

## Structures of polychlorinated naphthalenes and oxynaphthalenes and their $^{13}\text{C}$ NMR chemical shifts

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The increment scheme for calculating chemical shifts of polysubstituted naphthalenes is based on 1- and 2-substituted heterosubgraphs which describe the main part of the substituent effect. The influence of several substituents on  $^{13}\text{C}$  NMR chemical shifts have been described by two-particle increments corresponding to 1,2- and 2,3-*ortho*-disubstituted heterosubgraphs (the steric interaction of substituents in the same ring) and also to 1,4-conjugation of the substituents. Conjugation of two benzene rings required the introduction of a two-particle 1,8-heterosubgraph to the increment system. The systems of two-particle increments were obtained for polychlorinated naphthalenes, oxynaphthalenes, and polychlorinated oxynaphthalenes. Predicted  $^{13}\text{C}$  NMR spectra of polychlorinated naphthalenes not included in the increment analysis proved to be in good agreement with independent measurements.

**Key words:**  $^{13}\text{C}$  NMR chemical shifts, electronic and steric effects, increment scheme, polyoxynaphthalenes, polychlorinated naphthalenes, polychlorinated oxynaphthalenes.

It has been shown previously<sup>1-4</sup> that  $^{13}\text{C}$  NMR chemical shifts are related to the topology of a molecule by a limited set of parameters even for polysubstituted compounds. This makes it possible to simulate NMR spectra for all of the compounds of the class under consideration. In the present work we used the previously reported method for simulating  $^{13}\text{C}$  NMR spectra of organohalogen compounds based on two-particle increment schemes<sup>5-7</sup> for polychlorinated naphthalenes (PCN), polyoxynaphthalenes (PON), and polychlorinated oxynaphthalenes (PCON).

### Experimental

PCN, PON, and PCON were synthesized as described previously.<sup>8-11</sup>

The  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  for PCN,<sup>8,10</sup> PON,<sup>10,11</sup> and PCON,<sup>8</sup> and in acetone- $d_6$  for PON.<sup>10</sup>

Multiple-parameter regression analysis was carried out using the  $^{13}\text{C}$  NMR data for PCN and PON (Table 1). The conventional least-squares method was supplemented by the known technique of the adjustment of multiple-parameter linear regression.<sup>12</sup> The standard error was 0.46 ppm for PCN and 0.44 ppm for PON. Increments for PCON were obtained from the increments for PCN and PON according to the additive scheme and are in satisfactory agreement with the experimental data.

### Results and Discussion

In ecological problems PCN are often similar to polychlorinated dibenzo-*para*-dioxins (PCDD), although the former are less common. Chromatographic analysis of PCN requires 75 reference compounds that must be characterized by  $^{13}\text{C}$  NMR. The analysis of PON and PCON is substantially more complicated due to the rapid increase in the number of standards that need to be prepared and characterized. In solving ecological problems PCN are often found together with polychlorinated biphenyls (PCB); chromatographic peaks and NMR signals of these compounds occur in overlapping regions. In this connection the possibility of assigning a group of characteristic  $^{13}\text{C}$  NMR signals to each of the compounds is of particular assistance.

In a previous study of  $^{13}\text{C}$  NMR spectra of oxy- and polychlorinated oxybenzenes<sup>4,13</sup> it was shown that steric and electronic Cl—O interactions in PCDD are similar to those occurring in monocyclic aromatic systems, and corrections caused by the effect from the other ring are generally small. The  $^{13}\text{C}$  NMR spectra for PCN and PCDD are generally similar. 1- and 2-substituted naphthalene subgraphs as the basis elements of the increment scheme determine the transfer of the effect of substituents in two types of polycyclic compounds.<sup>14,15</sup>

