Thermodynamic Properties and Relative Stability of Polychlorinated Thianthrenes by Density Functional Theory

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Thermodynamic parameters, including total electronic energy (E_t), enthalpy ($H^\ominus$), entropy ($S^\ominus$), Gibbs free energy ($G^\ominus$), and standard heat capacity at constant volume ($C^\ominus{}_v$) for 75 polychlorinated thianthrenes (PCTAs) in the ideal gas state at 298.15 K and 101.325 kPa, have been computed using density functional theory at the B3LYP/6-31G* level with the Gaussian 98 program. The relations of these thermodynamic parameters with the number and position of chlorine substitution (N_{PCS}) were discussed. It was suggested that E_t, $S^\ominus$, $H^\ominus$, $G^\ominus$, and $C^\ominus{}_v$ of PCTAs vary greatly with the number and position of chlorine substitution. The values of molar heat capacity at constant pressure ($C_{p,m}$) at temperatures from (200 to 1800) K for PCTA congeners were calculated using a statistical thermodynamics calculation program based on Gaussian output files, and the temperature dependence relation of them was obtained using the least-squares method. The standard enthalpy of formation ($\Delta_f H^\ominus$) and the standard Gibbs energy of formation ($\Delta_f G^\ominus$) were obtained by designing an isodesmic reaction. On the basis of the magnitude of the relative standard Gibbs energy of formation ($\Delta_{R,f}G^\ominus$), the relative stability of PCTA isomers was theoretically proposed in this work and then compared with that of polychlorinated dibenzo-*p*-dioxin (PCDD) isomers.

Introduction

Many kinds of polycyclic aromatic sulfur heterocycles occur in the environment among the polycyclic aromatic compounds. Polychlorinated thianthrenes (PCTAs), polychlorinated dibenzothiophenes, and polychlorinated diphenylsulfide are three different groups of chlorinated polycyclic aromatic sulfur heterocycles which can be considered as sulfur analogues of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and polychlorinated diphenylethers, respectively. Structures of these compounds are shown in Figure 1. PCTAs, polychlorinated dibenzothiophenes, and polychlorinated diphenylsulfide are environmentally and toxicologically interesting compounds due to their structural similarity to corresponding oxygen analogues.[1] Some PCTA congeners have been observed in pulp mill effluent and stack gas samples,[2,3] and the separation of PCTAs[4] has been studied with capillary gas chromatography/mass spectrometry (HRGC−MSD). However, few studies of thermodynamic data for PCTAs have been reported.

Thermodynamic data of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, polychlorinated biphenyls, polychlorinated naphthalenes, and polybrominated naphthalenes[5−9] have been calculated, and the data evaluated via the first principle are greatly different from those using AM1 and PM3. Moreover, it has been found that the isomers with low free energy have a high ratio of formation; i.e., the ratio of formation for isomers is consistent with their relative stabilities. At the same time, it was found that thermodynamic properties of these compounds have good relations with the number and position of Cl substitution (N_{PCS}).

In this study, the thermodynamic properties (total electronic energy (E_t), standard entropy ($S^\ominus$), standard heat capacity at constant volume ($C^\ominus{}_v$), standard heat capacity at constant press ($C^\ominus{}_p$), the standard enthalpy of formation ($\Delta_f H^\ominus$), and the standard Gibbs energy of formation ($\Delta_f G^\ominus$) in the ideal gas state at 298.15 K and 101.325 kPa) were computed for all 75 PCTAs theoretically. The purpose of this study is to discuss the correlation of these thermodynamic properties with N_{PCS} and the temperature dependence of molar heat capacity at constant pressure ($C_{p,m}$). Furthermore, according to the magnitude of the relative Gibbs energy of formation ($\Delta_{R,f}G^\ominus$), the theoretical relative stability order of the isomers was proposed.

Computational Method

Geometry optimizations and energy calculations for all 75 PCTA molecules were performed using density functional theory (DFT) at the B3LYP/6-31G* level with the Gaussian 98 program.[10] Frequency calculations were then carried out for all of the possible geometries to ensure they are minimal on the potential energy surface. In this study, all the molecules refer to their ideal gas state at 298.15 K and 101.325 kPa, and the thermodynamic properties of them are obtained from the Gaussian output files.

The thermal energy ($E_{thermal}$) was calculated as the sum of zero-point energy and thermal energy corrections for molecular translation (E_{trans}), rotation (E_{rot}), and vibration (E_{vib}) at 298.15 K. The enthalpy ($H^\ominus$), at 298.15 K and 101.325 kPa, was obtained by adding RT to the total electronic energy (E_t) and thermal energy. These data, as well as the Gibbs free energy ($G^\ominus$), were obtained from the Gaussian output file in hartrees and then converted to kilojoules per mole (1 hartree = 2625.50 kJ·mol^{-1}). As for the notation in this paper, PCTA congeners with one to eight chlorine atoms are represented by MCTA,

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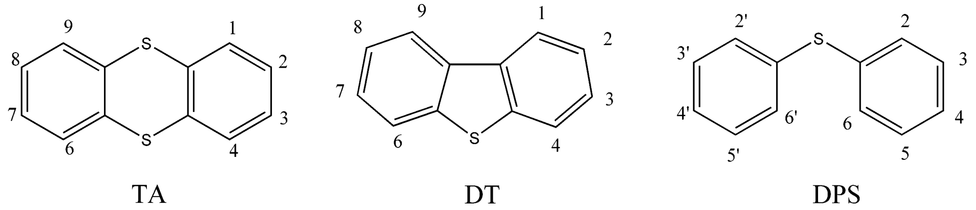

Figure 1. Molecular structures and atomic numbering of thianthrene (TA), dibenzothiophene (DT), and diphenylsulfide (DPS).

