

Short Communication

Crystal Structure of 2,3,3',4,5'-Pentachlorobiphenyl (PCB 108)

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Research interest on polychlorinated biphenyls (PCBs) is connected with the environmental problems that the worldwide industrial use of them has caused. The chemical persistence and lipophilic nature of PCBs contributes to their bioaccumulation in higher trophic levels in the food chain including man.^{1,2} The toxicity of coplanar PCB congeners (tetra-, penta- and hexa-) and the relatively high amounts of these found in the environment is causing risk to humans and wildlife.^{3,4} Non-ortho-substituted tetra-, penta- and hexa-chlorobiphenyls, especially 3,3',4,4',5-pentachlorobiphenyl (PCB 126), have been shown to be very toxic. The toxicity of these has been explained mainly in terms of their molecular dimensions and coplanar conformation resembling that of 2,3,7,8-tetrachlorodibenzodioxin.^{5,6} We herein report the crystal structure of mono-ortho-substituted 2,3,3',4,5'-pentachlorobiphenyl. The synthesis, structure verification (¹H and ¹³C NMR, IR and mass spectra) and toxicity studies (AHH induction) of the title compound has been reported earlier.^{7,8}

Experimental

Synthesis. 2,3,3',4,5'-Pentachlorobiphenyl was synthesized by an aromatic arylation method^{7,9,10} starting from 3,5-dichloroaniline and an excess of 1,2,3-trichlorobenzene followed by dropwise addition of isopentyl nitrite; at the same time the temperature was slowly raised to 130°C. Two isomers, 2,3,3',4,5'- and 3,3',4,5,5'-pentachlorobiphenyl were formed in the ratio 5:1. The excess of 1,2,3-trichlorobenzene was removed by distillation at reduced pressure. The products were purified by eluting them through a basic Al₂O₃ column with hexane and the isomers were separated on a charcoal column. The mix-

ture was eluted into the charcoal column first with hexane-CH₂Cl₂ (2°) and the elution was continued until all the 2,3,3',4,5'-pentachlorobiphenyl had been eluted. The charcoal column trapped 3,3',4,5,5'-pentachlorobiphenyl which was released in pure form by reversed elution with toluene.

Crystal data. C₁₂H₅Cl₅, *M*_r = 326.44, triclinic, *P*1, *a* = 7.955(1), *b* = 12.056(3), *c* = 6.929(1) Å, α = 102.93(1), β = 97.41(1), γ = 88.74(2)°, *V* = 642.1(2) Å³, *Z* = 2, *D*_x = 1.688 Mg m⁻³, λ(MoKα) = 0.7107 Å, μ = 1.108 mm⁻¹, *F*(000) = 324, *T* = 296 ± 1 K, final *R* = 0.035 and *R*_w = 0.043 for 2027 unique observed reflections and 174 parameters.

The unit cell was determined by least-squares refinement of 25 carefully centered independent reflections (18 < 2θ < 28°) measured at room temperature on an Enraf-Nonius CAD4 diffractometer. The data were corrected for Lorentz and polarization effects and for absorption (DIFABS,¹¹ min. and max. coefficients 0.722 and 1.251, respectively).

Data collection, structure determination and refinement. A total of 2431 reflections were collected (2θ_{max} = 50°) giving 2254 unique reflections (*R*_{int} = 0.005), of which 2027 were considered observed according to the criteria *I* < 3σ(*I*). The three intensity standards checked after every 400 reflections did not show any intensity decay. The structure was solved by direct methods by using the SHELXS86¹² program and subsequent Fourier synthesis. Full-matrix least-squares refinement on *F*, non-H atoms were refined anisotropically and the hydrogen atoms with isotropic temperature factors. A weighting scheme based on the Chebychev polynomial {*w* = *w*' - [1.0 - (Δ*F*/6σ*F*)²]}², where *w*' = Chebychev polynomial for *F*_c with three coefficients (5.33, 1.88 and 3.66)} was applied. The final difference Fourier map did not show any peak higher

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Table 1. Fractional coordinates with e.s.d.s in parentheses and equivalent isotropic temperature^a factors for PCB 108.

