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2,2′,4,4′,6,6′-Hexachlorobiphenyl

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Abstract. $C_{12}H_4Cl_6$, monoclinic, $C2/c$, $a = 21{\cdot}474$ (9), $b = 8{\cdot}409$ (2), $c = 15{\cdot}793$ (5) Å, $\beta = 91{\cdot}90°$, $Z = 8$, $D_c = 1{\cdot}68$ Mg m^{-3}, $U = 2851{\cdot}8$ Å^3, $\mu(\text{Cu } K\alpha) = 11{\cdot}10$ mm^{-1}. The final R and R_w are 0·051 and 0·058 respectively on 1248 reflections. The two benzene rings are planar and twisted about the C(1)—C(1′) bond with a dihedral angle of 87·3°. The C(1)—C(1′) bond length is 1·477 (8) Å, which is a normal C—C single-bond length between two sp^2 hybridized C atoms. The ring angles at C(1) and C(1′) are 115·9 (6) and 115·2 (6)°, respectively, but those at C(4) and C(4′) are both 120·5°. None of the *ortho*-substituted Cl atoms are closer than 3·94 Å to each other. The long molecular axis Cl(4)···Cl(4′) is slightly bent in the plane of one of the benzene rings.

Introduction. 2,2′,4,4′,6,6′-Hexachlorobiphenyl (see Fig. 1 for numbering system) was purchased from Analabs, North Haven, Connecticut, USA (the purity was ≥98% as previously reported by McKinney, Chae, Gupta, Moore & Goldstein, 1976). The sample contained large plate-like crystals from which a fragment measuring approximately 0·38 × 0·21 × 0·16 mm was cut and mounted along its longest dimension (the *b* axis) on a glass fiber. Precession and Weissenberg photographs showed the following systematic absences: *hkl* for *h* + *k* odd, and *h0l* for *l* odd; these indicate the space group to be either $C2/c$ or Cc. The centrosymmetric space group, $C2/c$, was assumed (Donohue, 1971), and found to be correct as seen by the successful refinement (see below). The intensity data were collected using Cu $K\alpha$ radiation,* $\lambda(\text{Cu } K\alpha_1) = 1{\cdot}5405$ Å, on a four-circle Picker automatic diffractometer equipped with a pulse-height analyzer and a scintillation counter. A 0·5 mil (127 μm) Ni foil was used to filter the $K\beta$ radiation. The cell constants were obtained by a least-squares refinement of the setting angles of 12 general reflections. The intensity data were corrected for background, Lorentz and polarization effects, and for absorption of the diffracted beam. The linear absorption coefficient, μ, is 11·10 mm^{-1} for Cu $K\alpha$ radiation. The transmission coefficients were in the range 0·09 to 0·32. 1248 reflections above 3σ were observed.

The structure was solved by direct methods using the multi-solution computer program *MULTAN* (Main, Woolfson & Germain, 1971), and difference Fourier syntheses. The positional and anisotropic temperature parameters for the 18 non-hydrogen atoms and positional and isotropic temperature parameters for the four hydrogen atoms were refined using Ibers's version of Busing, Martin & Levy's (1962) full-matrix least-squares program *ORFLS*. The function minimized was $\sum w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o)^2$. Atomic scattering factors for Cl and C including those for the anomalous dispersion of Cl were taken from *International Tables for X-ray Crystallography* (1974) and for H from Stewart, Davidson & Simpson (1965). Examination of the data near the end of the refinement indicated that the secondary-extinction correction was not needed. 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 0·051 and 0·058, respectively, based on 1248 observations and 179 variables. No attempt was made to refine the structure in the alternative noncentrosymmetric space group since the results obtained were internally consistent and in agreement with those reported for similar compounds (see below). A final difference Fourier map contained no peak greater than 0·30 e Å^{-3}.

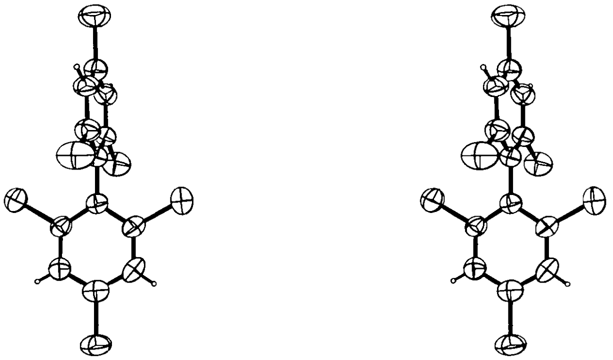

Fig. 1. A stereoview of a 2,2′,4,4′,6,6′-hexachlorobiphenyl molecule.