Table 1. Experimental and Computed Thermodynamic Parameters of the Substances in the Ideal Gas State at 298.15 K[a]

	$\Delta_f H^\ominus$	$\Delta_f G^\ominus$	$H^\ominus$	$G^\ominus$
compound	kJ·mol^{-1}	kJ·mol^{-1}	hartree	hartree
benzene	82.92[b]	129.66[b]	−232.14258[d]	−232.17302[d]
chlorobenzene	51.10[b]	98.50[b]	−691.74731[d]	−691.78290[d]
thianthrene	158.08[c]	275.96[c]	−1258.30019[d]	−1258.34801[d]

[a] $\Delta_f H^\ominus$ is the standard enthalpy of formation of the compound; $\Delta_f G^\ominus$ is the standard Gibbs energy of formation of the compound; $H^\ominus$ is the standard enthalpy; and $G^\ominus$ is the standard Gibbs energy. [b] Taken from ref 13. [c] Taken from ref 14. [d] Obtained from B3LYP/6-31G* calculations.

DCTA, tri-CTA, TCTA, penta-CTA, hexa-CTA, hepta-CTA, and octa-CTA, respectively. Prefix numbers represent the positions (see Figure 1) of chlorine substitution (e.g., 2,3,7,8-TCTA or simply 2,3,7,8-T).

Isodesmic reactions were used successfully to obtain thermodynamic data for PBDDs[11] and PBDEs[12] in previous studies. Similarly, isodesmic reaction 1 was designed to calculate the $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$ of PCTAs in this study.

$$\text{thianthrene} + n\cdot\text{chlorobenzene} = \text{PCTA} + n\cdot\text{benzene} \quad (1)$$

The standard enthalpy change of the reaction ($\Delta_r H^\ominus$) is equal to the sum of the standard enthalpies of the products as obtained from DFT calculations minus the sum of the standard enthalpies of reactants

$$\Delta_r H^\ominus = [H^\ominus_{\text{PCTA}} + nH^\ominus_{\text{benzene}}] - [H^\ominus_{\text{thianthrene}} + nH^\ominus_{\text{chlorobenzene}}] \quad (2)$$

The sum of the standard enthalpies of formation for the products minus that of the reactants also yields $\Delta_r H^\ominus$

$$\Delta_r H^\ominus = [\Delta_f H^\ominus_{\text{PCTA}} + n\Delta_f H^\ominus_{\text{benzene}}] - [\Delta_f H^\ominus_{\text{thianthrene}} + n\Delta_f H^\ominus_{\text{chlorobenzene}}] \quad (3)$$

By substituting eq 3 into eq 2, $\Delta_f H^\ominus_{\text{PCTA}}$ could be obtained by eq 4

$$\Delta_f H^\ominus_{\text{PCTA}} = H^\ominus_{\text{PCTA}} + nH^\ominus_{\text{benzene}} - nH^\ominus_{\text{chlorobenzene}} - H^\ominus_{\text{thianthrene}} - n\Delta_f H^\ominus_{\text{benzene}} + n\Delta_f H^\ominus_{\text{chlorobenzene}} + \Delta_f H^\ominus_{\text{thianthrene}} \quad (4)$$

Similarly, $\Delta_f G^\ominus_{\text{PCTA}}$ could be obtained by eq 5

$$\Delta_f G^\ominus_{\text{PCTA}} = G^\ominus_{\text{PCTA}} + nG^\ominus_{\text{benzene}} - nG^\ominus_{\text{chlorobenzene}} - G^\ominus_{\text{thianthrene}} - n\Delta_f G^\ominus_{\text{benzene}} + n\Delta_f G^\ominus_{\text{chlorobenzene}} + \Delta_f G^\ominus_{\text{thianthrene}} \quad (5)$$

The experimental values of $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$ for thianthrene, chlorobenzene, and benzene taken from the literature[13,14] are listed in Table 1, which also presents the values of $H^\ominus$ and $G^\ominus$ calculated at the B3LYP/6-31G* level for these compounds.

To test how well our calculations reproduce the thianthrene skeleton, the energetics for the reaction 2diphenylsulfide → thianthrene + 2benzene have been calculated at the B3LYP/6-31G* level and compared with the corresponding experimental ones. The calculated values of $\Delta_r H^\ominus$ and $\Delta_r G^\ominus$ are −9.96 and −30.17 kJ·mol^{-1}, respectively, and the corresponding experimental ones (obtained from the $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$ of diphenylsulfide, thianthrene, and benzene) are −6.14 and −26.40 kJ·mol^{-1}, respectively. It can be seen that the discrepancies between calculated values and experimental ones for $\Delta_r H^\ominus$ and $\Delta_r G^\ominus$ are both less than 4 kJ·mol^{-1}, which shows that the method used in this study is feasible.