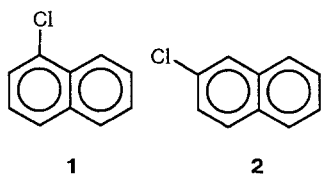
**Table 1.** Experimental (calculated)  $^{13}\text{C}$  NMR chemical shifts (ppm, from TMS) of some polysubstituted naphthalenes. New assignments of signals based on the calculated  $^{13}\text{C}$  NMR chemical shifts are given in brackets

Position of the substituent	Reference	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
1-Cl	<sup>a</sup> 8	131.9 [C-9] (131.2)	126.1 (126.8)	125.7 [C-6] (126.6)	126.1 (127.0)	128.2 (128.1)	127.0 [C-7] (125.9)	126.7 [C-3] (126.4)	124.4 (124.4)	130.9 [C-1] (131.5)	134.6 (134.2)
2-Cl	<sup>a</sup> 8	126.6 (126.3)	131.6 (131.4)	126.7 [C-6] (126.4)	129.5 (129.0)	127.8 (127.5)	126.1 [C-3] (126.9)	127.0 (127.5)	126.7 (126.9)	134.0 (134.0)	131.6 (131.7)
1,2-Cl <sub>2</sub>	<sup>a</sup> 8	129.4 (129.5)	131.7 (131.3)	126.6 (125.9)	128.1 (128.2)	127.9 (128.3)	127.2 (126.7)	127.7 (127.7)	124.6 (124.2)	130.3 (130.9)	132.6 (132.3)
1,4-Cl <sub>2</sub>	<sup>a</sup> 8	130.9 (130.9)	125.9 [C-6] (128.3)	125.9 (128.3)	130.9 (130.9)	125.0 (125.4)	127.7 [C-2] (126.2)	127.7 (126.2)	125.0 (125.0)	131.6 (132.1)	131.6 (132.1)
1,5-Cl <sub>2</sub>	<sup>a</sup> 8	131.9 (131.3)	127.0 [C-3] (126.5)	126.7 [C-2] (126.9)	123.7 (124.3)	131.9 (131.3)	127.0 (126.5)	126.7 (126.9)	123.7 (124.3)	132.3 (132.1)	132.3 (132.1)
1,8-Cl <sub>2</sub>	<sup>a</sup> 8	130.4 (130.3)	130.8 (130.3)	126.1 (126.3)	128.5 (127.8)	128.5 (127.8)	126.1 (126.3)	130.8 (130.3)	130.4 (130.3)	127.5 (127.1)	137.2 (136.8)
2,3-Cl <sub>2</sub>	<sup>a</sup> 8	127.0 (127.1)	130.1 (130.9)	130.1 (130.9)	127.0 (127.1)	126.9 (127.0)	128.8 (128.2)	128.8 (128.2)	126.9 (127.0)	132.3 (132.1)	132.3 (132.1)
2,6-Cl <sub>2</sub>	<sup>a</sup> 8	126.5 (126.5)	132.0 (132.1)	127.9 (127.6)	128.6 (128.6)	126.5 (126.5)	132.0 (132.1)	127.9 (127.6)	128.6 (128.6)	132.2 (132.1)	132.2 (132.1)
2,7-Cl <sub>2</sub>	<sup>a</sup> 8	125.7 (125.9)	132.8 (132.6)	127.0 (127.1)	129.2 (129.2)	129.2 (129.2)	127.0 (127.1)	132.8 (132.6)	125.7 (125.9)	134.5 (134.3)	129.7 (129.9)
1,2,3-Cl <sub>3</sub>	<sup>a</sup> 8	129.4 [C-9] (130.3)	130.4 [C-3] (130.8)	131.4 [C-2] (130.4)	127.3 [C-1] (126.8)	127.3 (127.8)	127.9 (127.9)	127.7 (128.4)	124.8 (124.3)	130.1 (129.1)	132.0 (132.7)
