Calculation of Thermodynamic Properties of Polychlorinated Phenoxathiins

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Thermodynamic properties, including entropy (S^{Θ}), heat capacity at constant volume (C^{Θ}_{v}), enthalpy (H^{Θ}), and Gibbs free energy (G^{Θ}) for 135 polychlorinated phenoxathiins (PCPTs) in the ideal gas state at 298.15 K and 101.325 kPa, have been computed using density functional theory (DFT) at the B3LYP/6-31G* level with the Gaussian 98 program. The standard enthalpy of formation ($\Delta_f H^{\Theta}$) and the standard Gibbs free energy of formation ($\Delta_f G^{\Theta}$) were obtained by designing an isodesmic reaction. The relations of S^{Θ}, C^{Θ}_{v}, $\Delta_f H^{\Theta}$, and $\Delta_f G^{\Theta}$ with the number and position of chlorine substitution (N_{PCS}) are discussed. It is suggested that S^{Θ}, C^{Θ}_{v}, $\Delta_f H^{\Theta}$, and $\Delta_f G^{\Theta}$ of PCPTs vary greatly with the number and position of chlorine substitution. The values of heat capacity at constant pressure (C^{Θ}_{p}) at temperatures (200 to 1800) K for PCPT 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. On the basis of the magnitude of the relative standard Gibbs free energy of formation ($\Delta_{R,f} G^{\Theta}$), the relative stability of PCPT isomers was theoretically proposed in this work and then compared with that of polychlorinated dibenzothiophene (PCDT) isomers.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) belong to the most often mentioned chemical pollutants because of their extreme toxicity and ubiquitous contamination in the global environment through atmospheric transport.[1] Polychlorinated thianthrenes (PCTAs), sulfur analogues of PCDDs, have also been observed in environmental samples.[2,3] Polychlorinated phenoxathiins (PCPTs) are also one group of chlorinated tricyclic aromatic heterocycles which can be considered a one-sulfur substituted compound of PCDDs or a one-oxygen substituted compound of PCTAs and are somewhat similar to polychlorinated dibenzothiophenes (PCDTs). The separation of PCPTs[4] has been studied with capillary gas chromatography/mass spectrometry (HRGC−MSD) although they have not yet been found in environmental samples. The structures and atom numbering of dibenzo-*p*-dioxin (DD), thianthrene (TA), phenoxathiin (PT), and dibenzothiophene (DT) are shown in Figure 1.

Thermodynamic properties (e.g., enthalpy of formation, $\Delta_f H$, and Gibbs free energy of formation, $\Delta_f G$) are important for studying the formation and distribution of dioxin and dioxin-like compounds. However, experimental values of thermodynamic properties for them are scarce due to limited availability of pure compounds and to experimental difficulties. Therefore, theoretical calculations are helpful for estimating the thermodynamic properties of them. Density functional theory (DFT) calculations have been performed on PCDDs,[5,6] PCTAs,[7] polychlorinated dibenzofurans (PCDFs),[8] polybrominated dibenzo-*p*-dioxins (PBDDs),[9] and polybrominated diphenyl ethers (PBDEs)[10] to obtain thermodynamic data of them. Although the thermodynamic properties of PT were studied experimentally,[11] to our knowledge, no studies of thermodynamic data for PCPTs have been reported.

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In this study, the thermodynamic properties (entropy (S^{Θ}), heat capacity at constant volume (C^{Θ}_{v}), heat capacity at constant pressure (C^{Θ}_{p}), enthalpy of formation ($\Delta_f H^{\Theta}$), and Gibbs free energy of formation ($\Delta_f G^{\Theta}$) in the ideal gas state at 298.15 K and 101.325 kPa) were computed for all 135 PCPTs using DFT. The purpose of this study is to obtain a set of thermodynamic values for PCPTs and to discuss the correlation of these thermodynamic properties with N_{PCS} and the temperature dependence of heat capacity at constant pressure (C^{Θ}_{p}). Furthermore, according to the magnitude of the relative standard Gibbs free energy of formation ($\Delta_{R,f} G^{\Theta}$), the theoretical relative stability order of the isomers was proposed.

Computational Method

The structure of phenoxathiin (PT) was studied previously using the X-ray[12] method and calculated using ab initio[13] or density functional theory (DFT)[14] methods. In this paper, the structure of PT was optimized at the DFT B3LYP/6-31G* level. It was found that the differences between measured and our calculated bond lengths are within 0.01 Å in general, and the calculated bond angles are in good agreement with X-ray results. Furthermore, we have calculated the values of $\Delta_r H^{\Theta}$ for the three reactions dibenzodioxin + dibenzothiophene → phenoxathiin + dibenzofuran, thianthrene + dibenzofuran → phenoxathiin + dibenzothiophene, and thianthrene + dibenzodioxin → 2phenoxathiin at the B3LYP/6-31G* level and compared them with experimental ones to test the feasibility of the method used by us. The calculated values of $\Delta_r H^{\Theta}$ are (11.81, −11.55, and 0.26) kJ·mol^{-1}, respectively, and the corresponding experimental ones are (19.01, 5.21, and 24.22) kJ·mol^{-1}, respectively. It can be seen that the calculated values of $\Delta_r H^{\Theta}$ are all less than the corresponding experimental ones, and the largest discrepancy of 23.96 kJ·mol^{-1} is for the third reaction. This result is satisfactory considering the fact that the third reaction is the sum of the other two reactions. To find a more accurate method, the values of $\Delta_r H^{\Theta}$ for these reactions have also been calculated at the B3LYP/6-311G** level, and the results [(11.58, −10.59,

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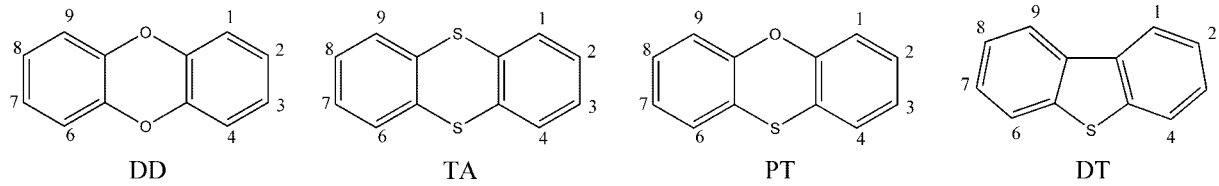

Figure 1. Molecular structures and atomic numbering of dibenzo-*p*-dioxin (DD), thianthrene (TA), phenoxathiin (PT), and dibenzothiophene (DT).

and 0.99) kJ·mol^{-1}] are very close to those at the B3LYP/6-31G* level. So, throughout this paper, geometry optimizations and energy calculations for all 135 PCPT molecules were performed at the B3LYP/6-31G* level with the Gaussian 98 program.[15] Frequency calculations were then carried out for all of the possible geometries to ensure they are minima 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. H^Θ and G^Θ were obtained in hartrees and then converted to kJ·mol^{-1} (1 hartree = 2625.50 kJ·mol^{-1}). As for the notation in this paper, PCPT congeners with one to eight chlorine atoms are represented by MCPT, DCPT, tri-CPT, TCPT, penta-CPT, hexa-CPT, hepta-CPT, and octa-CPT respectively. Prefix numbers represent the positions (see Figure 1) of chlorine substitution (e.g., 2,3,7,8-TCPT or simply 2,3,7,8-T).