The positions of Cl substitution (PCS) include the number of Cl atoms on the different positions of the parent compound and the number of relative positions for these Cl atoms. The numbers of the positions of Cl substitution (PCS) are defined as follows: the number of chlorine atoms at positions α (1, 4, 6, and 9 being α positions) and β (2, 3, 7, and 8 being β positions) are defined as N_α and N_β; the number of chlorine atoms at relative ortho, meta, and para positions are symbolized as N_o, N_m, and N_p; and the number of dichlorine atoms at positions 1 and 9 (or 4 and 6) synchronously is $N_{1,9}$, respectively. Moreover, the parameters mentioned above are defined as a general designation, N_{PCS}, and listed in Table 2.

Using the GQSARF 2.0 program,[15] N_{PCS} was taken as a theoretical descriptor to establish the correlation equations between the calculated thermodynamic parameters and N_{PCS}. From these correlative equations, the main influencing factors on these thermodynamic parameters can be found.

Results and Discussion

Relation of Thermodynamic Parameters with the Number and Position of Chlorine Substitution (N_{PCS}). The values of total electronic energies (E_t) and other thermodynamic quantities ($H^\ominus$, $G^\ominus$, $S^\ominus$, and $C^\ominus_v$) calculated for 75 PCTAs in the ideal gas state at 298.15 K and 101.325 kPa are listed in Table 2 together with the values of $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$ calculated from eqs 4 and 5. The correlation equations of E_t, $H^\ominus$, $G^\ominus$, $S^\ominus$, and $C^\ominus_v$ with position of chlorine substitution (N_{PCS}) were obtained using the GQSARF 2.0 program[15] and are indicated in Table 3, where R^2 is the squared correlation coefficient and SE is the standard error. From Table 3, the following conclusions can be drawn: (1) the correlations between these thermodynamic parameters and N_{PCS} are very well due to the corresponding R^2 values very close to 1.0000, which all clearly represent the influence of the number and position of chlorine substitution on these values. These equations with a large R^2 value show that thermodynamic properties have good relations with positions of Cl substitution (N_{PCS}) for PCTAs. (2) The higher the number of chlorine atoms is, the lower the value of E_t, $G^\ominus$, and $H^\ominus$ is. Furthermore, there is an order of the decrease at positions: $N_\alpha < N_\beta$. This indicates that congeners with Cl substitution in α positions have a stronger