1,2,3,4-Cl <sub>4</sub>	<sup>a</sup> 8	130.1 (130.2)	130.3 (130.3)	130.3 (130.3)	130.1 (130.2)	125.4 (125.5)	128.7 (128.8)	128.7 (128.8)	125.4 (125.5)	130.0 (130.0)	130.0 (130.0)
1,4,5,8-Cl <sub>4</sub>	<sup>a</sup> 9	131.0 (130.4)	131.0 (130.7)	131.0 (130.7)	131.0 (130.4)	131.0 (130.4)	131.0 (130.7)	131.0 (130.7)	131.0 (130.4)	130.5 (129.3)	130.5 (129.3)
1,2,3,4,6-Cl <sub>5</sub>	<sup>a</sup> 9	130.3 (130.1)	130.4 (130.2)	131.3 (131.0)	129.3 (129.5)	127.2 (126.3)	135.4 (134.0)	129.6 (129.0)	124.4 (123.7)	128.5 (128.1)	130.1 (130.3)
1,2,3,4,5,8-Cl <sub>6</sub>	<sup>a</sup> 9	130.2 (129.2)	134.5 (134.4)	134.5 (134.4)	130.2 (129.2)	130.3 (130.2)	131.8 (131.9)	131.8 (131.9)	130.3 (130.2)	129.3 (127.7)	129.3 (127.7)
1,2,3,5,6,7-Cl <sub>6</sub>	<sup>a</sup> 9	131.0 (130.5)	132.1 (132.2)	133.4 (132.5)	124.6 (123.9)	131.0 (130.5)	132.1 (132.2)	133.4 (132.5)	124.6 (123.9)	129.1 (128.5)	129.1 (128.5)
Cl <sub>8</sub>	<sup>a</sup> 8 <sup>a</sup> 9	128.7 129.7 [C-9,10] (129.6)	135.0 135.3 [C-2,3,6,7] (135.5)	135.0 135.3 (135.5)	128.7 129.7 [C-1,4,5,8] (129.6)	128.7 129.7 (129.6)	135.0 135.3 (135.5)	135.0 135.3 (135.5)	128.7 129.7 (129.6)	129.4 129.0 (129.2)	129.4 129.0 (129.2)
1-OH	<sup>a</sup> 10 <sup>b</sup> 10	151.2 153.9 (151.2)	108.8 108.8 (108.9)	125.8 126.9 (126.0)	120.8 119.8 (120.6)	127.7 128.2 (127.5)	126.5 126.8 (126.6)	125.3 125.3 (125.3)	121.5 122.9 (121.5)	124.4 125.8 (124.4)	134.8 135.8 (134.8)
2-OH	<sup>a</sup> 10 <sup>b</sup> 10	109.6 109.7 (109.7)	153.4 156.0 (153.4)	117.8 119.1 (118.4)	129.9 130.2 (129.8)	127.8 128.4 (127.6)	123.7 123.6 (123.8)	126.6 126.9 (126.8)	126.4 126.9 (126.1)	134.7 135.9 (135.2)	129.1 129.3 (128.9)
1,5-(OH) <sub>2</sub>	<sup>b</sup> 10	153.6 (153.8)	109.3 (109.2)	125.6 (125.4)	114.2 (114.5)	153.6 (153.8)	109.3 (109.2)	125.6 (125.4)	114.2 (114.5)	127.2 (126.7)	127.2 (126.7)
2,3-(OH) <sub>2</sub>	<sup>a</sup> 11	110.2 (110.2)	144.0 (144.0)	144.0 (144.0)	110.2 (110.2)	126.2 (126.4)	124.2 (124.4)	124.2 (124.4)	126.2 (126.4)	129.5 (130.4)	129.5 (130.4)
2,6-(OH) <sub>2</sub>	<sup>b</sup> 10	110.0 (110.0)	153.8 (153.6)	119.4 (118.9)	128.4 (128.5)	110.0 (110.0)	153.8 (153.6)	119.4 (118.9)	128.4 (128.5)	130.5 (130.4)	130.5 (130.4)

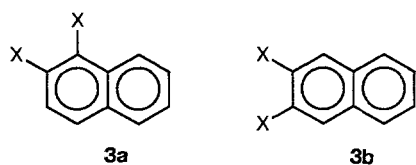
Table 1. Continued.

