The increment scheme for the prediction of ^{13}C NMR chemical shifts in polychlorinated dibenzo-*p*-dioxins

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A topological method for the calculation of ^{13}C NMR chemical shifts was developed for polychlorinated dibenzo-*p*-dioxins (PCDD). Based on previous results for polychlorinated benzenes and polyhydroxybenzenes, the collective influence of the substituents on carbon chemical shifts is presented as the sum of two-particle increments. The increments only of two new monosubstituted graphs have to be added to those known for PCDD spectra: 1-Cl—DD and 2-Cl—DD. All structural situations in the ^{13}C NMR chemical shifts of the whole class of 75 PCDD can be covered with a few model compounds. The coefficients of the increment scheme are independent of the change of $CDCl_3$ for acetone-d_6, so it may be a new reliable criterion for recognizing PCDD by ^{13}C NMR, in spite of the close resemblance of NMR spectra of aromatic compounds.

Key words: ^{13}C NMR chemical shifts, increment scheme, polychlorinated dibenzo-*p*-dioxins.

^{13}C NMR spectroscopy is rarely used for studying polychlorinated dibenzo-*p*-dioxins (PCDD)[1—5] and related compounds many of which have not yet been studied.

For resolving and interpreting the ^{13}C NMR spectrum of an unknown compound, the spectra of several related compounds and a method for generalizing their main spectral features to reliably predict the spectrum of any compound in the whole class must be available. This method is provided by the suggested system[6—9] of two-particle increment schemes, which relates various combinations of two substituents to the changes in chemical shifts (CS) in the ^{13}C NMR CS of polysubstituted compounds.[8,9] Conventional one-particle increment schemes are too rough to simulate the ^{13}C NMR spectra of polysubstituted compounds and a many-particle approach leads to an unlimited increase in the number of increments. We show that adequately chosen two-particle increments describe the collective effects of substituents on CS of C atoms of polysubstituted compounds with good accuracy.

Previously[10] the topological properties of the ^{13}C NMR of PCDD were generalized on the basis of the sole experimental data[1] available at that time. The new ^{13}C NMR spectra of PCDD[2] have made it possible to improve the increment scheme for CS calculation.[10] The calculations of all 75 PCDD were performed in this work, taking into account the increment scheme[2] and new experimental data.[4,5]

Results and Discussion

The ^{13}C NMR spectra of PCDD obtained so far have been at the limit of the sensitivity of the instruments. Therefore, in the experiments[1,3—5] the signals were accumulated with a small time delay, and the whole set of signals was not always obtained due to the difference in the relaxation times t_1 for different C nuclei: the C—O and C—Cl signals that are characteristic of PCDD are the most intense. Nevertheless, the calculations make it possible to determine the positions of all of the signals (Tables 1 and 2), and they can be found in further NMR studies, using impulse sequences. Such a multilevel NMR analysis is necessary, because the PCDD spectra overlap the spectra of aromatic compounds, and only a structural criterion such as the increment scheme of ^{13}C NMR CS makes it possible to establish their structures.

The main structural peculiarities of ^{13}C NMR CS of PCDD have been previously revealed.[10] We have attempted to calculate the full spectra of the compounds measured in Ref. 1 and most toxic PCDD, which have not been studied by the ^{13}C NMR method. The low solubility of highly chlorinated PCDD did not allow the authors of new NMR measurements[3] to obtain the full spectra for all compounds; however, on the whole there were enough signals to determine the increments of all of the main combinations of two substituents, with which one can determine the ^{13}C NMR CS of any C

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Table 1. Experimental and calculated ^{13}C NMR chemical shifts of some PCDD