Isodesmic reactions were used successfully to obtain thermodynamic data for PCDDs,[5,6] PBDDs,[9] and PBDEs[10] in previous studies. Similarly, isodesmic reaction 1 was designed to calculate $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$ of PCPTs in this study.

$$\text{phenoxathiin} + n\cdot\text{chlorobenzene} = \text{PCPT} + n\cdot\text{benzene} \quad (1)$$

The standard enthalpy change of the reaction ($\Delta_r H^\Theta$) 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

$$\Delta_r H^\Theta = [H^\Theta_{\text{PCPT}} + n\text{H}^\Theta_{\text{benzene}}] - [H^\Theta_{\text{phenoxathiin}} + nH^\Theta_{\text{chlorobenzene}}] \quad (2)$$

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

$$\Delta_r H^\Theta = [\Delta_f H^\Theta_{\text{PCPT}} + n\Delta_f H^\Theta_{\text{benzene}}] - [\Delta_f H^\Theta_{\text{phenoxathiin}} + n\Delta_f H^\Theta_{\text{chlorobenzene}}] \quad (3)$$

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

$$\Delta_f H^\Theta_{\text{PCPT}} = H^\Theta_{\text{PCPT}} + nH^\Theta_{\text{benzene}} - nH^\Theta_{\text{chlorobenzene}} - H^\Theta_{\text{phenoxathiin}} - n\Delta_f H^\Theta_{\text{benzene}} + n\Delta_f H^\Theta_{\text{chlorobenzene}} + \Delta_f H^\Theta_{\text{phenoxathiin}} \quad (4)$$

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

$$\Delta_f G^\Theta_{\text{PCPT}} = G^\Theta_{\text{PCPT}} + nG^\Theta_{\text{benzene}} - nG^\Theta_{\text{chlorobenzene}} - G^\Theta_{\text{phenoxathiin}} - n\Delta_f G^\Theta_{\text{benzene}} + n\Delta_f G^\Theta_{\text{chlorobenzene}} + \Delta_f G^\Theta_{\text{phenoxathiin}} \quad (5)$$

The experimental values of $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$ for phenoxathiin, chlorobenzene, and benzene taken from the literature[11,16] are listed in Table 1, which also presents the values of H^Θ and G^Θ calculated at the B3LYP/6-31G* level for these compounds.

Table 1. Experimental and Computed Thermodynamic Properties of the Substances in the Ideal Gas State at 298.15 K and 101.325 kPa[a]

	$\Delta_f H^\Theta$	$\Delta_f G^\Theta$	H^Θ	G^Θ
compound	kJ·mol^{-1}	kJ·mol^{-1}	hartree	hartree
phenoxathiin	61.55[b]	177.69[b]	−935.32436[d]	−935.37158[d]
benzene	82.92[c]	129.66[c]	−232.14258[d]	−232.17302[d]
chlorobenzene	51.10[c]	98.50[c]	−691.74731[d]	−691.78290[d]

[a] $\Delta_f H^\Theta$ is the standard enthalpy of formation of the compound; $\Delta_f G^\Theta$ is the standard Gibbs free energy of formation of the compound, H^Θ is the standard enthalpy; and G^Θ is the standard Gibbs free energy. [b] Taken from ref 11. [c] Taken from ref 16. [d] Obtained from B3LYP/6-31G* calculations.

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 position for these Cl atoms. The numbers of the positions of Cl substitution (PCS) are defined as follows: the number of chlorine atoms at positions 1 (1 and 9 being 1 positions), 2 (2 and 8 being 2 positions), 3 (3 and 7 being 3 positions), and 4 (4 and 6 being 4 positions) is defined as N_1, N_2, N_3, and N_4; the number of chlorine atom pairs at relative ortho, meta, and para positions is symbolized as N_o, N_m, and N_p, respectively. For 1,2,3,4,6,7,8,9-octa-CPT, N_1, N_2, N_3, N_4, N_o, N_m, and N_p equal 2, 2, 2, 2, 6, 4, and 2, 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,[17] N_{PCS} values were taken as theoretical descriptors to establish the correlation equations between the calculated thermodynamic properties and N_{PCS}. From these correlative equations, the main influencing factors on these thermodynamic properties can be found.

Results and Discussion

Relations of Thermodynamic Properties with N_{PCS}. The values of thermodynamic quantities (S^Θ, C^Θ_v, H^Θ, and G^Θ) calculated for 135 PCPTs in the ideal gas state at 298.15 K and 101.325 kPa are listed in Table 2 together with the values of $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$ calculated from eqs 4 and 5. The correlation equations of S^Θ, C^Θ_v, $\Delta_f H^\Theta$, and $\Delta_f G^\Theta$ with N_{PCS} were obtained using the GQSARF 2.0 program[17] 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 properties and N_{pcs} are very good due to the corresponding R^2 values very close to 1.000, which all clearly represent the influence of the number and position of chlorine substitution on these values. These equations with large R^2 show that thermodynamic properties have good relations with positions of Cl substitution (N_{PCS}) for PCPTs. (2) The higher the number of chlorine atoms is, the lower the value of $\Delta_f H^\Theta$ or $\Delta_f G^\Theta$ is. Furthermore, there is an order of the decrease at positions of $N_1 < N_4 < N_3 \approx N_2$. (3) Although the number of relative positions has only a slight influence on the values of S^Θ and $C_v{}^\Theta$ for PCPT congeners, they affect the values of $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$ remarkably. For example, if N_o is increased by one, the increase of $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$ can reach (12.66 and 13.14) kJ·mol^{-1}, respectively.