Position of the substituent	Reference	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
2,7-(OH) <sub>2</sub>	<sup>b</sup> 10	108.5 (108.4)	156.4 (156.5)	116.1 (116.0)	130.1 (130.1)	130.1 (130.1)	116.1 (116.0)	156.4 (156.5)	108.5 (108.4)	137.5 (136.8)	124.4 (124.1)
1-Cl,2-OH	<sup>a</sup> 8	113.7 (112.9)	149.4 (150.0)	117.2 (117.1)	128.2 (128.4)	128.4 (128.4)	124.1 (123.6)	127.5 (127.0)	122.8 (123.4)	131.1 (131.8)	129.5 (129.4)
1-Cl,4-OH	<sup>a</sup> 8	123.6 (123.0)	125.7 (126.9)	108.7 (109.2)	150.6 (151.3)	122.1 (122.1)	126.0 (125.3)	127.6 (126.8)	124.5 (124.7)	131.6 (133.2)	125.5 (125.6)
1-Cl,8-OH	<sup>a</sup> 8	127.2 (127.0)	127.5 (129.5) [C-4]	125.4 (127.0)	128.6 (127.2) [C-2]	120.9 (121.3)	127.6 (126.1)	113.1 **	152.8 **	119.8 **	137.0 **
2-Cl,1-OH	<sup>a</sup> 8	147.1 (146.2)	113.6 (114.0)	126.1 (125.0)	122.2 (122.2)	127.6 (127.6)	126.7 (126.6) [C-7]	125.9 (126.8) [C-6]	120.9 (120.8)	124.6 (124.2)	133.3 (133.4)
1,6-Cl <sub>2</sub> ,2-OH	<sup>a</sup> 8	113.5 (113.2)	149.7 (149.5)	118.5 (118.5)	124.6 (129.1) [C-8]	127.5 (127.4)	130.1 (128.3) [C-4]	128.4 (127.2) [C-6]	126.9 (125.1) [C-7]	129.5 (131.3) [C-10]	130.1 (129.7) [C-9]
2,4-Cl <sub>2</sub> ,1-OH	<sup>a</sup> 8	146.4 (146.3)	112.7 (113.1)	125.4 (125.9)	124.9 (124.6) [C-5]	124.4 (124.9) [C-4]	127.7 (126.8)	126.9 (126.5)	122.5 (121.6)	123.4 (124.1)	130.3 (131.3)

\* Solvent: a — CDCl<sub>3</sub>, b — acetone. \*\* The data were used to obtain 1-Cl, 8-OH mixed increments, therefore, the calculated and the experimental values are identical.

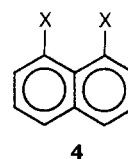


In Ref. 8 all of the variations of the <sup>13</sup>C NMR chemical shifts in polysubstituted naphthalenes were associated with these effects. However, judging by the great errors in the reproduction of the experimental data, this approach is too simple. Experiments<sup>2-4,16</sup> have shown that additional factors, *i.e.*, 1,2- or 2,3-*ortho*-disubstituted subgraphs (with equal effects of **3a** and **3b**), should be taken into account to simulate the steric interactions of substituents in the same ring as well as the effects of the *para*-conjugation of substituents (in positions 1, 4).



