

Research Article

DFT Calculation on 76 Polychlorophenazines: Their Thermodynamic Function and Implication of Cl Substituted Position

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Thermodynamic functions, including enthalpy (H^θ) and entropy (S^θ) for 76 polychlorophenazines (PCPZs) in the gas state at 298.15 K and 101.325 kPa, have been calculated using the B3LYP/6-31G* level with Gaussian 03 program, and considered on solvation affects. Total free energy in water (G_w) was calculated with the same program. Based on these data, the isodesmic reactions were designed to calculate the standard formation heat ($\Delta_f H^\theta$) and standard free energy of formation in water ($\Delta_f G_w^\theta$). The dependences of these thermodynamic parameters on the numbers and positions of chlorine substitution (N_{PCS}) were discussed. It is suggested that S^θ , $\Delta_f H^\theta$, and $\Delta_f G_w^\theta$ of PCPZs varied greatly with N_{PCS} . Moreover, the values of molar heat capacity at constant pressure ($C_{p,m}$) from 200 to 1800 K for PCPZ congeners were calculated using a statistical thermodynamics calculation program based on Gaussian output files, and the temperature-dependence relation of $C_{p,m}$ was obtained using the least-squares method. In addition, according to the relative magnitude of their $\Delta_f G_w^\theta$, the relative stability order of PCPZ congeners was theoretically proposed.

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1. Introduction

Phenazine (PZ) shows properties of a wide range in significant applications [1, 2]. Natural and synthetic phenazines have attracted considerable attention because of their interesting biological activities [3], that is, antibiotic and anticancer agents [4, 5]. Halosubstituted phenazines are useful as herbicides [6]. Because of their increasing dosage of chlorophenazines in recent years, their concentrations in the environment have also increased. Using the in vitro bioassay for dioxin-like activity showed that TBPZ has an ED_{50} of 10^{-7} M [7]. It can draw the conclusion that polychlorophenazines also have dioxin-like activity. For studying their generation, degradation, and environmental risk, it is important to know the thermodynamic properties of PCPZs. In addition, solvation has huge effect on organic reactivity/stability, and these studies were reported previously. For example, Warshel [8] studied computer modeling of chemical reactions in enzymes and solutions; Bren et al.

[9] studied the reaction between chloroethylene oxide and guanine; Kranjc and Mavri [10] reported the calculations of the activation free energy for a chemical reaction between ethylene oxide and guanine; Florián and Warshel [11] calculated chemical processes in aqueous solution using a new parameterization of the Langevin dipole (LD) model.

We have studied the thermodynamic properties for PCDFs, PCPTs, PBDF, PBNs and PCDTs [12–16]. The purpose of the study was to calculate the thermodynamic properties for 76 PCPZs. And considered on solvation affects, total free energy in water (G_w) was calculated with the same program. Then, the relationship between these parameters and the numbers and positions of chlorine substitution (N_{PCS}) were studied. By designing isodesmic reactions, the standard enthalpies of formation ($\Delta_f H^\theta$) and the standard Gibbs energies of formation in water ($\Delta_f G_w^\theta$) for all PCPZs were also obtained. On the basis of the relative magnitude of their $\Delta_f G_w^\theta$, the relative stability order of PCPZ congeners was theoretically proposed and then compared with that of

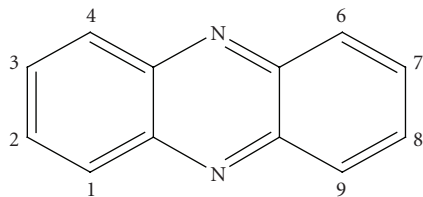


FIGURE 1: The numbering of the C-atoms.

polychlorinated dibenzo-p-dioxin (PCDD) isomers. Finally, the $C_{p,m}$ values of PCPZ congeners were calculated using statistical thermodynamics calculation program at 200–1800 K.

