PREDICTION OF ENVIRONMENTAL PARTITION COEFFICIENTS FOR 135 CONGENERS OF POLYCHLORINATED DIBENZOTIOPHENES (PCDTs)

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Introduction

Polychlorinated dibenzothiophenes (PCDTs) are an important group of persistent organic pollutants (POPs), which have been found to be a highly diversed group of chemical compounds. This group includes many substances more or less harmful to people and animals lives. The molecule of thiophene contains two benzene rings joined together with a five–membered carbon ring in which one carbon atom was replaced with one sulphur atom As a result of the replacement of hydrogen atoms by chlorine the group named PCDTs comes into being. Owing to eight carbon atoms which are open for attachment of chlorines, this group consists of a grate number of congeners. There are 135 congeners from mono- to octa- substituted thiophenes. Their molecular weights are in the range between 218.71 to 459.83 [g*mol^{-1}]. Showing all of 135 PCDTs congeners is possible only in theory, because, it is known that not everyone of them corresponds with the facts.

In the literature, primarily the polychlorinated dibenzothiophenes (PCDTs) derived from dibenzofurans are mentioned as proof for the presence of sulphur-analogues of the polychlorinated dioxins and furans[1,4,5].

The major sources of PCDTs in the environment are combustion and metallurgy, especially emission from municipal and hazardous waste incinerators as well as industrial incinerators. The other known sources are PCB incineration and metal reclamation. There are also many potential sources of this compounds for example: automobile exhaust, wood combustion, oil/gas heating, chemical production of PCB, trichlorobenzene sulphonates and sewage sludge. Some congeners have also been found in stuck gas and fly ashes[1,2,3,5,6,7,8,9].

PCDTs as a group of POPs are interesting due to their structural resemblance to PCDFs and PCDDs. The knowledge of their toxic effect is quite scarce, but we can suspect that this resemblance might have also been noticed in computer modelling of their chosen physico-chemical properties. PCDTs appeared considerable less toxic than TCDD and more toxic than PCDFs or PCBs[5]. Furthermore, the replacement of oxygen atom by sulphur greatly decreases the potency of a compound to induce AHH/EROD activity[1,5]. Acute toxicity is rarely reported in humans, fish, or wildlife, as a result of exposure to low levels of a single PAH compound. All of POPs are in general more frequently associated with chronic risks[1,7].

The current knowledge on sulphur analogue compounds of the standard PCDD/Fs seems not to be wary various. The toxicological relevance of this group of compounds is not well

examined and known. PCDTs should be considered as equally harmful and toxic as PCDD/Fs as long as no better data is available[1,5,10].

Moreover, in conclusions we would like to recommend that the harmful influence of PCDTs on the environment is not known enough to talk about them as a separate group of compounds. This fact makes us compare this group to similar groups such as PCDDs and others. That is why, we generally will consider possible similarities of physical-chemical properties between PCDTs and TCDD as the most toxic dioxin. The more similar their properties will turn out, the more possible it will be that their toxic effects might be the same. So that, environmental partition coefficients describing mobility potential were calculated for 135 congeners of PCDTs to check the hypothesis about the possible similarities in this values to dioxins and other better known dioxin – like compounds used as references.

Methods and Materials

In the first step MOPAC input files were prepared using Fujitsu CAChe Worksystem Pro 5.04 package[17]. An initial geometry was optimized and quantum – mechanical descriptors were calculated on the level of semi – empirical Parametric Method 5 (PM5) in MOPAC2002[18] as a part of CAChe package.

Next, based on optimized molecules, constitutional, geometrical and empirical descriptors were computed using Dragon package[11]. Then based on informations computed in CAChe and DRAGON matrix of 239 descriptors was built. These values quantitatively describe molecular structures of the congeners[12].

In the next part of this work Principal Component Analysis (PCA) with normalized VARIMAX rotation was performed[13,14,15,16]. It allowed to eliminate redundancy in data and to reduce the total number of variables.

In the next stage principal components extracted before were used as variables in prediction of log K_{OA}, log K_{OW} and K_H. Multiple regression was used as a method of prediction.

Defined chemometric models describing relationships between structure of congeners and predicted parameters, were validated using the cross – validation algorithm.

All operations were performed in STATISTICA 6.0 package[19].

Results and Discussion

The matrix of structural and physico – chemical 239 descriptors completed for 135 PCDTs and 50 "reference" compounds was autoscaled and PCA was performed.

As a result 10 principal components were chosen to the model which explained 90.59 % (44.51 % + 19.91 % + 10.20 % + 4.20 % + 3.82 % + 2.27 % + 1.66 % + 1.58 % + 1.41 % + 1 %) of the total variance in structural data. The first principal component (PC1) is mainly influenced by variables describing mass and size of the molecule and energy of LUMO. The second PC is influenced by variables depended on differences in character of bonds in molecule. The third component is connected with structural features related to central branching. The others depend on less important parameters.

In the next stage, the factors (PCs) extracted by PCA method and data collected for "reference" compounds[20 – 36], models of relationships between the structure and logarithm of n – octanol/air partition coefficient logarithm of n – octanol/water and Henry's constant were identified

and then validated (Table 1.). The predicted values for 135 congeners of PCDTs are presented in Table 2.

