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Quantum topological method studies on the thermodynamic properties of polychlorinated phenoxazines

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HIGHLIGHTS

- Novel quantum topological indices $PY_{1,2}$ derived from molecular structure.
- Quantum topological method on quantitative structure–property relationships of Phx and 135 PCPXs.
- Model is statistically significant and shows good stability for data variation tested by leave-one-out cross-validation.

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ABSTRACT

The novel quantum topological indices $PY_{1,2}$ were derived from molecular structure combined with the effect of atom space, the character of bonding atoms (such as equilibrium electro-negativity) and the branching effect between the atoms. The quantitative structure–property relationships (QSPRs) were proposed between $PY_{1,2}$ and the thermodynamic properties ($\triangle_f H^\theta$, $\triangle_f G^\theta$ and $\Delta_f G_R^\theta$) of phenoxazine (Phx) and 135 kinds of polychlorinated phenoxazines (PCPXs), by Multiple linear regression (MLR) analysis method. The high-quality prediction models were evidenced by the correlation coefficient *R*, the standard error of estimate *S*, the Fisher statistic value and the cross-validated correlation coefficient RCV. With the new QSPR model, we are able to predict a wide range of thermodynamic properties of an extensive number of molecules. And the model is statistically significant and shows good stability for data variation as tested by the leave-one-out cross-validation (LOO-CV).

Introduction

Polychlorinated phenoxazines (PCPXs) are kinds of common persistence of polychlorinated organic pollutants (PCOPs), and they are priority control pollutants in the black (gray) listed in the European Union, the United States, Germany, and many other environmental agency identified with Polychlorinated Dibenzo-p-dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDEs), polychlorinated naphthalenes (PCNs) [1–3]. Almost all PCPXs have carcinogenic, teratogenic or mutagenic effects, because of residues in the natural environment for a long time and enrichment by the food chain. And they have serious impact on human health and the environment ecosystem. In recent years, other kinds of halogenated tricyclic aromatic compounds had gradually attracted the attention of the researchers, as the environment pollution behavior of dioxins has been studied more and deeply [4–7]. However, mostof these studies focused on the physical and chemical properties [8,9]. And there are very few studies on PCPXs and their thermodynamic properties (such as standard heat of formation $\Delta_f H^\theta$, standard free energy of formation $\Delta_f G^\theta$ and relatively free energy of formation $\Delta_f G_R^\theta$) [10].

Phenoxazine (PhX), also known as 2,3,5,6-diphenyl oxazine, is shown in Fig. 1.

Because the structures of many PCPXs are similar, the PCPXs would have 135 possible structures, according to the number of chlorine atoms and different replace locations of Phx. If the physical and chemical properties or thermodynamic properties of each PCPXs compounds are determined, it is not realistic in terms of both manpower and material resources. Phx and 135 PCPXs would produce some experiment errors in the process of experimental

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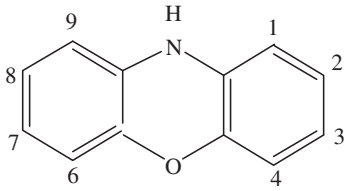

Fig. 1. Chemical structure of Phx and the numbering system for C atoms.

measurement [10,11]. If quantitative structure–property relationships (QSPRs) method can be studied on the physical and chemical properties or thermodynamic properties of Phx and 135 PCPXs, it would be a simple, practical and effective means. In addition, QSPRs are important tools in computational chemistry to represent explain and, most importantly, predict a variety of physicochemical, industrial and environmental properties [12–15].

The recent studies show that the topological indices have been widely used in QSPRs research and play an important role in many fields [13,16,17]. Most of the topological indices were based on the distance matrixes, such as Hosoya index, Balaban index, Hyper-Wiener index, Detour index, Hyper-Detour index, Harary index, Pasareti index, and Verhalom index. However, these distance matrices consisted of the shortest distances from vertex i to all other $(n-1)$ vertices in the molecular graphs, and the shortest distance of two adjacent atoms vertex was regarded as "1". In fact, the topological space distances from vertex i to all other $(n-1)$ vertices is not "1" [18,19]. At the same time, most of the topological indices could not reveal the real connection among atoms, and are not suitable for heteroatom-containing and multiple bond organic compounds [13].

Based on our previous work [18–23], including successful proposition of some topological indices, such as the w_m index [19], the PX_m index [20], the ^mTp index [21], the NP_m index [22], and the ND index [23]. In this paper, the novel quantum topological indices $PY_{1,2}$ of Phx and 135 PCPXs were proposed combined with the theory of quantum chemistry and topological chemistry. And the novel quantum topological indices $PY_{1,2}$ can describe each atom branching effect and encode information of the whole molecular chemical environment, employing the character of the bonding atoms , such as equilibrium electro-negativity and the topological space distances between the atoms. At the same time, the aim of this work was to establish new QSPR models for predicting the thermodynamic properties and to find the structural factors which affect the thermodynamic properties ($\triangle_f H^\theta$, $\triangle_f G^\theta$ and $\Delta_f G_R^\theta$) of Phx and 135 PCPXs. The stability and predictive power of these models were validated using leave-one-out cross-validation (LOO-CV) and external test. The results show that there are good correlations between $PY_{1,2}$ and the thermodynamic properties of Phx and 135 PCPXs, and the QSPR models have good stability and predictive power using LOO-CV and external test.

