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The Prediction of NMR ^{13}C Chemical Shifts for Mixed Cl,Br-Benzenes in Frame of Two-Particle Increments

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Introduction

The carbon NMR spectroscopy is well known as a power physical-chemistry method of structural determination of unknown compounds. Earlier we showed that in polysubstituted aromatic compounds¹⁻⁹⁾, NMR ^{13}C shifts and molecular structures are connected by a limited number of parameters. This allows to reconstruct NMR spectra of all species under studying including unknown. 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.

Results and discussion

Our method of simulating NMR ^{13}C spectra of organohalogen compounds in frame of mono- and two-particle increment scheme⁵⁾ 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 oxybenzenes²⁻⁴⁾, polychlorinated dibenzo-p-dioxins⁵⁾, polychlorinated naphthalenes⁶⁾, polychlorinated⁷⁾ and polybrominated biphenyls⁸⁾.

But it is evident that future ecological problems will be connected with analysis of pollutants with different halogens in one molecule. Now we offer the next step of this program: the analysis of NMR ^{13}C spectra of mixed polyhalogenated benzenes with Cl and Br. This step is very important for study of great number Cl,Br-dioxins, -furans and -diphenyls and other 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 published data¹⁰⁻¹²⁾ and our own NMR ^{13}C measurements.

After the corresponding regression analysis we found out that all homogeneous mono- and two-particle increments coincide with those obtained in paper¹⁾, so the last column of the Table 1 contains new increments for Cl-Br influence.

Table 1.

Two-particle increments of ortho-halogens in benzene ¹³C chemical shifts

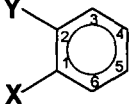
	Carbon under influence	X=Cl Y=Cl	X=Br Y=Br	X=Cl Y=Br
	C ₁	-1.21	-1.07	-2.05
	C ₂	-1.21	-1.07	0.00
	C ₃	0.77	0.46	1.24
	C ₆	0.77	0.46	-0.69

Table 2 demonstrates some examples of using the presented increment scheme.

Several discrepancies in Table 2 between experimental and calculated chemical shifts show that we need in some extension of the group of model compounds for better statistic, but in very limited amounts. After such an extension the presented increment scheme will include all structural features which determine the changes in NMR ¹³C chemical shifts.

Table 2.

The experimental (our data and ref¹⁰⁻¹²⁾) and calculating NMR ¹³C chemical shifts of some polyhalogenated benzenes (solvent CDCl₃)

Substituent positions	¹³ C, ppm from TMS					
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
1-Br,2-Cl, ref. ¹²⁾	122.56	134.58	130.14	127.31	127.84	133.53
	122.54	134.50	130.43	127.88	128.43	133.80
calc.	122.95	135.21	129.83	127.73	127.88	132.76
1-Br,3-Cl, ref. ¹¹⁾	122.75	131.49	135.13	127.34	130.75	129.74
	123.30	132.09	135.70	127.83	131.24	130.28
calc.	123.07	131.76	135.23	127.04	130.42	129.91
1-Br,4-Cl, ref. ¹⁰⁾	120.27	132.75	130.19	133.17		
	120.29	132.76	130.17	133.24		
calc.	120.53	131.76	129.04	132.54		
1-Br,2,6-Cl ₂	123.50	136.40	128.30	128.40		
calc.	123.52	136.21	127.54	127.54		
1-Br,2,6-Cl ₂	124.00	134.00	132.23	127.95	129.36	131.99
calc.	123.84	133.67	133.33	128.50	128.57	131.84

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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.

The increment scheme, which will be obtained after studying of some else compounds, may be algorithmized and transformed to a corresponding service program for the personal computer.

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.

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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 compd.* 1992; **8**: 39-41.
- 4) Dostovalova V.I. and L.A.Fedorov. The prediction of NMR ^{13}C spectra of polybrominated oxygenated benzenes. *Organohalogen compd.* 1993; **11**: 191-194.
- 5) Fedorov L.A. and V.I.Dostovalova. NMR approach to structure analysis of aromatic toxicants in environment. *Chemosphere* 1995; **30**(7): 1311-1329.
- 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 compd.* 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 compd.* 1994; **19**, 195-197.
- 8) Dostovalova V.I. and L.A.Fedorov. The prediction of NMR ^{13}C chemical shifts for polysubstituted benzenes with different halogens. *Organohalogen compd.* 1995; **23**: 151-153.
- 9) Dostovalova V.I. and L.A.Fedorov. Elucidation of brominated biphenyls structures in the framework of the common method for prediction of ^{13}C NMR chemical shifts for polysubstituted benzenes. *Organohalogen compd.* 1995; **26**, 431-433.
- 10) Bromilov J., R.T.C.Brownlee, D.J.Craik, M.Sadek and R.W.Taft. *J Org Chem* 1980; **45**, 2429-2438.
- 11) Bromilov J., R.T.C.Brownlee, D.J.Craik and M.Sadek. *Magn Reson Chem* 1986; **24**, 862-871.
- 12) Bremser W., F.Hardt, L.Ernst, B.Franke and W.Fachinger. *Carbon-13 NMR spectral data*. Weinheim: VCH, 1987.