The Program of NMR ^{13}C Chemical Shifts Calculations for Aromatic Pollutants. Calculated ^{13}C spectra of all PCDDs

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Results and discussion

The ^{13}C NMR spectroscopy is one of leading methods for structural elucidation of unknown organic compounds, especially polysubstituted ones.

Table 1.

The calculated NMR ^{13}C spectra of all PCDDs

	Positions of Cl	C-1a	C-1	C-2	C-3	C-4	C-4a
	nil	142.2	116.2	126.2			
1	1	138.86	121.34	121.34	123.02	114.48	142.85
2	2	142.53	116.56	128.15	123.43	116.62	140.98
3	1,2	139.96	120.49	127.82	123.62	114.90	141.63
4	1,3	137.64	121.76	124.31	127.57	114.84	143.18
5	1,4	139.51	119.62	123.90	123.90	119.62	139.51
6	1,6	138.28	121.59	124.91	123.38	114.38	142.27
7	1,7	138.46	121.47	124.94	123.46	114.90	142.55
8	1,8	138.56	121.76	124.92	123.48	114.61	142.45
9	1,9	138.28	121.24	124.84	123.45	114.73	142.27
10	2,3	141.31	117.75	126.77	126.77	117.75	141.31
11	2,7	142.13	116.69	128.61	123.87	117.04	140.68
12	2,8	142.23	116.98	128.59	123.89	116.75	140.58
13	1,2,3	138.74	121.68	126.44	126.96	116.03	141.96
14	1,2,4	140.61	118.77	127.24	124.50	120.04	138.29
15	1,2,6	139.38	120.74	128.25	123.98	114.80	141.05
16	1,2,7	139.56	120.62	128.28	124.06	115.32	141.33
17	1,2,8	139.66	120.91	128.26	124.08	115.03	141.23
18	1,2,9	139.38	120.39	128.18	124.05	115.15	141.05
19	1,3,6	137.06	122.01	124.74	127.93	114.74	142.60
20	1,3,7	137.24	121.89	124.77	128.01	115.26	142.88
21	1,3,8	137.34	122.18	124.75	128.03	114.97	142.78
22	1,3,9	137.06	121.66	124.67	128.00	115.09	142.60
23	1,4,6	138.93	119.87	124.33	124.26	119.52	138.93
24	1,4,7	139.11	119.75	124.36	124.34	120.04	139.21
25	1,7,8	138.16	121.89	125.38	123.92	115.03	142.15
26	2,3,7	140.91	117.88	127.23	127.21	118.17	141.01

It allows to distinguish isomer signals and detect compounds in mixtures. Such a problem is of great importance for ecological chemistry, essentially concerning recognizing of hazardous pollutants. It is practically impossible to synthesize and investigate every of those compounds especially such as their metabolites and congeners, though using reference compounds and data bases is necessary in traditional analytical methods.

In this aspect the NMR ^{13}C spectroscopy is the unique method because of its capability to identify different compounds and also their mixtures and to predict (to simulate) spectra of unknown compounds even if spectra are inaccessible. So we offered some process of combination the chromatography with NMR ^{13}C in order to avoid a synthesis of unlimited number of references[1].

NMR spectroscopy is a method of extremely high resolution because NMR signal can reflect small structure changes. NMR ^{13}C spectrum contains a set of signals according to a number of carbons in a compound, and those positions (chemical shifts) depend on molecular structure only, so NMR ^{13}C spectrum is a distinct portrait of a molecule.

Some time ago we had suggested a new method of simulating of NMR ^{13}C spectra in polysubstituted aromatics[1], using two-particle increment scheme.