Table 1. Models of predicted values

No. model	Dependent value	Model	n	s	D	F	Q^2_{CV}
1.	log K_{OA}	log K_{OA} = 9.78(±0.01) + 1.12(±0.08) PC1 + 0.24 (±0.06)PC3 – 1.11(±0.36) PC4 – 0.19(±0.06)PC7 + 0.15(±0.06)PC9	18	0.27	98 %	132.69	0.98
2.	K_H	K_H= 0.16 (± 0.12) – 0.72(± 0.09) PC3 + 0.6 (±0.06) PC5	29	0.54	84 %	70.57	0.78
3.	log K_{OW}	Log K_{OW} = 6.32(±0.07) + 0.89(±0.04)PC1–0.24(±0.03) PC2	31	0.27	94 %	231.18	0.93

Table 2. Predicted values of log K_{OA}, K_H, log K_{OW} for polychlorinated dibenzotiophenes.

PCDT no.	Pattern	log K_{OA}	K_H	log K_{OW}	PCDT no.	Pattern	log K_{OA}	K_H	Log K_{OW}
1.	1	8.05	0.03	4.95	69.	1,3,6,8	10.79	-0.3	6.43
2.	2	8.15	0.11	4.94	70.	1,3,6,9	7.37	0.09	6.29
3.	3	8.31	-0.03	5.03	71.	1,3,7,8	11.15	-0.37	6.47
4.	4	7.95	-0.02	4.98	72.	1,3,7,9	7.49	-0.38	6.36
5.	1,2	8.85	-0.03	5.46	73.	1,4,6,7	10.82	-0.57	6.51
6.	1,3	8.84	-0.09	5.47	74.	1,4,6,8	10.69	-0.31	6.47
7.	1,4	8.45	0.06	5.43	75.	1,4,6,9	7.48	-0.47	6.38
8.	1,6	8.78	-0.09	5.44	76.	1,4,7,8	10.89	-0.33	6.46
9.	1,7	9.1	-0.26	5.51	77.	1,6,7,8	10.98	-0.33	6.45
10.	1,8	8.95	-0.1	5.46	78.	2,3,4,6	10.72	-0.31	6.45
11.	1,9	6.5	-0.57	5.3	79.	2,3,4,7	11.05	-0.31	6.45
12.	2,3	9.14	-0.19	5.51	80.	2,3,4,8	10.76	-0.31	6.43
13.	2,4	8.76	-0.09	5.48	81.	2,3,6,7	11.09	-0.55	6.54
14.	2,6	8.91	-0.25	5.51	82.	2,3,6,8	10.83	-0.38	6.45
15.	2,7	9.21	-0.24	5.46	83.	2,3,7,8	11.2	-0.82	6.61
16.	2,8	8.87	-0.58	5.58	84.	2,4,6,7	10.81	-0.35	6.42
17.	3,4	9.03	-0.16	5.52	85.	2,4,6,8	10.7	-0.78	6.58
18.	3,6	9.06	-0.22	5.5	86.	3,4,6,7	10.98	-1.03	6.56
19.	3,7	9.13	-0.76	5.57	87.	1,2,3,4,6	11.23	-0.36	6.97
20.	4,6	8.74	-0.65	5.59	88.	1,2,3,4,7	11.56	-0.29	6.97
21.	1,2,3	10.33	-0.31	5.97	89.	1,2,3,4,8	11.24	-0.32	6.93
22.	1,2,4	9.85	-0.15	5.93	90.	1,2,3,4,9	8.16	-0.01	6.78
23.	1,2,6	10.07	-0.2	5.93	91.	1,2,3,6,7	11.64	-0.39	6.97
24.	1,2,7	10.13	-0.3	5.95	92.	1,2,3,6,8	11.44	-0.19	6.92

