

THE SIMULATION OF NMR ^{13}C SPECTRA OF POLYCHLORINATED DIOXINS

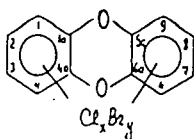
V.I. Dostovalova,

A.N. Nesmeyanov Institute of Organoelement Compounds,
USSR Academy of Sciences, 28 Vavilov Str., 117813 Moscow, USSR

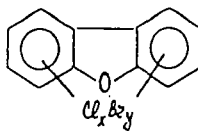
L.A. Fedorov,

V.I. Vernadski Institute of Geochemistry and Analytical Chemistry,
USSR Academy of Sciences, 19 Kosygin Str., 117975 Moscow, USSR

There are well known difficulties in the analysis of organohalogenic compounds in the environment because of their large diversity. Thus the whole family of the so called polyhalogenated dibenzodioxins (I) and dibenzofuranes (II) includes several thousand compounds [1]. Obviously, it is practically impossible to synthesis and investigate each such compound and, moreover, related ones or metabolites.



(I)



(II)

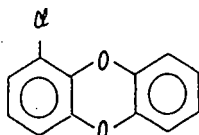
In this aspect the ^{13}C NMR spectroscopy is a unique analytical method, because of its capability to identify different compounds, even in mixtures, by their spectra. In addition, the spectra of unknown compounds can be predicted by mathematical calculations.

In reports [2-5] we described the method of a simulation of NMR ^{13}C spectra of organohalogen compounds - homogeneous and mixed halogenalkanes [2,3] and homogeneous halogenic benzenes [4,5] in the frame of mono- and two-particle increment scheme. In the present report we developed this method for the prediction of NMR ^{13}C spectra of polychlorinated dioxins (I, $x \neq 0$, $y = 0$).

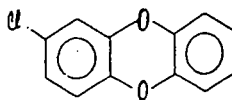
For this purpose it was necessary to work in consecutive order the similar methods for the calculation of NMR ^{13}C chemical shifts of polyoxygensubstituted benzenes (to be published), including the calculation of the unsubstituted dibenzodioxin NMR ^{13}C spectra of polychlorinated phenoles, anisoles, catecholes and diphenylic ethers (to be published).

At the final stage it was found that for the analysis of NMR ^{13}C chemical shifts in polychlorinated dioxins we must additionally consider only two new entites (III) and (IV)

- each with one chlorine atom:



(III)



(IV)

It can be seen that additional influences of chlorine-oxygen steric and electronic interactions in dioxins has no analogy with monocyclic aromatic systems.

As a statistical data base we used NMR ^{13}C of several low toxic chlorinated dioxins ($l, x \neq 0, y = 0$) [6], and experimental and calculated chemical shifts are given in the top part of the table. The results are quite satisfactory and some differences between experimental and calculated values may be caused by slight angle changes in the middle dioxin ring containing two oxygen atoms.

The result so obtained may be applied for a calculating of ^{13}C spectra for acutely toxic dioxins (including the 2,3,7,8-isomer) which are not yet investigated by NMR ^{13}C (the bottom of the table). One can pick out some important aspects of analytical and other applications of our method. Firstly it is evident that the experimental data concerning six low-toxic compounds can be used for obtaining the inaccessible information about the rest (69) polychlorinated dioxins ($l, x \neq 0, y = 0$). Such examples for 5 very highly toxic dioxins are shown in the table. We suppose also that the calculation accuracy may be increased on the more expanded basis of NMR ^{13}C experimental data of some new polychlorinated dioxins.

Secondly the present method may be easily developed for the simulation of NMR ^{13}C spectra of all polybrominated dioxins ($l, x = 0, y \neq 0$), if one can give only the minimal set of experimental data.

Then it is possible, in principle, to do a similar analysis for NMR ^{13}C spectra of mixed Cl, Br-dioxins (I, $x \neq 0$, $y \neq 0$) and to calculate the spectrum for every one of more than 1,500 of these compounds, and also develop the method for related compounds, containing some other substituents in addition to halogen atoms: OH (metabolites), alkyl groups and so on.

And at last the obtained results permit to identify the spectrum of an individual isomer in NMR ^{13}C spectra mixtures, for instance, of tetrachlorinated dioxins. It can be seen from table, that 1,2,3,4- and 2,3,7,8- Cl_4 -dioxins have evidently different spectra.

Finally it is necessary to note that the empirical scheme for spectral pattern calculations, suggested in [2-5] and in the present report, may have the general significance for the prediction NMR ^{13}C spectra for some sufficiently broad congener of inaccessible compounds by using the limited data base for accessible ones.

It is important also that the scheme mentioned above may be algorithmized and transformed to a corresponding service program for the personal computer.

References:

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The calculated and experimental [6] NMR ^{13}C chemical shifts
of some chlorinated dibenzodioxins

Chlorine positions	^{13}C , ppm from TMS											
	1a	1	2	3	4	4a	6a	6	7	8	9	9a
1-	140.1	124.0	123.6	124.4	113.7	142.5	143.2	116.7	124.4	124.8	116.4	143.2
exp.	141.0	-	123.0	124.0	114.0	143.0	143.0	116.0	124.0	124.0	116.0	143.0
2,7-	141.6	117.1	125.0	123.7	117.0	141.8						
exp.	-	116.0	-	123.0	117.0	-						
1,3-	137.4	122.9	124.0	128.7	114.8	142.9	143.7	116.7	123.3	123.6	116.2	140.8
exp.	-	124.0	124.0	-	115.0	143.0	143.0	116.0	124.0	124.0	116.0	141.0
2,3-	140.8	117.2	126.9				141.0	116.1	124.3			
exp.	141.0	117.0	126.0				141.0	116.0	124.0			
1,2,4-	141.4	119.1	127.2	125.3	120.5	141.0	140.7	116.6	123.6	124.5	116.9	144.7
exp.	140.0	119.0	127.0	124.0	119.0	140.0	140.0	116.0	124.0	124.0	116.0	
1,2,3,4-	138.8	120.9	126.4				138.9	116.7	124.5			
exp.	138.0	119.0	126.0				140.0	116.0	125.0			
2,3,7,8,-	141.2	118.3	125.1									
1,2,3,7,8,-	139.7	122.6	124.7	126.2	115.8	140.9	142.2	118.5	126.3	125.1	118.3	140.4
1,2,3,4,7,8-	139.9	121.3	124.8							126.3	119.0	141.4
1,2,3,6,7,8-	138.9	123.0	123.5	127.7	116.0	141.9						
1,2,3,7,8,9-	140.9	122.8	124.7	126.5	116.3	140.1						