Theoretical study on the molecular structures and thermodynamic properties of polychlorinated pyrenes

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ABSTRACT

Geometric molecular structures of 287 polychlorinated pyrenes (PCPY) were optimized using density functional theory (DFT) at the B3LYP/6-311G(d,p) level and their thermodynamic properties in the ideal gas state, such as standard heat capacity at constant volume (C_v°), standard entropy (S°), standard enthalpy of formation ($\Delta_f H^\circ$) and standard Gibbs free energy of formation ($\Delta_f G^\circ$), were computed. The relations of C_v°, S°, $\Delta_f H^\circ$ and $\Delta_f G^\circ$ with the number and position of chlorine atoms have also been explored, from which the relative stability of PCPY congeners was theoretically proposed according to the magnitude of the relative standard Gibbs free energy of formation ($\Delta_{r,f} G^\circ$). It was found that some of PCPY isomers are in a nonplanar configuration. With increasing the number of chlorine atoms, the values of $\Delta_f H^\circ$ and $\Delta_f G^\circ$ of the most stable PCPY isomers decrease initially and then increase quickly. The values of $\Delta_f H^\circ$ and $\Delta_f G^\circ$ of PCPY congeners with the same number of chlorine atoms show a strong dependence on the positions of chlorine atoms. The relative thermodynamic stability of PCPY isomers is determined mainly by intramolecular adjacent Cl$\cdots$Cl nuclear repulsive interaction between Cl atoms at two different six-membered rings.

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1. Introduction

As one kind of raw material for organic synthesis, pyrene (PY) is extensively utilized for preparing dye, synthetic resin, engineering plastic and so on. In addition, PY is also one of the 16 polycyclic aromatic hydrocarbons (PAHs) that are taken as priority pollutants by EPA of the United States of America. Compounds where one or several hydrogen atoms of PAHs are substituted with chlorine atoms are called as chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs). Some Cl-PAHs may have greater toxicity and mutagenic action than those of corresponding PAHs [1,2], and the determination of Cl-PAHs in environmental samples has attracted people's attention greatly. Chlorinated compounds of PY, namely polychlorinated pyrenes (PCPYs), have been detected in several kinds of environmental samples. Haglund et al. reported the determination of monochlorinated pyrenes in urban air, snow and automobile exhaust samples [3]. Nilsson et al. found out 1- and 4-monochlorinated pyrenes in urban atmosphere samples [4]. Wang et al. detected 18 kinds of Cl-PAHs in laboratory-scale incinerator, including some mono- and dichlorinated pyrene compounds [5]. Recently, the determination of PCPYs in urban atmosphere samples was reported and their photochemical degradation behaviors were studied [6–9].

Thermodynamic properties (such as the enthalpy of formation $\Delta_f H$, Gibbs free energy of formation $\Delta_f G$, and so on) are important for studying the formation and distribution of Cl-PAHs and other environmental pollutants and their behaviors in environment and organisms. The experimental studies of thermodynamic properties of pyrene (PY) have been reported [10]. Since PCPYs have many isomers, it is difficult to conduct experimental studies, and thus the relevant thermodynamic data are very rare. Therefore, theoretical calculation becomes one of the important ways to obtain thermodynamic property data of these substances. In recent years, density functional theory (DFT) method has been greatly and successfully applied in theoretical calculation and prediction for thermodynamic property of environmental pollutants. At B3LYP/6-31G∗∗ level, Lee et al. calculated the enthalpy of formation and Gibbs free energy of formation of 75 polychlorinated dibenzo-*p*-dioxins (PCDD) isomers, and the calculation results conformed well to the experimental values [11]. With three different methods, Li et al. estimated entropy, heat capacity at constant pressure, enthalpy of formation and Gibbs free energy of formation of 75 polybrominated dibenzo-*p*-dioxins (PBDD) isomers [12]. Out of them, the calculation results with DFT method (at the B3LYP/6-31G∗ level) are the most accurate. We have obtained the thermodynamic properties of polychlorinated anthracenes and polychlorinated fluoranthenes with DFT method [13,14].