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* Mo $K\alpha$ radiation, which would be a better choice for this highly absorbing crystal, was not available to us. The data were, however, corrected for absorption errors.

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Table 1. *Positional parameters and their e.s.d.'s for 2,2′,4,4′,6,6′-hexachlorobiphenyl*

	x	y	z
Cl(2)	0·2361 (1)	0·4584 (3)	0·2815 (1)
Cl(4)	0·2651 (1)	−0·0450 (2)	0·4842 (1)
Cl(6)	0·4652 (1)	0·2364 (3)	0·3597 (2)
Cl(2′)	0·3783 (1)	0·6527 (2)	0·4093 (1)
Cl(4′)	0·4544 (1)	0·8540 (3)	0·1095 (1)
Cl(6′)	0·3715 (1)	0·2571 (2)	0·1416 (1)
C(1)	0·3490 (3)	0·3396 (8)	0·3246 (4)
C(2)	0·2851 (3)	0·3245 (8)	0·3334 (4)
C(3)	0·2589 (4)	0·2114 (8)	0·3829 (5)
C(4)	0·2973 (3)	0·1033 (8)	0·4235 (4)
C(5)	0·3607 (4)	0·1113 (10)	0·4157 (5)
C(6)	0·3856 (3)	0·2285 (8)	0·3674 (4)
C(1′)	0·3754 (3)	0·4646 (8)	0·2709 (4)
C(2′)	0·3904 (3)	0·6151 (8)	0·3028 (4)
C(3′)	0·4137 (3)	0·7344 (9)	0·2546 (5)
C(4′)	0·4247 (3)	0·7052 (9)	0·1715 (5)
C(5′)	0·4120 (3)	0·5593 (11)	0·1369 (5)
C(6′)	0·3877 (3)	0·4415 (8)	0·1864 (4)
HC(3)	0·220 (3)	0·207 (8)	0·384 (4)
HC(5)	0·381 (2)	0·043 (7)	0·436 (3)
HC(3′)	0·421 (3)	0·846 (8)	0·285 (4)
HC(5′)	0·421 (3)	0·533 (8)	0·092 (4)

The final positional parameters, and their e.s.d.'s, are given in Table 1.* A stereoscopic drawing of the molecule is shown in Fig. 1.

Discussion. Polychlorinated biphenyls (PCB's) have been used in a wide variety of industrial applications in the US from 1930 to 1970, when their usage was voluntarily restricted to closed systems. They are widely distributed in the environment and have been found in tissues of wildlife and humans (Riseborough, Rieche, Peakall, Herman & Kirven, 1968; Biros, Walker & Medbery, 1970). Previous studies in our laboratories have shown that there is a wide variation in the toxicity of different hexachlorobiphenyl isomers of PCB's (McKinney *et al.*, 1976; Biocca, Moore, Gupta & McKinney, 1975). We have, therefore, decided to determine the conformation and molecular structure of several of these compounds in order to assist in elucidating their structure–activity relationships. The crystal structure of the title compound described in the present report is the first in the series of biphenyls to be examined and represents the maximum *ortho* effect, an effect which tends to prevent coplanarity of the two phenyl rings in the molecule.

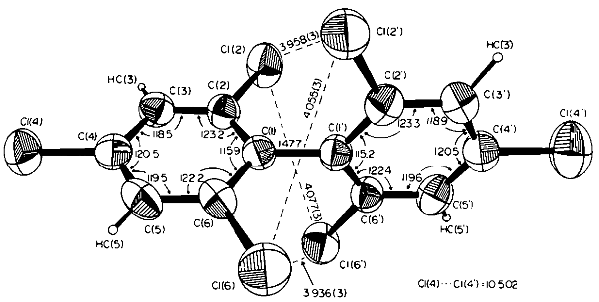

Fig. 2. A view of the 2,2′,4,4′,6,6′-hexachlorobiphenyl molecule showing the atom-numbering system and some important intramolecular distances (Å) and angles (°). C and Cl atoms are shown with 50% probability thermal ellipsoids, and H atoms as small circles of arbitrary size.

