

**SYNTHESIS AND STRUCTURE ELUCIDATION OF SOME PCB DERIVATIVES:
NMR, MS AND X-RAY DIFFRACTION STUDY OF
POLYCHLOROBIPHENYLS.**

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INTRODUCTION

Polychlorobiphenyls (PCBOH) as oxidation products and metabolites of PCBs are precursors for polychlorobiphenylanisoles (PCBA) formed via biomethylation found in the environment. PCBOHs may also be intermediates for highly toxic polychlorodibenzofurans (PCDF) formed for example in an accidental PCB capacitor fire. Synthesis of some PCBOHs is of great importance in structural studies of environmentally important compounds, as the model compounds for the analysis of the environmental samples and for the pyrolytic studies^{1,2}.

EXPERIMENTAL

Compounds: 2',3,4',5',6-pentachlorobiphenyl-2-ol **1**, 2,2',4',5,5'-pentachlorobiphenyl-3-ol **2**, 2,2',4',5,5'-pentachlorobiphenyl-4-ol **3**, 2',4,4',5,5'-hexachlorobiphenyl-2-ol **4**, 2',3',4,4',5,6,6'-heptachlorobiphenyl-2-ol **5**, 2,2',3',4,4',5,5'-heptachlorobiphenyl-3-ol **6**, 2,2',3,3',4',5,5'-heptachlorobiphenyl-4-ol **7**, 2',3',4,4',5,5',6,6'-oktachlorobiphenyl-2-ol **8**.

Synthesis: The synthesis of PCBOHs followed a known aromatic arylation procedure of Cadogan³ which has successively been used for preparing PCBs and PCBAs⁴⁻⁶. Eight PCBAs were coupled from three different polychloroanisoles and four different polychloroanilines. The respective PCBOHs were prepared from PCBAs by demethylation with borontribromide in dichloromethane. In some coupling reactions several isomers were formed and the separation of each was carried out as polychlorobiphenyls by flash chromatography on silica gel n-hexane/CH₂Cl₂ as an eluent.

Mass spectrometry: The molecular weight and the degree of chlorination of the compounds **1 - 8** were determined by MS. The instrument used was WG Auto Spec mass Spectrometer at 70 eV.

NMR spectroscopy: ¹H NMR spectra of compounds **1 - 8** were recorded in CDCl₃-solutions TMS as an internal standard. The instrument used was a JEOL GSX FT NMR spectrometer at 270.13 MHz at 30°C. The assignment and the coupling constants of the proton spectra are given in Table 1.

X-Ray diffraction: Crystal structure of **4** and **8** was analysed. Intensity data were collected on an Enraf Nonius CAD4 diffractometer at room temperature using MoK α radiation and $\omega/2\theta$ scan mode. The structures were solved by direct methods using the SHELXS program⁷. The final refinements were carried out by full matrix least-squares using the CRYSTALS program⁸, anisotropically for all non-H-atoms. The hydroxylic hydrogen atoms were located from ΔF map and refined as riding atoms with fixed isotropic temperature factor ($U = 0.08 \text{ \AA}^2$) whilst the rest H-atoms were calculated to their idealized positions ($C - H = 1.0 \text{ \AA}$) and refined as riding atoms with fixed isotropic temperature factor ($U = 0.08 \text{ \AA}^2$). The atomic scattering factors were taken from Ref. 9. In addition to quoted programs the SCHAKAL¹⁰ program was used.

RESULTS AND DISCUSSION

Mass spectra of compounds **1** - **8** gave the molecular ions and number of chlorine substituents. The spectra were referred with the literature⁴.

¹H NMR chemical shifts and coupling constants of eight polychlorinated biphenyls **1** - **8** measured in CDCl₃ at 30 °C are collected in Table 1. The assignment of the signals is based on the characteristic aromatic interproton coupling constants, comparison between similarly substituted rings and the chemical shifts of related biphenyls^{11,12}.

In compounds **1** - **4** characterized by the same 2',4',5'-trichlorosubstitution, the ¹H NMR chemical shifts of two protons in 3'- and 6'-positions (these protons can be observed via their typical five-bond *para*-coupling varying from 0.27 Hz to 0.32 Hz) stay in the limits of 0.007 ppm (2 Hz) and 0.061 ppm (17 Hz), respectively. This finding suggests, that the more flexible chemical shift is associated to the proton 6', which is influenced by the *ortho*-substituent in the other ring. The proton 3' is more separated from these steric influences. Consequently, its chemical shift stays almost constant. However, the total variation in the proton 6' is small in comparison with the chemical shift difference of 0.23 ppm of these *para*-protons. Thus, the inter-ring interactions can not change the order of the chemical shifts of these protons.

According to a previous article¹², the assignment of the ¹H NMR chemical shift of the protons 3' and 6' is opposite as proposed above. In order to ascertain the correct assignment, also ¹³C NMR and ¹H-¹³C COSY spectra have been measured and compared with literature¹¹. A COSY contour plot shows unambiguously, that the order $\delta[H(6')] < \delta[H(3')]$ given in literature for both ¹H and ¹³C NMR chemical shifts of 2,4,5-trisubstituted biphenyls is not same as observed in this study for biphenyl-2-ols containing the similarly substituted phenyl moiety.