Table 2. Thermodynamic Properties of PCPTs from DFT Calculations and N_{PCS}

molecule	S^{Θ} J·mol^{-1}·K^{-1}	C^{Θ}_{v} J·mol^{-1}·K^{-1}	H^{Θ} hartree	G^{Θ} hartree	$\Delta_f H^{\Theta}$ kJ·mol^{-1}	$\Delta_f G^{\Theta}$ kJ·mol^{-1}	$\Delta_{R,f} G^{\Theta}$ kJ·mol^{-1}	N_1	N_2	N_3	N_4	N_o	N_m	N_p
PT	415.82	174.79	−935.32436	−935.37158	61.55	177.69	0	0	0	0	0	0	0	
					MCPT									
1	444.92	190.74	−1394.92451	−1394.97504	41.73	163.39	8.48	1	0	0	0	0	0	0
2	446.21	191.13	−1394.92760	−1394.97827	33.64	154.91	0.00	0	1	0	0	0	0	0
3	446.27	191.13	−1394.92732	−1394.97800	34.36	155.61	0.70	0	0	1	0	0	0	0
4	445.68	190.97	−1394.92548	−1394.97609	39.20	160.63	5.72	0	0	0	1	0	0	0
					DCPT									
1,2	473.87	206.63	−1854.52272	−1854.57653	27.04	154.26	20.95	1	1	0	0	1	0	0
1,3	475.32	207.10	−1854.52622	−1854.58020	17.84	144.62	11.31	1	0	1	0	0	1	0
1,4	475.30	207.00	−1854.52462	−1854.57859	22.06	148.84	15.54	1	0	0	1	0	0	1
1,6	475.39	206.99	−1854.52540	−1854.57938	20.00	146.76	13.46	1	0	0	1	0	0	0
1,7	475.34	207.07	−1854.52719	−1854.58117	15.30	142.08	8.77	1	0	1	0	0	0	0
1,8	475.24	207.03	−1854.52732	−1854.58129	14.96	141.77	8.46	1	1	0	0	0	0	0
1,9	474.34	206.71	−1854.52335	−1854.57721	25.39	152.46	19.16	2	0	0	0	0	0	0
2,3	474.79	206.96	−1854.52556	−1854.57948	19.57	146.51	13.20	0	1	1	0	1	0	0
2,4	475.87	207.30	−1854.52739	−1854.58143	14.78	141.40	8.09	0	1	0	1	0	1	0
2,6	476.11	207.30	−1854.52844	−1854.58251	12.02	138.56	5.26	0	1	0	1	0	0	0
2,7	476.25	207.41	−1854.53022	−1854.58431	7.33	133.84	0.53	0	1	1	0	0	0	0
2,8	476.34	207.39	−1854.53042	−1854.58451	6.83	133.31	0.00	0	2	0	0	0	0	0
3,4	474.78	206.94	−1854.52338	−1854.57729	25.31	152.25	18.94	0	0	1	1	1	0	0
3,6	476.30	207.34	−1854.52812	−1854.58221	12.85	139.34	6.03	0	0	1	1	0	0	0
3,7	476.33	207.42	−1854.52992	−1854.58401	8.14	134.62	1.32	0	0	2	0	0	0	0
4,6	475.98	207.21	−1854.52609	−1854.58014	18.20	144.78	11.48	0	0	0	2	0	0	0
					tri-CPT									
1,2,3	502.36	222.53	−2314.11954	−2314.17659	15.97	148.88	28.57	1	1	1	0	2	1	0
1,2,4	503.57	222.81	−2314.12175	−2314.17894	10.16	142.71	22.39	1	1	0	1	1	1	1
1,2,6	504.21	222.84	−2314.12343	−2314.18069	5.75	138.11	17.80	1	1	0	1	1	0	0
1,2,7	503.83	222.89	−2314.12515	−2314.18236	1.25	133.72	13.41	1	1	1	0	1	0	0
1,2,8	503.92	222.89	−2314.12527	−2314.18250	0.92	133.37	13.05	1	2	0	0	1	0	0
1,2,9	503.11	222.62	−2314.12124	−2314.17837	11.51	144.20	23.88	2	1	0	0	1	0	0
1,3,4	503.99	222.92	−2314.12152	−2314.17875	10.78	143.20	22.89	1	0	1	1	1	1	1
1,3,6	505.22	223.26	−2314.12682	−2314.18419	−3.14	128.92	8.61	1	0	1	1	0	1	0
1,3,7	505.62	223.38	−2314.12856	−2314.18598	−7.71	124.23	3.91	1	0	2	0	0	1	0
1,3,8	505.57	223.38	−2314.12873	−2314.18614	−8.14	123.81	3.49	1	1	1	0	0	1	0
1,3,9	504.82	223.10	−2314.12478	−2314.18210	2.23	134.40	14.09	2	0	1	0	0	1	0
1,4,6	504.87	223.14	−2314.12508	−2314.18241	1.43	133.59	13.27	1	0	0	2	0	0	1
1,4,7	505.41	223.25	−2314.12699	−2314.18439	−3.60	128.40	8.09	1	0	1	1	0	0	1
1,4,8	505.23	223.24	−2314.12722	−2314.18459	−4.19	127.87	7.55	1	1	0	1	0	0	1
1,4,9	504.77	222.98	−2314.12319	−2314.18051	6.40	138.59	18.28	2	0	0	1	0	0	1
2,3,4	503.11	222.80	−2314.12034	−2314.17748	13.87	146.55	26.24	0	1	1	1	2	1	0
2,3,6	504.88	223.13	−2314.12615	−2314.18349	−1.39	130.77	10.45	0	1	1	1	1	0	0
2,3,7	505.31	223.26	−2314.12791	−2314.18529	−6.00	126.03	5.72	0	1	2	0	1	0	0
2,3,8	505.06	223.22	−2314.12815	−2314.18550	−6.63	125.48	5.16	0	2	1	0	1	0	0
2,3,9	504.27	222.91	−2314.12507	−2314.18234	1.44	133.78	13.47	1	1	1	0	1	0	0
2,4,6	505.94	223.50	−2314.12779	−2314.18525	−5.70	126.15	5.83	0	1	0	2	0	1	0
2,4,7	506.50	223.63	−2314.12971	−2314.18723	−10.73	120.95	0.63	0	1	1	1	0	1	0
2,4,8	506.07	223.58	−2314.13000	−2314.18747	−11.49	120.32	0.00	0	2	0	1	0	1	0
2,4,9	505.37	223.26	−2314.12693	−2314.18432	−3.43	128.59	8.27	1	1	0	1	0	1	0
3,4,6	504.96	223.14	−2314.12378	−2314.18112	4.85	136.99	16.67	0	0	1	2	1	0	0
3,4,7	505.08	223.22	−2314.12576	−2314.18311	−0.35	131.75	11.43	0	0	2	1	1	0	0
3,4,8	504.73	223.17	−2314.12610	−2314.18342	−1.26	130.94	10.63	0	1	1	1	1	0	0
3,4,9	503.76	222.84	−2314.12312	−2314.18033	6.56	139.06	18.74	1	0	1	1	1	0	0
					TCPT									
1,2,3,4	530.49	238.33	−2773.71356	−2773.77380	12.27	150.98	42.65	1	1	1	1	3	2	1
1,2,3,6	532.05	238.68	−2773.72004	−2773.78046	−4.74	133.51	25.17	1	1	1	1	2	1	0
1,2,3,7	532.74	238.83	−2773.72171	−2773.78220	−9.12	128.92	20.58	1	1	2	0	2	1	0
1,2,3,8	532.49	238.79	−2773.72185	−2773.78232	−9.50	128.62	20.28	1	2	1	0	2	1	0
1,2,3,9	531.58	238.49	−2773.71795	−2773.77832	0.73	139.13	30.79	2	1	1	0	2	1	0
1,2,4,6	534.10	239.05	−2773.72205	−2773.78270	−10.03	127.61	19.27	1	1	0	2	1	1	1
1,2,4,7	533.84	239.12	−2773.72392	−2773.78454	−14.93	122.79	14.45	1	1	1	1	1	1	1
1,2,4,8	533.78	239.07	−2773.72408	−2773.78470	−15.37	122.37	14.03	1	2	0	1	1	1	1
1,2,4,9	533.02	238.79	−2773.72015	−2773.78068	−5.04	132.92	24.58	2	1	0	1	1	1	1
1,2,6,7	532.49	238.69	−2773.72098	−2773.78145	−7.22	130.90	22.56	1	1	1	1	2	0	0
1,2,6,8	533.63	239.06	−2773.72473	−2773.78533	−17.06	120.72	12.38	1	2	0	1	1	1	0
1,2,6,9	533.13	238.80	−2773.72105	−2773.78159	−7.41	130.52	22.18	2	1	0	1	1	0	1
1,2,7,8	532.82	238.78	−2773.72285	−2773.78335	−12.12	125.90	17.56	1	2	1	0	2	0	0
1,2,7,9	533.07	238.90	−2773.72256	−2773.78310	−11.37	126.57	18.24	2	1	1	0	1	1	0
1,2,8,9	531.71	238.43	−2773.71908	−2773.77946	−2.24	136.12	27.78	2	2	0	0	2	0	0
1,3,4,6	534.28	239.10	−2773.72176	−2773.78244	−9.27	128.31	19.97	1	0	1	2	1	1	1
1,3,4,7	533.82	239.14	−2773.72367	−2773.78429	−14.28	123.45	15.11	1	0	2	1	1	1	1
1,3,4,8	533.70	239.09	−2773.72391	−2773.78452	−14.91	122.85	14.51	1	1	1	1	1	1	1
1,3,4,9	533.07	238.83	−2773.72003	−2773.78057	−4.74	133.21	24.87	2	0	1	1	1	1	1
1,3,6,7	534.19	239.19	−2773.72428	−2773.78494	−15.88	121.73	13.39	1	0	2	1	1	1	0
1,3,6,8	535.17	239.53	−2773.72810	−2773.78887	−25.90	111.42	3.08	1	1	1	1	0	2	0

