Calculated NMR ^{13}C Spectra of Polyhalogenated Biphenyls (Cl and Br)

Dostovalova Valentina I.[a] and Fedorov Lev A.[b]

[a] A.N.Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences, 28 Vavilov Str., 117813 Russia, Moscow.

[b] V.I.Vernadski Institute of Geochemistry and Analytical Chemistry Russian Academy of Sciences, 19 Kosygin Str., 117975 Russia, Moscow.

1. Introduction

As is known ^{13}C NMR chemical shifts in polysubstituted compounds are related with molecular structures by a limited number of parameters, so it enables to reconstruct NMR spectra of all species of interest[1]. Earlier we created the method of simulating ^{13}C NMR spectra of organohalogen compounds with mono- and two-particle increment scheme which was used for prediction of ^{13}C NMR spectra of wide group of polysubstituted organohalogen aromatics, include polychlorinated (PCB)[2] and polybrominated biphenyls (PBB)[3]. Data of this research and also of mixed substituted polyhalogenated benzenes[4] allow us to predict ^{13}C NMR for biphenyls, containing Cl and Br simultaneously (PCBBs).

2. Discussion

Tables 1 and 2 show some ^{13}C NMR spectra for respectively four- and five-substituted PCBBs of two types: high-toxic compounds with halogens in 3,4,5,3',4'-positions, and low- toxic biphenyls, with halogen in *ortho*-position. Fig.1 demonstrates changes, occurring in spectra of two pairs of five-substituted PCBBs when *para*-halogen passed to *ortho*-position. The spectra find out essential distinctions, thus, the solution of a 4-Hal or 5-Hal and other conhener mixture can be investigated by various methods of 2D-^{13}C NMR spectroscopy for recognition of signals, belonging to one substance, and then to identify each compound by comparison of experimental and calculated data.

3. 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.

2) Dostovalova V.I. and L.A.Fedorov. The elucidation of chlorinated biphenyls structures by prediction of NMR ^{13}C chemical shifts. *Organohalogen compd.* 1994; **19**, 195-197.

3) Dostovalova V.I. and Fedorov L.A. Elucidation of brominated Biphenyl structures in the framework of the common method for prediction of NMR ^{13}C chemical shifts for polysubstituted benzenes. *Organohalogen compd.* 1995; **26**, 431-433.

4) Fedorov L.A. and V.I.Dostovalova. The prediction of NMR ^{13}C chemical shifts for Mixed Cl,Br-benzenes in frame of two-particle Increments. *Organohalogen compd.* 1996; **28**, 456-458.

