

CALCULATED NMR ^{13}C SPECTRA OF POLYCHLORINATED
DIPHENYL ETHERS

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Introduction

Some years ago we had offered a new method of revealing of topological factors of ring carbon shielding changing in NMR ^{13}C spectra of polysubstituted benzenes and a new predictive increment scheme for ^{13}C chemical shifts for some homogeneously substituted benzenes^{1,2)} and polyhalogenated oxybenzenes³⁾. Many-particle increments⁴⁾ were replaced with two-particle ones^{2,3)}, and such an approach became very effective for prediction of NMR ^{13}C spectra for wide classes of polyhalogenated aromatic ecopollutants⁵⁾, including polychlorinated dibenzo-*p*-dioxines (PCDDs)⁶⁾, polychlorinated naphthalenes^{5,7)}, polychlorinated⁸⁾ and polybrominated⁹⁾ biphenyls.

In this report we calculate the NMR ^{13}C spectra of many polychlorinated diphenyl ethers (PCDEs) and compare with available experimental data¹⁰⁾.

Results and discussion

Many times we pointed out that it is possible to combine our method with chromatography for creating a new technics for structure analysis of aromatic compounds without synthesis of references⁵⁾.

Now we had applied our results to numerous set of PCDEs (widespread ecopollutants that have been found in fishes, birds, humans etc), only using increments for substituted benzenes.

Table 1 contains calculated ^{13}C NMR spectra for 28 compounds. PCDEs are considered as a benzene with two types of substituents - Cl and OPh. As a whole the fitting is very good, but of course some deviations exceed permissible error (1 ppm).

It is well known that ortho-chlorinated benzene rings in PCDEs undergo the serious steric effect, which may lead to some distortion of total electron density in the vicinity of oxygen and to addition shielding of ortho-carbons. Nevertheless it is evidently that in solution all these molecules are in the free rotation in NMR time scale because of symmetry of corresponding experimental spectra.

Additional sterical increments for PCDEs may be obtained just from observed deviations (3-5 ppm) between experimental chemical shifts and our calculations performed in frame of free rings approach. However, it is necessary preliminary to revise some assignments of NMR ^{13}C signals¹⁰⁾ in those cases, when deviations are large enough, but experimental data contain corresponding signals.

These results may be used in ecological projects for investigation of environmentally important pollutants.

Table 1. Calculated ^{13}C NMR chemical shifts for 28 polychlorinated diphenyl ethers

	PCDE	C-1,1'	C-2,2'	C-3,3'	C-4,4'	C-5,5'	C-6,6'
1	2,3	154.52	127.72	134.65	125.28	129.20	117.77
	2',4'	151.62	129.62	130.36	128.68	128.51	120.31
2	2,4	151.62	129.62	130.36	128.68	128.51	120.31
	2',4'	151.62	129.62	130.36	128.68	128.51	120.31
3	2,4	151.62	129.62	130.36	128.68	128.51	120.31
	3',5'	159.29	117.68	136.55	123.82	136.55	117.68
4	2,4	151.62	129.62	130.36	128.68	128.51	120.31
	2',6'	147.45	131.09	128.51	126.13	128.51	131.09
5	3,4	156.75	120.99	134.65	128.11	131.82	118.37
	3',4'	156.75	120.99	134.65	128.11	131.82	118.37
6	2,3,4	151.54	129.18	131.02	128.24	128.43	118.46
	2',4'	154.16	128.93	135.86	123.18	129.20	117.77
7	2,3,4	151.87	124.78	131.02	128.24	129.20	118.46
	3',4'	157.16	120.99	134.65	126.78	131.82	118.37
8	2,4,5	152.31	127.77	131.82	127.47	132.80	121.08
	2',4'	156.47	125.72	130.36	128.68	128.51	120.91
9	2,4,5	152.31	127.77	131.82	127.47	132.80	121.08
	2',5'	153.75	127.08	131.05	124.51	134.01	119.62
10	2,4,5	152.31	127.77	131.82	127.47	132.80	121.08
	3',4'	157.16	120.99	134.65	126.78	131.82	118.37
11	2,3,4	152.23	121.83	131.71	127.55	135.78	117.77
	2',3',4'	152.23	121.83	131.71	127.55	135.78	117.77
12	2,3,4	152.56	117.43	131.71	127.55	136.55	117.77
	2',4',6'	146.70	129.24	131.05	129.61	134.01	126.28
13	2,4,5	152.31	127.77	131.05	128.68	134.01	120.31
	2',3',4'	152.31	129.62	135.86	128.68	129.20	118.46
14	2,4,5	152.31	127.77	131.05	128.68	134.01	120.31
	2',4',5'	152.31	127.77	131.05	128.68	134.01	120.31
15	2,4,5	152.31	127.77	131.05	128.68	134.01	120.31
	2',4',6'	146.01	131.78	128.51	130.30	128.51	131.78
16	2,4,5	152.31	127.77	131.05	128.68	134.01	120.31
	3',4',5'	157.85	117.60	136.11	123.15	136.11	117.60
17	2,4,6	146.01	131.78	128.51	130.30	128.51	131.78
	2',4',6'	146.01	131.78	128.51	130.30	128.51	131.78
18	2,3,4,5	152.23	127.33	132.48	124.61	134.26	117.69
	2',4'	151.62	129.62	130.36	128.68	128.51	120.31
19	2,3,4,5	152.23	127.33	132.48	124.61	134.26	117.69
	3',4'	157.16	120.99	134.65	126.78	131.82	118.37
20	2,3,4,5	152.23	127.33	132.48	124.61	134.26	117.69
	2',3',4'	151.54	129.18	131.02	128.24	128.43	118.46
21	2,3,4,5	152.23	127.33	132.48	124.61	134.26	117.69
	2',3',5'	155.21	125.87	135.34	125.28	134.70	117.77
22	2,3,4,5	152.23	127.33	132.48	124.61	134.26	117.69
	2',4',5'	152.31	127.77	131.82	127.47	132.80	121.08
23	2,3,5,6	150.78	128.03	133.49	126.34	133.49	128.03
	2',3',4'	151.54	129.18	131.02	128.24	128.43	118.46
24	2,3,5,6	150.78	128.03	133.49	126.34	133.49	128.03
	2',4',5'	152.31	127.77	131.82	127.47	132.8	121.08

Table 1. Continuation

PCDE	C-1,1'	C-2,2'	C-3,3'	C-4,4'	C-5,5'	C-6,6'	
25	2,3,4,5	152.23	127.33	132.48	124.61	134.26	117.69
	2',3',4',5'	152.23	127.33	132.48	124.61	134.26	117.69
26	2,3,4,5	152.23	127.33	132.48	124.61	134.26	117.69
	2',3',5',6'	150.78	128.03	133.49	126.34	133.49	128.03
27	2,3,4,5,6	145.85	129.49	130.63	126.23	130.63	129.49
	2',3',4'	152.56	117.43	131.71	127.55	136.55	117.77
28	2,3,4,5,6	145.85	129.49	130.63	126.23	130.63	129.49
	2',3',4',5',6'	145.85	129.49	130.63	126.23	130.63	129.49

Conclusion

Contrary to PCDDs and polychlorinated naphthalenes with evident conjugative properties of two-ring plane aromatic systems we propose that substitution effects do not transmit from one to another benzene ring in PCDEs through conjugation. The mutual influence of ortho-substituents in different rings realizes only by sterical way.

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