2. Computational Methods

With Gaussian 03 program [17], geometry optimizations were performed at the B3LYP/6-31G* level at the state of 298.15 K and 101.325 kPa. And considered on solvation affects, total free energy in water (G_w) was calculated with the same program. In terms of the numbers and different positions of constituted chlorine atoms, there are 76 possible structural patterns of PCPZs. Standard enthalpies (H^θ), total free energy in water (G), and standard entropy (S^θ) for 76 PCPZs were obtained from the Gaussian output files. As for the notation in this paper, PCPZ congeners with one to eight chlorine atoms are represented by MCPZ, DCPZ, Tri-CPZ, TCPZ, Penta-CPZ, Hexa-CPZ, Hepta-CPZ, and Octa-CPZ, respectively. Prefix numbers represent the positions (see Figure 1) of chlorine substitution (e.g., 2,3,7,8-TCPZ or simply 2,3,7,8-).

Lee et al. [18] used the isodesmic reaction to calculate the $\Delta_f H$ and $\Delta_f G$ of PCDDs and obtained results consistent to experimental results. So it seems reasonable to expect that estimates of the thermodynamic properties of PCPZs, from DFT calculations based on isodesmic reactions, will be similarly accurate.

In this study, reaction 1 was designed for calculating $\Delta_f H^\theta$ and $\Delta_f G^\theta$:

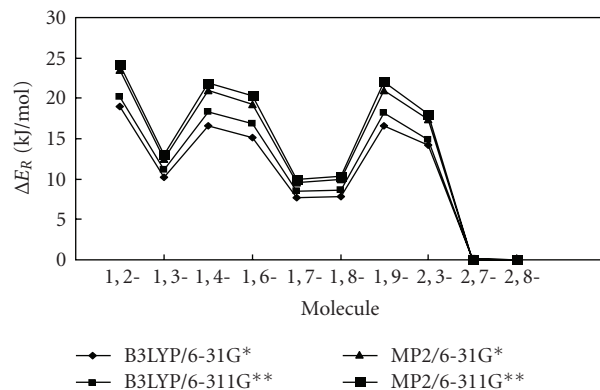
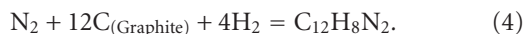


From the reaction above, $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of PCPZs can be obtained, as follows:

$$\begin{aligned} \Delta_f H_{\text{PCPZ}}^\theta &= H_{\text{PCPZ}}^\theta + nH_{\text{benzene}}^\theta - nH_{\text{chlorobenzene}}^\theta - H_{\text{PZ}}^\theta \\ &\quad - n\Delta_f H_{\text{benzene}}^\theta + n\Delta_f H_{\text{chlorobenzene}}^\theta + \Delta_f H_{\text{PZ}}^\theta, \end{aligned} \quad (2)$$

$$\begin{aligned} \Delta_f G_{\text{PCPZ}}^\theta &= G_{\text{PCPZ}}^\theta + nG_{\text{benzene}}^\theta - nG_{\text{chlorobenzene}}^\theta - G_{\text{PZ}}^\theta \\ &\quad - n\Delta_f G_{\text{benzene}}^\theta + n\Delta_f G_{\text{chlorobenzene}}^\theta + \Delta_f G_{\text{PZ}}^\theta. \end{aligned} \quad (3)$$

Equation (4) was used to calculate $\Delta_f G^\theta(\text{PZ})$:

FIGURE 2: The change tendency of ΔE for Di-PZs at different levels.

