TOWARDS A MORE COMPREHENSIVE APPROACH OF NINETEEN ATROPISOMERIC POLYCHLORINATED BIPHENYLS PERSISTENCE IN ENVIRONMENT

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Abstract: Nineteen polychlorinated biphenyls (PCBs) atropisomers, stable in the range of physiological temperatures, are representative as chiral persistent organic pollutants for biotope. This paper relates significant literature data on bio-concentration and bioaccumulation effects, observed or predicted, for these nineteen PCBs, with values concerning some of their thermodynamic and structural properties, calculated in precedent our works. As consequence of the adopted treatment results a better understanding of the variation of bio-concentration and bioaccumulation factors (BCFs and BAFs) for the considered 19 PCBs.

1. Introduction

Although the use of polychlorinated biphenyls (PCBs) was banned after 1980 in open applications the problems caused by theses hazardous chemicals persist. PCBs possess a low biodegradability which favors possibility to bioaccumulation and increased toxicity in rapport with parent molecules of the intermediates, formed during their lent degradation [1] PCBs can be described by general structural formula presented in fig 1. The structure consists of biphenyl that can have up to ten chlorine atoms attached. Therefore are 209 PCBs in all.

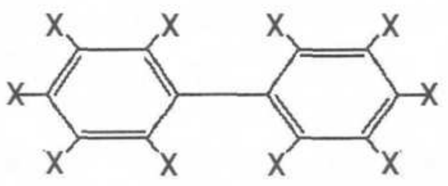

Fig. 1 The general structural formula of PCBs
X = H or Cl

Mullin et al. [2] realized in 1984 synthesis and have been determined chromatographic properties of all 209 PCB congeners. Bush and Barnard [3] obtained in 1995, gas-phase infrared spectra of all 209 biphenyl congeners using gas-chromatography with Fourier Transform infrared detection and internal standardization with a 13C labeled congener. Seventy eight of the 209 PCBs congeners which have chlorine substituents in ortho positions display an axial chirality, due to limited rotation of the phenyl group around the C1-C1' bond and are considered atropisomers [4]. Racemization or inter-conversion of enantiomers depends of energy barrier which limits the free rotation around this bond. Oki [4] predicted possibility of isolation for enantiomers which have a conversion energy barrier larger than 22.3 kcal/mol at 300K From [5-6] works results that only nineteen atropisomeric PCBs are stable at physiological temperatures (see Table 1) and have an influential role in partitioning, bio-concentration, bioaccumulation and toxicological activity. For this reason is necessary control in different phases and matrices of the PCBs concentration and bioaccumulation, in view of elaboration of adequate its removal methods. Thermal racemization and thermal degradation were studied in [6] for PCB136 and PCB176 by GC-MS hyphenated method. Nine of conformational stable atropisomeric PCBs are present in commercial mixtures (the so called Arochlors) above 1% concentration and for this reason are expected to be released in environment. Individual determination of ortho and non-ortho substituted PCBs in sediments by HPLC pre-separation and GC/ECD was performed in [7]. Other studies [8-12] demonstrate utility of PCBs chiral analysis in investigation of biotransformations within biota of Arctic food Webs. It is also necessary to mention the paper of Echols et al [13] which studied PCBs concentration and pattern in the Saginaw River using sediment caged fish and semi-permeable membrane devices. Knowledge of variation of PCBs content in transformators oil is a necessary information about function of these closed applications . In this direction we developed a specific strategy using high resolution hyphenated technique GC-MS, associated with identification of the PCBs characteristic mass spectra fragments [14]. Modeling and prediction of some PCBs physical properties from molecular descriptors (MDs) for all 209 congeners was firstly developed by Oberg [15]. Predicted PCBs properties: vapor pressure, water solubility, Henry laws coefficients. This Oberg approach [15] encouraged theoretical research to obtain PCBs properties or activity starting from different molecular descriptors using linear regression (LR), multiple linear regression (MLR) or quantitative structure - property/ activity relationship (QSPR/QSAR) methods. The PCBs properties/ activities investigated by these modeling methods are aqueous solubility [16], gas-particle partitioning in the atmosphere [17], photo-degradation half-life in n-hexane solution under UV radiation [18], n-octanol partition coefficient [19-22], vaporization [23], sublimation [24] and formation [25] enthalpies, dipole moments [25], frontier orbital energies [25], chromatographic retention indices [25-26], bio-concentration and bioaccumulation factors [27], toxicity and threshold limits of exposure values [28-29], health effects [30].

This paper correlates significant data, extracted from literature, on bio-concentration and bioaccumulation with values of thermodynamic and structural corresponding properties, calculated by us.

