

THE PREDICTION OF NMR ^{13}C SPECTRA OF POLYBROMINATED OXIGENATED BENZENES.

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Introduction

The ^{13}C NMR spectroscopy is nowadays one of main methods for the structure elucidation of unknown organic compounds. Such problem is of a great importance for ecological chemistry, especially concerning to recognizing of hazardous pollutants. Every big environmental center has a modern NMR spectrometer or even some system of them. NMR spectroscopy is a method of extremely high resolution because NMR signal can to reflect small structure changes. However it is well known that in nowday reality the mean instrument of ecological chemistry is the chromatography. The samples have been cleaned, deeply divided and identicated by comparing with references, which have to be specially synthesized. NMR spectrometers as a rule are used only for identification of model compounds. Contrary to one chromatography singlet requiring his own reference for identification, NMR ^{13}C spectrum contains a set of signals accordingly to number of unequivalent carbons in the compound, and positions of these signals (chemical shifts) do not depend in general on anything except molecular structure, so the NMR ^{13}C spectrum is a distinct portret of a molecule. Moreover the chromatography sometimes is a destructing method so e.g. hydroxy substituted compounds need in previous etherification, while NMR can analyse compounds without any transformation.

Approach

NMR ^{13}C chemical shifts are very informative physical properties of organic compounds, so it is evidently very important to generalize them in some standard manner to have a possibility of an unambiguous prediction NMR ^{13}C spectra for every structure and to avoid of a great part of modelling syntheses. Usually it has been doing in form of increment schemes, and the latter are essentially convenient for ecologists which are studying some sets of homologues and isomers. Conventional increment schemes based

at an additivity of mono-atomic influences, and such approach is not acceptable for polysubstituted molecules because of complicate steric and mesomeric effects. The introducing of different sets of poly-atomic increments is evidently closed way because of the avalanche-like amount of necessary parameters for real sets of compounds.

During last time we had shown at different examples¹⁻³ that many-atomic interactions in polysubstituted molecules may be expressed through two-particle increments, and had demonstrated such predictive increment schemes for carbon chemical shifts in polychlorinated dibenzo-p-dioxins^{4,5} and polychlorinated polyoxybenzenes⁶. There are next requirements to ¹³C NMR increment schemes in polysubstituted compounds:

- 1) The calculating reference must be universal (e.g. benzene, TMS).
- 2) Many-particle interactions must be expressed through two-particle increments, similarly to atom-atom potentials in molecular mechanics.
- 3) Mixed two-particle increments must be obtained from homogeneous ones. All these positions are extremely important for everyday using of increment scheme for structure recognition of really unknown aromatic compounds by NMR ¹³C.

Results and Discussion

Now we have performed such investigation, based only at published data, for the wide class of polybrominated benzenes with oxy-, methoxy- and phenoxy (one example) substituents. This class of aromatic ecotoxicants is unsufficiently known explored for the present, though it is so important as polychlorinated oxybenzenes because they are precursors of polybrominated dioxins. The traditional investigation of this new class of ecotoxicants will demand the whole set of individual chromatographic references, meanwhile two-particle increment scheme for NMR ¹³C chemical shifts can considerably simplify an identification of unknown compounds directly in some narrow fractions.

Available data^{7a-e} contain experimental values only for ¹³C spectra of 11 compounds (43 different chemical shifts), nevertheless we could obtain the increment scheme for ¹³C NMR chemical shifts predictive enough to reveal some opposit assignments in originals. The latter is an improvement of an acceptability of obtained increments for the description of NMR ¹³C spectra for all compounds of this class. However the restricted experimental volume does not allow to obtain good statistic for increments and to discuss the solvents influence.

