The ^{13}C NMR spectra of some polychlorinated dibenzo-*p*-dioxins. A calculation of ^{13}C chemical shifts

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The ^{13}C NMR spectra of a number of polychlorinated dibenzo-p-dioxins (PCDD) were measured. These and previously known spectra were used for the development of a method for calculation of ^{13}C NMR spectra of chloroaromatics in the framework of a two-particle increment scheme for carbon chemical shifts. The scheme one allows to calculate ^{13}C chemical shifts for all 75 PCDD.

Key words: polychlorinated dibenzo-p-dioxins, ^{13}C NMR chemical shifts, two-particle increments.

Low solubility and high toxicity are the principal reasons that prevent the application of ^{13}C and ^{1}H NMR spectroscopy[1,2] to studies of polychlorinated dibenzodioxins.

Previously,[3] we made a first attempt based on the data of Ref. 1 to generalize the topological characteristics of ^{13}C chemical shifts in PCDD in the framework of an increment scheme.[4,5] In this work we present new results of measurements of ^{13}C NMR spectra of PCDD which allowed us to improve the increment scheme of Ref. 3 and to predict the spectra for all 75 PCDD. Preliminary results of this study were reported in Refs. 6, 7.

Experimental

Dibenzo-p-dioxins chlorinated in the 1-, 2-, 2,3-, 1,2,3-, 2,3,7-, 1,3,7,8-, 1,2,3,7,8-, and 1,2,4,7,8- positions were synthesized according to known methods.[1,8,9]

The ^{13}C NMR spectra were recorded on a Gemini-200 NMR spectrometer (Varian). The working frequency for a carbon nucleus was 50.3 MHz. The measurements on 1-, 2-, and 1,2,3-chlorinated dioxins were performed at 19—22 °C, and for other derivatives, at 55 °C. The measurements were performed with wide-band H—C decoupling. The pulse duration was 5 μs; the build-up factor was within 1500—150000. Saturated solutions in $CDCl_3$ were used (2—6% for low-chlorinated dioxins and below 1% for tri- and higher chlorinated dioxins).

Results and Discussion

In this work we employed the topology of chemical shifts and their dependence on structure to predict the spectra of all 75 PCDD, in a way similar to that previously performed in Refs. 4, 5 for halogenated benzenes and oxybenzenes. The data are partially presented in Table 1.

The primary assignment of the signals was performed using the increment scheme.[3] The chemical shifts for 1- and 2,3-chlorinated dioxins were repeatedly measured and were found to agree well with the data of Ref. 1.

References

1. A. S. Kende, J. J. Wade, D. Ridge, and A. Poland, *J. Org. Chem.*, 1974, **39**, 931.
2. L. T. Gelbaum, D. G. Patterson, D. L. Ashley, and D. F. Groce, *Chemosphere*, 1988, **17**, 551.
3. V. I. Dostovalova and L. A. Fedorov, *Short papers of Proc. Int. Meeting DIOXIN-90*. Bayreuth (FRG), 1990, **2**, 125.
4. V. I. Dostovalova, L. A. Fedorov, and J. Paasivirta, *Magn. Reson. Chem.*, 1991, **29**, 830.
5. V. I. Dostovalova and L. A. Fedorov, *Magn. Reson. Chem.*, 1992, **30**, 1203.
6. L. A. Fedorov, V. I. Dostovalova, O. V. Arapov, and M. Yu. Malov, *Abstracts of 11th International Symposium on chlorinated dioxins, and related compounds*, Research Triangle Park, USA, 1991, Rep. 176.

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Table 1. The experimentally measured and calculated (given in brackets) ^{13}C NMR chemical shifts of certain PCDD.

Position of	Position of ^{13}C nucleus, ppm with respect to tetramethylsilane											
chlorine(s)	C-1a	C-1	C-2	C-3	C-4	C-4a	C-6a	C-6	C-7	C-8	C-9	C-9a
1	138.8	121.2	124.5	123.0	114.7	143.1	141.5	116.6	124.2	124.0	116.2	141.5
1 *	–	–	124.6	123.2	114.7	143.1	141.6	116.6	124.3	124.6	116.2	141.6
	(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	142.6	116.7	128.2	123.6	117.1	140.9	141.5	116.4	124.2	124.0	116.7	141.8
	(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	140.0	120.5	127.5	123.7	114.7	141.6	141.2	116.7	124.3	124.7	116.3	141.4
	(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 *	–	–	124.3	–	115.2	143.3	141.2	116.7	124.5	124.3	116.3	141.1
	(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	141.2	117.8	126.7	–	–	–	141.5	116.6	124.4	–	–	–
2, 3 *	141.1	117.5	126.3	–	–	–	141.1	116.3	124.2	–	–	–
	(141.3)	(117.8)	(126.8)	–	–	–	(141.5)	(116.8)	(124.5)	–	–	–
2, 7 *	–	116.6	–	123.9	117.0	–	–	–	–	–	–	–
	(142.1)	(116.7)	(128.6)	(123.9)	(117.0)	(140.7)	–	–	–	–	–	–
1, 2, 3 **	138.8	121.6	126.5	127.3	115.8	141.5	140.9	116.8	124.9	124.7	116.4	140.9
	(138.8)	(121.7)	(126.5)	(127.0)	(116.1)	(142.0)	(140.9)	(117.0)	(124.9)	(124.8)	(116.7)	(141.0)
1, 2, 4 *	140.7	119.6	127.2	124.1	119.6	–	140.7	116.9	124.9	124.8	116.9	140.7
	(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	140.8	117.9	126.9	127.2	117.9	141.0	141.9	117.0	129.2	124.4	117.3	140.2
	(140.9)	(117.9)	(126.7)	(127.2)	(117.4)	(141.0)	(141.8)	(117.1)	(129.1)	(124.3)	(117.2)	(140.3)
1, 2, 3, 4 *	138.9	119.9	126.9	–	–	140.4	116.6	125.0	–	–	–	–
	(139.4)	(120.0)	(126.7)	–	–	(140.4)	(116.9)	(125.3)	–	–	–	–
1, 3, 7, 8	137.2	122.4	125.1	128.8	115.5	–	140.3	118.3	127.7	127.7	117.9	140.3
	(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 **	140.8	–	–	–	–	–	–	–	–	–	–	–
	(140.6)	(118.3)	(127.7)	–	–	–	–	–	–	–	–	–
1, 2, 3, 7, 8	137.7	–	127.5	127.8	116.0	–	140.0	118.4	128.2	128.0	118.0	140.0
	(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	139.9	119.9	128.3	125.1	120.2	137.8	139.9	118.3	128.3	128.3	118.3	140.0
	(139.9)	(119.3)	(128.1)	(125.4)	(120.6)	(137.6)	(139.8)	(118.1)	(128.0)	(128.0)	(118.3)	(139.9)

*According to ref. 1.

**The spectrum was not employed in the increment scheme.

7. V. I. Dostovalova, L. A. Fedorov, O. A. Arapov, and M. Yu. Malov, *Short papers of Second Finnish-Russian seminar: chemistry, and ecology of organoelement compounds.* Juvaskyla, Finland, 1992, 12.
8. A. P. Gray, S. P. Cepa, I. J. Solomon, and O. Aniline, *J. Org. Chem.*, 1976, **41**, 2435.
9. A. E. Pohland and G. C. Yang, *J. Agric. Food. Chem.*, 1972, **20**, 1093.

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