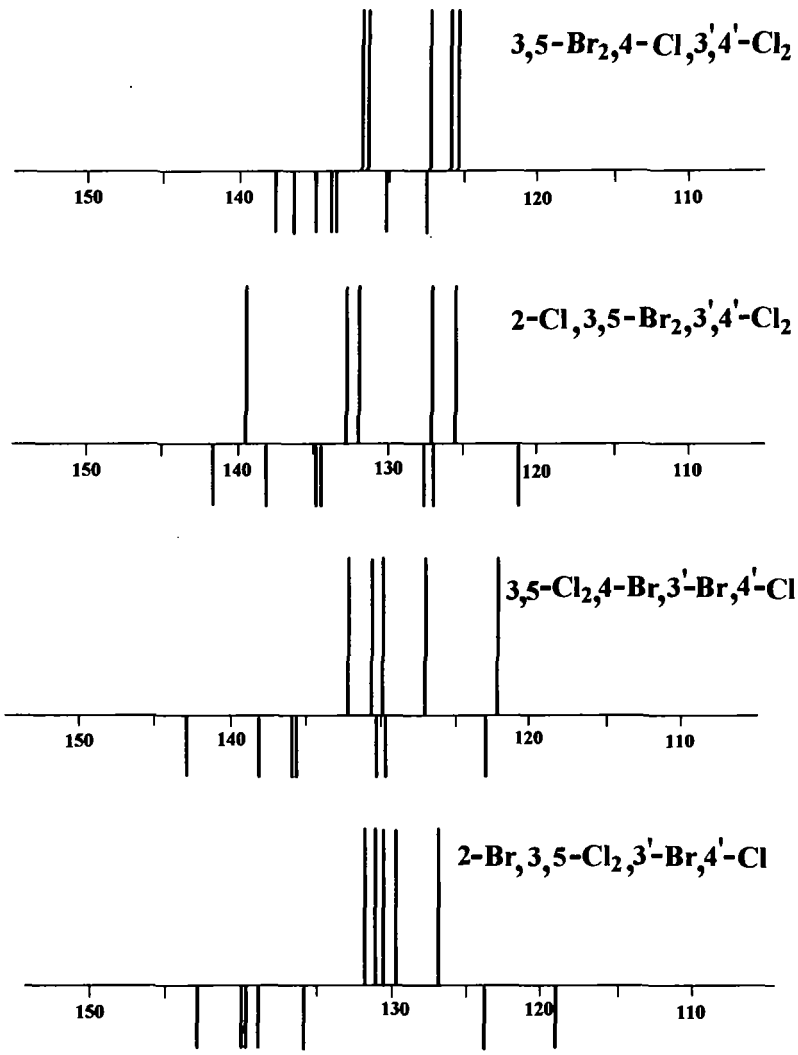

Fig. 1

^{13}C NMR spectra calculated for two pairs of five-substituted PCBBs when *para*-halogen passed to *ortho*-position (Cl for the 1-st pair and Br for the 2-nd.). The spectra are shown in TMS scale, in a mode of J-modulated spin echo, to distinguish C-atoms with hydrogen and without it.

Table 1. The calculated ^{13}C NMR chemical shifts for some high- and low-toxic tetrasubstituted PCBBs

	1	2	3	4	5	6	1'	2'	3'	4'	5'	6'
nil	140.6	126.75	128.37	126.87	128.37	126.75	140.6	126.75	128.37	126.87	128.37	126.75
						toxic PCBB						
3-Cl,4-Br,3',4'-Br_2	144.29	126.76	136.75	131.18	125.02	128.86	144.04	129.25	125.18	135.04	123.97	128.04
3,4-Cl_2 3',4'-Br_2	138.68	129.89	133.75	133.19	131.3	126.52	142.7	127.04	123.62	132.51	125.15	128.58
3-Br,4-Cl, 3',4'-Br_2,	139.14	132.01	123.80	139.16	131.3	127.51	144.4	127.18	125.3	135.47	124.09	127.97
3-Cl,4-Br, 3'-Br,4'-Cl	143.72	124.09	136.26	130.49	124.53	128.19	138.21	131.41	123.19	138.04	130.69	126.91
3-Cl,4-Br,3'-Cl,4'-Br	143.36	126.16	136.14	130.06	124.41	128.26	143.36	126.16	136.14	130.06	124.41	128.26
3-Cl,4-Br,3',4'-Cl_2	142.29	123.64	136.18	130.1	124.25	127.74	136.15	130.67	137.88	127.91	133.45	127.87
3-Br,4-Cl,3',4'-Cl_2	134.03	126.75	131.9	127.21	133.14	129.24	138.51	127.02	133.26	132.3	130.61	125.65
3-Br,4-Cl,3'-Br,4'-Cl	139.26	128.65	123.51	137.03	132.05	126.84	140.5	129.34	123.51	136.54	130.81	126.64
						mono-ortho-Hal PCBB						
2-Br,3-Cl,3',4'-Br_2	142.06	123.66	139.45	131.41	133.22	129.76	140.37	133.41	126.31	124.3	135.14	128.25
2,3-Cl_2,3',4'-Br_2	139.42	131.6	136.15	130.19	128.2	127.8	139.02	133.25	125.76	123.68	134.59	128.09
2-Cl,3-Br3',4'-Br_2	141.04	135. 5	126.4	132.25	128.97	128.79	139.95	133.85	126.37	124.8	135.2	128.69
2-Br,3-Cl,3'-Br,4'-Cl	141.09	121.19	138.96	130.92	132.93	129.29	141.54	131.91	123.89	135.91	131.19	127.21
2-Br,3-Cl, 3'-Cl,4'-Br	141.13	123.06	138.84	130.29	132.61	129.16	139.22	131.3	138.14	121.85	133.22	127.26
2-Br,3-Cl,3',4'-Cl_2	140.16	120.59	138.35	129.8	132.32	128.69	139.15	129.79	133.64	131.87	131.19	126.42
2-Cl,3-Br,3',4'-Cl_2	138.94	135.86	125.3	136.26	128.07	129.15	138.93	126.8	133.7	126.75	131.25	125.43
2-Cl,3-Br,3'-Br,4'-Cl	140.07	133.03	125.91	131.76	128.68	128.32	141.12	132.35	123.95	136.41	131.25	127.65