Position of the chlorine atom		TMS, δ											
		1a	1	2	3	4	4a	6a	6	7	8	9	9a
1-	[a]	138.8	121.2	124.5	123.0	114.7	143.1	141.5	116.6	124.2	124.0	116.2	141.5
	[b]	—	—	124.6	123.2	114.7	143.1	141.6	116.6	124.3	124.6	116.2	141.6
	[c]	138.4	120.5	124.5	123.7	114.8	142.9	141.3	116.3	124.2	124.5	116.1	141.1
intens.	[c]	(0.18)	(0.21)	(1.0)	(0.71)	(0.75)	(0.21)	(0.23)	(0.71)	(0.69)	(1.0)	(0.71)	(0.21)
calc.		138.9	121.2	124.5	123.4	114.5	142.9	141.6	116.5	124.1	124.0	116.1	141.6
2-	[a]	142.6	116.7	128.2	123.6	117.1	140.9	141.5	116.4	124.2	124.0	116.7	141.8
	[c]	142.3	116.1	127.7	123.6	117.2	140.7	140.9	116.1	124.3	124.2	116.1	141.3
intens.	[c]	(0.21)	(1.0)	(0.16)	(0.37)	(0.35)	(0.10)	(0.10)	(1.0)	(0.38)	(0.35)	(1.0)	(0.18)
calc.		142.5	116.6	128.2	123.4	116.6	141.0	141.8	116.3	124.1	124.0	116.6	141.9
1,2-	[a]	140.0	120.5	127.5	123.7	114.7	141.6	141.2	116.7	124.3	124.7	116.3	141.4
calc.		140.0	120.5	127.8	123.7	114.9	141.6	141.2	116.6	124.5	124.4	116.5	141.3
1,3-	[b]	—	—	124.3	—	115.2	143.3	141.2	116.7	124.5	124.3	116.3	141.1
	[c]	—	121.2	123.9	127.5	115.1	143.2	140.8	116.3	124.8	124.6	116.2	140.7
intens.	[c]	—	(0.27)	(0.66)	(0.29)	(0.75)	(0.29)	(0.27)	(1.0)	(0.98)	(0.86)	(0.95)	(0.35)
calc.		137.6	121.8	124.3	127.6	114.8	143.2	141.3	116.9	124.5	124.4	116.2	141.2
2,3-	[a]	141.2	117.8	126.7				141.5	116.6	124.4			
	[b]	141.1	117.5	126.3				141.1	116.3	124.2			
	[c]	141.2	117.6	125.8				140.8	116.2	124.5			
intens.	[c]	(0.24)	(0.70)	(0.28)				(0.23)	(0.98)	(1.0)			
calc.		141.3	117.8	126.8				141.5	116.8	124.5			
2,7-	[a]	—	116.6	—	123.9	117.0	—						
	[c]	142.0	116.3	128.0	123.9	117.6	140.8						
intens.	[c]	(0.41)	(1.00)	(0.29)	(0.88)	(0.70)	(0.23)						
calc.		142.1	116.7	128.6	123.9	117.0	140.7						
1,2,3-	[a]	138.8	121.6	126.5	127.3	115.8	141.5	140.9	116.8	124.9	124.7	116.4	140.9
	[d]	139.6	120.8	126.4	126.5	115.8	141.9	139.6	116.4	125.0	124.8	116.2	140.5
intens.	[c]	(0.70)	—	(0.54)	(0.27)	(0.81)	(0.23)	(0.70)	(0.94)	(1.0)	(0.82)	(0.83)	(0.34)
	[e]	138.8	121.7	126.5	127.0	116.0	142.0	140.9	117.0	124.9	124.8	116.7	141.0
1,2,4-	[b]	140.7	(119.6)	127.2	124.1	119.6	—	140.7	116.9	124.9	124.8	116.9	140.7
	[d]	139.6	118.5	126.5	124.0	120.0	—	140.3	116.0	125.2	125.0	116.0	140.3
calc.		140.6	118.9	127.2	124.5	120.0	138.2	140.7	116.5	124.8	124.7	117.2	140.3
2,3,7-	[a]	140.8	117.9	126.9	127.2	117.9	141.0	141.9	117.0	129.2	124.4	117.3	140.2
	[c]	140.6	117.6	126.1	126.3	117.6	140.8	141.4	117.4	128.3	124.2	116.4	139.8
intens.	[c]	(0.13)	(1.0)	(0.14)	(0.14)	(1.0)	(0.13)	(0.15)	(0.46)	(0.16)	(0.43)	(0.49)	(0.13)
calc.		140.9	117.9	126.7	127.2	118.2	141.0	141.8	117.1	129.1	124.3	117.2	140.3
1,2,3,4-	[b]	138.9	119.9	126.9				140.4	116.6	125.0			
	[d]	139.2	119.6	—				140.1	116.3	125.2			
calc.		139.4	120.0	126.7				140.4	116.9	125.3			
1,3,7,8-	[a]	137.2	122.4	125.1	128.8	115.5	—	140.3	118.3	127.7	127.7	117.9	140.3
	[c]	—	121.5	124.5	128.1	115.3	142.3	140.3	117.9	126.8	126.6	117.7	139.6
intens.	[c]	—	(0.48)	(0.90)	(0.40)	(1.0)	(0.43)	(0.51)	(0.85)	(0.40)	(0.42)	(0.86)	(0.62)
calc.		136.9	122.3	125.2	128.5	115.4	142.5	140.4	118.4	127.7	127.6	117.8	140.3
2,3,7,8-	[a]	140.8	—	—									
	[c]	139.6	117.6	126.9									
intens.	[c]*	(1.0)	(0.42)	(0.41)									
	[e]	140.6	118.3	127.7									
calc.		140.6	118.3	127.1									
1,2,3,7,8-	[a]	(137.7)	—	127.5	127.8	116.0	—	140.0	118.4	(128.2)	128.0	118.0	140.0
calc.		138.1	122.3	127.4	127.9	116.6	141.3	140.0	118.6	128.1	128.0	118.2	140.0
1,2,4,7,8-	[a]	139.9	119.9	128.3	125.1	120.2	137.8	139.9	118.3	128.3	128.3	118.3	(140.0)
calc.		139.9	119.3	128.1	125.4	120.6	137.6	139.8	118.1	128.0	128.0	118.3	139.9