2. Details on calculation methods and data selection

In this study are included a set of nineteen atropisomeric PCBs listed in the first column of Table 1 The bold character indicates the compound in accordance with IUPAC Convention and the positions of chlorine atoms in the both aryl rings are given in the brackets [1]. These compounds contain 4-8 chlorine atoms. For the calculation of log P (where P is partition coefficient, defined as the ratio of solubility of a chemical in water to its solubility in octanol) we used in [21-22] the incremental method of Ghose, Pritwchett and Crippen (GPC) implemented in Hyperchem [31]. For the studied compounds are considered the molecular structures optimized by molecular mechanics with MM+ force field. The electrostatic term was calculated by bond dipole approximation. Geometry optimization was done with the Polack-Ribiere algorithm and a 0.001kcal/mol.A gradient.

For the calculation of dipole moment and other structural and thermodynamic properties [25] have been used molecular mechanics MM+ and quantum semi-empirical AM1 methods, both included in Hyperchem [31] PCBs structures were optimized with AM1 method in the Restricted Hartree Fock (RHF) approximation *in vacuo*. Minimum energies structures were obtained using the Root Mean Square (RMS) gradient of 0.01kcal/mol.A.

Bio-concentration factor (BCF) of a chemical is defined as ratio of the concentration of that chemical in an organism (or in a certain tissue of organism) and the concentration of that chemical in aqueous environment, where respective organism lives. Determination of BCF can be based on the wet weight BCFw, or on lipid content BCFL of the aquatic organism or tissue [13].

Bioaccumulation factor (BAF) is defined as the ratio of the concentration of the chemical accumulated in organism (from food and direct exposure) to the concentration in the surrounding environment. This indicator is the more complex. It depends on nature of chemical compound, species, duration of exposure, concentration of that chemical in water and in food [27]. The BCF and BAF predicted values corresponding to 19 PCBs are extracted from [27]-a modeling study with partially ordered sets using quantitative super-structure/ activity relationships (QSSAR). These researchers collected 19 BAF data sets from study of Burkhard and coworkers [32] which measured BAF in the natural ecosystems for various fish species. Experimental values of BCF and BAF are presented in bold.

3. Discussion

Partition coefficient (log P) is the most used property to show how easily human or other organism can absorb and store a chemical [19-22]. It is included in the second category of descriptors [33] i.e. are significant for the energy of molecular interactions.

Table 1. BCFs, BAFs and PCBs dipole moment

PCB(Cl positions)	logBCF for fish	logBAF smelt adults	logBAF carp 10 year	Dipol mom. (D)
45(2,3,6,2')	4.64	**6.37**	6.96	1.392
84(2,3,6,2'.3')	5.10	7.07	7.53	2.082
88(2,,3,4,6,2')	5.16	7.09	7.53	1.908
91(2,3,6,2'4')	5.13	**7.26**	**7.66**	1.867
95(2,3,6,2'5')	5.15	7.13	7.57	0.933
131(2346,2'3')	5.53	**6.89**	**7.32**	2.077
132(234,2'3'6')	5.55	7.54	7.96	2.406
135(235,2'3'6')	5.53	7.61	8.08	1.585
136(236,2'3'6')	**5.43**	7.46	7.89	1.187
139(2346,2'4')	5.49	7.63	7.99	1.190
144(2346,2'5')	5.55	7.53	8.00	1.239
149(236,2'4'5')	5.57	**7.48**	**7.81**	1.717
171(2346,2'3'4')	5.80	7.89	8.34	1.846
174 (2345,2'3'6')	**5.80**	**7.84**	**8.18**	2.259
175(2346,2'3'5')	5.78	7.86	**9.02**	1.024
176(2346,2'3'6')	5.77	7.77	8.22	1.523
183(2346,2'4'5')	**5.84**	**7.93**	**8.33**	0.823
196(2345,2'3'4'6')	**5.92**	8.29	8.83	1.343
197(2346,2'3'4'6')	5.93	8.21	8.68	0.989

For this reason, values of calculated log P by GPC method for the 19 studied atropisomeric PCBs are extracted from [22]. It is necessary to mention that for high chlorinated compounds are no log P experimental data [33] and this shows the need for GPC calculations. But, is also necessary to observe that incremental GPC method give the same value for log P to the congeners, which contain the same number of chlorine atoms (i.e. having the same molecular weight).

In studied series of PCBs log P values increase progressive from 5.80 for PCB45 (a four- chlorinated biphenyl) to 6.32 for PCB84, PCB88, PCB91, PCB95 (five-chlorinated biphenyls), to 6.89 for PCB131, PCB132, PCB135, PCB136, PCB139, PCB144, PCB149 (six-chlorinated biphenyls) to 7.36 for PCB171, PCB174, PCB175, PCB176, PCB183 (hepta chlorinated biphenyls) and finally to 7.88: for PCB196 and PCB197 -both eight-chlorinated biphenyls. This means that all atropisomeric PCBs comprised in present study manifest a strong hydrophobic character. As consequence an aspect of "up-scale" variation for dependence

log BCF=f (log P) (1)

in conformity with data from Table 1 must be observed (in the case of PCB reference set from [22] linear dependences were preponderant). The high of stage is determined by difference between maximal and the minimal value of log BCF for the done group of atropisomers with the same log P value, i.e. with the same number of chlorine atoms and molecular weight .In the case of the most populated group - the hexa-chlorinated biphenyls-high of stage is 0.14 log.units.