Table 2. The calculated ^{13}C NMR chemical shifts for some high- and low-toxic pentasubstituted PCBBs

	1	2	3	4	5	6	1'	2'	3'	4'	5'	6'
nil	140.6	126.75	128.37	126.87	128.37	126.75	140.6	126.75	128.37	126.87	128.37	126.75
toxic PCBB												
3,5-Cl_2,4-Br,3',4'-Br_2,	145.84	124.72	137.12	130.99	130.31	130.66	142.21	129.0	125.1	134.85	123.89	127.79
3,4-Cl_2,5-Br,3',4'-Br_2	141.38	128.84	136.82	136.32	125.83	129.28	141.8	127.39	124.15	133.44	125.68	128.93
3,5-Br_2,4-Cl,3',4'-Br_2	141.84	130.96	126.87	142.29	125.83	130.27	143.5	127.53	125.83	136.4	124.62	128.32
3,5-Cl_2,4-Br,3'-Br,4'-Cl	145.27	122.05	136.63	130.3	129.82	129.99	136.38	131.16	123.11	137.85	130.61	126.66
3-Cl,4,5-Br,3'-Cl,4'-Br	146.06	125.11	138.43	132.32	117.87	132.17	142.46	126.51	136.67	130.99	124.94	128.61
3,5-Cl,4-Br,3',4'-Cl_2	143.84	121.60	136.55	129.91	129.54	129.54	134.32	130.42	137.8	127.72	133.37	127.62
3,5-Br,4-Cl,3',4'-Cl_2	136.73	125.7	134.97	130.33	127.67	132.0	137.61	127.37	133.79	133.23	131.14	126.0
3-Br,4,5-Cl,3'-Br,4'-Cl	140.81	126.61	125.34	135.63	136.33	128.17	138.67	129.09	123.43	136.35	130.73	126.39
mono-ortho-Hal PCBB												
2-Br,3,5-Cl,3',4'-Br_2	143.61	121.62	140.51	131.22	138.71	130.32	138.54	133.16	126.23	124.11	135.06	128.0
2,3-Cl_2,5-Br,3',4'-Br_2	142.12	130.55	137.98	133.52	122.73	131.25	138.12	133.6	126.29	124.61	135.12	128.44
2-Cl,3,5-Br,3',4'-Br_2	143.74	134.45	128.23	135.58	123.5	132.24	139.05	134.2	126.9	125.73	135.73	129.04
2-Br,3,5-Cl,3'-Br,4'-Cl	142.64	119.15	140.02	130.73	138.42	129.85	139.71	131.66	123.81	135.72	131.11	126.96
2,5-Br,3-Cl,3'-Cl,4'-Br	143.83	122.01	140.67	133.62	127.14	132.61	138.32	131.65	138.67	122.78	133.75	127.61
2-Br,3,5-Cl,3',4'-Cl_2	141.71	118.55	139.41	129.61	137.81	129.25	137.32	129.54	133.56	131.68	131.11	126.17
2-Cl,3,5-Br,3',4'-Cl_2	141.64	134.81	127.13	139.59	122.6	132.6	138.03	127.15	134.23	127.68	131.78	125.78
2,5-Cl,3-Br,3'-Br,4'-Cl	141.62	130.99	126.97	131.57	134.17	128.88	139.29	132.10	123.87	136.22	131.17	127.40