[a] Data from Ref. 5, $CDCl_3$; [b] See Ref. 1, $CDCl_3$; [c] See Ref. 6, acetone-d_6; [d] See Ref. 7, acetone-d_6; [e] These spectra were not used in the increment scheme.

* The values of the C(1a) and C(1) signals are probably mixed up in the text.[6]

atom in any PCDD. Full spectra are not necessary for determining the coefficients of the increment scheme. On the contrary, the use of only absolutely reliable signals decreases the error of increments because it decreases the uncertainty of the experiment and increases the reliability of the calculated spectra.

It has been previously[10] found that the effects of the steric and electronic interactions of Cl—O on ^{13}C NMR

Table 2. Experimental ^{13}C NMR chemical shifts of some PCDD calculated and assigned according to the suggested increment scheme

Position of the chlorine atom		TMS, δ											
		1a	1	2	3	4	4a	6a	6	7	8	9	9a
1,4-	[a]	139.6	119.6	124.8				141.3	116.2	124.6			
calc.		139.5	119.6	123.9				141.1	116.4	124.4			
2,8-	[b]	141.7	117.3	128.0	124.0	116.2	140.3						
intens.		(0.20)	(0.80)	(0.32)	(1.0)	(0.97)	(0.22)						
calc.		142.2	117.0	128.6	123.9	116.8	140.6						
1,7,8-	[b]	(139.6)	(120.7)	125.1	(125.1)	115.0	142.0	142.0	117.8	(126.5)	(124.3)	117.6	142.0
intens.	[b]	(0.28)	(0.15)	(1.0)	(0.96)	(0.92)	(0.25)	(0.25)	(0.76)	(0.19)	(0.96)	(0.86)	(0.25)
calc.		138.2	121.9	125.4	123.9	115.0	142.2	141.8	117.9	127.9	123.2	117.9	140.3
1,2,3,6-	[a]*	138.4	120.7	126.1	126.9	115.1	—	141.6	120.9	115.1	115.8	116.0	—
calc.		138.2	122.0	127.3	127.9	116.4	141.1	137.6	122.1	125.8	124.3	114.9	141.6
1,2,3,7-	[a]	—	120.9	126.7	128.3	115.8	—	141.0	117.4	(128.6)	124.5	116.3	139.4
calc.		138.4	121.9	126.9	127.4	116.5	141.7	141.3	117.4	129.5	124.7	117.1	139.7
1,2,3,8-	[a]	—	(121.0)	126.9	128.5	115.8	—	139.6	117.6	124.7	128.9	116.5	141.1
calc.		138.5	122.1	126.9	127.5	116.2	141.6	139.7	117.4	124.8	129.4	117.0	141.3
1,2,3,9-	[a]*	138.5	120.7	126.1	126.9	116.0	141.7	141.7	114.9	(118.1)	(116.0)	(114.9)	—
calc.		138.2	121.6	126.8	127.7	116.3	141.4	141.6	115.3	124.3	125.7	121.8	137.6
1,2,4,7-	[a]	—	118.6	126.9	124.4	119.4	137.9	140.8	116.4	128.9	124.4	117.5	—
calc.		140.2	118.9	127.7	125.0	120.5	138.0	141.0	116.8	129.4	124.7	117.2	139.5
1,2,4,8-	[a]	140.1	118.5	126.8	124.2	119.4	137.7	140.1	116.3	124.4	128.8	117.4	—
calc.		140.3	119.2	127.7	125.0	119.4	137.9	139.4	116.9	124.7	129.4	117.1	141.1
1,2,6,7-	[a]	138.9	120.0	(127.6)	124.4	115.4	140.5						
calc.		139.0	120.9	128.7	124.4	115.2	140.8						
1,2,7,8-	[b]	140.3	(119.7)	(127.4)	124.5	115.3	140.6	140.3	117.9	127.4	126.9	117.6	140.6
intens.	[b]	(0.47)	(0.37)	(0.44)	(0.90)	(1.0)	(0.42)	(0.47)	(0.86)	(0.44)	(0.33)	(0.86)	(0.42)