Table 2. Thermodynamic Parameters of PCTAs from DFT Calculations and N_{PCS}

	E_t	$H^\ominus$	$G^\ominus$	$S^\ominus$	$C^\ominus_v$	$\Delta_f H^\ominus$	$\Delta_f G^\ominus$	$\Delta_{R,f} G^\ominus$						
molecule	hartree	hartree	hartree	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	N_α	N_β	N_o	N_m	N_p	N_{19}
TA	−1258.47465	−1258.30019	−1258.34801	420.68	181.67	158.08	275.96		0	0	0	0	0	0
MCTA														
1	−1718.06611	−1717.90016	−1717.95199	455.95	197.81	139.51	260.28	8.78	1	0	0	0	0	0
2	−1718.06942	−1717.90342	−1717.95534	456.69	197.95	130.95	251.50	0.00	0	1	0	0	0	0
DCTA														
1,2	−2177.65556	−2177.49809	−2177.55317	484.55	213.64	126.31	251.97	22.10	1	1	1	0	0	0
1,3	−2177.65964	−2177.50217	−2177.55742	486.08	214.08	115.59	240.80	10.93	1	1	0	1	0	0
1,4	−2177.65629	−2177.49888	−2177.55406	485.44	213.94	124.23	249.62	19.75	2	0	0	0	1	0
1,6	−2177.65750	−2177.50006	−2177.55460	479.82	213.94	121.14	248.22	18.35	2	0	0	0	0	0
1,7	−2177.66062	−2177.50314	−2177.55840	486.17	214.05	113.06	238.23	8.36	1	1	0	0	0	0
1,8	−2177.66052	−2177.50304	−2177.55832	486.28	214.05	113.30	238.44	8.57	1	1	0	0	0	0
1,9	−2177.65682	−2177.49941	−2177.55460	485.57	213.93	122.86	248.21	18.34	2	0	0	0	0	1
2,3	−2177.65918	−2177.50164	−2177.55682	485.42	213.73	116.99	242.39	12.52	0	2	1	0	0	0
2,7	−2177.66380	−2177.50628	−2177.56097	481.12	214.16	104.81	231.49	1.62	0	2	0	0	0	0
2,8	−2177.66378	−2177.50625	−2177.56158	486.82	214.14	104.89	229.87	0.00	0	2	0	0	0	0
tri-CTA														
1,2,3	−2637.24410	−2637.09512	−2637.15345	513.12	229.48	115.46	246.01	26.33	1	2	2	1	0	0
1,2,4	−2637.24480	−2637.09587	−2637.15431	514.07	229.77	113.50	243.76	24.08	2	1	1	1	1	0
1,2,6	−2637.24684	−2637.09787	−2637.15628	513.87	229.71	108.25	238.58	18.89	2	1	1	0	0	0
1,2,7	−2637.24981	−2637.10082	−2637.15933	514.73	229.87	100.50	230.57	10.89	1	2	1	0	0	0
1,2,8	−2637.24970	−2637.10071	−2637.15922	514.72	229.86	100.79	230.87	11.18	1	2	1	0	0	0
1,2,9	−2637.24607	−2637.09714	−2637.15558	514.16	229.75	110.17	240.42	20.73	2	1	1	0	0	1
1,3,6	−2637.25070	−2637.10175	−2637.16036	515.64	230.18	98.07	227.87	8.18	2	1	0	1	0	0
1,3,7	−2637.25381	−2637.10482	−2637.16348	516.03	230.27	90.00	219.68	0.00	1	2	0	1	0	0
1,3,8	−2637.25374	−2637.10475	−2637.16344	516.34	230.31	90.18	219.77	0.09	1	2	0	1	0	0
1,3,9	−2637.25018	−2637.10124	−2637.15986	515.64	230.17	99.39	229.19	9.51	2	1	0	1	0	1
1,4,6	−2637.24703	−2637.09813	−2637.15664	514.78	230.00	107.56	237.62	17.94	3	0	0	0	1	1
1,4,7	−2637.25051	−2637.10158	−2637.16018	515.54	230.15	98.51	228.34	8.66	2	1	0	0	1	0
2,3,6	−2637.25013	−2637.10111	−2637.15962	514.73	229.82	99.73	229.80	10.12	1	2	1	0	0	0
2,3,7	−2637.25331	−2637.10425	−2637.16285	515.54	229.95	91.49	221.32	1.64	0	3	1	0	0	0
TCTA														
1,2,3,4	−3096.82784	−3096.68747	−3096.74897	541.03	245.24	116.91	252.55	41.48	2	2	3	2	1	0
1,2,3,6	−3096.83507	−3096.69461	−3096.75630	542.75	245.59	98.17	233.29	22.22	2	2	2	1	0	0
1,2,3,7	−3096.83812	−3096.69762	−3096.75933	542.92	245.67	90.27	225.35	14.28	1	3	2	1	0	0
1,2,3,8	−3096.83801	−3096.69752	−3096.75925	543.13	245.69	90.54	225.55	14.48	1	3	2	1	0	0
1,2,3,9	−3096.83447	−3096.69402	−3096.75569	542.48	245.57	99.70	234.91	23.84	2	2	2	1	0	1
1,2,4,6	−3096.83538	−3096.69497	−3096.75673	543.28	245.84	97.21	232.19	21.12	3	1	1	1	1	1
1,2,4,7	−3096.83872	−3096.69830	−3096.76017	544.32	246.02	88.47	223.13	12.06	2	2	1	1	1	0
1,2,4,8	−3096.83870	−3096.69827	−3096.76014	544.29	246.01	88.55	223.22	12.15	2	2	1	1	1	0
1,2,4,9	−3096.83525	−3096.69486	−3096.75664	543.56	245.86	97.51	232.40	21.33	3	1	1	1	1	1
1,2,6,7	−3096.83595	−3096.69548	−3096.75650	536.76	245.55	95.88	232.80	21.73	2	2	2	0	0	0
1,2,6,8	−3096.83976	−3096.69930	−3096.76114	544.01	245.96	85.85	220.60	9.53	2	2	1	1	0	0
1,2,6,9	−3096.83605	−3096.69566	−3096.75747	543.78	245.89	95.41	230.23	19.16	3	1	1	0	1	1
1,2,7,8	−3096.83914	−3096.69862	−3096.76037	543.30	245.64	87.65	222.61	11.54	1	3	2	0	0	0
1,2,7,9	−3096.83916	−3096.69873	−3096.76059	544.27	246.01	87.36	222.03	10.96	2	2	1	1	0	1
1,2,8,9	−3096.83504	−3096.69461	−3096.75633	542.94	245.61	98.17	233.24	22.17	2	2	2	0	0	1
1,3,6,8	−3096.84362	−3096.70316	−3096.76450	539.68	246.37	75.73	211.78	0.71	2	2	0	2	0	0
1,3,6,9	−3096.84000	−3096.69961	−3096.76158	545.20	246.29	85.04	219.44	8.37	3	1	0	1	1	1
1,3,7,8	−3096.84309	−3096.70256	−3096.76450	544.88	246.05	77.29	211.78	0.71	1	3	1	1	0	0
1,3,7,9	−3096.84318	−3096.70274	−3096.76477	545.69	246.41	76.82	211.07	0.00	2	2	0	2	0	1
1,4,6,9	−3096.83641	−3096.69608	−3096.75733	538.81	246.16	94.30	230.60	19.53	4	0	0	0	2	2
1,4,7,8	−3096.83983	−3096.69937	−3096.76126	544.48	245.96	85.67	220.29	9.22	2	2	1	0	1	0
2,3,7,8	−3096.84265	−3096.70204	−3096.76324	538.30	245.68	78.65	215.11	4.04	0	4	2	0	0	0
penta-CTA														
1,2,3,4,6	−3556.41827	−3556.28643	−3556.35129	570.63	261.31	101.00	241.23	26.74	3	2	3	2	1	1
1,2,3,4,7	−3556.42169	−3556.28979	−3556.35469	570.95	261.40	92.17	232.30	17.82	2	3	3	2	1	0
1,2,3,6,7	−3556.42403	−3556.29207	−3556.35700	571.21	261.39	86.20	226.26	11.77	2	3	3	1	0	0
1,2,3,6,8	−3556.42787	−3556.29590	−3556.36097	572.43	261.77	76.13	215.82	1.33	2	3	2	2	0	0
1,2,3,6,9	−3556.42424	−3556.29235	−3556.35739	572.18	261.68	85.46	225.23	10.74	3	2	2	1	1	1
1,2,3,7,8	−3556.42727	−3556.29524	−3556.36024	571.77	261.44	77.86	217.75	3.27	1	4	3	1	0	0
1,2,3,7,9	−3556.42733	−3556.29539	−3556.36049	572.69	261.81	77.48	217.10	2.61	2	3	2	2	0	1
1,2,3,8,9	−3556.42417	−3556.29227	−3556.35729	571.98	261.67	85.66	225.49	11.00	2	3	3	1	0	1
1,2,4,6,7	−3556.42427	−3556.29238	−3556.35742	572.25	261.70	85.38	225.13	10.65	3	2	2	1	1	1
1,2,4,6,8	−3556.42819	−3556.29629	−3556.36148	573.48	262.08	75.11	214.49	0.00	3	2	1	2	1	1
1,2,4,6,9	−3556.42463	−3556.29280	−3556.35795	573.23	261.99	84.29	223.74	9.26	4	1	1	1	2	2
1,2,4,7,8	−3556.42792	−3556.29596	−3556.36108	572.93	261.76	75.99	215.54	1.05	2	3	2	1	1	0
1,2,4,7,9	−3556.42809	−3556.29620	−3556.36141	573.69	262.11	75.35	214.67	0.19	3	2	1	2	1	1
1,2,4,8,9	−3556.42417	−3556.29227	−3556.35729	571.98	261.67	85.66	225.49	11.01	3	2	2	1	1	1

