J. Chem. Eng. Data **2010,** *55,* 1077–1086 **1077**

Density Functional Theory Calculation on Polychlorinated Anthraquinones: Their Gas Phase Thermodynamic Function and Implication of the Cl Substituted Position

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Using the Gaussian 03 program, the thermodynamic properties of 76 polychlorinated anthraquinones (PCAQNs) have been calculated by density functional theory (DFT) at the BHandHLYP/6-311G** level. On the basis of the output data of Gaussian, the isodesmic reactions are designed to calculate the standard enthalpy of formation and standard Gibbs energy of formation of PCAQN congeners. The relations of these thermodynamic parameters with the number and position of Cl atom substitution (N_{PCS}) are discussed, and the order of relative stability of PCAQN congeners is theoretically proposed according to the relative magnitude of their standard Gibbs energy of formation. The results were also compared with those of polychlorinated dibenzo-*p*-dioxins (PCDDs). In addition, the values of molar heat capacities at constant pressure ($C_{\mathrm{p,m}}$) from (200 to 1000) K for PCAQN congeners are calculated, and the temperature dependence relation of this parameter is obtained using the least-squares method. Finally, the toxicity orders of PCAQNs were predicted according to previous experience.

Introduction

Anthraquinone (9,10-dioxoanthracene, chemical formula: $C_{14}H_8O_2$, AQN), is an aromatic organic compound. The structure is similar to dibenzo-*p*-dioxin (DD) (see Figure 1). It is a derivative of anthracene and chemically fairly stable under normal conditions. AQN has the appearance of yellow or light gray to gray-green solid crystalline powder and is used in production of dyes, such as alizarin. Many natural pigments are derivatives of AQN. AQN is also used as a catalyst in the production of wood pulp in the pulp and paper industry. Seiji et al.[1] studied the quenching of bacteriochlorophyll fluorescence in chlorosomes from *Chloroflexus aurantiacus* by exogenous quinones, and the results showed quinones which exhibit a high quenching effect have sufficient hydrophobicity and one or more hydroxyl groups in the positions α of naphthoquinones (NQ) and AQN. Yen et al.[2] researched acute lethal toxicity of environmental pollutants to aquatic organisms. They found that the toxicity of naphthoquinone compounds to chlorella and carp was higher than that of AQN. A compound with a monochloride substitution on the AQN ring was less toxic to carp than those substituted with amine, hydroxyl, and dichlorine groups. Nitrobenzene compounds with an additional substitution group on the *p* position were extremely toxic to daphnia and carp. Bramble et al.[3] reported rat liver mitochondrial and microsomal tests for the assessment of quinone toxicity. Results of the mitochondrial and microsomal assay were statistically correlated with several quinone physicochemical parameters and qualitatively compared to the reduction potential. The biological response observed in both test systems appeared to be most strongly influenced by the reduction potential of the quinone. Biomechanisms of action were suggested on the basis of this relationship. To assess the ability of the mitochondrial and microsomal assays to indicate toxicity of the quinoid compounds, results were statistically correlated with literature derived toxicity data. It was concluded that the mitochoridrial assay appears to be a valid indicator of acute toxicity, whereas the microsomal assay better portends the potential for chronic toxicity. However, thermodynamic data of polychlorinated anthraquinones (PCAQNs) have not been reported.

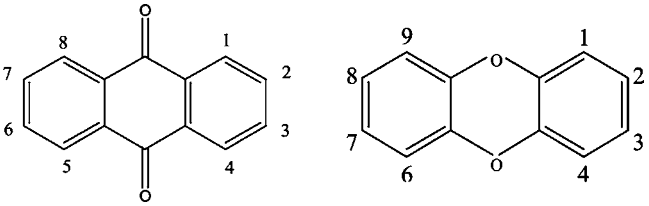

Figure 1. Structure and the systematic numbering of AQN and dibenzo-*p*-dioxin (DD).

In the past, density functional theory (DFT) calculations have been carried out on a number of polychlorodibenzofurans (PCDFs) using 6-31G* and 6-311G** basis sets to estimate their heats of formation on the basis of the known experimental values for dibenzofuran, benzene, and chlorobenzene.[4] Moreover, Zeng et al.[5] calculated the thermodynamic properties of 39 polybrominated diphenyl ethers (PBDEs) in the ideal gas state at the B3LYP/6-31G* level in Gaussian 03 program. Kroon et al.[6] predicted thermal decomposition mechanisms, temperatures, and the activation energies of the thermal breakdown reactions of ionic liquids using ab initio quantum chemical calculations (DFT-B3LYP). Larowe and Helgeson[7] calculated the thermodynamic properties of biomolecules at high temperatures and pressures. In addition, the thermodynamic data of polychlori-

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10.1021/je9003564

nated dibenzo-*p*-dioxins (PCDDs), PCDFs, polychlorinated biphenyls (PCBs), and polychlorinated phenoxathiins (PCPTs) have been calculated by DFT.[8−11] It was found that the isomers with lower free energy have higher formation ratio; that is, the formation ratios of isomers are consistent with their relative stabilities.