A view of the molecule with the atom-numbering system and some of the important intramolecular distances and angles is shown in Fig. 2. The bond distances and bond angles and their e.s.d.'s, not including the H atoms, are given in Table 2. The bond distances in the two phenyl rings are normal, and range from 1·364 to 1·396 Å (σ ~ 0·009 Å) with a mean of 1·375 Å. The two internal ring bond angles, at C(1) and C(1′), with values of 115·9 (6) and 115·2 (6)°, respectively, are significantly less than the ideal value of 120°. Similar values for this angle have been reported for 2,2′-dichlorobiphenyl, 116·2 (2)° (Rømming, Seip & Aanesen Øymo, 1974), decachlorobiphenyl, 118·7 (3)° (Pedersen, 1975), and biphenyl itself, 116·8° (Robertson, 1961), 117·9 (2)° (Charbonneau & Delugeard, 1976). This decrease of the ring angle at C(1) and C(1′) in the present molecule, and in decachlorobiphenyl, cannot be attributed to steric factors, since the two phenyl rings are almost perpendicular to

Table 2. *Bond distances* (Å) *and bond angles* (°) *not involving* H *atoms*

C(2)–Cl(2)	1·729 (7)	Cl(2)–C(2)–C(3)	118·0 (6)
C(4)–Cl(4)	1·731 (7)	C(2)–C(3)–C(4)	118·5 (7)
C(6)–Cl(6)	1·720 (7)	C(3)–C(4)–C(5)	120·5 (7)
C(2′)–Cl(2′)	1·738 (7)	Cl(4)–C(4)–C(3)	119·5 (6)
C(4′)–Cl(4′)	1·724 (7)	Cl(4)–C(4)–C(5)	120·0 (6)
C(6′)–Cl(6′)	1·735 (7)	C(4)–C(5)–C(6)	119·5 (7)
C(1)–C(2)	1·388 (8)	C(5)–C(6)–C(1)	122·2 (7)
C(2)–C(3)	1·365 (9)	Cl(6)–C(6)–C(5)	118·4 (6)
C(3)–C(4)	1·371 (9)	Cl(6)–C(6)–C(1)	119·3 (5)
C(4)–C(5)	1·373 (9)	C(2′)–C(1′)–C(6′)	115·2 (6)
C(5)–C(6)	1·366 (10)	C(1)–C(1′)–C(6′)	123·0 (6)
C(6)–C(1)	1·383 (9)	C(1)–C(1′)–C(2′)	121·8 (6)
C(1)–C(1′)	1·477 (8)	C(1′)–C(2′)–C(3′)	123·3 (7)
C(1′)–C(2′)	1·396 (9)	Cl(2′)–C(2′)–C(1′)	118·3 (5)
C(2′)–C(3′)	1·364 (9)	Cl(2′)–C(2′)–C(3′)	118·4 (6)
C(3′)–C(4′)	1·365 (10)	C(2′)–C(3′)–C(4′)	118·9 (7)
C(4′)–C(5′)	1·367 (10)	C(3′)–C(4′)–C(5′)	120·5 (7)
C(5′)–C(6′)	1·375 (10)	Cl(4′)–C(4′)–C(3′)	119·7 (6)
C(6′)–C(1′)	1·383 (9)	Cl(4′)–C(4′)–C(5′)	119·8 (6)
		C(4′)–C(5′)–C(6′)	119·6 (7)
C(2)–C(1)–C(6)	115·9 (6)	C(5′)–C(6′)–C(1′)	122·4 (7)
C(1′)–C(1)–C(6)	122·6 (6)	Cl(6′)–C(6′)–C(5′)	119·1 (6)
C(1′)–C(1)–C(2)	121·5 (6)	Cl(6′)–C(6′)–C(1′)	118·5 (5)
C(1)–C(2)–C(3)	123·2 (6)		
Cl(2)–C(2)–C(1)	118·8 (5)		