25.	1,2,8	10.07	-0.24	5.98	93.	1,2,3,6,9	8.13	0.06	6.77
26.	1,2,9	7.1	-0.13	5.77	94.	1,2,3,7,8	11.81	-0.34	7.05
27.	1,3,4	9.95	-0.2	5.95	95.	1,2,3,7,9	8.36	0.02	6.81
28.	1,3,6	10.06	-0.18	5.94	96.	1,2,3,8,9	7.98	0.05	6.74
29.	1,3,7	10.21	-0.29	5.96	97.	1,2,4,6,7	11.4	-0.46	6.96
30.	1,3,8	10.05	-0.22	5.93	98.	1,2,4,6,8	11.45	-0.24	7
31.	1,4,5	6.97	0.09	5.79	99.	1,2,4,6,9	7.98	-0.01	6.76
32.	1,4,6	9.84	-0.36	5.96	100.	1,2,4,7,8	11.59	-0.33	6.97
33.	1,4,7	10.12	-0.26	5.96	101.	1,2,4,7,9	7.98	0.08	6.74
34.	1,4,8	9.95	-0.18	5.94	102.	1,2,4,8,9	7.86	0.09	6.77
35.	1,4,9	7.08	-0.15	5.74	103.	1,2,6,7,8	11.53	-0.45	6.95
36.	1,6,7	10.33	-0.32	5.97	104.	1,2,6,7,9	8.24	-0.05	6.76
37.	1,6,8	10.15	-0.18	5.94	105.	1,3,4,6,7	11.44	-0.48	6.96
38.	1,7,8	10.33	-0.3	5.98	106.	1,3,4,6,8	11.42	-0.26	6.96
39.	2,3,4	9.93	-0.27	5.98	107.	1,3,4,6,9	8.14	0.02	6.79
40.	2,3,6	10.12	-0.28	5.98	108.	1,3,4,7,8	11.8	-0.32	7
41.	2,3,7	10.34	-0.23	6	109.	1,3,4,7,9	8.17	-0.03	6.78
42.	2,3,8	10.11	-0.3	5.95	110.	1,3,6,7,8	11.77	-0.3	6.98
43.	2,4,6	10.07	-0.3	5.99	111.	1,4,6,7,8	11.58	-0.43	6.98
44.	2,4,7	10.16	-0.29	5.96	112.	2,3,4,6,7	11.81	-0.48	7.03
45.	2,4,8	10.09	-0.24	5.99	113.	2,3,4,6,8	11.59	-0.35	7
46.	2,6,7	10.28	-0.36	5.97	114.	2,3,4,7,8	11.89	-0.37	7.08
47.	3,4,6	10.1	-0.38	6	115.	1,2,3,4,6,7	12.4	-0.38	7.53
48.	3,4,7	10.23	-0.44	5.98	116.	1,2,3,4,6,8	12.08	-0.27	7.47
49.	1,2,3,4	10.42	-0.26	6.44	117.	1,2,3,4,6,9	8.95	-0.06	7.31
50.	1,2,3,6	10.71	-0.24	6.4	118.	1,2,3,4,7,8	12.48	-0.31	7.54
51.	1,2,3,7	10.92	-0.26	6.45	119.	1,2,3,4,7,9	9.13	0	7.32
52.	1,2,3,8	10.68	-0.23	6.38	120.	1,2,3,4,8,9	8.83	-0.02	7.27
53.	1,2,3,9	7.54	0.09	6.25	121.	1,2,3,6,7,8	12.56	-0.41	7.54
54.	1,2,4,6	10.49	-0.25	6.43	122.	1,2,3,6,7,9	9.19	-0.18	7.33
55.	1,2,4,7	10.63	-0.24	6.39	123.	1,2,3,6,8,9	9.36	-0.62	7.44
56.	1,2,4,8	10.55	-0.12	6.41	124.	1,2,3,7,8,9	12.16	-0.43	7.5
57.	1,2,4,9	7.25	0.15	6.24	125.	1,2,4,6,7,8	9.07	-0.16	7.3
58.	1,2,6,7	10.94	-0.38	6.42	126.	1,2,4,6,7,9	9.05	-0.51	7.41
59.	1,2,6,8	10.69	-0.21	6.42	127.	1,2,4,6,8,9	12.48	-0.41	7.54
60.	1,2,6,9	7.34	-0.04	6.29	128.	1,3,4,6,7,8	9.12	-0.64	7.39
61.	1,2,7,8	10.84	-0.55	6.48	129.	1,3,4,6,7,9	9.26	-0.17	7.33
62.	1,2,7,9	7.37	0.1	6.23	130.	2,3,4,6,7,8	12.33	-0.82	7.65
63.	1,2,8,9	7.42	-0.41	6.37	131.	1,2,3,4,6,7,8	13.08	-0.42	8.04
64.	1,3,4,6	10.56	-0.25	6.41	132.	1,2,3,4,6,7,9	9.77	-0.18	7.79
65.	1,3,4,7	10.65	-0.26	6.39	133.	1,2,3,4,6,8,9	9.53	-0.12	7.75
66.	1,3,4,8	10.55	-0.22	6.38	134.	1,2,3,4,7,8,9	9.85	-0.2	7.8

67.	1,3,4,9	7.52	0.07	6.29	135.	1,4,2,3,4,6,7, 8,9	10.03	-0.74	8.43
68.	1,3,6,7	10.82	-0.32	6.39					

Conclusions

Prediction of logarithm of octanol/air partition coefficient (log K_{OA}), Henry's law constant (K_H), logarithm of octanol/water partition coefficient (log K_{OW}) for POPs (like PCDTs) is an area of many studies in recent time. Values of these parameters and other data like half – lives, activation enrgies of their degradation processes give the possibility of estimating the environmental (mainly atmospherical) transportation features of PCDTs.
Volatility of polychlorinated dibenzotiophenes is decreasing with higher substitution of chlorine. Monochlorosubstituted PCDTs characterized by log $K_{OA} \approx 8$, $-0.02 < K_H < 0.11$, log $K_{OW} \approx 5$ have similar properties to di- and trichlorodibenzo-*p*- dioxins and furans and biphenyls, which are classified as relatively low volatile substances. It can be good explanation for the lack of data on concentrations of high chlorinated PCDTs congeners in air samples.

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