Then

$$\begin{aligned} \Delta_r S^\theta &= S_{(\text{PZ})}^\theta - S_{(\text{N}_2)}^\theta - 12S_{(\text{C})}^\theta - 4S_{(\text{H}_2)}^\theta, \\ \Delta_r H^\theta &= \Delta_f H_{(\text{PZ})}^\theta - \Delta_f H_{(\text{N}_2)}^\theta - 12\Delta_f H_{(\text{C})}^\theta - 4\Delta_f H_{(\text{H}_2)}^\theta = \Delta_f H_{(\text{PZ})}^\theta, \\ \Delta_f G_{(\text{PZ})}^\theta &= \Delta_r H_{(\text{PZ})}^\theta - T\Delta_r S_{(\text{PZ})}^\theta. \end{aligned} \quad (5)$$

The experimental and calculated values of $\Delta_f H^\theta$, $\Delta_f G^\theta$, H^θ , G^θ , and S^θ for benzene, chlorobenzene, phenazine, graphite, nitrogen, and hydrogen are listed in Table 1.

3. Results and Discussions

In this work, the general structure of PZ is shown in Figure 1, and the numbering of the C-atoms in the phenyl rings is indicated. The numbers of chlorine atoms at positions 1(4, 6, 9) and 2(3, 7, 8) are defined as N_α and N_β , the pair numbers of chlorine at positions 1, 9 or 4, 6 are defined as $N_{1,9}$; the pair numbers of chlorine at ortho-, meta-, and para-positions are defined as N_o , N_m , and N_p , respectively. Moreover, the parameters mentioned above are defined as a general designation N_{PCS} .

3.1. Comparison of the Calculated Results at Different Levels

The S^θ of PZ, Mono-PZs, and Di-PZs were also calculated at the B3LYP/6-311G** level, and listed in Table 2. Seen from Table 2, the differences of S^θ between the calculated results at two different levels were small, in which the maximum discrepancy of S^θ is only $0.18 \text{ J} \cdot (\text{mol} \cdot \text{K})^{-1}$. Moreover, the values of E for ten Di-PZs were calculated at levels of B3LYP and MP2. Defined the most smallest value of E at each level as zero, the ΔE_R was obtained by the values of others minus the smallest value, and also listed in Table 2. The change tendency of ΔE_R for Di-PZs was shown in Figure 2.

In addition, compared ΔE as shown in Table 2 and Figure 2, it was found that ΔE of 1,2-PZ calculated using four methods are all maximum and that of 2,8-PZ are all minimum. And the discrepancy of ΔE between the two compounds, by MP2/6-311G**, MP2/6-31G*, B3LYP/6-311G**, and B3LYP/6-31G*, is $24.19 \text{ kJ} \cdot \text{mol}^{-1}$, 23.44

TABLE 1: Thermodynamic data used for calculating $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of PCPZs.

Number	Formula or name	$\Delta_f H^\theta / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f G^\theta / (\text{kJ} \cdot \text{mol}^{-1})$	$H^\theta / (\text{Hartree})$	$G^\theta / (\text{Hartree})$	$S^\theta / (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$
1	Benzene(PhH)	82.9 ^a	129.66 ^a	-232.14258	-232.17302	—
2	Chlorobenzene(CB)	51.8 ^a	99.07 ^a	-691.74731	-691.78288	—
3	Phenazine(PZ)	237.0 ^a	—	-571.425835	-571.470458	93.916
4	Graphite(C)	0	—	—	—	5.74 ^a
5	Nitrogen(N ₂)	0	—	—	—	45.77 ^a
6	Hydrogen(H ₂)	0	—	—	—	130.57 ^a

^aData from [19] and other data from B3LYP/6-31G* calculations.

TABLE 2: Comparison of S^θ and ΔE_R calculated at different levels.