Atom	x/a	y/b	z/c	U (iso)
Cl(2)	0.55867(9)	0.35207(5)	0.12172(8)	0.0549
Cl(3)	0.70202(9)	0.59089(5)	0.3319(1)	0.0581
Cl(4)	0.89896(8)	0.63191(5)	0.7629(1)	0.0606
Cl(3')	0.80971(8)	-0.14919(5)	0.2542(1)	0.0596
Cl(5')	0.17575(7)	0.00788(6)	0.17886(9)	0.0559
C(1)	0.6894(2)	0.2824(2)	0.4553(3)	0.0375
C(2)	0.6650(2)	0.3726(2)	0.3609(3)	0.0384
C(3)	0.7288(2)	0.4810(2)	0.4532(3)	0.0403
C(4)	0.8174(3)	0.4989(2)	0.6439(3)	0.0445
C(5)	0.8427(3)	0.4102(2)	0.7392(4)	0.0509
C(6)	0.7799(3)	0.3035(2)	0.6461(3)	0.0466
C(1')	0.6224(2)	0.1652(2)	0.3650(3)	0.0362
C(2')	0.7343(3)	0.0738(2)	0.3470(3)	0.0393
C(3')	0.6711(3)	-0.0352(2)	0.2757(3)	0.0404
C(4')	0.5001(3)	-0.0570(2)	0.2216(3)	0.0412
C(5')	0.3917(3)	0.0343(2)	0.2413(3)	0.0390
C(6')	0.4496(3)	0.1446(2)	0.3108(3)	0.0406
H(5)	0.903(4)	0.423(3)	0.872(5)	0.080(9)
H(6)	0.799(3)	0.254(2)	0.710(4)	0.051(7)
H(2')	0.850(3)	0.088(2)	0.386(3)	0.041(6)
H(4')	0.460(3)	-0.129(2)	0.178(4)	0.052(7)
H(6')	0.376(3)	0.206(2)	0.325(4)	0.046(6)

^a $U(\text{iso}) = [U(11) \times U(22) \times U(33)]^{1/3}$ H-atoms refined isotropically.

than $0.35 \text{ e } \text{\AA}^{-3}$.

The scattering factors were taken from Ref. 13. All calculations were performed on a 486-PC (66 MHz) and the refinements and all subsequent calculations were done using the CRYSTALS¹⁴ program (PC-version). The figures were drawn using the program SCHAKAL.¹⁵ Final atomic coordinates with e.s.d.s in parentheses with equivalent isotropic temperature factors are listed in Table 1 and bond distances and angles in Table 2. Lists of anisotropic temperature factors, least-squares planes and structure factors are available from the authors on request.

Results and discussion

The bond distances and angles are normal (Table 2). The molecule adopts a non-coplanar conformation (Fig. 1), which is reasonable because of an *ortho*-chlorine substituent.

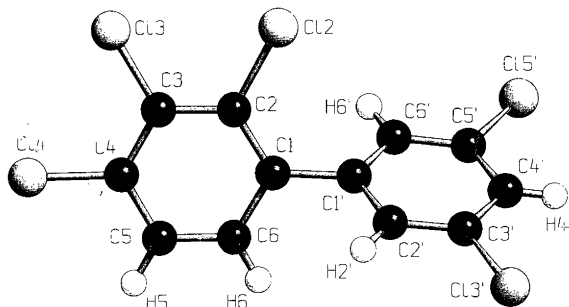


Fig. 1. A view of PCB 108 with labelling scheme.

Table 2. Bond distances (Å) and angles (°) for PCB 108 with e.s.d.s in parentheses.