calc.		139.3	121.1	128.7	124.5	115.5	140.9	140.3	118.2	127.7	127.6	118.1	140.4
1,2,8,9-	[a]	138.9	119.6	(127.3)	124.3	115.1	140.5						
calc.		139.1	120.8	128.6	124.5	115.3	140.7						
1,4,7,8-	[b]	138.6	119.4	124.8				140.1	117.8	126.9			
intens.	[b]	(0.23)	(0.38)	(0.81)				(0.36)	(1.0)	(0.32)			
calc.		138.8	120.2	124.8				140.2	117.9	127.6			
«7»	[a]*	141.3	116.1	124.1	124.3	116.1	142.3	141.1	117.2	127.7	123.5	116.1	140.7
calc. -H8		137.9	120.3	127.9	127.9	120.6	138.0	138.8	119.5	128.9	126.0	120.7	136.4
calc. -H9		138.2	120.8	128.0	127.9	120.5	138.1	136.9	122.4	128.1	128.7	116.8	140.1
«8»	[a]*	142.3	116.1	124.1	124.3	116.1	141.3	140.7	116.1	123.5	127.7	117.2	141.1
calc.		137.6	120.7	128.4	128.4	120.7	137.6	137.6	120.7	128.4	128.4	120.7	137.6

Note. We believe that the numbers presented in parentheses are unreliable. They resemble the numbers they should be, but the divergences from the calculated values are too large. At the same time, it should be taken into account that the first ^{13}C NMR of PCDD were carried out at the limits of sensitivity and relatively intense noise can be measured instead of the expected weak signal. This enhances the role of the objective method for the selection of useful signals. The suggested increment scheme can be used as such a method.

* This substance has been named incorrectly. [a] See Ref. 7, acetone-d_6. [b] See Ref. 6, acetone-d_6.

CS of PCDD are not exactly the same as those of polysubstituted benzenes. Therefore, three values of CS of non-substituted dioxin were taken as the reference point instead of ^{13}C NMR CS of non-substituted benzene. The Cl—Cl interaction, however, exerts the same effect on the PCDD spectra as that of polychlorinated benzenes[8] and hydroxybenzenes.[9] Finally, two new heterographs with one Cl atom, 1-Cl— and 2-Cl—DD, should be considered in addition to the topological peculiarities of polychlorinated benzenes and hydroxybenzenes for the analysis of ^{13}C NMR CS in PCDD.

Only the role of the solvents remained unclear. The ^{13}C NMR spectra of PCDD solutions measured and calculated in Ref. 3 were obtained in $CDCl_3$ (see Table 1). Acetone was used later[4,5] for measurements of the same spectra and exerted no specific effect on their CS (see Table 1). This fact allowed the authors[5] to make assignments analogous to our assignments. Only slight divergences due to the noise were observed between the measurements of Refs. 3 and 5. When the "signal/noise" ratio is small in the accumulation of weak signals, the noise envelope disguises the vertex of the useful signal and somewhat shifts the peak of intensity from its true value.