Table 2 Continued

molecule	S^Θ / J·mol^{-1}·K^{-1}	C^Θ_v / J·mol^{-1}·K^{-1}	H^Θ / hartree	G^Θ / hartree	$\Delta_f H^\Theta$ / kJ·mol^{-1}	$\Delta_f G^\Theta$ / kJ·mol^{-1}	$\Delta_{R,f} G^\Theta$ / kJ·mol^{-1}	N_1	N_2	N_3	N_4	N_o	N_m	N_p
1,3,6,9	534.46	239.26	−2773.72450	−2773.78519	−16.45	121.08	12.75	2	0	1	1	0	1	1
1,3,7,8	534.08	239.19	−2773.72624	−2773.78689	−21.03	116.62	8.28	1	1	2	0	1	1	0
1,3,7,9	534.48	239.35	−2773.72605	−2773.78674	−20.53	117.00	8.66	2	0	2	0	0	2	0
1,4,6,7	534.06	239.08	−2773.72256	−2773.78320	−11.36	126.30	17.96	1	0	1	2	1	0	1
1,4,6,8	535.52	239.47	−2773.72637	−2773.78719	−21.38	115.84	7.50	1	1	0	2	0	1	1
1,4,6,9	534.28	239.11	−2773.72277	−2773.78344	−11.91	125.67	17.34	2	0	0	2	0	0	2
1,4,7,8	534.08	239.09	−2773.72473	−2773.78538	−17.06	120.59	12.25	1	1	1	1	1	0	1
2,3,4,6	533.86	239.04	−2773.72059	−2773.78122	−6.20	131.51	23.18	0	1	1	2	2	1	0
2,3,4,7	533.36	239.08	−2773.72250	−2773.78307	−11.21	126.65	18.32	0	1	2	1	2	1	0
2,3,4,8	533.36	239.08	−2773.72280	−2773.78337	−12.01	125.85	17.51	0	2	1	1	2	1	0
2,3,4,9	532.57	238.75	−2773.71976	−2773.78024	−4.02	134.07	25.73	1	1	1	1	2	1	0
2,3,6,7	533.86	239.06	−2773.72363	−2773.78425	−14.17	123.54	15.21	0	1	2	1	2	0	0
2,3,6,8	534.95	239.43	−2773.72750	−2773.78825	−24.33	113.05	4.72	0	2	1	1	1	1	0
2,3,7,8	533.81	239.09	−2773.72567	−2773.78629	−19.52	118.20	9.86	0	2	2	0	2	0	0
2,4,6,7	535.10	239.43	−2773.72526	−2773.78603	−18.46	118.88	10.55	0	1	1	2	1	1	0
2,4,6,8	536.23	239.79	−2773.72915	−2773.79004	−28.67	108.34	0.00	0	2	0	2	0	2	0
3,4,6,7	533.79	239.02	−2773.72128	−2773.78190	−8.01	129.72	21.38	0	0	2	2	2	0	0
				penta-CPT										
1,2,3,4,6	560.40	254.48	−3233.31369	−3233.37733	−7.50	136.49	25.92	1	1	1	2	3	2	1
1,2,3,4,7	560.94	254.61	−3233.31554	−3233.37924	−12.34	131.49	20.91	1	1	2	1	3	2	1
1,2,3,4,8	560.73	254.59	−3233.31573	−3233.37941	−12.86	131.03	20.46	1	2	1	1	3	2	1
1,2,3,4,9	560.04	254.32	−3233.31183	−3233.37542	−2.60	141.50	30.92	2	1	1	1	3	2	1
1,2,3,6,7	560.84	254.57	−3233.31738	−3233.38107	−17.19	126.67	16.09	1	1	2	1	3	1	0
1,2,3,6,8	562.53	254.99	−3233.32113	−3233.38501	−27.02	116.33	5.75	1	2	1	1	2	2	0
1,2,3,6,9	561.76	254.71	−3233.31746	−3233.38125	−17.39	126.19	15.62	2	1	1	1	2	1	1
1,2,3,7,8	561.30	254.65	−3233.31925	−3233.38299	−22.10	121.62	11.05	1	2	2	0	3	1	0
1,2,3,7,9	561.69	254.80	−3233.31901	−3233.38279	−21.45	122.16	11.59	2	1	2	0	2	2	0
1,2,3,8,9	560.23	254.35	−3233.31552	−3233.37914	−12.30	131.74	21.16	2	2	1	0	3	1	0
1,2,4,6,7	562.06	254.83	−3233.31941	−3233.38324	−22.52	120.97	10.40	1	1	1	2	2	1	1
1,2,4,6,8	564.05	255.31	−3233.32315	−3233.38720	−32.33	110.57	0.00	1	2	0	2	1	2	1
1,2,4,6,9	562.68	254.94	−3233.31955	−3233.38345	−22.87	120.44	9.86	2	1	0	2	1	1	2
1,2,4,7,8	562.63	254.94	−3233.32146	−3233.38535	−27.90	115.43	4.85	1	2	1	1	2	1	1
1,2,4,7,9	563.18	255.10	−3233.32118	−3233.38513	−27.16	116.01	5.43	2	1	1	1	1	2	1
1,2,4,8,9	561.52	254.65	−3233.31775	−3233.38152	−18.15	125.51	14.93	2	2	0	1	2	1	1
1,3,4,6,7	562.97	254.98	−3233.31910	−3233.38303	−21.69	121.54	10.96	1	2	2	2	1	1	
1,3,4,6,8	564.29	255.38	−3233.32288	−3233.38696	−31.63	111.20	0.63	1	1	1	2	1	2	1
1,3,4,6,9	563.40	255.09	−3233.31927	−3233.38325	−22.14	120.96	10.39	2	0	1	2	1	1	2
1,3,4,7,8	562.88	255.01	−3233.32123	−3233.38515	−27.30	115.95	5.38	1	1	2	1	2	1	1
1,3,4,7,9	563.51	255.19	−3233.32099	−3233.38498	−26.65	116.41	5.84	2	0	2	1	1	2	1
1,3,4,8,9	561.58	254.66	−3233.31772	−3233.38149	−18.06	125.58	15.00	2	1	1	1	2	1	1
2,3,4,6,7	562.84	254.96	−3233.31794	−3233.38186	−18.65	124.61	14.04	0	1	2	2	3	1	0