Cl(2)–C(2)	1.728(2)	Cl(3)–C(3)–C(4)	120.1(2)
Cl(3)–C(3)	1.176(2)	C(2)–C(3)–C(4)	119.2(2)
Cl(4)–C(4)	1.729(2)	Cl(4)–C(4)–C(3)	120.6(2)
Cl(3')–C(3')	1.736(2)	Cl(4)–C(4)–C(5)	119.3(2)
Cl(5')–C(5')	1.735(2)	C(3)–C(4)–C(5)	120.1(2)
C(1)–C(2)	1.386(3)	C(4)–C(5)–C(6)	120.1(2)
C(1)–C(6)	1.394(3)	C(4)–C(5)–H(5)	119.7(2)
C(1)–C(1')	1.492(3)	C(6)–C(5)–H(5)	120.2(2)
C(2)–C(3)	1.396(3)	C(1)–C(6)–C(5)	121.4(2)
C(3)–C(4)	1.388(3)	C(1)–C(6)–H(6)	119.4(2)
C(4)–C(5)	1.376(3)	C(5)–C(6)–H(6)	119.1(2)
C(5)–C(6)	1.376(3)	C(1)–C(1')–C(2')	119.2(2)
C(5)–H(5)	0.96(3)	C(1)–C(1')–C(6')	121.2(2)
C(6)–H(6)	0.91(3)	C(2')–C(1')–C(6')	119.5(2)
C(1')–C(2')	1.394(3)	C(1')–C(2')–C(3')	119.2(2)
C(1')–C(6')	1.390(3)	C(1')–C(2')–H(2')	119.2(1)
C(2')–C(3')	1.378(3)	C(3')–C(2')–H(2')	121.6(1)
C(2')–H(2')	0.94(2)	Cl(3')–C(3')–C(2')	119.4(2)
C(3')–C(4')	1.379(3)	Cl(3')–C(3')–C(4')	118.6(2)
C(4')–C(5')	1.377(3)	C(2')–C(3')–C(4')	112.1(2)
C(4')–H(4')	0.90(3)	C(3')–C(4')–C(5')	117.8(2)
C(5')–C(6')	1.377(3)	C(3')–C(4')–H(4')	121.3(2)
C(6')–H(6')	0.93(3)	C(5')–C(4')–H(4')	120.9(2)
		Cl(5')–C(5')–C(4')	118.3(2)
C(2)–C(1)–C(6)	117.8(2)	Cl(5')–C(5')–C(6')	119.7(2)
C(6)–C(1)–C(1')	118.5(2)	C(4')–C(5')–C(6')	122.0(2)
Cl(2)–C(2)–C(1)	120.4(2)	C(1')–C(6')–C(5')	119.4(2)
Cl(2)–C(2)–C(3)	118.2(2)	C(1')–C(6')–H(6')	118.6(2)
C(1)–C(2)–C(3)	121.3(2)	C(5')–C(6')–H(6')	121.6(2)
Cl(3)–C(3)–C(2)	120.7(2)		

ent. The dihedral angle between the benzene planes is 58.2° , which is larger than the corresponding angle in biphenyl¹⁶ (42°) but smaller than in *ortho*-disubstituted polychlorobiphenyl derivatives^{17,18} ($75\text{--}82^\circ$). The *ortho*-chlorine in the title compound prevents the molecule from adopting a coplanar conformation, thus explaining the low toxicity of the compound. The benzene rings are planar, the max. deviation from the calculated least-squares plane being -0.003 \AA . Thus no overcrowding effect due to the chlorine substituents is observed. The molecules are packed (Fig. 2) in the unit cell so that the more substituted benzene rings stack face-to-face creating bilayers of the compound in the crystal lattice. There

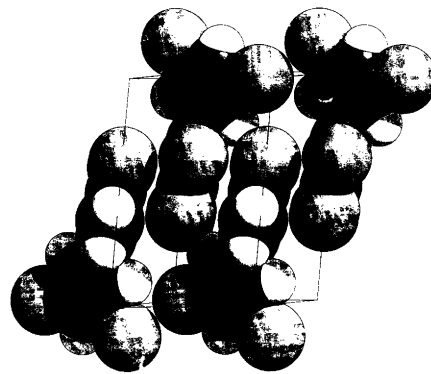


Fig. 2. A packing view with van der Waals radii. The *a*-axis is horizontal and the *b*-axis is vertical.

are no contacts shorter than the van der Waals radii of the atoms.

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