

Thermodynamic and physicochemical properties *vs.* some ecotoxicological features of polychlorinated naphthalenes

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Abstract

Geometry, electrostatic potential surfaces and basic thermodynamic and physicochemical characteristics such as standard enthalpies of formation ($\Delta_f H^\circ$), standard free enthalpies of formation ($\Delta_f G^\circ$), entropies (S°), heat capacities (C_p°), energies of LUMO and HOMO and dipole moments have been computed for all 75 congeners of chloronaphthalene (CNs, PCNs). Chloronaphthalene congeners nos.: 5, 9, 10, 12, 27, 41, 45, 47, 65, 66, 70 and 72 have minima at C_{2v} symmetry; nos.: 6, 11, 36, 42, 67 and 71 at C_{2h} symmetry; nos.: 46, 48 and 75 at D_{2h} symmetry and all other congeners at C_s symmetry.

All congeners of CNs are thermodynamically unstable and the absolute values of $\Delta_f H^\circ$ and $\Delta_f G^\circ$ decrease with an increasing degree of chlorination. LUMO energies of CNs are negative which suggest that corresponding anions are stable.

Dipole moments of highly symmetric CNs (C_{2v} and D_{2h}) are negligible while those of less symmetric derivatives reach 1.925 [D]. The physicochemical characteristics such as enthalpies, free enthalpies of formation, HOMO and LUMO energies and dipole moments were correlated with known bioaccumulation factors (BAF) of chloronaphthalene congeners in herring living in Baltic Sea.

Key words: Polychlorinated naphthalenes, thermodynamic and physicochemical properties, relations with ecotoxicological features.

Introduction

Useful physical properties and chemical inertness of polychlorinated naphthalenes (PCNs), similarly to chlorobiphenyls (PCBs) or chloroterphenyls (PCTs), made these substances interesting for electric, energy and others industries (1). Polychlorinated naphthalenes are lipophilic, toxic and relatively persistent substances under environmental conditions. Their main sources are related to various industrial appliances, thermal degradation and chlorination processes (1-2). Among 75 congeners of chloronaphthalenes only a few are relatively resistant to biodegradation and these biomagnify in animals occupying higher position in marine food web. Many of them are also bioaccumulated in lower food web organisms (3-6).

Only limited data concerning the biological activity of different chloronaphthalene congeners (7-9) are available. Also relations between structure, physicochemical and other features and persistency or pliancy to metabolism were only occasionally investigated.

Nevertheless, we attempted to relate them to theoretically predicted properties of PCNs. For this purpose, we optimized geometry of molecules and calculated electrostatic potential surfaces and values of selected thermodynamic and physicochemical properties using the semiempirical methods. The obtained data were correlated with available ecotoxicological characteristics of individual isomers or congeners of chloronaphthalene.

Materials and Methods

Geometry optimizations were carried out on the level of the semiempirical PM3 method (10) using the EF technique (11) implemented in the MOPAC 93 program package (12). Values of thermodynamic and physicochemical quantities were extracted directly from MOPAC 93 data files (13). Electrostatic potential surfaces were drawn using the SPARTAN v. 4.0 program (14).

The values of bioaccumulation factor (BAF) of PCNs in herring were taken from different papers (4, 5).

Results and Discussion

The constitution symmetry and basic thermodynamic and physicochemical properties such as standard enthalpies of formation ($\Delta_f H^\circ$), standard free enthalpies of formation ($\Delta_f G^\circ$), entropies (S°), heat capacities (C_p°), energies of HOMO and LUMO and dipole moments of chloronaphthalene congeners are summarized in Table 1. The surfaces of an electrostatic potential surrounding four selected pentachloronaphthalenes, which are relatively persistent under environmental conditions and do not have two vicinal (adjacent) carbon atoms unsubstituted with chlorine (4, 16) are shown in Figures 1 and 2.

Congeners nos.: 5, 9, 10, 12, 27, 41, 45, 47, 65, 66, 70 and 72 have one C_2 rotation axis (rotation by 180°) and two vertical planes (C_{2v} point group); nos.: 6, 11, 36, 42, 67 and 71 - one C_2 rotation axis and one horizontal plane (C_{2h} point group); nos.: 46, 48 and 75 - three C_2 rotation axis and one horizontal plane (D_{2h} point group), while others - one plane (C_s point group).

The standard enthalpy of formation ($\Delta_f H^\circ$) equals the amount of heat exchanged upon the formation of a compound from stable forms of elements under pressure of 1 atm. and temperature of 298 K. Therefore, the more negative value of the enthalpy of formation the more thermodynamically stable the molecule is. All congeners of chloronaphthalene are thermodynamically unstable, although the absolute values of $\Delta_f H^\circ$ and $\Delta_f G^\circ$ decrease with an increasing degree of chlorination (Table 1). It means that less chlorinated chloronaphthalenes should easier decompose than more chlorinated.