Dioxin-like chemicals are a family of ubiquitous environmental contaminants known to produce a broad spectrum of toxic effects in animals, some of which include carcinogenicity, teratogenicity, immunotoxicity, and endocrine toxicity. PCAQNs also are one of dioxin-like chemicals. To provide basic data for studying their formation, degradation, and the environmental risk of these dioxin-like chemicals, we attempt to study the thermodynamic properties and the order of relative stability of dioxin-like chemicals.

In this study, the thermodynamic properties for the 76 PCAQNs were calculated with DFT. By designing isodesmic reactions, the standard enthalpies of formation ($\Delta_f H^\theta$) and the standard Gibbs energies of formation ($\Delta_f G^\theta$) for all PCAQNs were also obtained. Then, the relationships between these parameters and the numbers and positions of Cl substitution (N_{PCS}) were studied. According to the relative magnitude of their $\Delta_f G^\theta$, the relative stability order of PCAQN congeners was theoretically proposed. On the basis of results, we compared the volumes, predicted toxicity, and stability of PCAQNs with the corresponding results of PCDDs. Finally, the $C_{p,m}$ values at (200 to 1000) K for PCAQN congeners were calculated using a statistical thermodynamics calculation program.[12]

Theory and Calculations

Theoretical calculations of the thermodynamic properties for 76 PCAQNs in the gaseous phase were performed by DFT methods with the Gaussian 03 program.[13] All of the quantum mechanical computations were performed using the procedure of BHandHLYP/6-311G**. The term opt freq refers to the optimization of the molecular structure (opt) followed by frequencies calculations (freq) performed at the stationary points on the potential energy surface, and both calculations were made at the same BHandHLYP/6-311G** level. The standard state entropy (S^θ), as well as the absolute enthalpy (H^θ) and Gibbs free energies (G^θ), was obtained directly from DFT calculations (Gaussian's output file).

In this paper, PCAQN isomers with one to eight chlorine atoms are represented by the notation MCAQN, DCAQN, TriCAQN, TCAQN, penta-CAQN, hexa-CAQN, hepta-CAQN, and OCAQN, respectively. In addition, the positions of Cl substitution (PCS) consist of the number of the substituting Cl atoms on different positions of the parent compound and the number of relative positions of these Cl atoms. The numbers of chlorine atoms at positions 1, 4, 5, and 8 were defined as N_α, the positions of 2, 3, 6, and 7 as N_β, the pair numbers of chlorine atoms at positions 1,8 or 4,5 as $N_{1,8}$ and $N_{4,5}$, and the pair numbers of the ortho, meta, and para positions of chlorine atoms on one benzene ring as N_o, N_m, and N_p, respectively. Moreover, the parameters mentioned above are defined as a general designation of N_{PCS}, where N is the number of Cl atom substitutions and the subscript PCS indicates the positions.

Because no experimental data of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ for PCAQNs is available, in this study, reaction 1 was designed for calculating $\Delta_f H^\theta$ and $\Delta_f G^\theta$. Lee et al.[14] used the isodesmic reaction to calculate the $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of PCDDs and obtained results consistent to experimental results. It seems reasonable to expect that estimates of the thermodynamic properties of PCAQNs, from DFT calculations based on isodesmic reactions, will be similarly accurate.

$$\text{AQN} + n\ \text{chlorobenzene} = \text{PCAQN} + n\ \text{benzene} \tag{1}$$

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

$$\Delta_r H^\theta = [H^\theta_{PCAQN} + nH^\theta_{benzene}] - [H^\theta_{AQN} + nH^\theta_{chlorobenzene}] \tag{2}$$

Similarly, following eq 3 also yields $\Delta_r H^\theta$:

$$\Delta_r H^\theta = [\Delta_f H^\theta_{PCAQN} + n\Delta_f H^\theta_{benzene}] - [\Delta_f H^\theta_{AQN} + n\Delta_f H^\theta_{chlorobenzene}] \tag{3}$$

So eq 4 could be obtained from eq 3 and eq 2:

$$\Delta_f H^\theta_{PCAQN} = H^\theta_{PCAQN} + nH^\theta_{benzene} - nH^\theta_{chlorobenzene} - H^\theta_{AQN} - n\Delta_f H^\theta_{benzene} + n\Delta_f H^\theta_{chlorobenzene} + \Delta_f H^\theta_{AQN} \tag{4}$$