2,3,4,6,8	563.80	255.32	−3233.32182	−3233.38585	−28.84	114.13	3.56	0	2	1	2	2	2	0
2,3,4,6,9	562.35	254.92	−3233.31909	−3233.38295	−21.67	121.74	11.17	1	1	1	2	2	1	1
2,3,4,7,8	562.30	254.93	−3233.32017	−3233.38402	−24.50	118.92	8.35	0	2	2	1	3	1	0
2,3,4,7,9	562.47	255.05	−3233.32077	−3233.38464	−26.08	117.30	6.72	1	1	2	1	2	2	0
2,3,4,8,9	560.77	254.54	−3233.31745	−3233.38113	−17.37	126.51	15.93	1	2	1	1	3	1	0
				hexa-CPT										
1,2,3,4,6,7	589.48	270.41	−3692.91093	−3692.97787	−19.66	129.85	14.33	1	1	2	2	4	2	1
1,2,3,4,6,8	590.57	270.77	−3692.91470	−3692.98176	−29.55	119.64	4.12	1	2	1	2	3	3	1
1,2,3,4,6,9	589.78	270.49	−3692.91112	−3692.97809	−20.15	129.28	13.75	2	1	1	2	3	2	2
1,2,3,4,7,8	589.33	270.42	−3692.91299	−3692.97992	−25.07	124.48	8.96	1	2	2	1	4	2	1
1,2,3,4,7,9	589.77	270.58	−3692.91280	−3692.97977	−24.55	124.87	9.34	2	1	2	1	3	3	1
1,2,3,4,8,9	588.17	270.11	−3692.90940	−3692.97620	−15.65	134.25	18.73	2	2	1	1	4	2	1
1,2,3,6,7,8	589.64	270.48	−3692.91373	−3692.98069	−27.02	122.44	6.92	1	2	2	1	4	2	0
1,2,3,6,7,9	590.27	270.60	−3692.91393	−3692.98096	−27.54	121.73	6.21	2	1	2	1	3	2	1
1,2,3,6,8,9	589.81	270.51	−3692.91414	−3692.98112	−28.09	121.32	5.80	2	2	1	1	3	2	1
1,2,3,7,8,9	588.53	270.23	−3692.91192	−3692.97875	−22.25	127.54	12.02	2	2	2	0	4	2	0
1,2,4,6,7,8	591.28	270.81	−3692.91576	−3692.98290	−32.33	116.65	1.13	1	2	1	2	3	2	1
1,2,4,6,7,9	591.37	270.85	−3692.91598	−3692.98314	−32.92	116.02	0.50	2	1	1	2	2	2	2
1,2,4,6,8,9	591.42	270.82	−3692.91617	−3692.98333	−33.41	115.52	0.00	2	2	0	2	2	2	2
1,3,4,6,7,8	591.22	270.83	−3692.91549	−3692.98263	−31.62	117.37	1.85	1	1	2	2	3	2	1
1,3,4,6,7,9	591.77	270.92	−3692.91580	−3692.98300	−32.45	116.38	0.86	2	0	2	2	2	2	2
2,3,4,6,7,8	590.90	270.80	−3692.91442	−3692.98152	−28.81	120.28	4.75	0	2	2	2	4	2	0
				hepta-CPT										
1,2,3,4,6,7,8	617.96	286.27	−4152.50722	−4152.57740	−29.33	125.88	1.19	1	2	2	2	5	3	1
1,2,3,4,6,7,9	618.84	286.43	−4152.50743	−4152.57770	−29.87	125.08	0.39	2	1	2	2	4	3	2
1,2,3,4,6,8,9	618.45	286.34	−4152.50762	−4152.57785	−30.37	124.69	0.00	2	2	1	2	4	3	2
1,2,3,4,7,8,9	616.93	286.03	−4152.50560	−4152.57566	−25.07	130.45	5.76	2	2	2	1	5	3	1
				octa-CPT										
1,2,3,4,6,7,8,9	645.09	301.82	−4612.09911	−4612.17236	−27.43	133.88	0.00	2	2	2	2	6	4	2

Temperature Dependence of Heat Capacity at Constant Pressure (C^Θ_p). To our knowledge, the values of C^Θ_p at different temperatures for PCPT congeners have not been reported. So the values of C^Θ_p were calculated using a statistical thermodynamics calculation program at temperatures (200 to 1800) K based on the Gaussian output files; however, these C^Θ_p

Table 3. Correlation Equations of Thermodynamic Properties with N_{PCS}, the Squared Correlation Coefficient (R^2), and the Standard Error (SE) of the Correlation Equations

property	unit	equation	R^2	SE
S^Θ	$J\cdot mol^{-1}\cdot K^{-1}$	$S^\Theta = 415.757 + 29.283N_1 + 30.232N_2 + 30.3787N_3 + 30.215N_4 - 1.602N_o - 0.203N_m - 0.118N_p$	1.000	0.209
$C^\Theta{}_v$	$J\cdot mol^{-1}\cdot K^{-1}$	$C^\Theta{}_V = 174.824 + 15.955N_1 + 16.255N_2 + 16.297N_3 + 16.210N_4 - 0.411N_o + 0.018N_m - 0.019N_p$	1.000	0.030
Δ_fH^Θ	$kJ\cdot mol^{-1}$	$\Delta_fH^\Theta = 57.469 - 16.132N_1 - 26.298N_2 - 25.698N_3 - 19.629N_4 + 12.659N_o + 3.008N_m$	0.996	1.22
Δ_fG^Θ	$kJ\cdot mol^{-1}$	$\Delta_fG^\Theta = 174.675 - 11.721N_1 - 21.120N_2 - 20.564N_3 - 15.495N_4 + 13.137N_o + 3.068N_m + 2.133N_p$	0.994	0.93

values are not listed in the paper because of the length of the article and are given in the Supporting Information.