Molecule	$S^\theta / \text{J} \cdot (\text{mol} \cdot \text{K})^{-1}$			$\Delta E_R / \text{kJ} \cdot \text{mol}^{-1}$			
	B3LYP/6-31G*	B3LYP/6-311G**	Diff	B3LYP/6-31G*	B3LYP/6-311G**	MP2/6-31G*	MP2/6-311G**
PZ	93.92	94.04	0.12	—	—	—	—
1-	100.97	101.07	0.10	—	—	—	—
2-	101.21	101.33	0.12	—	—	—	—
1,2-	107.85	107.97	0.12	19.00	20.12	23.44	24.19
1,3-	108.22	108.40	0.18	10.17	11.11	12.51	13.00
1,4-	108.09	108.26	0.17	16.61	18.30	20.91	21.88
1,6-	108.11	108.28	0.17	15.10	16.79	19.29	20.29
1,7-	108.26	108.36	0.11	7.67	8.44	9.50	9.98
1,8-	108.23	108.39	0.16	7.87	8.69	9.92	10.41
1,9-	108.08	108.25	0.17	16.55	18.25	21.01	21.97
2,3-	107.98	108.16	0.18	14.17	14.86	17.38	18.06
2,7-	108.39	108.52	0.13	0.10	0.10	0.02	0.05
2,8-	108.35	108.52	0.17	0.00	0.00	0.00	0.00

$\text{kJ} \cdot \text{mol}^{-1}$, $20.12 \text{ kJ} \cdot \text{mol}^{-1}$, and $19.00 \text{ kJ} \cdot \text{mol}^{-1}$, respectively. The values of ΔE calculated using four methods are different, but the order of the relative magnitude and the change tendency of ΔE are accordant. So the relative stability order of PCPZ congeners proposed at the B3LYP/6-31G* level was feasible theoretically.

3.2. Relation of the Numbers and Positions of Chlorine Substitute (N_{PCS}) to S^θ

Up to date, there hasn't been experimental thermodynamic data of PCPZs reported systematically. In this work, S^θ can be directly obtained from the output files of Gaussian programs and presented in Table 3.

Using multiple linear regression method of the SPSS 12.0 for windows program, the relation between N_{PCS} and S^θ can be seen in (6). The squared regression coefficient R^2 is 1000 and standard deviation SD is 0.05. From the equation, the number of chlorine substitute has obvious effect on entropy, but the spatial effect of chlorine on the parameter S^θ is minor and the decrease effect is ortho \gg meta $>$ para. S^θ value is increased about $7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ when increasing each chlorine atom to PCPZs:

$$S^\theta = 93.93 + 7.11N_\alpha + 7.22N_\beta - 0.01N_{1,9} - 0.38N_o - 0.05N_m + 0.00N_p, \quad R^2 = 1.000 \text{ SD} = 0.05. \quad (6)$$

3.3. Calculated Results of $\Delta_f H^\theta$ and $\Delta_f G_w^\theta$ Value and Relative Stability of Isomer Groups

With the isodesmic reactions, $\Delta_f H^\theta$ and $\Delta_f G_w^\theta$ of PCPZs were obtained and presented in Table 3. Using multiple linear regression method, the correlation expressions of $\Delta_f H^\theta$ and $\Delta_f G_w^\theta$ to N_{PCS} were summarized and presented in (7) and (8), respectively. The correlations of (7) is very well due to the corresponding larger r^2 as well as (8), both of which represent the influence of the number of chlorine on the value of $\Delta_f H^\theta$ and $\Delta_f G_w^\theta$ clearly:

$$\Delta_f H^\theta = 235.08 - 19.89N_\alpha - 26.47N_\beta + 1.57N_{1,9} + 12.91N_o + 3.12N_m + 1.97N_p, \quad R^2 = 0.997 \text{ SD} = 1.16, \quad (7)$$

$$\Delta_f G_w^\theta = 392.87 + 22.31N_\alpha + 14.24N_\beta + 12.94N_o + 5.03N_m, \quad R^2 = 0.997 \text{ SD} = 2.83. \quad (8)$$

It is suggested that $\Delta_f H^\theta$ and $\Delta_f G_w^\theta$ of PCPZs varied greatly with the positions of chlorine substitution, with an order of decrement for these parameters being position $\beta >$ position α . It was also found that $\Delta_f H^\theta$ and $\Delta_f G_w^\theta$ increase with two chlorines at the same aromatic ring, and the increase effect order is ortho \gg meta $>$ para.