Table 1. (Continuation)

	Positions of Cl	C-6a	C-6	C-7	C-8	C-9	c-9a
	nil	142.2	116.2	126.2			
1	1	141.62	116.45	124.03	123.96	116.10	141.62
2	2	141.80	116.33	124.06	124.04	116.62	141.90
3	1,2	141.22	116.58	124.49	124.40	116.52	141.32
4	1,3	141.32	116.87	124.47	124.42	116.23	141.22
5	1,4	141.04	116.35	124.39	124.39	116.35	141.04
6	1,6	138.28	121.59	124.91	123.38	114.38	142.27
7	1,7	141.95	116.81	128.58	123.79	116.52	140.40
8	1,8	140.40	116.87	123.86	128.51	116.46	141.95
9	1,9	142.27	114.73	123.45	124.84	121.24	138.28
10	2,3	141.50	116.75	124.50	124.50	116.75	141.50
11	2,7	142.13	116.69	128.61	123.87	117.04	140.68
12	2,8	140.58	116.75	123.89	128.59	116.98	142.23
13	1,2,3	140.92	117.00	124.93	124.86	116.65	140.92
14	1,2,4	140.64	116.48	124.85	124.83	116.77	140.74
15	1,2,6	137.88	121.72	125.37	123.82	114.80	141.97
16	1,2,7	141.55	116.94	129.04	124.23	116.94	140.10
17	1,2,8	140.00	117.00	124.32	128.95	116.88	141.65
18	1,2,9	141.87	114.86	123.91	125.28	121.66	137.98
19	1,3,6	137.98	122.01	125.35	123.84	114.51	141.87
20	1,3,7	141.65	117.23	129.02	124.25	116.65	140.00
21	1,3,8	140.10	117.29	124.30	128.97	116.59	141.55
22	1,3,9	141.97	115.15	123.89	125.30	121.37	137.88
23	1,4,6	137.70	121.49	125.27	123.81	114.63	141.69
24	1,4,7	141.37	116.71	128.94	124.22	116.77	139.82
25	1,7,8	140.73	118.00	127.20	127.13	117.65	140.73
26	2,3,7	141.83	117.11	129.05	124.33	117.17	140.28

Table 1. (Continuation)

	Positions of Cl	C-1a	C-1	C-2	C-3	C-4	C-4a
27	1,2,3,4	139.39	119.96	126.63	126.63	119.96	139.39
28	1,2,3,6	138.16	121.93	126.87	127.32	115.93	141.38
29	1,2,3,7	138.34	121.81	126.90	127.40	116.45	141.66
30	1,2,3,8	138.44	122.10	126.88	127.42	116.16	141.56
31	1,2,3,9	138.16	121.58	126.80	127.39	116.28	141.38
32	1,2,4,6	140.03	119.02	127.67	124.86	119.94	137.71
33	1,2,4,7	140.21	118.90	127.70	124.94	120.46	137.99
34	1,2,4,8	140.31	119.19	127.68	124.96	120.17	137.89
35	1,2,4,9	140.03	118.67	127.60	124.93	120.29	137.71
36	1,2,6,7	138.98	120.87	128.71	124.42	115.22	140.75
37	1,2,6,8	139.08	121.16	128.69	124.44	114.93	140.65
38	1,2,6,9	138.80	120.64	128.61	124.41	115.05	140.47