Table 2. (Continued)

molecule	E_{t} hartree	$H^{\ominus}$ hartree	$G^{\ominus}$ hartree	$S^{\ominus}$ $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$C^{\ominus}_{\mathrm{v}}$ $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$\Delta_{\mathrm{f}}H^{\ominus}$ $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{\mathrm{f}}G^{\ominus}$ $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{\mathrm{R,f}}G^{\ominus}$ $\mathrm{kJ \cdot mol^{-1}}$	N_{α}	N_{β}	N_{o}	N_{m}	N_{p}	N_{19}
hexa-CTA														
1,2,3,4,6,7	−4016.00708	−4015.88375	−4015.95186	599.22	277.15	89.40	234.52	15.23	3	3	4	2	1	1
1,2,3,4,6,8	−4016.01095	−4015.88761	−4015.95586	600.42	277.51	79.26	224.02	4.73	3	3	3	3	1	1
1,2,3,4,6,9	−4016.00747	−4015.88418	−4015.95239	600.09	277.41	88.26	233.12	13.83	4	2	3	2	2	2
1,2,3,4,7,8	−4016.01075	−4015.88733	−4015.95547	599.47	277.15	80.01	225.05	5.76	2	4	4	2	1	0
1,2,3,6,7,8	−4016.01203	−4015.88857	−4015.95608	593.90	277.20	76.75	223.46	4.17	2	4	4	2	0	0
1,2,3,6,7,9	−4016.01231	−4015.88892	−4015.95719	600.62	277.50	75.83	220.53	1.24	3	3	3	2	1	1
1,2,3,6,8,9	−4016.01215	−4015.88876	−4015.95702	600.59	277.50	76.25	220.97	1.68	3	3	3	2	1	1
1,2,3,7,8,9	−4016.01137	−4015.88793	−4015.95607	599.50	277.20	78.43	223.46	4.17	2	4	4	2	0	1
1,2,4,6,7,9	−4016.01261	−4015.88930	−4015.95708	596.29	277.85	74.82	220.82	1.53	4	2	2	2	2	2
1,2,4,6,8,9	−4016.01257	−4015.88924	−4015.95766	601.92	277.82	74.97	219.29	0.00	4	2	2	2	2	2
hepta-CTA														
1,2,3,4,6,7,8	−4475.59502	−4475.48018	−4475.55149	627.34	292.91	80.12	230.27	1.60	3	4	5	3	1	1
1,2,3,4,6,7,9	−4475.59544	−4475.48066	−4475.55210	628.50	293.21	78.87	228.67	0.00	4	3	4	3	2	2
OCTA														
1,2,3,4,6,7,8,9	−4935.17814	−4935.07191	−4935.14572	649.35	308.61	83.21	240.22		4	4	6	4	2	2

Table 3. Correlation Equations of Thermodynamic Parameters with N_{PCS}

parameter	unit	equation	R^2	SE
E_{t}	hartree	$E_{\mathrm{t}} = -1258.48470 - 459.58716N_{\alpha} - 459.58865N_{\beta}$	1.0000	0.004
$G^{\ominus}$	hartree	$G^{\ominus} = -1258.35882 - 459.59898N_{\alpha} - 459.60039N_{\beta}$	1.0000	0.004
$H^{\ominus}$	hartree	$H^{\ominus} = -1258.31099 - 459.59572N_{\alpha} - 459.59683N_{\beta}$	1.0000	0.004
$S^{\ominus}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$S^{\ominus} = 425.6021 + 29.5618N_{\alpha} + 30.2560N_{\beta} - 1.7250N_{\mathrm{o}}$	0.9980	1.960
$C^{\ominus}_{\mathrm{v}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$C^{\ominus}_{\mathrm{v}} = 43.4712 + 3.8561N_{\alpha} + 3.8790N_{\beta} - 0.09548N_{\mathrm{o}}$	1.0000	0.010

interaction force compared to those with Cl substitutions in the β positions. (3) The number of relative positions has only a slight influence on the values of $S^{\ominus}$ and $C^{\ominus}_{\mathrm{v}}$ for PCTA congeners (because parameters N_{o}, N_{m}, and N_{p} have hardly any influence on the values of E_{t}, $G^{\ominus}$, and $H^{\ominus}$, they were not included in corresponding fitted equations).

