)
Cl(2)—C(4)—C(3)	119·8 (2)	Cl(5)—C(10)—C(9)	119·1 (2)
Cl(2)—C(4)—C(5)	119·2 (2)	Cl(5)—C(10)—C(11)	119·8 (2)
Cl(3)—C(5)—C(4)	122·0 (2)	Cl(6)—C(11)—C(10)	121·4 (2)
Cl(3)—C(5)—C(6)	120·0 (2)	Cl(6)—C(11)—C(12)	120·4 (2)
C(2)—C(1)—C(6)	117·9 (2)	C(8)—C(7)—C(12)	118·0 (2)
C(1)—C(2)—C(3)	120·1 (2)	C(7)—C(8)—C(9)	120·8 (2)
C(2)—C(3)—C(4)	120·4 (2)	C(8)—C(9)—C(10)	119·7 (2)
C(3)—C(4)—C(5)	121·0 (2)	C(9)—C(10)—C(11)	121·1 (2)
C(4)—C(5)—C(6)	118·0 (2)	C(10)—C(11)—C(12)	118·3 (2)
C(5)—C(6)—C(1)	122·5 (2)	C(11)—C(12)—C(7)	122·1 (3)
C(2)—C(1)—C(7)	122·3 (2)	C(8)—C(7)—C(1)	122·0 (2)
C(6)—C(1)—C(7)	119·7 (2)	C(12)—C(7)—C(1)	120·0 (2)
H(3)—C(3)—C(4)	122 (1)	H(9)—C(9)—C(10)	124 (1)
H(3)—C(3)—C(2)	117 (1)	H(9)—C(9)—C(8)	116 (1)
H(6)—C(6)—C(1)	119 (1)	H(12)—C(12)—C(7)	123 (1)
H(6)—C(6)—C(5)	119 (1)	H(12)—C(12)—C(11)	115 (1)

---

* Lists of atomic coordinates, structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42941 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Bond lengths and valence angles of the title compound are listed in Table 2; they have not been corrected for effects of thermal motion. The average free molecule in the conformation stated above would have C_2 symmetry with the twofold axis going through the centre of C(1)—C(7) and bisecting the phenyl interplanar angle. This symmetry is roughly displayed in the bond lengths and valence angles found in the crystal. If one, however, looks at the distances of the various atoms from the ring planes, significant deviations from twofold symmetry occur, for instance C(1) and C(7) 0·072 and 0·141 Å and Cl(2) and Cl(5) 0·061 and 0·009 Å (see Table 1). Further inspection of Table 2 shows the *ortho* and *meta* C—Cl bonds to be shorter than the *para* C—Cl bonds, and reveals the inequivalence of various distances and angles within one phenyl ring. The *para* C—Cl bonds (mean 1·737 Å) are close to the standard C—Cl length [1·740 (1) Å] (Domenicano, Vaciago & Coulson, 1975). Deviations from D_{6h} symmetry in the phenyl rings are significant but complex. A detailed analysis of the endocyclic valence angles according to Domenicano & Murray-Rust (1979) cannot be made due to lack of knowledge of the parameters pertaining to a trichlorophenyl substituent, which is not coplanar with the phenyl group and hence weakly conjugated.

References

BASTIANSEN, O., KVESETH, K. & MØLLENDAL, H. (1979). *Top. Curr. Chem.* **81**, 99–172.

DOMENICANO, A. & MURRAY-RUST, P. (1979). *Tetrahedron Lett.* pp. 2283–2286.

DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* B**31**, 1630–1641.

FRENZ, B. A. (1978). *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64–71. Delft Univ. Press.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

RØMMING, C., SEIP, H. M. & AANESEN ØYMO, I.-M. (1974). *Acta Chem. Scand. Ser. A*, **28**, 507–514.

STØLEVIK, R. & THINGSTAD, Ø. (1984). *J. Mol. Struct. Theochem.* **106**, 333–353.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1986). C**42**, 1178–1181

Structure of (*Z*)-*N*-Benzoyl-α,β-dehydroleucine

BY V. BUSETTI

Dipartimento di Chimica Organica, Università di Padova, Via Marzolo 1, 35100 *Padova, Italy*

AND D. AJÒ* AND A. VITTADINI

Istituto di Chimica e Tecnologia dei Radioelementi del CNR, Corso Stati Uniti 4, 35100 *Padova, Italy*

(*Received* 5 *December* 1985; *accepted* 4 *March* 1986)

Abstract. $C_{13}H_{15}NO_3$, $M_r = 233·27$, triclinic, $P\bar{1}$, $a = 22·914$ (4), $b = 11·282$ (3), $c = 5·056$ (2) Å, $\alpha = 95·30$ (5), $\beta = 93·04$ (5), $\gamma = 95·13$ (5)°, $V = 1293·8$ (7) Å^3, $Z = 4$, $D_x = 1·198$, $D_m = 1·170$ g cm^{-3} (by flotation in aqueous KBr solution), Mo $K\alpha$ radiation (monochromatized by a graphite plate), $\lambda = 0·71069$ Å, μ(Mo $K\alpha$) = 0·797 cm^{-1}, $F(000) = 496$, $T = 298$ K, $R = 5·54$% for 3106 reflections with $I > 3\sigma(I)$. There are two independent molecules in the asymmetric unit. They are approximate enantiomers $\{\varphi[C(O_2)–C–N–C] = -51·7$, $\psi[N–C–C–O(H)] = -29·6°$ for molecule *A*; $\varphi = 55·9$, $\psi = 25·8°$ for molecule *B*$\}$ linked in pairs by hydrogen bonds through the carboxylic groups.

Introduction. α,β-Unsaturated amino-acid derivatives are present in many natural peptides, several of which exhibit biological activities (Ajò, Granozzi, Tondello & Del Pra, 1980, and references therein). The α,β-double bond in dehydro-amino-acid derivatives represents, in addition to the amino and carboxy groups, the introduction of a third reactive function into the molecule, which makes this class of compounds particularly interesting because of their unusual conformational and electronic features (Ajò, Casarin, Bertoncello, Busetti, Ottenheijm & Plate, 1985, and references therein).

Conformational studies of α,β-unsaturated amino-acid derivatives are of interest not only from a biological point of view, but also in order to investigate the mechanism of their asymmetric hydrogenation

---

* To whom correspondence should be addressed.

0108-2701/86/091178-04$01.50