39	1,2,7,8	139.26	121.04	128.72	124.52	115.45	140.93
40	1,2,7,9	138.98	120.52	128.64	124.49	115.57	140.75
41	1,2,8,9	139.08	120.81	128.62	124.51	115.28	140.65
42	1,3,6,8	136.76	122.43	125.18	128.39	114.87	142.20
43	1,3,6,9	136.48	121.91	125.10	128.36	114.99	142.02
44	1,3,7,8	136.94	122.31	125.21	128.47	115.39	142.48
45	1,3,7,9	136.66	121.79	125.13	128.44	115.51	142.30
46	1,4,6,9	138.35	119.77	124.69	124.69	119.77	138.35
47	1,4,7,8	138.81	120.17	124.80	124.80	120.17	140.15
48	2,3,7,8I	140.61	118.30	127.67	127.67	118.30	140.61
49	1,2,3,4,6	138.81	120.21	127.06	126.99	119.86	138.81
50	1,2,3,4,7	138.99	120.09	127.09	127.07	120.38	139.09
51	1,2,3,6,7	137.76	122.06	127.33	127.76	116.35	141.08
52	1,2,3,6,8	137.86	122.35	127.31	127.78	116.06	140.98
53	1,2,3,6,9	136.81	122.27	129.65	128.19	115.41	140.80
54	1,2,3,7,8	138.04	122.23	127.34	127.86	116.58	141.26
55	1,2,3,7,9	137.76	121.71	127.26	127.83	116.70	141.08
56	1,2,3,8,9	137.86	122.00	127.24	127.85	116.41	140.98
57	1,2,4,6,7	139.63	119.15	128.13	125.30	120.36	137.41
58	1,2,4,6,8	139.73	119.44	128.11	125.32	120.07	137.31
59	1,2,4,6,9	139.45	118.92	128.03	125.29	120.19	137.13
60	1,2,4,7,8	139.91	119.32	128.14	125.40	120.59	137.59
61	1,2,4,7,9	139.63	118.80	128.06	125.37	120.71	137.41
62	1,2,4,8,9	139.73	119.09	128.04	125.39	120.42	137.31
63	1,2,3,4,6,7	138.41	120.34	127.52	127.43	120.28	138.51
64	1,2,3,4,6,8	138.51	120.63	127.50	127.45	119.99	138.41
65	1,2,3,4,6,9	138.23	120.11	127.42	127.42	120.11	138.23
66	1,2,3,4,7,8	138.69	120.51	127.53	127.53	120.51	138.69
67	1,2,3,6,7,8	137.46	122.48	127.77	128.22	116.48	140.68
68	1,2,3,6,7,9	137.18	121.96	127.69	128.19	116.60	140.50
69	1,2,3,6,8,9	137.28	122.25	127.67	128.21	116.31	140.40
70	1,2,3,7,8,9	137.46	122.13	127.70	128.29	116.83	140.68
71	1,2,4,6,7,9	139.05	119.05	128.49	125.73	120.61	136.83
72	1,2,4,6,8,9	139.15	119.34	128.47	125.75	120.32	136.73
73	1,2,3,4,6,7,8	138.11	120.76	127.96	127.89	120.41	138.11
74	1,2,3,4,6,7,9	137.83	120.24	127.88	127.86	120.53	137.93
75	1,2,3,4,6,7,8,9	137.53	120.66	128.32	128.32	120.66	137.53