General aspect of dependence:

log BAF=f (log P) (2)

for the smelt adults and carp 10 years is the same as dependence log BCF=f(log P), but, the high of stage is much larger.

For example, in the same group of hexa-chlorinated biphenyls high of stage is 0.64 log.units for smelt adults and 0.66 log .units for carp 10 years.

Experimental values of log BAF for carp 10 years are larger than those of log BCF in the same group of hexa-chlorinated compounds with 1.79 log.units. It is obvious that experimental values of log BAF for smelt adults are larger than those of log BCF for fish with 1.36 log.units. This type of difference between log BAF for carp 10 years values and log BCF values respectively log BAF for smelt adults and log BCF increase in the group of hepta and octa chlorinated biphenyls. This in accord with a general statement from toxicology [33]: concomitantly with increase of molecular weight and hydrophobicity the pollutant will be absorbed in more significant measure in lipidic tissues, presenting a greater toxic risk (as consequence it is expected that corresponding threshold limit of exposure will be smaller for PCB196, PCB197 than for PCB132).

In this study for explaining the variation of bio-concentration and bioaccumulation factors we use also a property from third category [33], dipole moment. Values of this electronic level property, very sensible to chlorine positions in biphenyl, are listed in the fourth column of Table 1. It is obvious that values of dipole moment varies from 0.823D for PCB183 to 2.409D for PCB132. This shows the possibility to use this electronic level property to explain some variation of BCF and BAF values within the group of atropisomers which contain the same number of chlorine atoms. Indeed from examination of the data within a group with the same number of chlorine atoms (i.e. with the same log P value and the same molecular weight) we observe that maximal values of BCF and BAF appear to compounds characterized by the minimal or medium values of dipole moments i.e. at reduced PCB polarity. This explain the increased persistence in environment by bio-concentration and bioaccumulation for: PCB45, PCB135, PCB136, PCB139, PCB144, PCB183, PCB196, PCB197 in accord with experimental data from [3], [8], [11-12].

To confirm this explanation we selected in the Table 2 the values of other electronic level molecular properties which can help to discriminate between BCF and BCF values of the PCBs atropisomers having the same log P. In Table 2 in the first column is marked the order number of corresponding PCB from actual 19 atropisomers set (listed in Table 1) Energies of frontier orbital Elumo are extracted from our precedent work [25]. Values of vertical electro-negativity Xv, and of vertical hardness Nv are obtained in conformity with Koopman theory [33] from values of Ehomo and Elumo.

Thus: Iv= -Ehomo (3)

EAv= -Elumo (4)

and Xv=1/2(Iv+EAv) (5)

Nv=1/2(Iv-EAv) (6)

Table 2.PCB's electronic level molecular properties

Crt. no.	Elumo (eV)	Xv	Nv
1	-0.422	4.986	4.564
2	-1.000	5.309	4.309
3	-0.662	5.165	4.503
4	-0.553	5.104	4.551
5	-0.576	5.034	4.518
6	-0.751	5.229	4.478
7	-0.586	5.142	4.556
8	-0.594	5.114	4.520
9	-0.513	5.086	4.513
10	-0.763	5.263	4.500
11	-0.728	5.215	4.487
12	-0.599	5.116	4.577
13	-0.832	5.326	4.494
14	-0.753	5.242	4.489
15	-0842	5.273	4.431
15	-0.762	5.222	4.460
17	-0.841	5.272	4.431
18	-0.905	5.353	4.448
19	-0.839	5.319	4.480

Passing to the discussion which use the new electronic level criteria, listed in Table 2 (surely, in association with data about BCF and BAF values from Table 1) is evidently their utility in special for estimation of log BAF variation within a done group of atropoisomeric PCBs. We remember that BAF indicator is more complex being dependent of nature of chemical. Using Elumo property (which is in relation of direct proportionality with affinity for electron of certain atropisomeric PCB) we observe that high values of BAF appear in the case of hexa-chlorinated biphenyls to PCB135, PCB139, PCB144. These compounds are characterized by medium values of Elumo (0.594 - 0.728). Using Xv (i.e. vertical electro-negativity) in the same group the higher values of BAF correspond to medium values of this calculated property comprised between 5.114 - 5.263. After the third criteria Nv (i.e so called vertical hardness) the estimation is similar. In the near future electronic level properties will offer more opportunities in explanation of atropisomeric PCBs health effects, where quality of electron donor or electron acceptor of certain compound is very important.

4. Conclusions

For the set of nineteen atropisomeric PCBs, stable at physiological temperatures, we have been related literature experimental and predicted data on their bio-concentration and bioaccumulation factors with values of some thermodynamic (partition coefficients) and structural electronic level properties (dipole moments, frontier orbitals energies, vertical electronegativity and vertical hardness), calculated by us.

A better understanding of the nineteen atropisomeric PCBs environment persistence is obtained on this basis.

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