

**THE ELUCIDATION OF THE STRUCTURE OF POLYCHLORINATED NAPHTHALENS AND OXYNAPHTHALENES BY PREDICTION OF NMR  $^{13}\text{C}$  CHEMICAL SHIFTS**

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The carbon NMR had already shown its undoubted advantage over others physical-chemistry methods in structural determination of unknown compounds. Earlier we had shown that even in polysubstituted compounds<sup>1,2</sup> NMR  $^{13}\text{C}$  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  $^{13}\text{C}$  NMR structural analysis is mainly based on the topological dependence of chemical shifts, and large volume of spectra predictions has been achieved with empirical increment schemes. The latter must however have some contradictory properties: an accuracy being enough in view of high resolution of NMR, a reliable predictivity and a sufficient simplicity in direct using or in programming for expert systems.

Our method of a simulation of NMR  $^{13}\text{C}$  spectra of organohalogen compounds in frame of mono- and two-particle increment scheme is presented now for the prediction of NMR  $^{13}\text{C}$  spectra of polychlorinated naphthalenes, polyoxygenated naphthalenes and then - of polychlorinated oxynaphthalenes (OR = OH, OMe and OPh).

Naphthalens are dioxin-like compounds, and chromatographic determination only of polychlorinated species demands 75 references, which in their turn are to be identified with the same NMR method. The situation for oxy-substituted naphthalenes is significantly more complicative because of vast number of references which are to be synthesized and recognized. Moreover, in ecological problems naphthalenes under consideration are usually accompanying parent biphenyls which have close chromatographic and NMR signal regions. So it is necessary to use NMR possibility to characterize every compound with a definite group of signals, so individual as a finger-print.

Before dioxins proper we had investigated NMR  $^{13}\text{C}$  spectra of oxy- and polychlorinated polyoxybenzenes<sup>2,3</sup> and it was shown that the influences of chlorine-oxygen steric and electronic interactions in dioxins are almost similar to

those in monocyclic aromatic systems except of some corrections to the fixed position and the specific orientation of oxygen lone pairs in dioxins.

NMR spectral features for naphthalenes are similar to peculiarities of dioxins spectra<sup>4,5</sup>: it is also important to consider 1- and 2-substituted heterographs as base elements of an increment scheme and 1,2- or 2,3-ortho disubstituted heterographs with equal effects as a model of substituents steric interactions.

But naphthalene two-ring system demonstrates more expressive conjugative properties than in dioxins case because the intermediate oxygen-containing ring in the latter suppresses the conjugating of two benzene rings. That's why the system of base elements for NMR <sup>13</sup>C increment scheme for polysubstituted naphthalenes contains in addition 1,8-two-particle heterosubgraph.

For the development of our method of construction of increment scheme for prediction of NMR <sup>13</sup>C spectra we had used only published data<sup>6</sup> and consequently applied our approach firstly to polychlorinated naphthalenes<sup>6,7</sup> than to polyoxygenated<sup>6,8</sup> and finally to polychlorinated oxynaphthalenes<sup>6</sup>. In spite of limited number of model compounds we had the opportunity to predict NMR <sup>13</sup>C spectra of some polychlorinated naphthalenes which were not used for increment analysis, and our calculations were in good accordance with measurements performed by V.Nikifirov<sup>7</sup>. Except of this we succeeded in reassignment of signals of some polychlorinated naphthalenes, and further in polychlorinated oxynaphthalenes<sup>6</sup>. So we can declare that our generalization of NMR <sup>13</sup>C chemical shifts is predictive enough to distinct similar for the first sign spectra of different relative compounds. Of course we need in some expansion of the group of model compounds, but in very limited amounts. After this the presented increment scheme will include all structural features which determine the changes in NMR <sup>13</sup>C chemical shifts. Nevertheless, even existing data are enough entrust that the direction of structure recognizing by spectra prediction is very promising, because it is in general significantly more economic as in synthetic so in person aspect.

The Table demonstrates some examples of using the presented increment scheme, and calculating carbon chemical shifts show the necessary reassignment of some signals (in simple brackets).

