# POLYCHLORINATED PYRENES (PCPYS) – SIMILARITIES TO ANOTHER POPS

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## Introduction

Polychlorinated pyrenes (PCPYs) are relatively less studied group of persistent organic pollutants (POPs). The persistency of PCPYs depends on the place of chlorine in the pyrene nuclei. There are two possibilities: chlorine atoms substituted as result of the substitution reaction, and chlorine atoms added during the addition mechanism. Generally, chlorosubstituted pyrenes (Cl-S PCPYs) are much more stable compounds than chloroadded congeners (Cl-A PCPYs)[2,9,15,16].

Both Cl-S – and Cl-A PCPYs are produced mainly due to antropogenic thermal and no-thermal processes, such as heating in domestic systems, municipal waste incineration, in automobile exhaust, chlorine disinfections of tap water and pulp bleaching[2,9,15,16]. Natural process of chlorination of pyrene is possible also, especially in soil, during UV irradiation, but it of much less significance when compared to mentioned anthropogenic sources [19].

Toxicity of some congeners of PCPYs was confirmed in a few studies. Chloropyrenes are mutagenic in the *Salmonella typhimurium* test[1]. Monochloropyrenes are characterized by the photoinduced acute toxicity, based on the response of *Daphnia magna*[20]. Also mono- and dichloropyrenes are embriotoxic when nanoinjected to sea trout (*Salmo trutta*) eggs test[8].

Based on the assumption, that the structure of a molecule is responsible for its property, especially toxicity, it could be interesting to compare some structural descriptors computed for chloropyrenes with analogous descriptors computed for another toxic POPs[7]. This comparison is the main aim of the following study. Because Cl-S PCPYs are much more persistent in the environment than Cl-A PCPYs our investigation focused on persistent congeners only.

## Methods and Materials

At the beginning, a structural data matrix for all possible 281 chloropyrene congeners and 56 'reference' POPs was prepared. Geometry optimization and all quantum-chemical computation were done on the level of semi-emipirical Parametric Method 3 (PM3) using MOPAC2000 Fujitsu software[4,17,18]. Structural descriptors used in the study were: molecular connectivity indices of the zero, first, and the second order; total dipole moment; dipole vectors: X, Y, and Z; energy of HOMO and LUMO; molecular weight and refraction; solvent accessible surface area; logarithm of the *n*-octanol/ water partition coefficient; valence molecular indices of the zero, first, and the second order; kappa indices of the first, second, and the third order; standard heat of formation[3,5,6,10,11,12,14]. In assumption, these variables quantitatively describe molecular structures of the compounds – their topology, shape, energy, polarity, and lipophilicity.

Next, this multivariate space of the data was explored using Principal Component method[10,13]. In effect of reduction of dimensions, it was possible to observe similarities and differences between both, changeability of the structural descriptors and chemical compounds.

**Results and discussion**

Principal Component Analysis of (337 x 20) data matrix resulted in a five-dimensional model which was explained 92 % (60 % + 16 % + 6 % + 6 % + 5 %) of the total variance. Factor matrix obtained after Varimax rotation indicates strong correlations between principal components and congeners.

The first principal component (PC) is determined by variables describing mass and size of the molecule and energy of LUMO. The second PC is strongly influenced by variables depending on differences in character of bonds in the molecule, while the next (PC3-PC5) components are connected with polarity (table 1).

