

2,2',3,3',6,6'-Hexachloro-5-nitro-1,1'-biphenyl (5-Nitro PCB 136)

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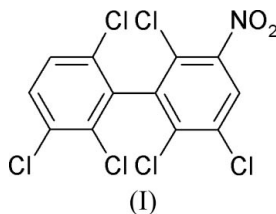
Key indicators

Single-crystal X-ray study
 $T = 90$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in main residue
 R factor = 0.042
 wR factor = 0.100
Data-to-parameter ratio = 15.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{12}\text{H}_3\text{Cl}_6\text{NO}_2$, has a dihedral angle of $83.92(8)^\circ$ between the benzene rings. It was obtained as an intermediate in the synthesis of 3-hydroxy PCB 136 by nitration of PCB 136.

Comment

Polychlorinated biphenyls (PCBs) are mixtures of up to 209 individual chlorinated compounds known as congeners. Due to their high stability, good electrical resistance and insulating properties, they were manufactured industrially between 1929 and 1977 for several commercial applications such as in dielectric fluids and as insulators for transformers and capacitors (Robertson & Hansen, 2001). PCBs are resistant to biodegradation and thus remain in the environment where they bioaccumulate, raising concerns about their impact on wildlife and human health. Recent findings implicate PCB congeners having multiple *ortho* substitutions with adverse human health effects. For example, PCB 136 (2,2',3,3',6,6'-hexachlorobiphenyl) has been associated with cognitive deficits in laboratory animals and humans (Kodavanti, 2004; Schantz *et al.*, 2003). Until now the investigation of the mechanism(s) by which multiple *ortho*-substituted PCBs cause cognitive deficits has been limited (Lehmler, Robertson, Garrison & Kodavanti, 2005).



As part of our efforts to investigate the neurotoxicity of PCB 136 and its hydroxylated metabolites, we obtained the title compound, (I), as an intermediate in the synthesis of 5-hydroxy PCB 136 by nitration of PCB 136. The crystal structure of (I) confirms earlier reports that this nitration reaction results in the 5-nitro-substituted PCB 136 (Waller *et al.*, 1999). The dihedral angle between the benzene rings in (I) is $83.92(8)^\circ$, smaller than the calculated dihedral angle of 90° in aqueous solution [calculated with *MM2* using GB/SA water solvent continuum as implemented by *MACROMODEL* 5.0 (Still *et al.*, 1990)]. This difference between solid-state and the calculated dihedral angle is probably due to crystal packing effects which are also observed in other PCB congeners (Kania-Korwel *et al.*, 2004; Lehmler, Parkin & Robertson, 2001; Miao *et al.*, 1997; Rømming *et al.*, 1974; Singh *et al.*, 1986).

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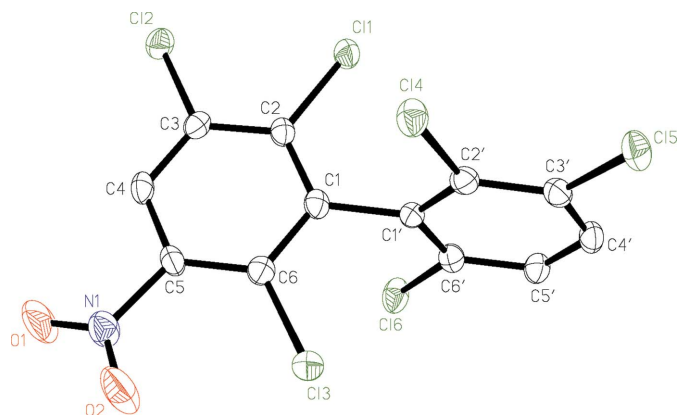


Figure 1
View of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

and PCB derivatives (Lehmler, Parkin & Robertson, 2002; Lehmler, Robertson & Parkin, 2001, 2005; Lehmler, Robertson, Parkin & Brock, 2002; McKinney & Singh, 1988; Rissanen *et al.*, 1988a,b).

Experimental

The title compound, (I), was synthesized by nitration of PCB 136 using a known experimental procedure (Waller *et al.*, 1999). Yellow crystals were obtained upon recrystallization from methanol.

Crystal data

$C_{12}H_3Cl_6NO_2$	$D_x = 1.879 \text{ Mg m}^{-3}$
$M_r = 405.85$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3326 reflections
$a = 12.1073 (2) \text{ \AA}$	$\theta = 1.0\text{--}27.5^\circ$
$b = 16.3810 (5) \text{ \AA}$	$\mu = 1.20 \text{ mm}^{-1}$
$c = 7.5813 (4) \text{ \AA}$	$T = 90.0 (2) \text{ K}$
$\beta = 107.4219 (14)^\circ$	Block cut from rod, yellow
$V = 1434.62 (9) \text{ \AA}^3$	$0.25 \times 0.20 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	2544 reflections with $I > 2\sigma(I)$
ω scans at fixed $\chi = 55^\circ$	$R_{\text{int}} = 0.027$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.742$, $T_{\text{max}} = 0.796$	$h = -15 \rightarrow 15$
5940 measured reflections	$k = -21 \rightarrow 21$
3280 independent reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 1.8622P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta\sigma)_{\text{max}} = 0.002$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.65 \text{ e \AA}^{-3}$
3280 reflections	$\Delta\rho_{\text{min}} = -0.41 \text{ e \AA}^{-3}$
207 parameters	
H-atom parameters constrained	

There is a ring-flip disorder of the NO_2 -substituted ring that leads to a partial occupancy Cl sitting near the N atom and a partial NO_2

group sitting over the corresponding Cl. Some distortion of the C–N bond is to be expected in such cases. To counter this, restraints were used in the refinement to keep all the C–Cl bonds approximately the same and to keep the major and minor NO_2 components approximately the same. The C–N bonds of both parts were also subject to similarity restraints. The minor disorder parts were refined with isotropic displacement parameters because of the low occupancy. H atoms were placed in geometrically idealized positions and constrained using a riding model in which the C–H distance was fixed at 0.95 \AA , with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO-SMN (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL (Sheldrick, 1994); software used to prepare material for publication: SHELX97-2 (Sheldrick, 1997) and local procedures.

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