The signals of PCDD occupy two rather narrow spectral ranges from 144 to 136 ppm and from 130 to 114 ppm, where the signals of other classes of aromatic compounds are also present (see Tables 1 and 2). The spectra of some PCDD isomers are identical (for example, 1,7- and 1,8-DCDD, 2,7- and 2,8-DCDD, *etc.*), not positions, but only the numbers of the signals differ. Reliable measurements[5] completely confirmed the coefficients of the increment scheme.[2]

Thus, the spectra of PCDD calculated by this scheme are close to the true spectra. This makes it possible to compare each large deviation of CS for the PCDD, which were measured for the first time with the indicated intensities of the signals and with assignments to only three main types of C atoms (see Ref. 4), with the assignments made similarly but without the indicated intensities of the signals.[5]

Compounds with high symmetry have fewer signals in their spectra (see Table 2). For 1,4,7,8-TCDD, the experimental data exactly coincide with the calculated data despite the different solvents. For 2,3,7,8-TCDD, the intensities of the C(1) and C(2) signals are mixed up.[4] In addition, there are signals that are systematically shifted 1 ppm up field compared to our measurements and the data of the calculation (see Table 1). It seems that not the central signal of the multiplet of acetone-d_6, but the signal next to it was taken as the reference point.

The spectra of two TCDD (1,2,3,6/1,2,3,9), whose signals were assigned[5] probably due to their different ratios in an inseparable mixture (see Table 2),[4] are of interest. Although the intensities of individual signals have not previously[5] been presented, only the signals with CS 115.1, 115.8, 116.0 and 114.9, 116.0 and 118.1 ppm correspond to proton-substituted C atoms. These spectra contain no noticeable signals within the 123.5—125.5 ppm band corresponding to the signals of the C(7) and C(8) atoms in similar fragments (C(2) and C(3) in 1-Cl—DD, C(3), C(7) in 1,2,8-Cl(3)—DD and in 1,2,8,9-TCDD, *etc.*). It is evident that both of the compounds stated as TCDD[5] are not really TCDD.

It is not possible to select similar sets of signals from the calculated spectra of PCDD with 2,3,7,8-Cl-substitution. Both 2,3,7,8-TCDD (does not suit due to high symmetry) and 1,2,3,7,8-PnCDD (large deviation of the spectrum from the calculated spectrum) could have served as such PCDD. Since for other PCDD[4,5] there is close agreement between the experimental and calculated data, this pair of substances cannot be PCDD. Judging from the synthesis,[11] these substances could be aromatic compounds containing a nitro group, because in this case ^{13}C and ^{1}H NMR CS are within the range that is usual for nitrobenzenes.[12] Moreover, when describing the synthesis and spectra of PCDD, researchers[13] have referred to the general properties of the spectral mixture as of the ABC type and mentioned that the ^{1}H NMR spectrum of the "1,2,3,6—1,2,3,9" mixture, unlike other PCDD, "does not exhibit similar splitting".

The validity of the increment scheme discussed can be seen in an analysis of the spectra of the two following compounds.[5] The first of them is considered to be a Cl(7)—DD and the second is considered to be a Cl(8)—DD. In the ^{1}H NMR spectrum the singlet for Cl(7)—DD is observed and no signal for Cl(8)—DD [11] is seen, so these substances could be completely described if the corresponding ^{13}C NMR data were available. However, the spectrum of only one rather than two substances was obtained[5] (see Table 2). This compound contains 10 carbon signals. Four of them belong to the heterocyclic C atoms (140.7, 141.1, 141.3, and 142.3 ppm), two signals are assigned to the adjacent C atoms (116.1 and 117.2 ppm), and the remaining signals correspond to the peripheral C atoms (123.5, 124.1, 124.3, and 127.7 ppm). Only one signal (127.7 ppm) of the ten signals corresponds to the C atom of C—Cl, while the C atoms at the 2,3,7,8-positions are bonded to hydrogen atoms. Thus, the ^{13}C NMR spectra denoted[5] as Cl(7)—DD and Cl(8)—DD compounds (see Table 2) do not confirm the structures claimed. It is likely that the researchers[5] dealt with Cl(7)-DD and Cl(8)-DD compounds with about 98 % purity (see Ref. 3), while the remaining 2 % were also PCDD, but were poorly chlorinated. Due to the low solubility of highly chlorinated PCDD, an excess of the compounds was taken[5] for the preparation of the saturated solution for NMR studies, but the relatively easily soluble admixture dissolved. According to the calculation by the increment scheme, this admixture could be a 2,7—2,8-DCDD mixture (see Table 1 and 2). This example shows that analysis by the NMR method with slightly soluble substances should be confirmed by multi-level checking of the results, especially when these compounds are used as chromatographic references.