**Table 1.** Table of loadings

| Variable | PC1 | PC2 | PC3 | PC4 | PC5 |
|---|---|---|---|---|---|
| Molecular connectivity index of zero order, $^{0}\div$ | **1.00**[a] | 0.01 | 0.01 | 0.03 | -0.04 |
| Molecular connectivity index of first order, $^{1}\div$ | **0.94** | 0.28 | -0.01 | 0.05 | -0.01 |
| Molecular connectivity index of second order, $^{2}\div$ | **0.95** | 0.24 | 0.00 | 0.03 | -0.03 |
| Total dipole moment of the molecule | -0.07 | 0.17 | -0.63 | 0.60 | 0.06 |
| Dipole vector X | -0.02 | -0.12 | **0.90** | 0.16 | 0.04 |
| Dipole vector Y | -0.12 | -0.14 | -0.13 | **-0.90** | 0.01 |
| Dipole vector Z | 0.10 | 0.04 | -0.02 | -0.02 | **-0.93** |
| Energy of HOMO | 0.26 | **0.91** | -0.11 | 0.10 | -0.04 |
| Logarithm of the n-octanol/water partition coefficient | **0.97** | 0.03 | -0.01 | -0.01 | -0.02 |
| Energy of LUMO | **-0.77** | -0.57 | 0.03 | -0.09 | 0.12 |
| Molecular refraction | **0.98** | 0.18 | -0.01 | 0.03 | 0.01 |
| Molecular weight | **0.96** | -0.21 | 0.03 | 0.03 | -0.10 |
| Kappa index of first order, $^{1}\hat{e}$ | **0.98** | -0.18 | 0.02 | 0.00 | 0.00 |
| Kappa index of second order, $^{2}\hat{e}$ | **0.84** | -0.42 | 0.01 | -0.09 | 0.20 |
| Kappa index of third order, $^{3}\hat{e}$ | 0.26 | **-0.75** | 0.03 | -0.22 | 0.41 |
| Solvent accessible surface area | **0.99** | -0.08 | 0.03 | -0.02 | 0.02 |
| Valence molecular index of zero order, $^{0}\div^{v}$ | **0.99** | -0.09 | 0.01 | 0.03 | -0.06 |
| Valence molecular index of first order, $^{1}\div^{v}$ | **0.99** | 0.11 | 0.00 | 0.04 | -0.03 |
| Valence molecular index of second order, $^{2}\div^{v}$ | **0.99** | 0.08 | 0.00 | 0.03 | 0.01 |
| Standard heat of formation | -0.08 | **0.85** | -0.10 | -0.01 | 0.20 |

[a] **Marked** loadings are > 0.70

Analyzing the corresponding score plot (Figure 1), which is a projection of the future space on the plane restricted by the two first principal components, it could be observed that, there is not significant difference in distribution of studied compounds along PC1. It means, that these pollutants are characterized by similar mass/size properties, and in consequence, probably by similar abilities to be transported in the environment.

The second principal component (PC2) classifying all studied compounds into two prominent groups (with positive and negative values of the PC2). It is interesting, that POPs known as 'dioxin-analogues' are situated opposite PAHs and Cl-PAHs (chloropyrenes) on the plot. This observation might suggest that the mechanism of toxic action of chloropyrene congeners were similar rather to

PAHs than the dioxin. Additionally, this mechanism is not determined by mass, size, and shape, but probably by character of the bounds and electron distribution in the molecule.

Next components (not shown) groups together compounds with similar values of dipole vector X (PC3), dipole vector Y (PC4), and dipole vector Z (PC5), which is probably not such significant as the pervious observation.

In the future works the mechanism of the toxic action of PCPYs will be studied in detail.

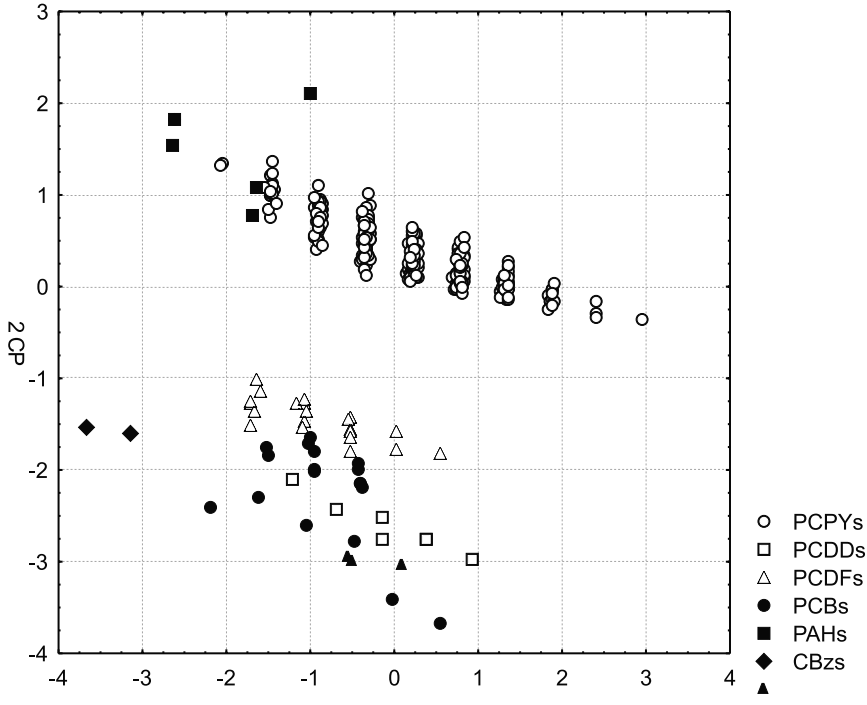


**Figure 1.** The score plot of PC2 *vs.* PC1

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