Temperature Dependence of Molar Heat Capacity at Constant Pressure ($C_{p,m}$). To our knowledge, the values of $C_{\mathrm{p,m}}$ at different temperatures (T) for PCTA congeners have not been reported. So, the values of $C_{\mathrm{p,m}}$ were calculated using a statistical thermodynamics calculation program at temperatures (200 to 1800 K) based on Gaussian output files; however, these $C_{\mathrm{p,m}}$ values were not listed in the paper because of the length of the article.

On the basis of the calculated values of $C_{\mathrm{p,m}}$ of all PCTAs at different temperatures (T), the relations between $C_{\mathrm{p,m}}$ and temperature were obtained using the least-squares method and listed in Table 4. A, B, and C are regression coefficients, and D is a constant. From Table 4, the following conclusions can be drawn: (1) There are very good relationships between $C_{\mathrm{p,m}}$ and temperature (T, $1/T$, and $1/T^2$) for almost all PCTA congeners. The correlation coefficients (r^2) are all very close to or equal to 1.0, and the standard deviations (SE) are all low, which indicates that the calculated $C_{\mathrm{p,m}}$ values in this study can be used to predict $C_{\mathrm{p,m}}$ of PCTAs at different temperatures. Moreover, the SE values decrease with the increasing number of Cl atoms. (2) For the same isomer group, the $C_{\mathrm{p,m}}$ values are close to each other at the same temperature because their regression coefficients are close to each other.

Relative Stability of Isomer Groups. It has been known that the isomers with higher free energies are less stable than those with lower free energies. On the basis of the lowest $\Delta_{\mathrm{f}}G^{\ominus}$ in each PCTA isomer group, the relative formation free energies ($\Delta_{\mathrm{R,f}}G^{\ominus}$) of PCTAs were obtained and are also listed in Table 2. For comparison of these parameters, the most stable and the least stable isomers in the seven categories of congeners are summarized and listed in Table 5. It is obvious that the relative thermodynamic stability of PCTAs with the same degree of chlorination is determined by the intramolecular chlorine repulsion effect. The most stable isomers have no or the minimum number of nearest chlorine atoms, whereas the least stable isomers have the maximum number of nearest chlorine atoms at the same aromatic ring.

It can be seen from Table 5 that the least stable isomers in DCTAs, tri-CTAs, TCTAs, penta-CTAs, hexa-CTAs, and hepta-CTAs are all those with chlorine atoms located on near positions. On the contrary, the chlorine atoms in the most stable isomers are reasonably distributed at two aromatic rings, and they are relatively far away from each other. For MCTAs, the 1-MCTA isomer is less stable than the 2-MCTA isomer by an amount of 8.78 $\mathrm{kJ \cdot mol^{-1}}$. For DCTAs, the 2,8-DCTA is the most stable, whereas the 1,2-DCTA is the least stable with a difference of 22.10 $\mathrm{kJ \cdot mol^{-1}}$ in their energy values. Similarly, the 1,3,7-, 1,3,7,9-, 1,2,4,6,8-, 1,2,4,6,8,9-, and 1,2,3,4,6,7,9- are the most stable isomers with differences of (26.33, 41.48, 26.74, 15.23, and 1.60) $\mathrm{kJ \cdot mol^{-1}}$ from the least stable isomers 1,2,3-, 1,2,3,4-, 1,2,3,4,6-, 1,2,3,4,6,7-, and 1,2,3,4,6,7,8- for tri-CTAs, TCTAs, penta-CTAs, hexa-CTAs, and hepta-CTAs, respectively. The chlorine substituent at the adjacent positions on the same aromatic ring seems to destabilize the isomers, and the resulting steric effect may be one of the important sources of the relative instabilities of the PCTAs apart from the associated electrostatic effects.

Comparison with PCDDs. By comparison with the relative stability of isomer groups of PCDDs reported previously,[5] one can see that for isomer groups with the number of Cl atoms being odd both the most stable and the least stable isomers are in agreement. However, when the number of Cl atoms is even, both the most stable isomers and the least stable isomers are not consistent except for the isomer group with four chlorine atoms. This result may originate from the structural difference between PCTAs and PCDDs. It was found that all 75 PCTA molecules have a nonplanar geometrical configuration, whereas PCDD molecules are all in a planar configuration. If the number