On the basis of the calculated values of $C^\Theta{}_p$ of all PCPTs at different temperatures, the relations between $C^\Theta{}_p$ and temperature were obtained using the least-squares method and are listed in Table 4. *A* is a constant, and *B*, *C*, and *D* are regression coefficients. The following conclusions can be drawn: (1) There are very good relationships between $C^\Theta{}_p$ and temperature (*T*, 1/*T*, and $1/T^2$) for almost all PCPT congeners. The correlation coefficients (R^2) are all equal to 1.000, and the standard errors (SE) are all low, which indicates that the calculated $C^\Theta{}_p$ values in this study can be used to predict $C^\Theta{}_p$ of PCPTs at different temperatures. Moreover, the standard error (SE) values decrease with the increasing number of Cl atoms. (2) For the same isomer group, the $C^\Theta{}_p$ 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. Although it is estimated that the uncertainties of the calculated values for Δ_fG^Θ are about 10 $kJ\cdot mol^{-1}$, they are approximately uniform for all isomers. So, based on the lowest Δ_fG^Θ in each PCPT isomer group, the relative standard Gibbs free energies of formation ($\Delta_{R,f}G^\Theta$) of PCPTs 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 PCPTs 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 DCPTs, tri-CPTs, TCPTs, penta-CPTs, hexa-CPTs, and hepta-CPTs 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 MCPTs, the 1-MCPT isomer is less stable than the 2-MCPT by an amount of 8.48 $kJ\cdot mol^{-1}$. For DCPTs, the 2,8-DCPT is the most stable, while the 1,2-DCTA is the least stable with a difference of 20.95 $kJ\cdot mol^{-1}$ in their values of Gibbs free energy. Similarly, the 2,4,8-, 2,4,6,8-, 1,2,4,6,8-, 1,2,4,6,8,9-, and 1,2,3,4,6,8,9- are the most stable isomers with differences of (28.57, 42.65, 30.92, 18.73, and 5.76) $kJ\cdot mol^{-1}$ from the least stable isomers 1,2,3-, 1,2,3,4-, 1,2,3,4,9-, 1,2,3,4,8,9-, and 1,2,3,4,7,8,9- for tri-CPTs, TCPTs, penta-CPTs, hexa-CPTs, and hepta-CPTs, 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 PCPTs apart from the associated electrostatic effects. Furthermore, it was found that the differences of Δ_fG^Θ in each PCPT isomer group are mainly due to the differences of Δ_fH^Θ, since the largest differences of Δ_fH^Θ in MCPTs, DCPTs, tri-CPTs, TCPTs, penta-CPTs, hexa-CPTs, and hepta-CPTs are (8.10, 20.22, 27.47, 40.93, 29.73, 17.76, and 5.30) $kJ\cdot mol^{-1}$, respectively, while the corresponding differences of TS^Θ in these isomer groups are only (0.38, 0.73, 1.10, 1.72, 1.19, 0.97, and 0.46) $kJ\cdot mol^{-1}$, respectively. The differences of Δ_fG^Θ, Δ_fH^Θ, and TS^Θ are all listed in Table 5 for comparison.

Comparison with PCDTs. Unlike PCDDs and PCTAs which both have 75 different isomers, PCPTs have 135 different isomers. So in this work, the relative stability of isomer groups of PCPTs is compared with that of isomer groups of PCDTs reported recently.[18] The most stable isomers and the least stable ones in each isomer group for PCPTs and PCDTs are listed in Table 5. Seemingly, most stable isomers are consistent in two congeners only for isomers with four chlorine atoms; however, two classes of compounds have the common character that the most stable isomers have no or the minimum number of nearest chlorine atoms. Furthermore, careful observation of Table 2 can lead to the result that the most stable isomers in PCDTs are the second, the third, or the fourth stable isomers in PCPTs, and the mean value of the differences of their Gibbs free energies with that of most stable isomers is only 1.05 $kJ\cdot mol^{-1}$. As for the least stable isomers, they are all those with chlorine atoms located on near positions in DCPTs, tri-CPTs, TCPTs, penta-CPTs, hexa-CPTs, and hepta-CPTs, and by comparison, they are all those with chlorine atoms attached to 1, 9 simultaneously in DCDTs, tri-CDTs, TCDTs, penta-CDTs, hexa-CDTs, and hepta-CDTs. This is because the distances between 1 and 9 carbon atoms and hence the distances between chlorine atoms at 1 and 9 positions in PCDTs are much shorter than those in PCPTs. Consequently, the repulsion effects of Cl atom substituents at the 1 and 9 positions in PCDTs are more remarkable. For instance, the distance of Cl atoms (3.139 Å) for 1,9-DCDT is much shorter than that of 1,9-DCPT (4.160 Å), while the distance between 1 and 9 carbon atoms (3.458 Å) for 1,9-DCDT is also much shorter than that of 1,9-DCPT (4.542 Å).

Conclusion

The structures of 135 PCPT molecules were fully optimized at the B3LYP/6-31G* level, and the entropy (S^Θ), heat capacity at constant volume ($C^\Theta{}_v$), enthalpy (H^Θ), and Gibbs free energy (G^Θ) of them were consequently obtained. The standard enthalpy of formation (Δ_fH^Θ) and the standard Gibbs free energy of formation (Δ_fG^Θ) were obtained by designing isodesmic reactions. The results showed that S^Θ, $C^\Theta{}_v$, Δ_fH^Θ, and Δ_fG^Θ are all greatly dependent on the number and position of chlorine substitution (N_{PCS}). According to the magnitude of the relative standard Gibbs energy of formation ($\Delta_{R,f}G^\Theta$), the relative stability order of the isomers in each isomer group was determined. The temperature dependence relation of heat

Table 4. Temperature Dependence of Heat Capacity at Constant Pressure and the Standard Error (SE) of the Correlation Equations