Of the PCPZ compounds in each isomer group, the isomers with lower relative standard Gibbs energy of formation are relatively more stable, whereas those with the

TABLE 3: Thermodynamic parameters by B3LYP/6-31G* for PCPZs.

Molecular	S^θ	$\Delta_f H^\theta$	$\Delta_f G_w^\theta$	$\Delta_f G_{w,R}^\theta$	Constant	$C_{p,m}, J \cdot (\text{mol} \cdot \text{K})^{-1}$			N_α	N_β	N_o	N_m	N_p	$N_{1,9}$
	$J \cdot (\text{mol} \cdot \text{K})^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$		$10^3 T$	$10^4 T^{-1}$	$10^6 T^{-2}$						
PZ	93.9	237.0 ^a	398.9		575.69	2.15	1.67	1.54	0	0	0	0	0	0
1-	101.0	216.3	416.30	5.60	582.01	1.24	1.62	1.46	1	0	0	0	0	0
2-	101.2	208.7	410.71	0.00	581.67	1.18	1.61	1.46	0	1	0	0	0	0
1,2-	107.9	200.4	440.95	18.52	588.57	4.71	1.56	1.39	1	1	1	0	0	0
1,3-	108.2	191.5	434.08	11.65	588.22	4.63	1.56	1.39	1	1	0	1	0	0
1,4-	108.1	198.1	437.34	14.92	588.44	4.65	1.56	1.39	2	0	0	0	1	0
1,6-	108.1	196.6	435.79	13.37	588.40	4.66	1.56	1.39	2	0	0	0	0	0
1,7-	108.3	189.0	429.11	6.68	588.03	4.58	1.55	1.38	1	1	0	0	0	0
1,8-	108.2	189.2	429.03	6.60	588.06	4.59	1.55	1.38	1	1	0	0	0	0
1,9-	108.1	198.0	438.74	16.32	588.45	4.67	1.56	1.39	2	0	0	0	0	1
2,3-	108.0	195.4	438.28	15.85	588.24	4.64	1.56	1.38	0	2	1	0	0	0
2,7-	108.4	181.2	422.90	0.48	587.70	4.51	1.55	1.38	0	2	0	0	0	0
2,8-	108.3	181.1	422.43	0.00	587.69	4.51	1.55	1.38	0	2	0	0	0	0
1,2,3-	114.7	190.7	474.61	26.97	595.38	8.27	1.51	1.32	1	2	2	1	0	0
1,2,4-	115.0	184.9	467.91	20.27	595.19	8.17	1.51	1.32	2	1	1	1	1	0
1,2,6-	115.0	181.3	460.39	12.75	594.97	8.13	1.50	1.32	2	1	1	0	0	0
1,2,7-	115.1	173.6	453.76	6.12	594.59	8.04	1.50	1.31	1	2	1	0	0	0
1,2,8-	115.1	173.7	454.56	6.92	594.61	8.06	1.50	1.31	1	2	1	0	0	0
1,2,9-	115.0	182.6	464.38	16.73	595.03	8.15	1.50	1.32	2	1	1	0	0	1
1,3,6-	115.3	172.6	454.84	7.20	594.67	8.06	1.50	1.31	2	1	0	1	0	0
1,3,7-	115.5	164.8	447.84	0.19	594.33	8.00	1.50	1.31	1	2	0	1	0	0
1,3,8-	115.5	164.9	447.64	0.00	594.31	7.99	1.50	1.31	1	2	0	1	0	0