Thus, the empirical schemes for calculating CS suggested previously[8,9] and in this work make it possible to predict the ^{13}C NMR spectra of all PCDD isomers.

Experimental

^{13}C NMR spectra (see Table 1) were measured on a Varian Gemini-200 NMR spectrometer (the working frequency with respect to the ^{13}C nucleus was 50.3 MHz) at room temperature (19—22 °C) for 1-, 1,2-, and 1,2,3-chlorinated dioxins and at 55 °C for other compounds, in a regime of broad-band H—C decoupling (pulse duration was 5 μs, number of scans was 1500—150000). Saturated $CDCl_3$ solutions were used: 2—6 % for low chlorinated dioxins and lower than 1 % for compounds with three and more chlorine atoms.

A multi-parameter linear regression analysis was performed by the standard method of regularization of the system of linear equations.[14] 22 parameters remained non-zero at the end of the calculations. The number of points was 58. The standard error was 0.238.

References

1. A. S. Kende, J. J. Wade, D. Ridge, and A. Poland, *J. Org. Chem.*, 1974, **39**, 931.
2. L. A. Fedorov, V. I. Dostovalova, O. V. Arapov, and M. Yu. Malov, in *Abstracts of 11th International Symposium on Chlorinated Dioxins and Related Compounds*, Research Triangle Park, USA, 1991, 176.

3. V. I. Dostovalova, L. A. Fedorov, O. A. Arapov, and M. Yu. Malov, in *Short Papers of the Second Finnish—Russian Seminar: Chemistry and Ecology of Organometallic Compounds*, Jyvaskyla, Finland, 1992, 12.
4. J. Grainger, Z. Liu, S. Sirimanne, V. L. Francis, and D. G. Patterson, *Organohalogen Compounds*, 1993, **11**, 207.
5. J. Grainger, Z. Liu, S. Sirimanne, V. L. Francis, and D. G. Patterson, in *Short papers of the 13th International Symposium on Chlorinated Dioxin and Related Compounds*, Vienna, ANA, 1993, 38.
6. V. I. Dostovalova, F. K. Velichko, T. T. Vasil'eva, N. V. Kruglova, and R. Kh. Freidlina, *Org. Magn. Reson.*, 1981, **16**, 251.
7. V. I. Dostovalova, S. S. Zlotsky, D. L. Rakhmankulov, and A. B. Terent'ev, *Magn. Reson. Chem.*, 1985, **25**, 1.
8. V. I. Dostovalova, L. A. Fedorov, and J. Paasivirta, *Magn. Reson. Chem.*, 1991, **29**, 830.
9. V. I. Dostovalova and L. A. Fedorov, *Magn. Reson. Chem.*, 1992, **30**, 1203.
10. V. I. Dostovalova and L. A. Fedorov, *Organohalogen Compounds*, 1990, **2**, 125.
11. D. L. Ashley, V. V. Reddy, and D. G. Patterson, *Magn. Reson. Chem.*, 1989, **27**, 117.
12. P. Savarino, V. I. Dostovalova, L. A. Fedorov, G. Viskardi, R. Karpingiano, and E. Barny, *Zh. Strukt. Khim.*, 1992, **33**, 91 [*J. Struct. Chem.*, 1992, **33** (Engl. Transl.)].
13. L. T. Gelbaum, D. G. Patterson, D. L. Ashley, and D. F. Groce, *Chemosphere*, 1988, **17**, 551.
14. A. N. Tikhonov and V. Ya. Arsenin, *Metody resheniya nekorrectnykh zadach* [*The Methods for Solving Incorrect Problems*], Nauka, Moscow, 1974, 224 (in Russian).

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