In this paper, we have used DFT-B3LYP/6-311G(d,p) method to optimize the molecular geometric structures of 287 polychlorinated pyrene (PCPY) isomers. In consideration of isodesmic reaction, their

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various thermodynamic properties were calculated and obtained. In addition, the relations between these property parameters and the number and position of chlorine atoms have also been explored. The relative stability of PCPY isomers was obtained according to the magnitude of the relative standard Gibbs free energy of formation.

2. Computational methods

DFT-B3LYP/6-311G(d,p) method was used to optimize the molecular geometric structures of 287 polychlorinated pyrene (PCPY) isomers. With vibration analysis, they were confirmed to be the minimum points in the potential energy surface, and the standard thermodynamic properties (heat capacity at constant volume (C_v°), entropy (S°), enthalpy (H°) and Gibbs free energy (G°)) of these substances in the ideal gas state at 298.15 K and 101.325 kPa were obtained. The above calculation was conducted with Gaussian 03 program [15]. For molecular structure of the parent compound PY and its carbon atom number, refer to Fig. 1. For convenience, PCPY isomers containing 1 to 10 Cl atoms were represented with MCPY, DCPY, tri-CPY, TCPY, penta-CPY, hexa-CPY, hepta-CPY, octa-CPY, nona-CPY and deca-CPY, respectively. The number in prefix represents the position of Cl atom. For example, 1-MCPY means that one H atom at the C atom of positions 1 is substituted with Cl.

The thermodynamic properties of PCDD [11] and PBDD [12] in gaseous state were calculated previously by designing isodesmic reaction and the obtained results conform to experiment well. In this paper, standard enthalpy of formation ($\Delta_f H^\circ$) and standard Gibbs free energy of formation ($\Delta_f G^\circ$) of PCPY were calculated by designing isodesmic reactions (1a–d) where pyrene ($C_{16}H_{10}$, PY) and chlorobenzene (C_6H_5Cl, CB) or 1,2 or 1,3 or 1,4-dichlorobenzene ($C_6H_4Cl_2$, DB) in gas phase react to produce PCPY ($C_{16}H_{10-n}Cl_n$, PCPY) and benzene (C_6H_6, PhH).
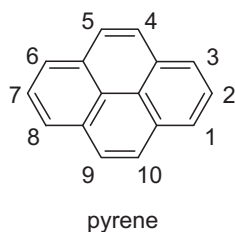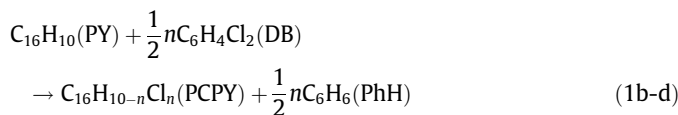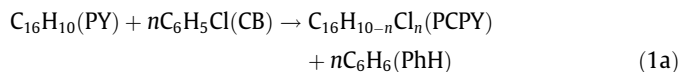

Fig. 1. Molecular structure and atomic numbering for C atoms of pyrene (PY).

$$C_{16}H_{10}(PY) + nC_6H_5Cl(CB) \rightarrow C_{16}H_{10-n}Cl_n(PCPY) + nC_6H_6(PhH) \quad (1a)$$

$$C_{16}H_{10}(PY) + \frac{1}{2}nC_6H_4Cl_2(DB) \rightarrow C_{16}H_{10-n}Cl_n(PCPY) + \frac{1}{2}nC_6H_6(PhH) \quad (1b\text{-}d)$$

1,2 or 1,3 or 1,4-Dichlorobenzene isomers instead of chlorobenzene were included in order to eliminate errors that might arise from neglecting Cl–Cl interaction effects [19,20]. With H° of each substance obtained in the theoretical calculation, the standard reaction enthalpy change ($\Delta_r H^\circ$) of Eqs. (1a–d) could be obtained based on Eqs. (2a–d):

$$\Delta_r H^\circ = [H^\circ_{PCPY} + nH^\circ_{PhH}] - [H^\circ_{PY} + nH^\circ_{CB}] \quad (2a)$$

$$\Delta_r H^\circ = \left[H^\circ_{PCPY} + \frac{1}{2}nH^\circ_{PhH}\right] - \left[H^\circ_{PY} + \frac{1}{2}nH^\circ_{DB}\right] \quad (2b\text{-}d)$$

