

Density functional theory studies on the molecular structures and thermodynamic properties of polychlorinated anthracenes

Xiao Lan Zeng*, Yan Wang, Xiu Lan Zhang, Yong Sheng Yu

College of Chemistry and Chemical Engineering, Xinyang Normal University, Henan Xinyang 464000, People's Republic of China

ARTICLE INFO

Article history:

Received 15 February 2009

Accepted 7 April 2009

Available online 16 April 2009

Keywords:

Polychlorinated anthracenes (PCANs)

Molecular structures

Thermodynamic properties

Relative stability

Density functional theory (DFT)

ABSTRACT

Geometric molecular structures of 287 polychlorinated anthracenes (PCANs) were optimized using density functional theory (DFT) at the B3LYP/6-311G(d,p) level and their thermodynamic properties in the ideal gas state (heat capacity at constant volume (C_v^0), entropy (S^0), enthalpy (H^0), Gibbs energy (G^0), standard enthalpy of formation ($\Delta_f H^0$) and standard Gibbs energy of formation ($\Delta_f G^0$)) were computed. The relations of C_v^0 , S^0 , $\Delta_f H^0$ and $\Delta_f G^0$ with the number and position of chlorine atoms were also explored. According to the magnitude of the relative standard Gibbs energy of formation ($\Delta_r G^0$), the relative stability of PCAN congeners was theoretically proposed. It was found that some PCAN isomers have a planar configuration while others adopt a nonplanar configuration. Both the values of C_v^0 and S^0 increase with successive chlorination while the values of $\Delta_f H^0$ and $\Delta_f G^0$ of the most stable PCAN isomers decrease initially and then increase with increasing the degree of chlorination. The values of $\Delta_f H^0$ and $\Delta_f G^0$ of PCAN congeners with the same number of chlorine atoms show a strong dependence on the position of chlorine substitution. The relative thermodynamic stability of PCAN isomers is determined mainly by relative magnitude of intramolecular delocalized π bond and Cl–Cl nuclear repulsive interaction.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Chlorinated polycyclic aromatic hydrocarbons (CIPAHs) are a group of compounds comprising polycyclic aromatic hydrocarbons with three or more rings and one or more chlorine atoms attached to the ring system. The detection of CIPAHs in environmental samples has been attracting attention from a viewpoint of environmental pollution and toxicology, since some of them are known to have strong toxicity and mutagenic properties. Anthracene (AN) is one of the simplest tricyclic aromatic hydrocarbons, the structure and atomic numbering of which are shown in Fig. 1. Polychlorinated anthracenes (PCANs) have been detected in environmental samples of various origins. Ishaq et al. identified the existence of mono-heptachlorosubstituted anthracenes in vapor and particulate air samples from urban road tunnels [1]. Wang et al. investigated emissions of CIPAHs from a laboratory-scale tube-type furnace at various temperatures and detected 18 CIPAHs, in which mono- and dichlorinated anthracenes are included [2]. Recently, Ohura et al. reported the determination of concentrations of CIPAHs including PCANs in urban air and in emissions from the scorching of polyvinylidene chloride (PVDC) film [3–5].

Some studies have been conducted to measure the presence of PCANs in the environment and their behavior of photochemical

degradation [6], however, to the best of our knowledge, no study on their thermodynamic properties has been reported. This is due to the limited availability of pure compounds and to experimental difficulties. Therefore, theoretical calculations are helpful for estimating thermodynamic properties of PCANs. Density functional theory (DFT) calculations have been performed on polychlorinated dibenzo-*p*-dioxins (PCDDs) [7], polybrominated dibenzo-*p*-dioxins (PBDDs) [8], polychlorinated naphthalenes (PCNs) [9] and polybrominated diphenyl ethers (PBDEs) [10] to obtain their thermodynamic data. Here, DFT calculations on PCANs are presented to predict their geometric molecular structures and to estimate their thermodynamic properties in the ideal gas state at 298.15 K and 100 kPa. The intent of the present work is to obtain a set of thermodynamic values for PCANs and to discuss the relation of these thermodynamic properties with the number and position of Cl atoms. Moreover, the theoretical relative stability order of the isomers for PCANs was proposed based on the magnitude of the relative standard Gibbs energy of formation.

2. Computational methods

The values of the standard enthalpy of reaction ($\Delta_r H^0$) for the three related reactions anthracene \rightarrow phenanthrene, 2chlorobenzene \rightarrow 1,2-dichlorobenzene + benzene and 1,2-dichlorobenzene \rightarrow 1,4-dichlorobenzene was calculated at the B3LYP/6-311G(d,p) level and compared with experimental ones to ascertain

* Corresponding author. Tel.: +86 0376 6390702.