Quantum mechanical calculations provide also values of energy of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and dipole moments. The energies HOMO of CNs differ only slightly and changes of these do not correlate with a degree of chlorination. The negative energy of HOMO and LUMO approximate according to the Koopman's theory. The first ionization potential and electron affinity of molecules respectively. The dipole moments are more dependent on the constitution and less on degree of chlorination of molesules. Hence, the congeners of chloronaphthalene with chlorine atoms distributed symmetrically exhibit minimal values of

dipole moments and those with chlorine atoms distributed non-symmetrically - the highest values of this quantity. More chlorinated CN congeners will easier attract an electron than less chlorinated ones. However, all chlorinated naphthalenes should form thermodynamically stable negative ions.

The electrostatic potential surrounding molecules reflects ability to interact with nucleophilic or electrophilic reagents. Blue colour indicates positive and red negative values of the electrostatic potential (Figs. 1 and 2)

The deeper the colour is, the more distinctive is the ability to chemical interactions. The regions of highly positive potential are susceptible to nucleophilic substitution and negative potential - to electrophilic substitution. As these reactions should indicate chemical degradation of PNs, the thorough analysis of electrostatic potential around molecules enables preliminary insight into reactivity, possibilities of interaction and degradation of their derivatives.

Congeners of chloronaphthalene having two vicinal (adjacent) carbon atoms unsubstituted with chlorine (NVC - CIPCN) such as nos.: 42, 52, 58, 60, 61, 64, 67, 68, 69, 71, 72, 73, 74 and 75 that are considered the most persistent, have lower values of standard enthalpy of formation, standard free enthalpy and dipole moments, and higher values of entropy and heat capacity on the average, when compared to congeners with other patterns of substitution with chlorine.

The environmental persistency and behavior of organohalogenated pollutants, especially when related to the abiotic matrices, are highly determined by their various physicochemical features like low hydrophilicity and high lipophilicity, low vapor pressure, and a high $\log K_{ow}$ or $\log K_{d/s}$ values. Regressive analysis indicates that bioaccumulation factors (BAF) of PCNs in herring feeding on plankton positively correlate with some physicochemical and thermodynamical properties of these substances such as standard free enthalpies, energies of LUMO and HOMO and dipole moments.