Meanwhile, there is relationship shown as Eqs. (3a–d) between $\Delta_r H^\circ$ for Eqs. (1a–d) and $\Delta_f H^\circ$ of each substance:

$$\Delta_r H^\circ = [\Delta_f H^\circ_{PCPY} + n\Delta_f H^\circ_{PhH}] - [\Delta_f H^\circ_{PY} + n\Delta_f H^\circ_{CB}] \quad (3a)$$

$$\Delta_r H^\circ = [\Delta_f H^\circ_{PCPY} + \frac{1}{2}n\Delta_f H^\circ_{PhH}] - [\Delta_f H^\circ_{PY} + \frac{1}{2}n\Delta_f H^\circ_{DB}] \quad (3b\text{-}d)$$

Combining Eqs (2a–d) and (3a–d), the calculation Eqs. (4a–d) for $\Delta_f H^\circ$ of PCPY could be obtained:

$$\Delta_f H^\circ_{PCPY} = H^\circ_{PCPY} + nH^\circ_{PhH} - nH^\circ_{CB} - H^\circ_{PY} - n\Delta_f H^\circ_{PhH} + n\Delta_f H^\circ_{CB} + \Delta_f H^\circ_{PY} \quad (4a)$$

$$\Delta_f H^\circ_{PCPY} = H^\circ_{PCPY} + \frac{1}{2}nH^\circ_{PhH} - \frac{1}{2}nH^\circ_{DB} - H^\circ_{PY} - \frac{1}{2}n\Delta_f H^\circ_{PhH} + \frac{1}{2}n\Delta_f H^\circ_{DB} + \Delta_f H^\circ_{PY} \quad (4b\text{-}d)$$

In the same way, the calculation Eqs. (5a–d) for $\Delta_f G^\circ$ of PCPY can be obtained:

$$\Delta_f G^\circ_{PCPY} = G^\circ_{PCPY} + nG^\circ_{PhH} - nG^\circ_{CB} - G^\circ_{PY} - n\Delta_f G^\circ_{PhH} + n\Delta_f G^\circ_{CB} + \Delta_f G^\circ_{PY} \quad (5a)$$

$$\Delta_f G^\circ_{PCPY} = G^\circ_{PCPY} + \frac{1}{2}nG^\circ_{PhH} - \frac{1}{2}nG^\circ_{DB} - G^\circ_{PY} - \frac{1}{2}n\Delta_f G^\circ_{PhH} + \frac{1}{2}n\Delta_f G^\circ_{DB} + \Delta_f G^\circ_{PY} \quad (5b\text{-}d)$$

Table 1
Thermodynamic data used to calculate $\Delta_f H^\circ$ and $\Delta_f G^\circ$ of PCPYs[a].

Compound	$\Delta_f H^\circ$/kJ mol^{-1}	$\Delta_f G^\circ$/kJ mol^{-1}	H°/hartree	G°/hartree	S°/J mol^{-1} K^{-1}
Pyrene	225.70[b]	329.72[c]	−615.69307[d]	−615.73808[d]	396.37[d]
Benzene	82.93[e]	129.73[e]	−232.20302[d]	−232.23347[d]	
Chlorobenzene	51.84[e]	99.23[e]	−691.83341[d]	−691.86900[d]	
1,2-Dichlorobenzene	30.20[f]	82.70[f]	−1151.458135[d]	−1151.496988[d]	
1,3-Dichlorobenzene	25.70[f]	78.60[f]	−1151.462100[d]	−1151.501105[d]	
1,4-Dichlorobenzene	22.50[f]	77.20[f]	−1151.462210[d]	−1151.500563[d]	
Graphite					5.74[g]
H$_2$					130.68[g]

[a] $\Delta_f H^\circ$ is the standard enthalpy of formation of the compound, $\Delta_f G^\circ$ is the standard Gibbs energy of formation of the compound, H° is the standard enthalpy, G° is the standard Gibbs energy and S° is the standard entropy.
[b] Taken from Ref. [10].
[c] Calculated from Eq. [8].
[d] Obtained from B3LYP/6-311G(d,p) calculations.
[e] Taken from Ref. [16].
[f] Taken from Ref. [17].
[g] Taken from Ref. [18].