	$C^{\Theta}_p = A + BT + CT^{-1} + DT^{-2}$						$C^{\Theta}_p = A + BT + CT^{-1} + DT^{-2}$				
	A	*B*	*C*	*D*			*A*	*B*	*C*	*D*	
molecule	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-2}	10^{5}J·mol^{-1}	10^{7}J·mol^{-1}·K	SE	molecule	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-2}	10^{5}J·mol^{-1}	10^{7}J·mol^{-1}·K	SE
PT	562.37	0.006619	−1.6191	1.5027	1.64						
MCPT											
1	569.45	0.003018	−1.5646	1.4293	1.47	3	569.20	0.003051	−1.5609	1.4241	1.46
2	569.23	0.003033	−1.5610	1.4241	1.45	4	569.41	0.002983	−1.5624	1.4256	1.45
DCPT											
1,2	576.97	−0.00072	−1.5121	1.3582	1.30	2,4	576.58	−0.00067	−1.5067	1.3516	1.28
1,3	576.59	−0.00063	−1.5085	1.3548	1.29	2,6	576.37	−0.00062	−1.5045	1.3470	1.27
1,4	576.70	−0.00065	−1.5091	1.3547	1.29	2,7	576.17	−0.00055	−1.5032	1.3457	1.28
1,6	576.58	−0.00063	−1.5079	1.3524	1.29	2,8	576.24	−0.00058	−1.5035	1.3461	1.28
1,7	576.37	−0.00056	−1.5065	1.3506	1.29	3,4	576.85	−0.00072	−1.5091	1.3535	1.28
1,8	576.46	−0.00059	−1.5070	1.3511	1.29	3,6	576.32	−0.00060	−1.5042	1.3469	1.28
1,9	576.68	−0.00062	−1.5104	1.3561	1.30	3,7	576.10	−0.00052	−1.5029	1.3453	1.28
2,3	576.64	−0.00063	−1.5086	1.3534	1.29	4,6	576.52	−0.00066	−1.5055	1.3480	1.27
tri-CPT											
1,2,3	584.61	−0.00448	−1.4608	1.2897	1.14	1,4,9	583.94	−0.00429	−1.4551	1.2821	1.14
1,2,4	584.44	−0.00445	−1.4589	1.2880	1.13	2,3,4	584.53	−0.00450	−1.4583	1.2857	1.12
1,2,6	584.12	−0.00437	−1.4556	1.2815	1.12	2,3,6	583.81	−0.00430	−1.4522	1.2765	1.12
1,2,7	583.94	−0.00431	−1.4544	1.2796	1.13	2,3,7	583.58	−0.00422	−1.4506	1.2748	1.12
1,2,8	584.03	−0.00435	−1.4548	1.2803	1.12	2,3,8	583.67	−0.00426	−1.4511	1.2751	1.12
1,2,9	584.23	−0.00437	−1.4578	1.2849	1.14	2,3,9	583.85	−0.00426	−1.4542	1.2799	1.13
1,3,4	584.35	−0.00442	−1.4579	1.2868	1.13	2,4,6	583.72	−0.00432	−1.4501	1.2744	1.10
1,3,6	583.76	−0.00428	−1.4523	1.2782	1.12	2,4,7	583.54	−0.00426	−1.4487	1.2729	1.10
1,3,7	583.54	−0.00421	−1.4508	1.2764	1.12	2,4,8	583.60	−0.00428	−1.4492	1.2735	1.10
1,3,8	583.63	−0.00425	−1.4510	1.2766	1.12	2,4,9	583.82	−0.00430	−1.4526	1.2788	1.12
1,3,9	583.80	−0.00425	−1.4541	1.2814	1.13	3,4,6	583.98	−0.00437	−1.4525	1.2763	1.11
1,4,6	583.84	−0.00430	−1.4528	1.2779	1.12	3,4,7	583.79	−0.00430	−1.4514	1.2751	1.11
1,4,7	583.64	−0.00424	−1.4514	1.2764	1.13	3,4,8	583.85	−0.00433	−1.4518	1.2755	1.11
1,4,8	583.72	−0.00427	−1.4518	1.2769	1.12	3,4,9	584.06	−0.00435	−1.4553	1.2808	1.13
TCPT											
1,2,3,4	592.68	−0.00840	−1.4118	1.2240	0.98	1,3,6,7	591.21	−0.00799	−1.3991	1.2061	0.97
1,2,3,6	591.82	−0.00815	−1.4047	1.2133	0.97	1,3,6,8	591.00	−0.00795	−1.3970	1.2045	0.96
1,2,3,7	591.61	−0.00809	−1.4030	1.2112	0.97	1,3,6,9	591.08	−0.00792	−1.3991	1.2073	0.98
1,2,3,8	591.72	−0.00813	−1.4036	1.2118	0.97	1,3,7,8	591.05	−0.00792	−1.3986	1.2057	0.97
1,2,3,9	591.90	−0.00813	−1.4067	1.2163	0.98	1,3,7,9	591.00	−0.00791	−1.3985	1.2071	0.97
1,2,4,6	591.58	−0.00809	−1.4023	1.2110	0.97	1,4,6,7	591.27	−0.00800	−1.3995	1.2058	0.97
1,2,4,7	591.40	−0.00804	−1.4010	1.2093	0.97	1,4,6,8	591.07	−0.00797	−1.3973	1.2042	0.96
1,2,4,8	591.49	−0.00807	−1.4016	1.2101	0.97	1,4,6,9	591.19	−0.00795	−1.4000	1.2079	0.98
1,2,4,9	591.69	−0.00808	−1.4048	1.2150	0.98	1,4,7,8	591.14	−0.00794	−1.3993	1.2060	0.98
1,2,6,7	591.62	−0.00809	−1.4030	1.2097	0.97	2,3,4,6	591.68	−0.00816	−1.4015	1.2084	0.96
1,2,6,8	591.38	−0.00805	−1.4006	1.2080	0.97	2,3,4,7	591.48	−0.00808	−1.4005	1.2071	0.96
1,2,6,9	591.51	−0.00804	−1.4029	1.2111	0.98	2,3,4,8	591.56	−0.00812	−1.4008	1.2075	0.96
1,2,7,8	591.40	−0.00801	−1.4018	1.2087	0.98	2,3,4,9	591.74	−0.00812	−1.4041	1.2127	0.97
1,2,7,9	591.40	−0.00801	−1.4020	1.2104	0.98	2,3,6,7	591.25	−0.00800	−1.3990	1.2043	0.97
1,2,8,9	591.81	−0.00811	−1.4057	1.2138	0.98	2,3,6,8	591.03	−0.00796	−1.3966	1.2025	0.96
1,3,4,6	591.47	−0.00806	−1.4014	1.2098	0.97	2,3,7,8	591.10	−0.00794	−1.3984	1.2039	0.97
1,3,4,7	591.33	−0.00801	−1.4005	1.2085	0.97	2,4,6,7	591.19	−0.00804	−1.3969	1.2023	0.95
1,3,4,8	591.39	−0.00804	−1.4009	1.2090	0.97	2,4,6,8	590.97	−0.00800	−1.3948	1.2009	0.94
1,3,4,9	591.62	−0.00806	−1.4042	1.2141	0.98	3,4,6,7	591.42	−0.00807	−1.3995	1.2043	0.96
penta-CPT											
1,2,3,4,6	599.86	−0.01205	−1.3556	1.1474	0.83	1,2,4,7,9	598.89	−0.01174	−1.3490	1.1406	0.84
1,2,3,4,7	599.67	−0.01200	−1.3542	1.1457	0.83	1,2,4,8,9	599.27	−0.01184	−1.3525	1.1439	0.84
1,2,3,4,8	599.74	−0.01203	−1.3545	1.1459	0.83	1,3,4,6,7	598.95	−0.01177	−1.3485	1.1379	0.83
1,2,3,4,9	599.93	−0.01204	−1.3576	1.1510	0.84	1,3,4,6,8	598.78	−0.01175	−1.3463	1.1363	0.82
1,2,3,6,7	599.28	−0.01186	−1.3517	1.1412	0.84	1,3,4,6,9	598.87	−0.01172	−1.3487	1.1396	0.84
1,2,3,6,8	599.05	−0.01182	−1.3492	1.1392	0.83	1,3,4,7,8	598.83	−0.01172	−1.3481	1.1377	0.84
1,2,3,6,9	599.17	−0.01181	−1.3515	1.1423	0.84	1,3,4,7,9	598.78	−0.01170	−1.3480	1.1394	0.84
1,2,3,7,8	599.14	−0.01181	−1.3509	1.1405	0.84	1,3,4,8,9	599.20	−0.01181	−1.3520	1.1431	0.84
1,2,3,7,9	599.10	−0.01180	−1.3509	1.1420	0.84	2,3,4,6,7	599.13	−0.01186	−1.3484	1.1363	0.82
1,2,3,8,9	599.49	−0.01190	−1.3544	1.1452	0.84	2,3,4,6,8	598.91	−0.01182	−1.3462	1.1347	0.81
1,2,4,6,7	599.08	−0.01181	−1.3499	1.1397	0.83	2,3,4,6,9	599.04	−0.01180	−1.3491	1.1385	0.83
1,2,4,6,8	598.86	−0.01178	−1.3472	1.1376	0.82	2,3,4,7,8	599.00	−0.01180	−1.3482	1.1365	0.83
1,2,4,6,9	598.95	−0.01174	−1.3498	1.1410	0.84	2,3,4,7,9	598.96	−0.01179	−1.3484	1.1381	0.83
1,2,4,7,8	598.92	−0.01175	−1.3489	1.1388	0.84	2,3,4,8,9	599.34	−0.01188	−1.3522	1.1418	0.83
hexa-CPT											
1,2,3,4,6,7	607.34	−0.01578	−1.3025	1.0751	0.72	1,2,3,6,8,9	607.00	−0.01563	−1.3015	1.0755	0.73
1,2,3,4,6,8	607.12	−0.01574	−1.3003	1.0736	0.71	1,2,3,7,8,9	607.20	−0.01569	−1.3032	1.0766	0.73
1,2,3,4,6,9	607.22	−0.01571	−1.3026	1.0768	0.73	1,2,4,6,7,8	606.81	−0.01561	−1.2986	1.0713	0.72
1,2,3,4,7,8	607.21	−0.01571	−1.3022	1.0751	0.72	1,2,4,6,7,9	606.65	−0.01553	−1.2987	1.0729	0.73
1,2,3,4,7,9	607.16	−0.01570	−1.3021	1.0766	0.72	1,2,4,6,8,9	606.74	−0.01556	−1.2994	1.0739	0.73
1,2,3,4,8,9	607.54	−0.01580	−1.3056	1.0800	0.73	1,3,4,6,7,8	606.74	−0.01559	−1.2980	1.0703	0.72
1,2,3,6,7,8	607.03	−0.01567	−1.3008	1.0731	0.72	1,3,4,6,7,9	606.55	−0.01550	−1.2979	1.0718	0.73
1,2,3,6,7,9	606.87	−0.01559	−1.3005	1.0742	0.73	2,3,4,6,7,8	606.87	−0.01566	−1.2978	1.0685	0.71
hepta-CPT											
1,2,3,4,6,7,8	615.11	−0.01959	−1.2520	1.0076	0.64	1,2,3,4,6,8,9	615.04	−0.01953	−1.2525	1.0101	0.65
1,2,3,4,6,7,9	614.91	−0.01949	−1.2514	1.0086	0.65	1,2,3,4,7,8,9	615.24	−0.01958	−1.2543	1.0113	0.65
octa-CPT											
1,2,3,4,6,7,8,9	623.29	−0.02349	−1.2054	0.9457	0.63						