E-mail address: zx16688@163.com (X.L. Zeng).

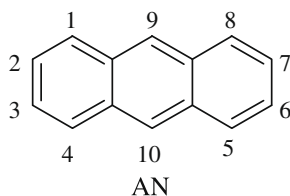


Fig. 1. Molecular structure and atomic numbering of anthracene (AN).

Table 1

Calculated and experimental values of $\Delta_r H^\theta$ for reactions anthracene \rightarrow phenanthrene, 2chlorobenzene \rightarrow 1,2-dichlorobenzene + benzene and 1,2-dichlorobenzene \rightarrow 1,4-dichlorobenzene.^a

Reaction	$\Delta_r H^\theta/\text{kJ mol}^{-1}$	
Anthracene \rightarrow phenanthrene	-20.06 ^b	-28.40 ^c
2Chlorobenzene \rightarrow 1,2-dichlorobenzene + benzene	14.80 ^b	9.45 ^c
1,2-Dichlorobenzene \rightarrow 1,4-dichlorobenzene	10.63 ^b	7.70 ^c

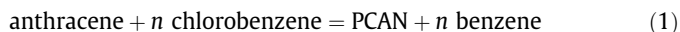
^a $\Delta_r H^\theta$ is the standard enthalpy of reaction.

^b Obtained from H^θ calculated at the B3LYP/6-311G(d,p) level.

^c Obtained from experimental values of $\Delta_r H^\theta$.

the quality of our method. The calculated and experimental values of $\Delta_r H^\theta$ are listed in Table 1, from which one can see that the discrepancies between calculated values and experimental ones are all less than 6 kJ mol⁻¹. So in this work, geometry optimizations and energy calculations for all 287 PCAN molecules were performed at the B3LYP/6-311G(d,p) level with Gaussian 98 program [11]. Frequency calculations were then carried out to ensure they are minima on the potential energy surface. In this study, all these molecules refer to their ideal gas state at 298.15 K and 100 kPa and their thermodynamic properties (C_v^θ , S^θ , H^θ and G^θ) are obtained from the Gaussian output files. The symmetry number has been built into the values for S^θ and G^θ . As for the notation in this paper, PCAN congeners with one to ten chlorine atoms are represented by MCAN, DCAN, tri-CAN, TCAN, penta-CAN, hexa-CAN, hepta-CAN, octa-CAN, nona-CAN and deca-CAN, respectively. Prefix numbers represent the positions (see Fig. 1) of chlorine substitution. (e.g., 1,2-DCAN).

Thermodynamic properties for PCDDs [7] and PBDDs [8] were computed using isodesmic reactions in previous study and were found to agree well with experimental results. Isodesmic reactions have also been used to obtain thermodynamic data for PCNs [9], PBDEs [10], polychlorinated thianthrenes (PCTAs) [12] and polychlorinated phenoxathiins (PCPTs) [13]. In this study, we use similar isodesmic reaction 1 to calculate $\Delta_r H^\theta$ and $\Delta_r G^\theta$ of PCANs.



Using the calculated values of the standard enthalpies (H^θ) of reactants and products and the experimental values of the standard enthalpies of formation ($\Delta_f H^\theta$) for anthracene, chlorobenzene and benzene, $\Delta_r H^\theta_{\text{PCAN}}$ could be calculated by Eq. (2):

$$\Delta_r H^\theta_{\text{PCAN}} = H^\theta_{\text{PCAN}} + nH^\theta_{\text{benzene}} - nH^\theta_{\text{chlorobenzene}} - H^\theta_{\text{anthracene}} - n\Delta_f H^\theta_{\text{benzene}} + n\Delta_f H^\theta_{\text{chlorobenzene}} + \Delta_f H^\theta_{\text{anthracene}} \quad (2)$$

From the calculated values of G^θ and the literature values of $\Delta_f G^\theta$, the similar Eq. (3) was used to calculate $\Delta_r G^\theta_{\text{PCAN}}$:

$$\Delta_r G^\theta_{\text{PCAN}} = G^\theta_{\text{PCAN}} + nG^\theta_{\text{benzene}} - nG^\theta_{\text{chlorobenzene}} - G^\theta_{\text{anthracene}} - n\Delta_f G^\theta_{\text{benzene}} + n\Delta_f G^\theta_{\text{chlorobenzene}} + \Delta_f G^\theta_{\text{anthracene}} \quad (3)$$

Since the experimental value for $\Delta_f G^\theta$ of anthracene was not available, Eq. (4) was used to calculate this quantity:

$$\Delta_r G^\theta_{\text{anthracene}} = \Delta_r H^\theta_{\text{anthracene}} - T \left[S^\theta_{\text{anthracene}} - \left(14S^\theta_{\text{graphite}} + 5S^\theta_{\text{H}_2} \right) \right] \quad (4)$$

where T is the specified temperature (298.15 K).