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Table 1. (Continuation)

	Positions of Cl	C-6a	C-6	C-7	C-8	C-9	c-9a
27	1,2,3,4	140.34	116.90	125.29	125.29	116.90	140.34
28	1,2,3,6	137.58	122.14	125.81	124.28	114.93	141.57
29	1,2,3,7	141.25	117.36	129.48	124.69	117.07	139.70
30	1,2,3,8	139.70	117.42	124.76	129.41	117.01	141.25
31	1,2,3,9	141.57	115.28	124.35	125.74	121.79	137.58
32	1,2,4,6	137.30	121.62	125.73	124.25	115.05	141.39
33	1,2,4,7	140.97	116.84	129.40	124.66	117.19	139.52
34	1,2,4,8	139.42	116.90	124.68	129.38	117.13	141.07
35	1,2,4,9	141.29	114.76	124.27	125.71	121.91	137.40
36	1,2,6,7	138.98	120.87	128.71	124.42	115.22	140.75
37	1,2,6,8	136.66	122.14	125.20	128.37	115.16	142.30
38	1,2,6,9	138.53	120.00	124.79	124.70	119.94	138.63
39	1,2,7,8	140.33	118.13	127.66	127.57	118.07	140.43
40	1,2,7,9	142.20	115.22	128.46	125.11	122.08	136.76
41	1,2,8,9	140.65	115.28	124.51	128.62	120.81	139.08
42	1,3,6,8	136.76	122.43	125.18	128.39	114.87	142.20
43	1,3,6,9	138.63	120.29	124.77	124.72	119.65	138.53
44	1,3,7,8	140.43	118.42	127.64	127.59	117.78	140.33
45	1,3,7,9	142.30	115.51	128.44	125.13	121.79	136.66
46	1,4,6,9	138.35	119.77	124.69	124.69	119.77	138.35
47	1,4,7,8	140.15	117.90	127.56	127.56	117.90	140.15
48	2,3,7,8I	140.61	118.30	127.67	127.67	118.30	140.61
49	1,2,3,4,6	137.00	122.04	126.17	124.71	115.18	140.99
50	1,2,3,4,7	140.67	117.26	129.84	125.12	117.32	139.12
51	1,2,3,6,7	138.68	121.29	129.15	124.88	115.35	140.35
52	1,2,3,6,8	136.36	122.56	125.64	128.83	115.29	141.90
53	1,2,3,6,9	138.23	120.42	125.23	125.16	120.07	138.23
54	1,2,3,7,8	140.03	118.55	128.10	128.03	118.20	140.03
55	1,2,3,7,9	141.90	115.64	128.90	125.57	122.21	136.36
56	1,2,3,8,9	140.35	115.70	124.95	129.08	120.94	138.68
57	1,2,4,6,7	138.40	120.77	129.07	124.85	115.47	140.17
58	1,2,4,6,8	136.08	122.04	125.56	128.80	115.41	141.72
59	1,2,4,6,9	137.95	119.90	125.15	125.13	120.19	138.05
60	1,2,4,7,8	139.75	118.03	128.02	128.00	118.32	139.85
61	1,2,4,7,9	141.62	115.12	128.82	125.54	122.33	136.18
62	1,2,4,8,9	140.07	115.18	124.87	129.05	121.06	138.50
63	1,2,3,4,6,7	138.10	121.19	129.51	125.31	115.60	139.77
64	1,2,3,4,6,8	138.51	120.63	127.50	127.45	119.99	138.41
65	1,2,3,4,6,9	138.23	120.11	127.42	127.42	120.11	138.23
66	1,2,3,4,7,8	139.45	118.45	128.46	128.46	118.45	139.45
67	1,2,3,6,7,8	137.46	122.48	127.77	128.22	116.48	140.68
68	1,2,3,6,7,9	139.33	119.57	128.57	125.76	120.49	137.01
69	1,2,3,6,8,9	137.01	120.84	125.83	128.50	119.22	139.33
70	1,2,3,7,8,9	140.68	116.83	128.29	127.70	122.13	137.46
71	1,2,4,6,7,9	139.05	119.05	128.49	125.73	120.61	136.83
72	1,2,4,6,8,9	136.73	120.32	125.75	128.47	119.34	139.15
73	1,2,3,4,6,7,8	136.88	122.38	128.13	128.65	116.73	140.10
74	1,2,3,4,6,7,9	138.75	119.47	128.93	126.19	120.74	136.43
75	1,2,3,4,6,7,8,9	137.53	120.66	128.32	128.32	120.66	137.53

Based at NMR ^{13}C spectra of a set of model compounds such increment schemes can reconstruct spectra for whole classes of compounds with an accuracy according to an experimental error. So it is possible to use them for recognizing structures of unknown compounds without special references and to have essentially new possibilities in operating with toxic and insoluble species.

The empirical increment schemes for NMR ^{13}C spectra calculations which developed now for polysubstituted benzenes, different pilyhalogenated oxybenzenes, PCDDs, PCB, PBB and naphthalenes, have common features[1]. They all provide prediction of NMR ^{13}C spectra for many thousands of unknown compounds on the basis of minimal information about known species.

For this purpose we created the corresponding service PC program, which can reproduce NMR ^{13}C spectrum for every compound from investigated classes[1].

The Table 1 demonstrates calculated NMR ^{13}C spectra for all PCDD, as an example of its capability. This program may be easily used for simulation of NMR ^{13}C spectra e.g. for all polybrominated dibenzo-*p*-dioxins if some minimal model volume of experimental data should be achieved. Such work may also be made for NMR ^{13}C spectra of some mixed Cl,Br-dioxins, and then spectra any of these 1400 compounds should be calculated. That can be done for parent structures: PCDF, PBDF and also for other dioxins-like compounds with another substituents, i.e. OH, Alk and so on.

Therefore we can obtain unlimited base of NMR ^{13}C for ecological pollutants. These results may be used in ecological projects for investigation of environmental pollutants, and one must perfectly understand what NMR can offer.

References

1) Fedorov L.A., and V.I.Dostovalova. NMR approach to structure analysis of aromatic toxicants in environment. *Chemosphere* 1995; **30**(7): 1311-1329.