THE PREDICTION OF ^{13}C NMR SPECTRA OF POLYOXYCHLORINATED
AROMATIC POLLUTANTS

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The ^{13}C spectroscopy is nowdays one of methods for the
structural elucidation of unknown organic compounds, including
hazardous pollutants. Compounds can be analysed in solutions,
isomer signals are distinguishing, species may be detected in
mixtures.

NMR can well cooperate with chromatography in creating of
the data bank of individual or mixed standards. The ^{13}C NMR
structural analysis mainly concerns chemical shifts because of
their topologival dependence, so the large volume of spectra
predictions has to be achieved with increment schemes. However
latters need in some contradictory properties: accuracy corres-
ponding to the high resolution of NMR, reliable predictivity
and sufficient simplicity in direct using or in programming for
the expert systems.

Simple additive estimating of ^{13}C NMR chemical shifts in
aromatic compounds is based on assumed independence of substi-
tuent influences and causes a discrepancy in experimental and
calculating data: collecltive contributions in ^{13}C chemical
shifts of oxygenated [1] and oxychlorinated aromatic pollutants
caused by electronic and especially by steric substituent
interactions are comparable with their individual increments
and limit the fitness of simple additive schemes.

Modern practical problems (signal assignments, theoretical
spectra calculations and construction of different expert sys-
tems - NMR or/and chromatographic) require some ways including
substituent interactions.

Recently[1-3] we offered a new method of revealing of
topological factors of ring carbon shielding changings in
polysubstituted benzenes and obtained the new predictive
increment scheme for ^{13}C shifts for some homogeniously
substituted benzenes $C_6H_{6-n}X_n$ (X = F, Cl, Br, CH_3 etc.) in
frame of two-particle interactions only.

Now the method offered in [1-3] we developed for a genera-
lization of ^{13}C NMR chemical shifts of a wide class of
practically important compounds - polyoxychlorinated benzenes
with hydroxy and methoxy substituents. The substituent
influence effects are obtained in form of individual and
collective increments. The final calculative massif had 135
experimental points (lines) and 21 parameters (columns),
standard error 0.67 ppm. Results are in a good agreement with
experimental data and allow to entrust to predictive capability
of obtained set of increments. The Table demonstrated some
examples of chemical shifts calculations.

Table

The experimental and predicted ^{13}C NMR spectra for some
oxychlorinated benzenes

Substituents positions							ppm from TMS					
							C-1	C-2	C-3	C-4	C-5	C-6
OH	Cl	Cl	OMe	Cl	-	(a)	151,5	119.9	129.5	147.1	127.8	116.3
						calc.	151.7	118.9	128.7	146.7	127.9	116.1
OH	Cl	Cl	OMe	-	Cl	(a)	144.8	123.1	120.9	150.5	113.0	121.2
						calc.	144.4	121.8	120.6	150.1	110.8	120.9
OH	Cl	·Cl	OMe	Cl	Cl	(a)	148.6	120.8	127.9	147.8		
						calc.	148.8	119.1	126.6	148.1		
OMe	Cl	-	OMe	-	-	(b)	149.4	123.0	112.7	153.9	113.3	116.2
						calc.	149.1	123.6	115.2	155.0	113.0	112.7

(a) acetone-d$_6$ [4]; (b) CDCl$_3$ [5];

During the calculating process the opposite assignment of
chemical shifts C-3 and C-6 in 1,4-OMe-2-Cl-C$_6$H$_3$ from the
catalogue [5]. Undoubtedly so small differences in chemical
shifts (112.7 and 116.2 ppm) can not be recognized with an
expert system based on the spectra compilations using the data
bank even very large one. Reliable results one can get only
with help of calculating methods which take into account
physico-chemical properties of compounds under consideration.
Such general procedure of topological analysis can be used
for the studying of any set of NMR data of different classes
of compounds. Calculations carried out for oxychlorinated
benzenes had shown the rightful of accepted suggestions and
the efficiency of choosen system of increments. In particular
nowdays there is no any other method for an identification of
NMR signals in these polysubstituted benzenes. The intermolecu-
lar hydrogen bonding was taken into account, so we had the
opportunity to calculate some examples of spectra in aceton-d$_6$,
the solvent with the specific solvatation of OH-groups.
In conclusion there must be noted some consequences
important for the practice. Detail studying of topological
properties of ^{13}C chemical shifts in polyoxychlorinated
benzenes already now can accompany to the chromatography in two

dimensions: the confirmation of references structures and in determination of structure of unknown compounds in the case of sufficient extraction of natural pollutants.

Besides this our method is a necessary step in analysis of spectra NMR of aromatic environmemtal pollutants so as polyhalogenated dioxins set[6]. It is must be emphasize that obtained increment scheme may be algorithming for the creating the ^{13}C NMR spectra simulating program for PC with better approaching to an experiment than known programs.

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