Principle concepts and methods

Molecular structure optimization and quantitative calculation

First, MOPAC 7.0 software was used to optimize the initial geometric parameters of molecular structures of Phx and 135 PCPXs by constructing and using AM1 semiempirical quantum chemistry methods. Then, the further geometric configuration optimization and vibration analysis were completed by using Gaussian03 software on the B3LYP/6-31+G (d) basis set, with the application of density functional theory (DFT). When the stable molecular Configuration forming, the potential energy surface scanning method was used to scan all possible bond angle, the dihedral angle, and the corresponding relationship between energy and geometric configuration will be set. On this basis, the spatial topological distance were calculated between individual atoms of Phx and 135 PCPXs [20].

Construction of the novel quantum topological indices $PY_{1,2}$

For a molecular graph maded of n vertices, its distance matrix $\boldsymbol{D}$, which is a symmetric matrix, can be given as: $D = [d_{ij}]_{n \times n}$, where d_{ij} are the length of the shortest path between the vertices i and j. However, the actual distance is not the shortest distance between the vertices i and j. So, in this paper, d_{ij} was revised by using the actual spatial topological distance sd_{ij}, which can be obtained from step A. therefore, the following distance matrix is 3D topological distance matrix $^3\boldsymbol{D}$.

$$ {}^3D = \begin{bmatrix} 0 & sd_{12} & \dots & sd_{1(n-1)} & sd_{1n} \\ sd_{21} & 0 & \dots & sd_{2(n-1)} & sd_{2n} \\ \dots & \dots & \dots & \dots & \dots \\ sd_{(n-1)1} & sd_{(n-1)2} & \dots & 0 & sd_{(n-1)n} \\ sd_{n1} & sd_{n2} & \dots & sd_{n(n-1)} & 0 \end{bmatrix} $$

According to molecular topological chemistry theory, each edge in the hydrogen-hidden graph is made of the chemical bond, the strength of which depends on the electro-negativity of the bonding atoms. As one of the main physicochemical parameters of atoms, electro-negativity represents the ability of atoms to obtain or lose electrons. The larger electronegativity of an atom, the stronger the ability of the atom to attract electrons. Based on Pauling electronegativity, the group electro-negativity x_G can be calculated by the method of step-wise addition, which can be expressed as the following [12–15,18–26].

The equilibrium of the first level (1 in Fig. 2): $\chi_0 = \frac{1}{n_{1l}} \sum_{l=1}^{n_{1l}} \chi_{1l}$

The equilibrium of the second level (2 in Fig. 2): $\chi_{1l} = \frac{1}{n_{2l}} \sum_{l=1}^{n_{2l}} \chi_{2l}$

.....

The equilibrium of the k-th level (k in Fig. 2): $\chi_{(k-1)1} = \frac{1}{n_{kl}} \sum_{l=1}^{n_{kl}} \chi_{kl}$

Then, the group electro-negativity χ_G is defined as:

$$ \chi_G = \frac{1}{n_{1l}} \sum_{l=1}^{n_{1l}} \left[\frac{1}{n_{2l}} \sum_{l=1}^{n_{2l}} \cdots \left(\frac{1}{n_{kl}} \sum_{l=1}^{n_{kl}} \chi_{kl} \right) \cdots \right] \quad (1) $$

where n is the sum of atom or group directly attached to the ground atom, which is the left atom next to the dotted line labeled 1, 2, 3,..., k,... of each level in Fig. 2. And $\sum_{l=1}^{n_{1l}} \chi_{1l}, \sum_{l=1}^{n_{2l}} \chi_{2l}, \dots, \sum_{l=1}^{n_{kl}} \chi_{kl}$ are the sum of electro-negativity of atom or group directly attached to the ground atom. We think that electro-negativity randomly changes in the formation of a molecule. As long as a molecule is formed, the electro-negativity of atom in the molecule is fixed, that is to say, the electro-negativity is in the state of equilibrium, which is called the equilibrium electro-negativity of atom. The definition of equilibrium electro-negativity χ_i for atom i is defined as following [27,28]:

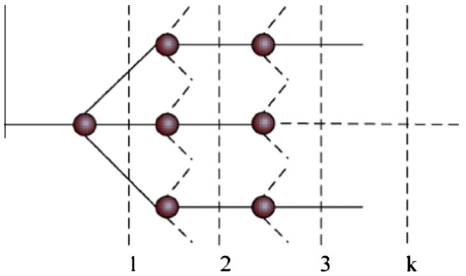

Fig. 2. The plot of group structure tree.