In two-particle approach the chemical shift of the k-th ring carbon α_k in polysubstituted benzene may be represented as:

$$C_k = C_0 + \sum (E_k(i)) + \sum (R_k(ij))$$

Here C_0 - the benzene chemical shift (128.5 ppm); $P_k(i)$ - the substituent's increment in X - monosubstituted benzenes; $R_k(ij)$ - additional effect contribution to the chemical shift α_k caused with i-th and j-th substituents nonadditivity influence.

In consecutive order there were used previous results obtained for polybrominated³ and polyoxygenated⁴ benzenes. Calculations were carried out only for mixed oxy-bromine two-particle increments using the similarity of bromine and chlorine effects in ¹³C NMR of organic compounds. So we had chosen for oxy-bromine increments the same form as for oxy-chlorine ones⁷ and had found them with help of known method of regularization of multiparameter linear regression. At the end of calculations only 19 nonzero parameters remain valid standard error was 0.87 ppm (Table 1).

The Table 2 demonstrates some examples of new increment scheme's possibilities. Results are in a good agreement with experimental data and allow to entrust to predictive capability of obtained set of increments.

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Table 1

The experimental and predicted¹³C NMR chemical shifts (ppm from TMS) for some brominated oxybenzenes.

Substituent position	Solv.	C-1	C-2	C-3	C-4	C-5	C-6
1-OH,2-Br [7a] calc.	C ₆ H ₁₂	153.3	110.7	132.3	121.7	129.7	116.6
		152.7	110.5	131.8	(121.4)	128.9	116.4
1-OMe,2-Br [7b] calc.	CCl ₄	155.8	111.9	133.1	121.3	127.9	111.5
		156.2	111.9	133.1	(122.1)	127.9	111.5
1-OH,4-Br [7b] calc. [7c]	CDCl ₃	153.9	117.2	132.5	113.2		
		154.9	(117.4)	(132.0)	111.8		
	DMSO	156.8	117.6	132.1	110.0		
1-OPh,4-Br [7b] calc.	CDCl ₃	156.5	120.3	132.5	115.6		
		155.4	(120.5)	(132.0)	114.8		
1-OH,2,6-Br ₂ [7b] calc.	CDCl ₃	149.3	110.0	131.9	122.3		
		150.5	110.9	131.7	122.7		
1-OMe,2,6-Br ₂ [7d] calc.	acet.	154.8	118.6	133.6	127.5		
		154.8	119.0	132.6	126.3		
1-OH,2,4-Br ₂ [7b] calc.	CDCl ₃	151.5	110.8	134.0	112.7	132.0	117.4
		151.7	111.1	134.6	112.8	132.4	117.6
1-OH,2,4,6-Br ₃ [7b] calc.	CDCl ₃	150.5	112.4	133.9	111.3		
		149.3	111.4	134.2	111.1		
1-OMe,2,4,6-Br ₃ [7b] calc.	CDCl ₃	153.7	118.9	134.9	117.3		
		153.7	119.5	135.1	117.5		
1-OH,2-OMe,4,5-Br ₂ [7e] calc.	CDCl ₃	145.3	146.3	115.2	115.0	113.6	119.0
		145.5	147.4	(115.9)	114.6	115.3	(119.2)
1,2-OMe ₂ ,3,4,5,6-Br ₄ [7f] cacl.	CDCl ₃	151.9		122.3	124.3		
		151.9		121.3	125.2		

The values in brackets did not demand mixed O-Br increments

Table 2

The mixed OR-Br increments additional to Br and OR ones

The structure element	C _k	Y-H	Y-Me	The structure element	C _k	Y-H	Y-Me
1-OY,2-Br	C ₁	-6.70	-6.70	1-OY,4-Br	C ₁	0.18	0.18
	C ₂	0.55	3.50		C ₂	-2.10	-2.10
	C ₃	-0.25	1.10	1-OY,2,6-Br ₂	C ₁	-5.64	-5.64
	C ₅	1.55	0.60		C ₂	0.40	10.00
	C ₆	-1.00	-4.40		C ₃	0.85	1.77
				C ₄	0.14	2.98	