Table 5. Most Stable and Least Stable Isomers in Different Isomer Groups for PCPTs and PCDTs and the Differences of $\Delta_f G^\ominus$, $\Delta_f H^\ominus$, and $TS^\ominus$ ($\Delta(\Delta_f G^\ominus)$, $\Delta(\Delta_f H^\ominus)$ and $\Delta(TS^\ominus)$) between the Most Stable and the Least Stable Isomers for PCPTs

			$\Delta(\Delta_f G^\ominus)$	$\Delta(\Delta_f H^\ominus)$	$\Delta(TS^\ominus)$
substance	most stable isomer	least stable isomer	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
MCPT	2-	1-	8.48	8.10	0.38
DCPT	2,8-	1,2-	20.95	20.22	0.73
tri-CPT	2,4,8-	1,2,3-	28.57	27.47	1.10
TCPT	2,4,6,8-	1,2,3,4-	42.65	40.93	1.72
penta-CPT	1,2,4,6,8-	1,2,3,4,9-	30.92	29.73	1.19
hexa-CPT	1,2,4,6,8,9-	1,2,3,4,8,9-	18.73	17.76	0.97
hepta-CPT	1,2,3,4,6,8,9-	1,2,3,4,7,8,9-	5.76	5.30	0.46
MCDT	3-	1-			
DCDT	3,7-	1,9-			
tri-CDT	2,4,7-	1,2,9-			
TCDT	2,4,6,8-	1,2,8,9-			
penta-CDT	1,3,4,6,8-	1,2,3,4,9-			
hexa-CDT	1,3,4,6,7,8-	1,2,3,4,8,9-			
hepta-CDT	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-			

capacity at constant pressure ($C^\ominus_p$) was also obtained. The values of $C^\ominus_p$ for the complete set of 135 PCPT congeners provided by this work should be valuable in further thermodynamics studies.

Supporting Information Available:

The values of $C^\ominus_p$ at temperatures (200 to 1800) K for PCPT congeners. This material is available free of charge via the Internet at http://pubs.acs.org.

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