1,3,9-	115.3	173.6	457.51	9.86	594.70	8.08	1.50	1.31	2	1	0	1	0	1
1,4,6-	115.2	180.4	461.27	13.63	594.95	8.11	1.50	1.32	3	0	0	0	1	1
1,4,7-	115.4	171.5	450.72	3.07	594.53	8.01	1.50	1.31	2	1	0	0	1	0
2,3,6-	115.1	176.5	458.91	11.26	594.69	8.09	1.50	1.31	1	2	1	0	0	0
2,3,7-	115.2	168.6	451.44	3.80	594.35	8.01	1.49	1.30	0	3	1	0	0	0
1,2,3,4-	121.4	187.7	511.64	37.59	602.62	11.92	1.46	1.26	2	2	3	2	1	0
1,2,3,6-	121.7	172.1	493.95	19.90	601.87	11.72	1.45	1.25	2	2	2	1	0	0
1,2,3,7-	122.0	164.3	489.41	15.36	601.48	11.64	1.44	1.24	1	3	2	1	0	0
1,2,3,8-	121.9	164.4	488.71	14.66	601.49	11.63	1.44	1.24	1	3	2	1	0	0
1,2,3,9-	121.8	173.3	497.72	23.66	601.91	11.74	1.45	1.25	2	2	2	1	0	1
1,2,4,6-	122.1	167.6	492.05	17.99	601.69	11.62	1.45	1.25	3	1	1	1	1	1
1,2,4,7-	122.2	158.9	481.24	7.19	601.31	11.54	1.45	1.24	2	2	1	1	1	0
1,2,4,8-	122.1	158.9	481.76	7.71	601.33	11.55	1.45	1.24	2	2	1	1	1	0
1,2,4,9-	122.1	167.7	491.84	17.78	601.74	11.64	1.45	1.25	3	1	1	1	1	1
1,2,6,7-	121.9	166.3	485.61	11.56	601.55	11.60	1.45	1.24	2	2	2	0	0	0
1,2,6,8-	122.2	157.6	480.07	6.01	601.29	11.55	1.44	1.24	2	2	1	1	0	0
1,2,6,9-	122.1	165.5	486.32	12.26	601.55	11.58	1.45	1.25	3	1	1	0	1	1
1,2,7,8-	122.0	161.5	484.21	10.15	601.29	11.56	1.44	1.24	1	3	2	0	0	0
1,2,7,9-	122.2	158.8	483.56	9.51	601.29	11.55	1.44	1.24	2	2	1	1	0	1
1,2,8,9-	121.8	167.6	490.32	16.26	601.61	11.62	1.45	1.24	2	2	2	0	0	1
1,3,6,8-	122.4	149.3	474.06	0.00	600.99	11.48	1.44	1.24	2	2	0	2	0	0
1,3,6,9-	122.3	157.0	480.35	6.29	601.24	11.51	1.45	1.24	3	1	0	1	1	1
1,3,7,8-	122.2	152.8	477.27	3.22	600.97	11.49	1.44	1.23	1	3	1	1	0	0
1,3,7,9-	122.4	150.0	476.43	2.37	600.99	11.49	1.44	1.24	2	2	0	2	0	1
1,4,6,9-	122.3	164.7	487.84	13.79	601.51	11.55	1.45	1.25	4	0	0	0	2	2
1,4,7,8-	122.1	159.6	480.73	6.68	601.22	11.52	1.44	1.24	2	2	1	0	1	0
2,3,7,8-	122.0	156.3	480.52	6.47	600.99	11.50	1.44	1.23	0	4	2	0	0	0
1,2,3,4,6-	128.5	170.6	536.64	25.09	609.15	15.38	1.40	1.18	3	2	3	2	1	1