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* Lists of structure factors, anisotropic thermal parameters, and bond distances and bond angles involving the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33961 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

each other in both compounds (see below), and the Cl···Cl separations at the *ortho* positions are all greater than the sum of their van der Waals radii (3·60 Å), as depicted in Fig. 2 for the title compound. The ring bond angles at the 2 and 6 positions in both phenyl rings are greater than 120°, mostly in response to the reduction in bond angles at the 1 position. The C(1)—C(1′) bond distance, 1·477 (8) Å, is almost identical with that calculated theoretically, 1·479 Å, for non-coplanar biphenyl (Dewar & Harget, 1970), and is not significantly different from the 1·489 Å (being within 2σ) determined by X-ray analysis for 2,2′-dichlorobiphenyl (Rømming *et al.*, 1974). It should be pointed out that Dewar & Schmeising (1968) suggest 1·485 Å as the length of a single bond between two sp^2-hybridized C atoms, which is within one e.s.d. of the value found in this work. The C—Cl bond distances range from 1·720 (7) to 1·783 (7) Å with a mean value of 1·730 Å, which is within 2σ of that found for decachlorobiphenyl, 1·718 Å (Pedersen, 1975), and for hexachlorobenzene, 1·715 (2) Å (Brown & Strydom, 1974).

The bond distances and bond angles involving the H atoms* are normal within the large experimental error always involved with X-ray data. The C—H distances range from 0·77 (6) to 1·06 (7) Å and the C—C—H angles from 115 (5) to 125 (5)°.

Deviations of atoms from the least-squares planes of the two phenyl rings and their χ^2 values are given in Table 3. It is apparent that both phenyl rings are planar with their substituent Cl atoms lying very close to the respective planes. The dihedral angle between the planes of the two rings is 87·3°, which is quite close to the value observed for decachlorobiphenyl, 86·6° (Pedersen, 1975). Therefore, with respect to each other, the planes of the two phenyl rings are almost perpendicular.

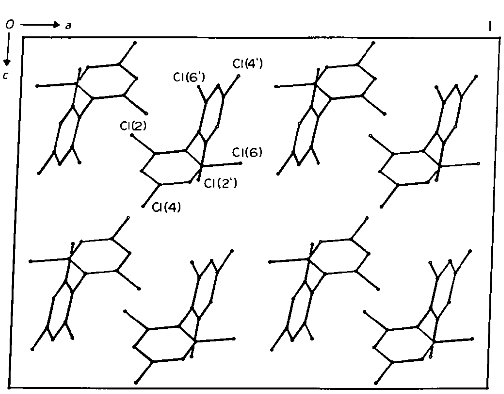

Fig. 3. Packing of 2,2′,4,4′,6,6′-hexachlorobiphenyl molecules in the crystal lattice viewed down the *b* axis.

Table 3. *Deviations* (Å) *of atoms from the least-squares planes through the two phenyl rings*

Plane I ($\chi^2 = 7\cdot73$)				Plane II ($\chi^2 = 5\cdot16$)			
C(1)*	−0·005	Cl(2)	0·020	C(1′)*	0·008	Cl(2′)	−0·044
C(2)*	0·013	Cl(4)	0·022	C(2′)*	−0·011	Cl(4′)	0·015
C(3)*	−0·011	Cl(6)	−0·012	C(3′)*	0·006	Cl(6′)	0·000
C(4)*	0·000	H(3)	0·035	C(4′)*	0·002	H(3′)	0·040
C(5)*	0·008	H(5)	0·081	C(5′)*	−0·004	H(5′)	−0·091
C(6)*	−0·005	C(1′)	0·010	C(6′)*	−0·001	C(1)	0·021
		C(4′)	−0·009			C(4)	0·087
		Cl(4′)	−0·015			Cl(4)	0·129

* Atoms included in the calculation of the least squares planes.

As has been observed previously for other biphenyl derivatives (Chawdhury, Hargreaves & Sullivan, 1968; Pedersen, 1975) the longest molecular axis is slightly bent, the angles Cl(4)—C(1)—Cl(4′) and Cl(4)—C(1′)—Cl(4′) both being 178·7 (2)°. This bending lies mainly in the plane of the ring containing atoms C(1) through C(6) since C(1′), C(4′) and Cl(4′) do not deviate significantly from plane I but C(1), C(4) and Cl(4) deviate by progressively larger amounts, *i.e.* 0·021, 0·087 and 0·129 Å, respectively, from plane II.

Packing of the molecules in the crystal lattice is shown in Fig. 3. There are only three short intermolecular contacts. These are (numbers in parentheses are the sums of the respective van der Waals radii): Cl(4)···Cl(4), 3·55 (3·60); Cl(6)···Cl(6′), 3·51 (3·60); and C(3)···Cl(2), 3·36 (3·50) Å.