Table 4. Temperature Dependence of Molar Heat Capacity at Constant Pressure

	$C_{p,m} = AT + BT^{-1} + CT^{-2} + D$					
molecule	A/J·mol^{-1}·K^{-2}	B/J·mol^{-1}	C/J·mol^{-1}·K	D/J·mol^{-1}·K^{-1}	R^2	SE
TA	0.0068	−157532.8650	14508153.0174	560.5237	0.9998	1.55
MCTA						
1	0.0030	−151869.0517	13726468.0571	567.7753	0.9999	1.36
2	0.0031	−151719.1093	13714155.5920	567.4971	0.9999	1.36
DCTA						
1,2	−0.0007	−146561.9110	12998871.0096	575.2713	0.9999	1.18
1,3	−0.0006	−146267.0099	12975384.2668	574.9544	0.9999	1.17
1,4	−0.0007	−146336.3810	12969854.2490	575.1616	0.9999	1.17
1,6	−0.0007	−146233.6014	12950201.7376	575.0310	0.9999	1.17
1,7	−0.0006	−146075.4532	12934176.4108	574.7561	0.9999	1.17
1,8	−0.0006	−146082.9762	12935282.7330	574.7673	0.9999	1.17
1,9	−0.0007	−146236.8597	12946774.3309	575.0879	0.9999	1.17
2,3	−0.0006	−146473.6555	13001022.1132	574.9575	0.9999	1.19
2,7	−0.0005	−145964.6748	12927672.5947	574.5110	0.9999	1.18
2,8	−0.0005	−145966.4966	12927737.0046	574.4958	0.9999	1.18
tri-CTA						
1,2,3	−0.0045	−141456.3855	12310605.8592	583.0277	0.9999	1.01
1,2,4	−0.0045	−141235.8199	12282830.4604	582.9012	0.9999	1.00
1,2,6	−0.0044	−140961.5181	12225445.1608	582.5638	0.9999	1.00
1,2,7	−0.0043	−140775.3642	12206074.4232	582.2778	0.9999	1.00
1,2,8	−0.0043	−140813.7437	12211597.7900	582.3386	0.9999	1.00
1,2,9	−0.0044	−140927.5825	12217688.0618	582.6004	0.9999	1.00
1,3,6	−0.0043	−140647.2429	12199547.5982	582.2414	0.9999	0.99
1,3,7	−0.0043	−140527.8206	12189271.1468	582.0076	0.9999	1.00
1,3,8	−0.0043	−140501.5907	12186385.4327	581.9868	0.9999	1.00
1,3,9	−0.0044	−140669.6790	12200701.5552	582.3073	0.9999	0.99
1,4,6	−0.0044	−140741.1379	12196037.9618	582.4614	0.9999	0.99
1,4,7	−0.0043	−140581.5104	12181789.2718	582.1947	0.9999	0.99
2,3,6	−0.0043	−140851.1924	12221856.1257	582.2760	0.9999	1.01
2,3,7	−0.0042	−140713.1933	12211098.4830	582.0206	0.9999	1.02
TCTA						
1,2,3,4	−0.0085	−136514.6061	11629302.3927	591.2669	0.9999	0.84
1,2,3,6	−0.0082	−135834.3329	11534295.6478	590.3248	0.9999	0.84
1,2,3,7	−0.0082	−135702.9853	11520578.3512	590.0774	0.9999	0.85
1,2,3,8	−0.0081	−135693.0463	11519990.3085	590.0712	0.9999	0.84
1,2,3,9	−0.0083	−135831.1014	11528947.1377	590.3647	0.9999	0.84
1,2,4,6	−0.0082	−135638.0205	11508188.3727	590.2207	0.9999	0.83
1,2,4,7	−0.0081	−135463.4953	11492638.2856	589.9504	0.9999	0.84
1,2,4,8	−0.0081	−135459.1152	11491719.1522	589.9406	0.9999	0.84
1,2,4,9	−0.0082	−135618.0032	11505525.4267	590.2041	0.9999	0.83
1,2,6,7	−0.0082	−135656.3319	11496146.8516	590.1170	0.9999	0.84
1,2,6,8	−0.0081	−135392.0557	11477010.8956	589.8260	0.9999	0.84
1,2,6,9	−0.0082	−135419.9957	11466656.4251	590.0055	0.9999	0.83
1,2,7,8	−0.0081	−135560.6242	11494398.8395	589.8356	0.9999	0.85
1,2,7,9	−0.0081	−135360.3948	11470418.9346	589.8542	0.9999	0.83
1,2,8,9	−0.0082	−135626.2407	11489488.2817	590.1652	0.9999	0.84
1,3,6,8	−0.0080	−135135.0834	11458883.9433	589.5371	0.9999	0.83
1,3,6,9	−0.0081	−135145.2588	11446272.3719	589.6811	0.9999	0.83
1,3,7,8	−0.0080	−135285.6061	11474157.8771	589.5180	0.9999	0.85
1,3,7,9	−0.0080	−135089.6220	11450770.1884	589.5318	0.9999	0.83
1,4,6,9	−0.0082	−135226.8777	11443672.6726	589.8868	0.9999	0.83
1,4,7,8	−0.0080	−135331.1512	11467177.5488	589.6904	0.9999	0.84
2,3,7,8	−0.0079	−135486.7033	11497213.4630	589.5177	0.9999	0.87
penta-CTA						
1,2,3,4,6	−0.0123	−130920.4169	10855157.3696	598.6014	1.0000	0.69
1,2,3,4,7	−0.0122	−130797.9197	10844625.2841	598.3478	1.0000	0.69
1,2,3,6,7	−0.0120	−130578.4272	10811635.3871	597.9203	1.0000	0.70
1,2,3,6,8	−0.0119	−130312.1253	10790888.7514	597.6069	1.0000	0.70
1,2,3,6,9	−0.0120	−130343.3933	10780803.8215	597.7874	1.0000	0.70
1,2,3,7,8	−0.0119	−130474.9938	10806998.6055	597.6106	0.9999	0.71
1,2,3,7,9	−0.0119	−130282.0414	10784394.2860	597.6312	1.0000	0.70
1,2,3,8,9	−0.0120	−130345.6424	10780446.3776	597.7880	1.0000	0.70
1,2,4,6,7	−0.0120	−130322.4209	10778244.7134	597.7650	1.0000	0.70
1,2,4,6,8	−0.0119	−130084.7625	10762286.1020	597.4885	1.0000	0.69
1,2,4,6,9	−0.0120	−130125.0293	10755294.3247	597.6451	1.0000	0.69
1,2,4,7,8	−0.0119	−130249.9419	10780293.4628	597.4862	1.0000	0.71
1,2,4,7,9	−0.0119	−130070.1518	10760623.4426	597.4880	1.0000	0.69
1,2,4,8,9	−0.0120	−130345.6424	10780446.3776	597.7880	1.0000	0.70

