THE ELUCIDATION OF CHLORINATED BIPHENYLS STRUCTURES BY THE PREDICTION OF NMR ^{13}C CHEMICAL SHIFTS

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INTRODUCTION

It is well known that even in polysubstituted compounds ^{13}C NMR chemical shifts and molecular structures are related by a limited number of parameters, so it is possible to reconstruct NMR spectra of all species of interest[1,2]. The ^{13}C NMR structural analysis is based on a topological dependence of chemical shifts, and spectra predictions are usually achieved with empirical increment schemes which must correspond to some contradictory necessities: an accuracy enough for high resolution of NMR, a reliable predictivity and a sufficient simplicity.

Our method of a simulation of ^{13}C NMR spectra of organohalogen compounds with respect to the mono− and two−particle increment scheme is presented here for the prediction of ^{13}C NMR spectra of polychlorinated biphenyls (PCB).

METHOD

The chromatographic determination of only the polychlorinated species required that 209 compounds be identified with the same NMR method. But e.g. oxy−substituted PCB need a much larger number of compounds which must be synthesized and characterized. More over, in ecological problems PCB are usually associated with parent aromatics with similar chromatographic and NMR properties.

By using ^{13}C NMR, however, it is possible to characterize every compound with a specific group of signals like a finger−print. Earlier we had analysed ^{13}C NMR spectra of oxybenzenes, polychlorinated and polybrominated polyoxybenzenes[2−4], dioxins[5,6] and naphthalenes[7] and showed that effects of steric and electronic substituents interactions are similar in all these aromatics.

The present analysis of NMR ^{13}C chemical shifts for PCBs revealed that PCBs can be considered as a benzene ring with two types of substituents: Cl and Ph. The only two−particle increments are related to well known Cl,Cl influences1) and three combinations of Cl−Ph: 2−, 3− and 4−Cl−biphenyls. To prove this assumption we had again included Ph−, Cl− and Cl,Cl − effects in PCB carbon chemical shift calculations and obtained the expected values[1,8]. It was found once more that effects of di−ortho−chlorines do not depend on their position relatively to ipso−carbon, contrary to authors[9] assumed different increments for every displacement of di−ortho

chlorines in two benzene rings of PCB despite to the physical sense of non − bonded interactions (here is the reason that their calculations had masked some erroneous signal assignments[10].

DISCUSSION
The problem of non − planar stable rotamers of ortho − substituted PCBs does not show any special effects, because two PCB rings quickly swing between potential barriers in NMR time scale and give an average spectrum for some quasi − planar structures.

Table 1 shows only examples of PCBs used to determine the increment scheme. It was enough to consider a few spectra of symmetrical molecules with unambiguous signal assignments, and some reliable measurements for unsymmetrical structures (for the stability of regression matrix). The resulting increment scheme has a standard error of 0.8 ppm and may be readily computerized.

This investigation is a part of a new approach to solving analytical problems in ecological chemistry by using NMR. It is possible to create new chromatographic procedures arranged with ^{13}C NMR for an identification of hundreds compounds PCB classes when a synthesis or even a separation of individual references are not beneficial. NMR also allows the study of molecular structures in some rectificated mixtures, so it is possible to correlate ^{13}C NMR spectra with chromatograms of mixtures to obtain combined characteristics without synthesis of reference compounds for the PCB − catalogue.

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Table 1

The experimental and calculated ^{13}C NMR chemical shifts for some PCBs (solvent CD$_2$Br$_2$ [10]), used in increments calculations

	δ ^{13}C ppm from TMS					
Clorine	1	2	3	4	5	6
positions	1'	2'	3'	4'	5'	6'
Nil	140.6	126.8	128.4	126.9		
calc.	140.3	127.3	128.5	127.5		
4 —	138.9	127.9	128.4	132.7		
	139.1	126.4	128.4	127.1		
calc.	139.0	128.5	128.5	127.6		
	139.3	128.5	128.5	127.6		
2,2' —	137.6	132.8	130.7	128.7	126.0	128.9
calc.	137.8	131.9	129.8	128.6	125.9	129.6
3,3' —	140.7	127.4	134.2	126.8	129.6	124.8
calc.	139.8	126.6	134.0	126.8	129.2	124.8
4,4' —	137.5	127.7	128.5	132.9		
calc.	138.2	128.1	128.5	133.5		
2,6,2',6' —	134.4	134.4	127.4	129.8		
calc.	135.2	134.1	127.2	129.6		
2,3,4,5,6 —	139.8	132.4	136.3	132.3		
	131.2	128.1	128.3	128.2		
calc.	141.3	132.7	134.6	133.5		
	132.7	127.3	128.5	128.4		
2,3,4,2',3',4' —	137.0	131.7	133.0	133.6	127.7	128.3
calc.	136.7	132.7	133.8	134.6	128.2	127.7
2,3,4,5,6,4' —	138.6	134.1	134.7	132.7		
	131.4	128.5	129.9	132.2		
calc.	137.7	134.1	134.7	131.4		
	138.0	128.5	129.6	131.0		
2,3,6,2',3',6' —	136.0	132.7	132.3	130.6	128.0	131.4
calc.	136.2	132.6	132.0	130.4	128.7	131.6
3,4,5,3',4',5' —	136.6	126.4	134.2	133.6		
calc.	137.1	126.3	134.0	132.1		