TABLE 3: Continued.

Molecular	S^θ	$\Delta_f H^\theta$	$\Delta_f G_w^\theta$	$\Delta_f G_{w,R}^\theta$	$C_{p,m}, J \cdot (\text{mol} \cdot \text{K})^{-1}$			N_α	N_β	N_o	N_m	N_p	$N_{1,9}$	
	$J \cdot (\text{mol} \cdot \text{K})^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$	Constant	$10^3 T$	$10^4 T^{-1}$							$10^6 T^{-2}$
1,2,3,4,7-	128.6	162.0	526.50	14.95	608.78	15.31	1.40	1.18	2	3	3	2	1	0
1,2,3,6,7-	128.6	157.4	519.92	8.37	608.48	15.20	1.39	1.17	2	3	3	1	0	0
1,2,3,6,8-	129.0	149.2	515.79	4.24	608.20	15.15	1.39	1.17	2	3	2	2	0	0
1,2,3,6,9-	128.9	156.8	520.97	9.42	608.45	15.17	1.39	1.17	3	2	2	1	1	1
1,2,3,7,8-	128.7	152.6	518.51	6.96	608.19	15.15	1.39	1.17	1	4	3	1	0	0
1,2,3,7,9-	128.9	150.0	517.98	6.44	608.20	15.15	1.39	1.17	2	3	2	2	0	1
1,2,3,8,9-	128.7	158.6	523.53	11.99	608.50	15.21	1.39	1.17	2	3	3	1	0	1
1,2,4,6,7-	128.9	153.1	517.96	6.42	608.31	15.10	1.39	1.18	3	2	2	1	1	1
1,2,4,6,8-	129.3	144.6	512.53	0.98	608.04	15.06	1.39	1.17	3	2	1	2	1	1
1,2,4,6,9-	129.2	152.4	518.64	7.10	608.29	15.08	1.40	1.18	4	1	1	1	2	2
1,2,4,7,8-	129.0	147.3	512.80	1.25	608.02	15.06	1.39	1.17	2	3	2	1	1	0
1,2,4,7,9-	129.3	144.7	511.55	0.00	608.03	15.05	1.39	1.17	3	2	1	2	1	1
1,2,4,8,9-	129.0	153.1	518.28	6.74	608.34	15.12	1.39	1.18	3	2	2	1	1	1
1,2,3,4,6,7-	135.4	156.3	563.76	23.06	615.78	18.87	1.35	1.11	3	3	4	2	1	1
1,2,3,4,6,8-	135.6	148.0	557.70	17.00	615.51	18.82	1.34	1.11	3	3	3	3	1	1
1,2,3,4,6,9-	135.5	155.7	564.27	23.56	615.77	18.84	1.35	1.11	4	2	3	2	2	2
1,2,3,4,7,8-	135.3	150.6	557.35	16.65	615.49	18.82	1.34	1.10	2	4	4	2	1	0
1,2,3,6,7,8-	135.5	149.1	557.52	16.82	615.39	18.80	1.34	1.10	2	4	4	2	0	0
1,2,3,6,7,9-	135.7	144.6	540.70	0.00	615.24	18.71	1.34	1.10	3	3	3	2	1	1
1,2,3,6,8,9-	135.6	144.8	553.46	12.76	615.24	18.70	1.34	1.11	3	3	3	2	1	1
1,2,3,7,8,9-	135.3	150.0	558.88	18.18	615.41	18.80	1.34	1.10	2	4	4	2	0	1
1,2,4,6,7,9-	136.0	140.4	550.28	9.58	615.12	18.62	1.34	1.11	4	2	2	2	2	2
1,2,4,6,8,9-	135.9	140.4	549.89	9.19	615.10	18.61	1.34	1.11	4	2	2	2	2	2
1,2,3,4,6,7,8-	142.1	148.2	599.58	4.08	622.73	22.48	1.29	1.04	3	4	5	3	1	1
1,2,3,4,6,7,9-	142.4	143.8	595.49	0.00	622.59	22.39	1.29	1.04	4	3	4	3	2	2
1,2,3,4,6,7,8,9-	148.7	147.4	641.63		630.04	26.15	1.24	0.98	4	4	6	4	2	2

^aData from [19].

