Elucidation of Brominated Biphenyl Structures in the Framework of the Common Method for Prediction of NMR ^{13}C Chemical Shifts for Polysubstituted Benzenes

Dostovalova Valentina I.[a] and Fedorov Lev A.[b]

[a] A.N.Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences, 28 Vavilov Str., 117813 Russia, Moscow.

[b] V.I.Vernadski Institute of Geochemistry and Analytical Chemistry Russian Academy of Sciences, 19 Kosygin Str., 117975 Russia, Moscow.

1. Introduction

^{13}C NMR chemical shifts and molecular structures in polysubstituted compounds 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 the aid of empirical increment schemes, which must meet some contradictory requirements: an accuracy enough for high resolution of NMR, reliable predictivity and sufficient simplicity.

Our method of simulating ^{13}C NMR spectra of organohalogen compounds in the context of the mono- and two-particle increment scheme is presented here for prediction of ^{13}C NMR spectra of polybrominated biphenyls (PBB).

Chromatographic determination of only polychlorinated or polybrominated species required that 209 compounds be identified with the same NMR method. But e.g. oxy-substituted PCB (and also PBB) need a much larger number of compounds, which must be synthesized and characterized. Moreover, in ecological problems PBB may be associated with parent aromatics with similar chromatographic and NMR properties.

However, using ^{13}C NMR, it is possible to characterize every compound with a specific group of signals. Earlier we had analyzed ^{13}C NMR spectra of oxybenzenes, polychlorinated and polybrominated polyoxybenzenes[2-4], polychlorinated dioxins[5,6] and naphthalenes[7] and PCB[8] 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 PBBs revealed that PBBs are completely similar to PCB and can be considered as a benzene ring with two types of substituents: Br and Ph; two-particle Br-Br increments[1] and three combinations of Br-Ph: 2-, 3- and 4-Br -biphenyls are enough for adequate description of NMR ^{13}C spectra of PBB.

2. Discussion

As in case of PCB[8], the problem of non-planar stable rotamers of ortho-substituted PBBs does not show any special effects, because two PBB 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 PBBs used to determine the increment scheme. It was enough to consider a few spectra of symmetrical molecules[9,10] with unambiguous signal assignments, and some reliable measurements for asymmetric structures (for stability of the regression matrix). The resulting increment scheme has a standard error of 0.6 ppm and may be readily computerized e.g. with the help of "Microsoft Excel".

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 of PBB classes when synthesis or even 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 PBB-catalogue.

Table 1. The experimental and calculated ^{13}C NMR chemical shifts for some PBBs solvent $CDCl_3$ [9,10]), used in increments calculations

	^{13}C, ppm from TMS					
Bromine positions	1 1'	2 2'	3 3'	4 4'	5 5'	6 6'
Nil	140.8	126.8	128.4	126.9		
calc.	140.3	126.3	128.5	127.0		
4-	140.0	128.7	131.8	121.5		
	140.1	126.9	128.8	127.6		
calc.	139.7	128.5	131.5	121.7		
	139.9	127.1	128.5	127.6		
4,4'-	139.0	128.5	132.1	122.0		
calc.	138.7	128.1	132.6	122.4		
2,6	143.1	124.5	131.8	129.8		
	141.2	128.2	129.2	128.1		
calc.	142.9	124.7	132.0	129.6		
	140.9	127.9	129.3	128.7		
2,4,6-	143.3	125.6	135.1	122.5		
	141.2	129.3	129.8	129.3		
calc.	143.6	125.1	136.1	122.9		
	141.4	129.7	128.3	129.0		
2,3,4,2',3',4'-	138.9	127.9	128.9	128.1	130.7	126.9
calc.	140.2	127.1	128.7	127.8	131.3	127.4

3. References

1) Dostovalova V.I., L.A.Fedorov, and J.Paasivirta. Prediction of carbon-13 chemical shifts of polysubstituted benzenes with homogeneous substituents. Magn Reson Chem 1991; **29**: 830-833.
2) Dostovalova V.I., and L.A.Fedorov. Application of topological analysis of ^{13}C chemical shifts to the elucidation of electronic and steric features of polyoxygenated benzenes with different substituents. Simulation of ^{13}C NMR spectra. Magn Reson Chem 1992; **30**: 1203-1211.
3) Dostovalova V.I., L.A.Fedorov and J.Paasivirta. The prediction of ^{13}C NMR spectra of polychlorinated aromatic pollutants. Organohalogen compounds 1992; **8**: 39-41.
4) Dostovalova V.I., and L.A.Fedorov. The prediction of NMR ^{13}C spectra of polybrominated oxigenated benzenes Organohalogen compounds 1993; **11**: 191-194.
5) Dostovalova V.I., and L.A.Fedorov. The simulation of NMR ^{13}C spectra of polychlorinated dioxins Organohalogen compounds 1990; **2**: 125-128.
6) Fedorov L.A., and V.I.Dostovalova. NMR approach to structure analysis of aromatic toxicants in environment. Chemosphere. 1995. in press
7) Dostovalova V.I., and L.A.Fedorov. The elucidation of the structure of polychlorinated naphthalenes and oxynaphthalenes by prediction of NMR ^{13}C chemical shifts. Organohalogen compounds 1993; **11**: 147-150.
8) Dostovalova V.I. and L.A.Fedorov. The elucidation of chlorinated biphenyls structures by prediction of NMR ^{13}C chemical shifts. Organohalogen compounds 1994; 19, 195-197.
9) Anklam E. ^{1}H and ^{13}C NMR studies of mono-and polybrominated biphenyls Magn Reson Chem 1989; **27**: 503-506.
10) Sovocool G.W., and N.K.Wilson. Differentiation of brominated biphenyls by carbon-13 nuclear magnetic resonance and GC/MS. J Org Chem 1982; 4032-4037.