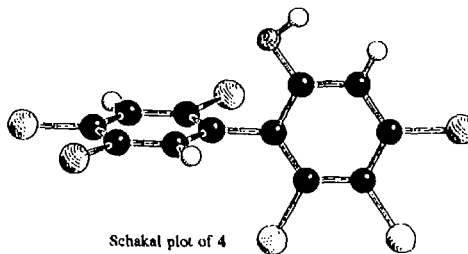
As suggested above, any substitution probably can not induce the effects of 0.23 ppm or more needed to change the order of the chemical shifts of H(3') and H(6') in biphenyl moiety. Thus, the ¹H-¹³C COSY experiment suggests, that the assignment of ¹H and ¹³C NMR chemical shifts given for 2,4,5-trichlorosubstituted ring in 2,2',3',4,5-pentachlorobiphenyl^{11,12} probably is not valid, because it is not in agreement with that of 2',4',5'-trichlorosubstituted ring in 2',3,4',5',6-pentachlorobiphenyl-2-ol. Thus, the ¹H or ¹³C NMR chemical shift assignment for protons/carbons 3' and 6' given in literature^{11,12} for chlorinated biphenyls is probably erroneous. Based on the above reasoning concerning the variation of the ¹H NMR chemical shifts of 2',4',5'-trisubstituted ring in compound **1**, it is probable that the assignment of ¹H NMR chemical shifts in 2,4,5-trichlorinated rings of chlorinated

biphenyls is wrong and should be *vice versa*. Consequently, the assignment of ^{13}C NMR chemical shifts¹¹ is correct.

Crystal structure analysis of **4** and **8** confirmed the structure analysis based on NMR measurements. In addition the twist angle between the phenyl rings is 82.06° in the case of **4** and 87.49° of **8**. Space group is $P2_1/n$ (no. 14, non std) and $P-1$ (no. 2) for **4** and **8** respectively. The final R_w was 0.058 for **4** and 0.072 for **8**.

TABLE 1. ^1H NMR chemical shifts and coupling constants of eight polychlorinated biphenyls measured in CDCl_3 at 30°C

Compound	Chemical shift, ppm	Coupling constant, Hz
1	H(4) 7.093	$^3\text{J}(\text{H4},\text{H5})$ 8.67
	H(5) 7.389	
	H(3') 7.678	$^5\text{J}(\text{H3}',\text{H6}')$ 0.27
	H(6') 7.405	
	OH(2) 5.70	
2	H(4) 6.878	$^4\text{J}(\text{H4},\text{H6})$ 2.42
	H(6) 7.165	
	H(3') 7.645	$^5\text{J}(3',6')$ 0.32
	H(6') 7.400	
	OH(3) 5.80	
3	H(3) 7.261	$^5\text{J}(\text{H3},\text{H6})$ 0.32
	H(6) 7.220	
	H(3') 7.631	$^5\text{J}(\text{H3}',\text{H6}')$ 0.33
	H(6') 7.400	
	OH 5.73	
4	H(3) 7.132	$^5\text{J}(\text{H3}',\text{H6}')$ 0.29
	H(3') 7.692	
	H(6') 7.398	
	OH(2) 6.29	
5	H(3) 7.058	
	H(5') 7.631	
	OH(2) 4.99	
6	H(6) 7.228	
	H(6') 7.350	
	OH(3) 7.29	
7	H(6) 7.026	
	H(6') 7.351	
	OH(4) 6.18	
8	H(3) 7.136	
	OH(2) 3.0	



CONCLUSIONS

^1H NMR spectroscopy combined with mass spectrometry and X-ray diffraction forms an excellent structure specific method in studying environmentally important chlorinated biphenyls and their derivatives. The full NMR spectral assignment is usually a tedious task demanding time consuming two-dimensional carbon-proton heteronuclear COSY experiments, comparative studies on related derivatives and structural isomers in order to find out all substituent effects on the chemical shifts and coupling constants. In spite of that, the assignment should be verified by other methods such as known synthetical routes in preparing the model compounds.

In this special case, the chemical shift correlated 2-D ^1H - ^{13}C COSY spectroscopy showed to be an useful method in assigning the ^1H and ^{13}C NMR spectra of 2',3,4',5',6-pentachlorobiphenyl-2-ol. The literature based assignment probably was erroneous and the new one being in agreement with the COSY spectrum is given.

The precise stereostructure elucidation is of great importance in determining the quantitative structure/activity relationships (QSAR) of chlorinated aromatics. ^1H and ^{13}C NMR has shown to possess excellent isomer specificity in determining the structures of chlorinated biphenyls,^{11,12} biphenylols¹³ and their derivatives such as chlorinated dibenzotriophenes.^{14,15} In addition, vicinal and long-range ^1H and ^{13}C NMR coupling constants exhibit well-known angular dependencies. These parameters can be useful in estimating the conformational preferences such as the coplanarity of the rings in PCB:s, which has been argued to be the major factor in effecting on the physiological activity of these compounds.

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