Table 4. (Continued)

	$C_{p,m} = AT + BT^{-1} + CT^{-2} + D$					
molecule	A/J·mol^{-1}·K^{-2}	B/J·mol^{-1}	C/J·mol^{-1}·K	D/J·mol^{-1}·K^{-1}	R^2	SE
hexa-CTA						
1,2,3,4,6,7	−0.0160	−125630.1853	10127671.2572	606.1743	1.0000	0.59
1,2,3,4,6,8	−0.0159	−125377.3675	10108790.8639	605.8746	1.0000	0.59
1,2,3,4,6,9	−0.0160	−125438.6871	10105314.6769	606.0485	1.0000	0.59
1,2,3,4,7,8	−0.0159	−125562.7154	10128134.8791	605.8784	1.0000	0.60
1,2,3,6,7,8	−0.0158	−125488.9585	10123305.2003	605.7001	1.0000	0.60
1,2,3,6,7,9	−0.0158	−125248.5414	10092184.8403	605.5673	1.0000	0.59
1,2,3,6,8,9	−0.0158	−125252.5808	10091989.9890	605.5722	1.0000	0.59
1,2,3,7,8,9	−0.0158	−125454.1625	10113356.3356	605.7151	1.0000	0.60
1,2,4,6,7,9	−0.0158	−125002.1024	10064019.2538	605.3984	1.0000	0.59
1,2,4,6,8,9	−0.0158	−125024.7901	10066917.3291	605.4108	1.0000	0.59
hepta-CTA						
1,2,3,4,6,7,8	−0.0198	−120555.6007	9440232.6314	613.9556	1.0000	0.55
1,2,3,4,6,7,9	−0.0198	−120361.9665	9418965.7042	613.8430	1.0000	0.54
OCTA						
1,2,3,4,6,7,8,9	−0.0239	−115684.1583	8768485.9038	622.2618	1.0000	0.57

Table 5. Most Stable and Least Stable Isomer in Different Isomer Groups

	most stable isomer	least stable isomer
MCTA	2-	1-
DCTA	2,8-	1,2-
tri-CTA	1,3,7-	1,2,3-
TCTA	1,3,7,9-	1,2,3,4-
penta-CTA	1,2,4,6,8-	1,2,3,4,6-
hexa-CTA	1,2,4,6,8,9-	1,2,3,4,6,7-
hepta-CTA	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

of Cl atoms is odd, both PCTA and PCDD molecules belong to the C_1 point group; however, when the number is even, PCTA molecules have different symmetry than PCDD molecules in general. Furthermore, to study how differently chlorination affects dibenzo-*p*-dioxin (DD) and thianthrene (TA), the energetics of the 75 reactions polychlorodibenzo-*p*-dioxins + thianthrene → dibenzo-*p*-dioxin + polychlorothianthrenes have been obtained theoretically. The mean values of calculated $\Delta_r G^{\ominus}$ in all isomer groups are positive and less than 3 kJ·mol^{-1} moreover. Although most of the mean values of calculated $\Delta_r H^{\ominus}$ are negative, the absolute values of them are less than 1 kJ·mol^{-1} in general. In addition, the values of $\Delta_r S^{\ominus}$ for all reactions are negative, which is partially because dibenzo-*p*-dioxin (DD) has different symmetry than thianthrene (TA); concretely, they belong to the D_{2h} and C_{2v} point group, respectively. Despite the difference between $\Delta_r H^{\ominus}$ and $\Delta_r G^{\ominus}$, the values of them are both small, which indicates that chlorination affects DD and TA to approximately the same extent.

Conclusion

The structures of 75 PCTA molecules were fully optimized at the B3LYP/6-31G* level, and the total electronic energy (E_t), enthalpy ($H^{\ominus}$), entropy ($S^{\ominus}$), Gibbs free energy ($G^{\ominus}$), and heat capacity at constant volume ($C^{\ominus}_v$) of them were consequently obtained. The results showed that all these thermodynamic parameters are greatly dependent on the number and position of chlorine substitution (N_{PCS}). The standard enthalpy of formation ($\Delta_f H^{\ominus}$) and the standard Gibbs energy of formation ($\Delta_f G^{\ominus}$) were obtained by designing isodesmic reactions. According to the magnitude of the relative standard Gibbs energy of formation ($\Delta_{R,f} G^{\ominus}$), the relative stability order of the isomers in each isomer group was determined. The temperature dependence relation of molar heat capacity at constant pressure ($C_{p,m}$) was also obtained. The values of $C_{p,m}$ for the complete set of 75 PCTA congeners provided by this work should be valuable in further thermodynamic studies.

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