higher relative standard Gibbs energy of formation are more unstable. Supposed the lowest $\Delta_f G_w^\theta$ of isomers with the same numbers of substituent to be zero, the relative standard Gibbs energies of formation ($\Delta_f G_{w,R}^\theta$) were obtained, by $\Delta_f G_w^\theta$ of other isomers minus the lowest $\Delta_f G_w^\theta$ of isomers with the same substituent numbers. Then, according to the magnitude of $\Delta_f G_{w,R}^\theta$, the theoretic relative stability orders of the isomers were proposed, and the most stable isomer and the most unstable one are listed in Table 4. As can be observed from Table 4, the most unstable isomers in MCPTs, DCPTs, Tri-CPTs, TCPTs, Penta-CPTs, Hexa-CPTs, and Hepta-CPTs are all those with chlorines being attached at the same aromatic ring and close to each other. On the contrary, the most stable isomers are all those with bromines replaced at two aromatic rings as possible, so that the bromines can be apart from each other.

We have calculated the gas phase thermodynamic functions of polychlorinated dibenzo-p-dioxins (PCDDs) via DFT method and designed isodesmic reactions [20]. The relative contents of isomers were found to correlate with the values of free energies, that is, the isomer with lower free energy has higher relative content. So it can be concluded that the formation ratio of isomer with lower $\Delta_f G_{w,R}^\theta$ is

TABLE 4: Most stable and unstable isomers in different isomer groups for PCPZs.

Compounds	The most stable isomer	The most unstable isomer
MCPT	2-	1-
DCPT	2,8-; 2,7-	1,2-
Tri-CPT	1,3,8-; 1,3,7-	1,2,3-
TCPT	1,3,6,8-	1,2,3,4-
Penta-CPT	1,2,4,7,9-	1,2,3,4,6-
Hexa-CPT	1,2,3,6,7,9-	1,2,3,4,6,7-
Hepta-CPT	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

higher, while the formation ratio of isomer with higher $\Delta_f G_{w,R}^\theta$ is lower, which is similar to that of PCDDs.

3.4. The Temperature Dependence of Molar Heat Capacity of PCPZs at Constant Pressure

The values of molar heat capacity at constant pressure ($C_{p,m}$) for PCPZs congeners haven't been reported. So, the values of $C_{p,m}$ were calculated using statistical thermodynamics

calculation program at 200 to 1800 K based on Gaussian output files.

Based on the calculated values of $C_{p,m}$ of PCPZs at different temperature (T), the relations between $C_{p,m}$ and temperature were obtained using the least-square method. Regression coefficients for 10^3T , 10^4T^{-1} , 10^6T^{-2} , and constant are listed in Table 3. From Table 3, the following conclusion can be drawn. (1) The $C_{p,m}$ values of PCPZs are in direct ratio to temperature T , T^{-1} , and T^{-2} . (2) All PCPZ congeners have very good relationships between $C_{p,m}$ and temperature (T , T^{-1} , and T^{-2}), and the correlation coefficients (r^2) are all very close or equal to 1.0. These indicated that a good correlation between $C_{p,m}$ values and T .

4. Conclusions

76 PCPZs were fully optimized at B3LYP/6-31G* level, and thus their H^θ , S^θ , and G_w were consequently obtained. In addition, the standard formation heat and standard formation free energy of each PCPZ molecule were calculated by isodesmic reactions. The result showed that all these thermodynamic parameters have close relationship with the numbers and positions of chlorine substituents (N_{PCS}). So, the enthalpies and Gibbs free energies of formation for 76 PCPZ congeners should be valuable in further thermodynamic modeling studies. According to the relative magnitude of their $\Delta_f G_w^\theta$, the order of relative stability of PCPZ congeners was theoretically proposed. Moreover, it is found that there is a very good relationship between $C_{p,m}$ and temperature for the PCPZ congeners. In a word, this work about thermodynamic properties is useful and significant for studying the generation, degradation, and potential environmental risk of PCPZs.

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