Table I. Symmetry and physicochemical properties of PCNs

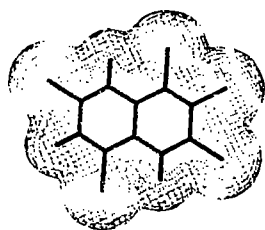
No	Structure	Point group symmetry	Standard enthalpy of formation*	Standard free enthalpy of formation	Entropy†	Heat capacity‡	Energy of LUMO (eV)	Energy of HOMO (eV)	Dipole moment (D)
1	1-MoCN	C _s	34.5	34.1	90.0	34.8	-0.620	-8.803	0.9020
2	2-MoCN	C _s	33.8	33.4	86.6	32.9	-0.605	-8.897	1.0653
3	1,2-DiCN	C _s	28.9	28.5	93.0	36.5	-0.779	-8.816	1.4528
4	1,3-DiCN	C _s	28.0	27.6	93.2	36.6	-0.802	-8.878	1.1443
5	1,4-DiCN	C _{2v}	28.7	28.3	93.2	36.5	-0.826	-8.770	0.3703
6	1,5-DiCN	C _{2h}	28.7	28.3	92.6	36.5	-0.816	-8.803	0.0045
7	1,6-DiCN	C _s	27.9	27.5	93.1	36.5	-0.801	-8.890	0.8288
8	1,7-DiCN	C _s	27.9	27.5	93.1	36.5	-0.799	-8.861	1.4809
9	1,8-DiCN	C _{2v}	31.3	30.9	92.1	36.5	-0.809	-8.719	1.5901
10	2,3-DiCN	C _{2v}	28.3	27.9	93.3	36.6	-0.757	-8.969	1.6016
11	2,6-DiCN	C _{2h}	27.1	26.7	92.9	36.6	-0.791	-8.910	0.0002
12	2,7-DiCN	C _{2v}	27.2	26.7	93.4	36.6	-0.784	-9.003	0.9071
13	1,2,3-TrCN	C _s	23.5	23.1	96.1	38.3	-0.922	-8.888	1.6744
14	1,2,4-TrCN	C _s	23.3	22.8	99.6	40.2	-0.971	-8.796	1.1003
15	1,2,5-TrCN	C _s	23.1	22.7	95.6	38.2	-0.961	-8.835	0.7581
16	1,2,6-TrCN	C _s	22.3	21.9	95.9	38.3	-0.951	-8.868	0.6126
17	1,2,7-TrCN	C _s	22.3	21.9	99.6	40.3	-0.943	-8.901	1.4829
18	1,2,8-TrCN	C _s	25.7	25.3	94.9	38.2	-0.954	-8.740	1.9075
19	1,3,5-TrCN	C _s	22.3	21.9	99.6	40.3	-0.982	-8.865	0.9654
20	1,3,6-TrCN	C _s	21.5	21.1	96.5	38.4	-0.969	-8.982	0.1835
21	1,3,7-TrCN	C _s	21.5	21.1	99.7	40.3	-0.971	-8.900	0.7930
22	1,3,8-TrCN	C _s	25.0	24.5	98.9	40.2	-0.977	-8.810	1.3579
23	1,4,5-TrCN	C _s	25.8	25.3	95.0	38.2	-1.002	-8.872	0.7249
24	1,4,6-TrCN	C _s	22.2	21.8	96.3	38.3	-0.990	-8.841	0.6647
25	1,6,7-TrCN	C _s	22.5	22.1	99.5	40.3	-0.939	-8.934	1.5452
26	2,3,6-TrCN	C _s	21.8	21.4	96.1	38.3	-0.929	-9.005	0.7789
27	1,2,3,4-TeCN	C _{2v}	18.8	18.4	102.3	42.0	-1.082	-8.816	1.5226
28	1,2,3,5-TeCN	C _s	17.8	17.4	102.2	42.0	-1.091	-8.886	1.3222
29	1,2,3,6-TeCN	C _s	17.1	16.6	99.1	40.0	-1.083	-8.953	0.6505
30	1,2,3,7-TeCN	C _s	17.0	16.6	102.4	42.0	-1.079	-8.939	1.1754
31	1,2,3,8-TeCN	C _s	20.5	20.1	101.5	42.0	-1.086	-8.813	1.8125
32	1,2,4,5-TeCN	C _s	20.4	20.0	101.3	42.0	-1.134	-8.759	0.9392
33	1,2,4,6-TeCN	C _s	16.8	16.4	102.4	42.0	-1.128	-8.846	0.2460
34	1,2,4,7-TeCN	C _s	16.8	16.4	102.5	42.0	-1.123	-8.880	0.6795
35	1,2,4,8-TeCN	C _s	20.4	20.0	101.3	41.9	-1.134	-8.741	1.2477
36	1,2,5,6-TeCN	C _{2h}	17.6	17.2	102.1	42.0	-1.099	-8.847	0.0016
37	1,2,5,7-TeCN	C _s	16.8	16.4	102.3	42.0	-1.114	-8.912	0.6734
38	1,2,5,8-TeCN	C _s	20.3	19.9	97.9	30.0	-1.134	-8.748	1.0359
39	1,2,6,7-TeCN	C _s	17.0	16.6	102.0	42.0	-1.077	-8.938	1.1703
40	1,2,6,8-TeCN	C _s	19.4	19.0	101.4	42.0	-1.114	-8.807	1.2450
41	1,2,7,8-TeCN	C _{2v}	20.2	19.8	101.2	41.9	-1.086	-8.780	1.9245
42	1,3,5,7-TeCN	C _{2h}	16.0	15.6	106.1	44.0	-1.139	-8.899	0.0017
43	1,3,5,8-TeCN	C _s	19.5	19.1	101.7	42.0	-1.154	-8.790	0.6856
44	1,3,6,7-TeCN	C _s	16.2	15.8	102.5	42.1	-1.100	-8.985	0.5550
45	1,3,6,8-TeCN	C _{2v}	18.7	18.3	102.0	42.0	-1.131	-8.907	0.5662
46	1,4,5,8-TeCN	D _{2h}	23.6	23.2	97.0	39.9	-1.180	-8.653	0.0035

Table 1, cont'd

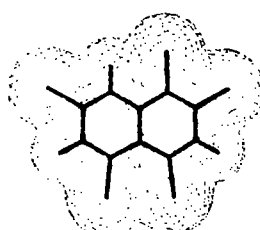
Table 1, continued.

