The Prediction of NMR ^{13}C Chemical Shifts for Polysubstituted Benzenes with Different Halogens

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

The carbon NMR has already shown its undoubted advantage over other physical-chemistry methods in structural determination of unknown compounds. Earlier we showed that in polysubstituted compounds[1-7] NMR ^{13}C shifts and molecular structures are connected by a limited number of parameters, and this allows to reconstruct NMR spectra of all species under studying. The ^{13}C NMR structural analysis is mainly based on the topological dependence of chemical shifts, and large volume of spectra predictions has been achieved with the aid of empirical increment schemes. However, those schemes must have some contradictory properties: an accuracy enough for high resolution of NMR, reliable predictivity and sufficient simplicity in direct using or in programming for expert systems.

2. Discussion

Our method of simulating NMR ^{13}C spectra of organohalogen compounds in the context of mono- and two-particle increment scheme was firstly developed for prediction of NMR ^{13}C spectra of polysubstituted benzenes with homogeneous substituents and this investigation became a basis for elucidation by NMR ^{13}C of various environmental aromatic pollutants as polychlorinated and polybrominated oxybenzenes[2-4], dioxins[4,5], naphthalenes[6], PCB[7].

Now we offer the next step of this program: the analysis of NMR ^{13}C spectra of polyhalogenated benzenes with Cl, F or Br, F in one molecule. This step is very important for study of great number of ecotoxicants with mixed halogen substitution. For the development of our method, in which two-particle increment scheme for prediction of NMR ^{13}C spectra is constructed, we used only published data[8-10].

After the corresponding regression analysis we found out that all homogeneous mono- and two-particle increments coincide with those obtained in paper[1], so for the present problem new increments shown at the Table 1 are almost enough.

Of course we need some extension of the group of model compounds, but in very limited amounts. After such an extension, the presented increment scheme will include all structural features which determine the changes in NMR ^{13}C chemical shifts. Nevertheless, even existing data are enough to trust that the direction of structure recognizing by spectra

prediction is very promising, because in general it is significantly more economic both in the synthesis and in the personnel aspects.

Table 1. Mixed increments for polyhalogenated benzenes

Increment	C_k	X=Cl	X=Br
	1	0.5	0.0
$R^{1,2}(X-F)$	2	-4.7	-7.0
	6	1.0	1.5
$R^{1,4}(X-F)$	1	0.0	-1.2

Table 2 demonstrates some examples of using the presented increment scheme. The resulting increment scheme has standard error of 0.45 ppm and may be algorithmized and transformed to a corresponding service program for the personal computer.

Table 2. The experimental[8-10] and calculating NMR ^{13}C chemical shifts of some polyhalogenated benzenes (solvent $CDCl_3$)

| Substituent positions | ^{13}C, ppm from TMS | | | | | |
	C_1	C_2	C_3	C_4	C_5	C_6
1-Cl,2,6-F_2	110.2	159.4	111.0	127.6		
calc.	110.5	159.4	111.9	128.8		
1-Cl,2,3,4,5,6-F_5	108.2	144.8	138.3	140.7		
calc.	106.3	142.8	136.7	140.8		
1,3,4,5,6-Cl_5,2-F	121.6	153.8	132.0	129.4		
calc.	122.7	153.0	133.6	128.3		
1-Br,2,3-F_2	111.7	149.6	152.4	117.7	126.1	129.6
calc.	111.4	147.3	152.3	116.4	125.8	128.9
1,2-Br_2,3,4,5,6-F_4	109.2		146.5		141.0	
calc.	108.5		147.3		141.8	
1,3-Br_2,2,4,5,6-F_4	94.8	152.5		149.0	(138.3)	
calc.	94.0	152.9		149.3	141.3	
1,4-Br_2,2,3,5,6-F_4	99.7	145.4				
calc.	100.8	145.7				
1-Br,2,3,4,5,6-F_5	94.7	145.4	138.4	141.3		
calc.	92.5	144.3	138.9	140.3		

Considering this investigation as a model we can suggest the new approach to solving of the analytical problem under consideration with an intensification of NMR part. It is possible to create new chromatographic procedures arranged with NMR ^{13}C for identification of hundreds compounds of aromatic classes when the synthesis or at least the separation of individual references is not beneficial.

2. 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) Fedorov L.A., and V.I.Dostovalova. NMR approach to structure analysis of aromatic toxicants in environment. Chemosphere. 1995. in press

6) 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.

7) 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.

8) Abraham R.J., D.F.Wileman, G.R.Bedford, and G.R.Greatbanks. J Chem Soc Perkin II. 1972, 12, 1733-1738.

9) Briggs J.M., and E.W.Randall. J Chem Soc Perkin II. 1973, 13, 1789-91.

10) Bremser W., A.Hardt, L.Ernst, B.Franke, and W.Fachinger. Carbon-13 NMR spectral data. Weinhaim: VCH, 1987.