Thermodynamic data used to calculate $\Delta_r H^\theta$ and $\Delta_r G^\theta$ of PCANs are listed in Table 2, which includes experimental values of $\Delta_r H^\theta$, $\Delta_r G^\theta$ and S^θ taken from literature [14–17] and calculated values of H^θ and G^θ at the B3LYP/6-311G(d,p) level.

3. Results and discussion

3.1. Geometric molecular structures of PCANs

The number of theoretically possible congeners for PCANs from MCAN to deca-CAN are (3, 15, 32, 60, 66, 60, 32, 15, 3 and 1), respectively, and the total number is 287. It is well-known that non-substituted anthracene molecule has a planar configuration. Our optimization calculations show that some of PCAN congeners adopt a planar configuration, while others have a nonplanar configuration. The configuration distribution of PCAN congeners is listed in Table A1 (see Appendix A), in which molecules represented with a sign “N” have a nonplanar configuration and the others are all in planar configuration. A closer inspection of Table A1 reveals that the PCAN molecules will have a nonplanar configuration if either H atoms at 1 and 9 positions or at 8 and 9 positions or at 4 and 10 positions or at 5 and 10 positions are substituted with Cl atoms synchronously. For the convenience of illumination, H or Cl atoms at position n ($n = 1-10$) are denoted as H_n or Cl_n. Obviously, nonplanar configuration originates from intramolecular Cl1–Cl9 (or Cl8–Cl9, Cl4–Cl10 and Cl5–Cl10) nuclear repulsive interaction. For DCAN, only 1,9-DCAN is in nonplanar configuration of which the dihedral angle Cl9C9C1Cl1 is 6.51° and the Cl1–Cl9 distance is only 3.069 Å. While in 1,2- and 2,3-DCAN the Cl1–Cl2 and Cl2–Cl3 distances are 3.184 and 3.209 Å, respectively. For tri-CAN, eight isomers with two Cl atoms located at 1 and 9 positions synchronously are in nonplanar configuration and the dihedral angle Cl9C9C1Cl1 of 1,8,9-tri-CAN isomer (33.34°) is the largest in all eight Cl9C9C1Cl1 dihedral angles, which also show that the molecular configuration is mainly determined by Cl1–Cl9 (or Cl8–Cl9, Cl4–Cl10 and Cl5–Cl10) nuclear repulsive interaction. Comparing the dihedral angles Cl9C9C1Cl1 of 1,2,9-tri-CAN (21.16°), 1,2,3,9-TCAN (22.98°) and 1,2,3,4,9-penta-CAN (28.91°) with that of 1,9-DCAN (6.51°) and comparing those of 1,2,7,8,9-tri-CAN (38.10°), 1,2,3,6,7,8,9-tri-CAN (38.86°), 1,2,3,4,5,6,7,8,9-tri-CAN (41.10°) with that of 1,8,9-tri-CAN isomer (33.34°), it can be seen that for molecules with nonplanar configuration other neighbor Cl–Cl repulsion affects distortion extent of PCAN molecules.

Table 2

Thermodynamic data used to calculate $\Delta_r H^\theta$ and $\Delta_r G^\theta$ of PCANs.^a

Compound	$\Delta_f H^\theta/\text{kJ mol}^{-1}$	$\Delta_f G^\theta/\text{kJ mol}^{-1}$	$H^\theta/\text{hartree}$	$G^\theta/\text{hartree}$	$S^\theta/\text{J mol}^{-1} \text{K}^{-1}$
Anthracene	230.10 ^b	331.67 ^g	-539.45144 ^d	-539.49532 ^d	393.10 ^e
Benzene	82.93 ^c	129.73 ^c	-232.20302 ^d	-232.23347 ^d	
Chlorobenzene	51.84 ^c	99.23 ^c	-691.83341 ^d	-691.86900 ^d	
Graphite					5.74 ^f
H ₂					130.68 ^f

^a $\Delta_f H^\theta$ is the standard enthalpy of formation of the compound, $\Delta_r G^\theta$ is the standard Gibbs energy of formation of the compound, H^θ is the standard enthalpy, G^θ is the standard Gibbs energy and S^θ is the standard entropy.

^b Taken from Ref. [14].

^c Taken from Ref. [15].

^d Obtained from B3LYP/6-311G(d,p) calculations.

^e Taken from Ref. [16].

^f Taken from Ref. [17].

^g Calculated from Eq. (4).

Download English Version:

<https://daneshyari.com/en/article/5417426>

Download Persian Version:

<https://daneshyari.com/article/5417426>

[Daneshyari.com](https://daneshyari.com)