No	Structure	Point group symmetry	Standard enthalpy of formation ^a	Standard free enthalpy of formation	Entropy ^f	Heat capacity ^l	Energy of LUMO (eV)	Energy of HOMO (eV)	Dipole moment (D)
47	1,4,6,7-TeCN	C _{2v}	16.9	16.5	102.5	42.003	-1.118	-8.895	1.0960
48	2,3,6,7-TeCN	D _{2h}	16.5	16.0	102.3	42.041	-1.062	-9.076	0.0018
49	1,2,3,4,5-PeCN	C _s	16.0	15.6	104.0	43.650	-1.236	-8.770	1.4222
50	1,2,3,4,6-PeCN	C _s	12.4	12.0	105.2	43.750	-1.229	-8.879	0.7429
51	1,2,3,5,6-PeCN	C _s	12.4	12.0	104.9	43.733	-1.219	-8.911	0.7203
52	1,2,3,5,7-PeCN	C _s	11.6	11.2	108.7	45.745	-1.239	-8.938	0.4951
53	1,2,3,5,8-PeCN	C _s	15.1	14.7	104.2	43.671	-1.253	-8.805	1.1565
54	1,2,3,6,7-PeCN	C _s	11.8	11.4	105.1	43.776	-1.205	-9.000	0.5393
55	1,2,3,6,8-PeCN	C _s	14.3	13.8	104.5	43.742	-1.235	-8.885	0.8862
56	1,2,3,7,8-PeCN	C _s	15.1	14.7	118.1	43.677	-1.213	-8.832	1.5390
57	1,2,4,5,6-PeCN	C _s	15.0	14.5	104.0	43.661	-1.250	-8.777	0.6428
58	1,2,4,5,7-PeCN	C _s	14.2	13.8	107.9	45.670	-1.276	-8.839	0.0160
59	1,2,4,5,8-PeCN	C _s	18.4	17.9	103.2	43.595	-1.301	-8.692	0.6706
60	1,2,4,6,7-PeCN	C _s	11.6	11.2	105.1	43.767	-1.244	-8.910	0.4712
61	1,2,4,6,8-PeCN	C _s	14.2	13.8	107.8	45.665	-1.280	-8.798	0.4573
62	1,2,4,7,8-PeCN	C _s	14.9	14.5	104.0	43.657	-1.255	-8.785	1.1045
63	1,2,3,4,5,6-HxCN	C _s	10.6	10.2	106.6	45.394	-1.353	-8.801	1.0113
64	1,2,3,4,5,7-HxCN	C _s	9.8	9.4	110.5	47.410	-1.373	-8.835	0.4879
65	1,2,3,4,5,8-HxCN	C _{2v}	14.0	13.6	105.8	45.323	-1.393	-8.714	1.0238
66	1,2,3,4,6,7-HxCN	C _{2v}	7.2	6.8	107.8	45.510	-1.343	-8.927	0.0324
67	1,2,3,5,6,7-HxCN	C _{2h}	7.2	6.8	111.2	47.462	-1.336	-8.957	0.0010
68	1,2,3,5,6,8-HxCN	C _s	9.8	9.4	110.3	47.386	-1.372	-8.839	0.4558
69	1,2,3,5,7,8-HxCN	C _s	9.8	9.4	110.2	47.380	-1.371	-8.825	0.7648
70	1,2,3,6,7,8-HxCN	C _{2v}	9.8	9.4	106.9	45.455	-1.331	-8.893	0.9535
71	1,2,4,5,6,8-HxCN	C _{2h}	13.1	12.7	109.2	47.314	-1.416	-8.720	0.0020
72	1,2,4,5,7,8-HxCN	C _{2v}	13.1	12.7	109.3	47.313	-1.412	-8.736	0.4416
73	1,2,3,4,5,6,7-HxCN	C _s	5.5	5.1	112.8	49.113	-1.461	-8.850	0.4125
74	1,2,3,4,5,6,8-HxCN	C _s	8.8	8.4	111.8	49.043	-1.501	-8.749	0.4446
75	1,2,3,4,5,6,7,8-OCN	D _{2h}	4.5	4.1	114.2	50.775	-1.583	-8.769	0.0002

^a(kcal/mol); ^f(cal/(mol K))

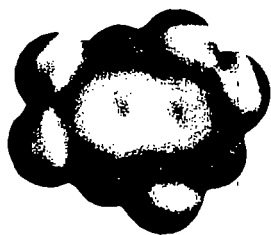


1,2,3,5,7-PeCN (No. 52)

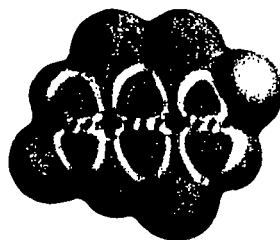


1,2,4,5,7-PeCN (No. 58)

Figure 1. Surfaces of the electrostatic potential around CNs nos. 52 and 58.



1,2,4,6,7-PeCN (No. 60)



1,2,4,6,8-PeCN (No. 61)

Figure 2. The electrostatic potential surfaces of CNs nos. 60 and 61.

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