We thank Professor D. J. Hodgson for providing the laboratory facilities.

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* See previous footnote.

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2-{[3-(Trifluoromethyl)phenyl]amino}-3-pyridinecarboxylic Acid* (Niflumic Acid)†

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Abstract. $C_{13}H_9F_3N_2O_2$, $P2_1/n$, a = 5·111 (2), b = 15·330 (2), c = 15·479 (2) Å, β = 95·5 (3)°, D_m = 1·51 (flotation), D_c = 1·55 Mg m^{-3}, Z = 4. The three planar groupings in the molecule, *i.e.* the two six-membered rings and the carboxyl group, are nearly coplanar. In the crystal structure the molecules exist as hydrogen-bonded dimers. In addition, there is an intramolecular hydrogen bond connecting the carboxyl group and the N atom which bridges the two six-membered rings.

Introduction. Fenamates (mefenamic acid, meclofenamic acid, flufenamic acid and niflumic acid) constitute an important recently developed group of analgesics which are believed to act, like other anti-inflammatory analgesics, through the inhibition of prostaglandin biosynthesis (Flower, 1974). The crystal structures of mefenamic acid and flufenamic acid have been determined (McConnell, 1973, 1976). As part of a programme of X-ray studies on analgesics and their interactions (Singh & Vijayan, 1977; Krishna Murthy, Vijayan & Brehm, 1979), we report here the crystal structure of niflumic acid.

Elongated needle-like crystals of the title compound were grown from a solution in tetrahydrofuran using a sample supplied by UPSA Laboratories, Agen, France. The data were collected on a CAD-4 computer-controlled diffractometer from a specimen of dimensions 1·0 × 0·3 × 0·2 mm using graphite-monochromated Cu radiation up to a Bragg angle of 72°. Of the 2373 unique reflections in this range, 1426 had $I > 3\sigma(I)$ and were subsequently used for structure determination and refinement. The data were corrected for Lorentz and polarization factors. The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971) and refined by the block-diagonal least-squares method using the modified version of a program originally written by R. Shiono. The heavy atoms and the H atoms were given anisotropic and isotropic temperature factors respectively. The refinement converged at R = 0·080. The weighting scheme was of the form $1/(a + bF_o + cF_o^2)$, where a = 1·28, b = –0·034 and c = 0·004. The scattering factors for the non-hydrogen atoms and the H atoms were taken from

Table 1. *Final coordinates* (×10⁴) *of the non-hydrogen atoms*

The standard deviations are given in parentheses.

	x	y	z
C(1)	8280 (19)	5434 (7)	7682 (7)
C(2)	6208 (19)	4949 (7)	7206 (8)
C(3)	4642 (21)	4432 (8)	7685 (9)
C(4)	5052 (22)	4391 (9)	8576 (9)
C(5)	7142 (24)	4871 (9)	8963 (9)
N(6)	8717 (17)	5385 (7)	8533 (6)
C(7)	5699 (20)	4992 (8)	6266 (8)
O(1)	7020 (16)	5407 (7)	5778 (5)
O(2)	3633 (16)	4529 (7)	5951 (6)
N(1)	9844 (16)	5955 (6)	7231 (6)
C(8)	11840 (19)	6546 (7)	7526 (7)
C(9)	12509 (19)	6761 (7)	8395 (7)
C(10)	14571 (21)	7353 (7)	8584 (7)
C(11)	15884 (21)	7738 (8)	7960 (8)
C(12)	15186 (22)	7533 (8)	7096 (9)
C(13)	13149 (20)	6946 (8)	6880 (7)
C(14)	15373 (22)	7556 (8)	9505 (8)
F(1)	17191 (18)	7029 (7)	9870 (6)
F(2)	13441 (17)	7527 (8)	10027 (6)
F(3)	16392 (22)	8352 (6)	9633 (6)

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* The systematic chemical name for niflumic acid given in our abstract (04.6–15) communicated to the Eleventh International Congress of Crystallography, Warszawa, 3–12 August 1978, is incorrect. The error is regretted.

† Structural Studies of Analgesics and Their Interactions. VI.

‡ Contribution No. 128 from the Molecular Biophysics Unit.

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