However, conjugation of the two benzene rings is much more pronounced in naphthalene than in PCDD, in which the intermediate ring formed by oxygen bridges suppresses the conjugation of the aromatic rings. Therefore, the system of increments for naphthalene should

be supplemented by a two-particle 1,8-heterosubgraph (**4**) whose effect is quite substantial.<sup>17</sup>



These increments were based on the experimental data for PCN<sup>8</sup> and PON,<sup>10</sup> which was then used for the calculations of the <sup>13</sup>C NMR spectra for other PCN,<sup>8,9</sup> oxynaphthalenes,<sup>10,11</sup> and PCON.<sup>8</sup> In spite of the small number of model compounds, we managed to predict the <sup>13</sup>C NMR spectra for a series of PCN not involved in the increment analysis with good agreement with experiment.<sup>9</sup> Table 1 shows examples of the application of the resulting increment scheme for the calculation of <sup>13</sup>C NMR chemical shifts in some polysubstituted naphthalenes.

The set of increments (Table 2) provides a standard error of 0.45 ppm and may be entered into a corresponding service program for a personal computer. Along with predicting spectra of uninvestigated compounds, this makes it possible to revise the assignment of signals for those PCN and PCON whose investigation involved uncertainty.<sup>8</sup> It should be emphasized that the assignment of the signals of polysubstituted compounds with the aid of statistically weighted increments for the <sup>13</sup>C NMR chemical shifts offers one more advantage. The fact is that the experimental data used were obtained with various NMR techniques, including spin-spin cou-

**Table 2.** Cl and OH one- and two-particle increments for  $^{13}\text{C}$  NMR chemical shifts in PCN, PON, and PCON (with respect to unsubstituted naphthalene:  $\delta(\text{C-1}) = 127.52$ ,  $\delta(\text{C-2}) = 126.30$ ,  $\delta(\text{C-9}) = 133.53$  ppm from TMS)

Position of the substituent	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
1-Cl	3.82	0.55	0.41	-0.30	0.79	-0.28	0.23	-2.74	-2.12	0.53
2-Cl	-1.00	5.16	0.17	1.69	0.12	0.01	1.25	-0.42	0.35	-1.85
1,2-Cl <sub>2</sub> *	-0.63	-0.63	-0.93	—	—	—	—	—	-0.93	—
1,8-Cl <sub>2</sub>	1.48	3.37	—	—	—	—	—	—	-7.11	6.94
1-OH	23.82	-17.40	0.17	-6.79	0.13	0.40	-0.67	-6.09	-8.56	1.64
2-OH	-17.66	27.24	-7.83	2.44	0.30	-2.35	0.55	-1.23	1.58	-4.78
1,2-(OH) <sub>2</sub> *	-4.15	-4.15	-1.92	—	—	—	—	—	-1.92	—
2,3-(OH) <sub>2</sub>	-1.92	-4.15	-4.15	-1.92	—	—	—	—	—	—
1-Cl,2-OH**	-1.73	3.96	-1.31	—	—	—	—	—	-1.51	—
1-Cl,8-OH	2.11	2.53	—	—	—	—	4.01	4.39	-3.12	1.22

\* The same increments with the corresponding cyclic rearrangement of C<sup>k</sup> are used for 2,3-X<sub>2</sub>.

\*\* The same increments are used for 1-OH, 2-Cl, 2-Cl, 3-OH and 2-OH, 3-Cl.

pling constants and multiple resonances. Since these constants are simultaneously affected by several factors they no longer contain unambiguous structural information. Therefore, their properties which have been determined for monosubstituted benzenes cannot be directly extended to more complex systems.

Thus, the method suggested for calculating  $^{13}\text{C}$  NMR chemical shifts allows one to distinguish between similar spectra of related compounds.

The accuracy of the calculations increases if the set of model derivatives used includes, for example, PON with OH groups in positions 1 and 8. In this case, the increment scheme reflects all of the basic information on the variation of  $^{13}\text{C}$  NMR chemical shifts throughout the given class of structures. Nevertheless, even the currently available data indicate that empirical calculations of the  $^{13}\text{C}$  NMR spectra are quite promising for determining the structure of molecules, since they provide good results and can be readily accomplished.

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