The resulting increment scheme has standard error 0.45 ppm and 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 the solving of the analytical problem under consideration with an intensification of NMR part. It is possible to create new chromatographic procedures arranged with NMR  $^{13}\text{C}$  for an identification of hundreds of compounds of naphthalene classes when the synthesis or at least the separation of individual references is not beneficial. Moreover NMR allows to study molecular structures in some ratified mixtures, so we can correlate NMR spectra with chromatogram of mixtures under consideration in order to obtain chromatographic characteristics without a synthesis of references. In this way we can develop the calculating methods for obtaining the catalogue of spectra NMR  $^{13}\text{C}$  for all compounds of the class under consideration.

#### References

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Table  
The experimental and calculating NMR  $^{13}\text{C}$  chemical shifts (ppm from TMS) of some  
polysubstituted naphthalenes (solvent  $\text{CDCl}_3$ )

Compound, ref.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
1,2,3,4- $\text{Cl}_4$ [6] calc.	130.1 130.2	130.3 130.3			125.4 125.5	128.7 128.8			130.0 130.0	
$\text{Cl}_8$ [6] • [7] calc.	128.7 129.7 (9,10) 129.6	135.0 135.3 (2,3,6,7) 135.5							129.4 129.0 (1,4,5,8) 129.2	
1,4,5,8- $\text{Cl}_4$ [7] calc.	130.9 130.4	131.0 130.7							130.5 129.3	
1,2,3,4,5,8- $\text{Cl}_6$ [7] calc.	129.3 129.2	134.5 134.4			130.3 130.2	131.8 131.9			129.3 127.7	
1,2,3,5,6,7- $\text{Cl}_6$ [7] calc.	131.0 130.5	132.1 132.2			133.4 132.5	124.6 123.9			129.1 128.5	
1,2,3,4,6- $\text{Cl}_5$ [7] calc.	130.3 130.1	130.4 130.2	131.3 131.0	129.3 129.5	127.2 126.3	135.4 134.0	129.6 129.0	124.4 123.7	128.5 128.1	130.1 130.3
1-OH [8] calc.	151.2 151.2	108.8 106.9	125.8 126.0	120.8 120.6	127.7 127.5	126.5 126.6	125.3 125.3	121.5 121.5	124.4 124.4	134.8 134.8
1,5-(OH) $_2$ [8] calc.	153.6 153.8	109.3 109.2	125.6 125.4	114.2 114.5					127.2 126.7	
2,3-(OH) $_2$ [8] calc.	110.2 110.2	144.0 144.0			126.2 126.4	124.2 124.4			129.5 130.4	
1- $\text{Cl}$ ,2-OH [6] calc.	113.7 112.9	149.4 150.0	117.2 117.1	128.2 128.4	128.4 128.4	124.1 123.6	127.5 127.0	122.8 123.4	131.1 131.8	129.5 129.4
1- $\text{Cl}$ ,4-OH [6] calc.	123.6 123.0	125.7 126.9	108.7 109.2	150.6 151.3	122.1 122.1	126.0 125.3	127.6 126.8	124.5 124.7	131.6 133.2	125.5 125.6
2- $\text{Cl}$ ,1-OH [6] • calc.	147.1 146.2	113.6 114.0	126.1 (7) 125.0	122.2 (6) 122.2	127.6 127.6	126.7 126.6	125.9 126.8	120.9 120.8	124.6 124.2	133.3 133.4
1,6- $\text{Cl}_2$ ,2-OH [6] • calc.	113.5 (8) 113.2	149.7 149.5	118.5 (4) 118.5	124.6 (6) 129.1	127.5 (7) 127.4	130.1 (10) 128.3	128.4 (9) 127.2	126.9 125.1	129.5 131.3	130.1 129.7
2,4- $\text{Cl}_2$ ,1-OH [6] • calc.	146.4 (5) 146.3	112.7 (4) 113.1	125.4 125.9	124.9 124.6	124.4 124.9	127.7 126.8	126.9 126.5	122.5 121.6	123.4 124.1	130.3 131.3

• - new assignment