Similarly, $\Delta_f G^\theta{}_{PCAQN}$ could be obtained by eq 5:

$$\Delta_f G^\theta_{PCAQN} = G^\theta_{PCAQN} + nG^\theta_{benzene} - nG^\theta_{chlorobenzene} - G^\theta_{AQN} - n\Delta_f G^\theta_{benzene} + n\Delta_f G^\theta_{chlorobenzene} + \Delta_f G^\theta_{AQN} \tag{5}$$

To obtain $\Delta_f G^\theta{}_{AQN}$, eq 6 was designed:

$$14C_{graphite} + 4H_2 + O_2 = C_{14}H_8O_2 \tag{6}$$

So:

$$\Delta_r S^\theta = S^\theta_{AQN} - 14S^\theta_C - 4S^\theta_{H2} - S^\theta_{O2} \tag{7}$$

$$\Delta_r H^\theta = \Delta_f H^\theta_{AQN} - 4H^\theta_C - 4H^\theta_{H2} - H^\theta_{O2} = \Delta_f H^\theta_{AQN} \tag{8}$$

$$\Delta_r G^\theta = \Delta_f G^\theta_{AQN} - 14G^\theta_C - 4G^\theta_{H2} - G^\theta_{O2} = \Delta_f G^\theta_{AQN} \tag{9}$$

$$\Delta_r G^\theta_{AQN} = \Delta_f G^\theta_{AQN} = \Delta_r H^\theta_{AQN} - T\Delta_r S^\theta_{AQN} = \Delta_f H^\theta_{AQN} - T\Delta_r S^\theta_{AQN} \tag{10}$$

The experimental values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ for benzene and chlorobenzene are listed in Table 1, including the calculated values of H^θ and G^θ at the BHandHLYP/6-311G** level. The experimental values of compounds mentioned above are taken from ref 15. At the B3LYP/6-31G* level, the mean absolute deviation of calculated thermochemical quantities from the experiment for a variety of compounds is 33.05 $\text{kJ}\cdot\text{mol}^{-1}$, and the standard deviation is 39.75 $\text{kJ}\cdot\text{mol}^{-1}$.[16] Since all of the values are from theoretical calculations, variables can be exactly repeatable.

To validate the precision of the method, we have calculated some thermodynamic data of halogen aroma compounds with experimental data[15] using the same method.[17] The calculated thermodynamic parameters and experimental ones are listed in Table 2. As seen from Table 2, the conclusions can be obtained: 2,2′-DCB, benzene, and 1,3-dichlorobenzene possess the largest discrepancies of $\Delta_f H^\theta$, S^θ, and $\Delta_f G^\theta$ with values of 14.8 $\text{kJ}\cdot\text{mol}^{-1}$, 17.5 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and −5.2 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. Furthermore, in our previous study,[18] we calculated $S_{T,m}$, $C_{p,m}$, $\Delta_0{}^T H_m/T$, and $\Delta_0{}^T G_m/T$ for 1- and 2-bromonaphthalenes, 2,3-dibromonaphthalene, and octabromonaphthalene (scale factor

Table 1. Thermodynamic Data Used for Calculating $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of PCAQNs

no.	name	$\Delta_f H^\theta$ / $kJ \cdot mol^{-1}$	$\Delta_f G^\theta$ / $kJ \cdot mol^{-1}$	H^θ / $kJ \cdot mol^{-1}$	G^θ / $kJ \cdot mol^{-1}$	S^θ / $J \cdot mol^{-1} \cdot K^{-1}$
1	benzene (PhH)	82.9[a]	129.66[a]	−609240.4	−609325.9	
2	chlorobenzene (CB)	51.8[a]	99.11[a]	−1815966.4	−1816060.7	
3	AQN (XX)	−119.4[a]	−6.26[b]	−1807234.6	−1807362.8	429.91
4	graphite (C)	0[a]				5.69[a]
5	hydrogen (H_2)	0[a]				130.52[a]
6	oxygen (O_2)	0[a]				204.93[a]

[a] Data from ref 15. [b] Predicted from eqs 6 to 10 and other data from BHandHLYP/6-311G** calculations.

Table 2. Differences between the Calculated and the Experimental Thermodynamic Parameters

		$\Delta H^\theta{}_f$			S^θ			$\Delta G^\theta{}_f$		
		$KJ \cdot mol^{-1}$			$J \cdot mol^{-1} \cdot K^{-1}$			$KJ \cdot mol^{-1}$		
number	name	exptl[a]	calcd	diff.	exptl[a]	calcd	diff.	exptl[a]	calcd	diff.
1	benzene	82.9			269.3	286.8	17.5	129.7	129.7	0.0
2	chlorobenzene	51.8			313.5	316.1	2.6	99.2	99.2	0.0
3	1,2-dichlorobenzene	30.0	35.5	5.5	341.5	344.0	2.5	82.7	83.9	1.2
4	1,3-dichlorobenzene	28.1	25.3	−2.8	343.5	345.4	1.9	78.6	73.4	−5.2
5	1,4-dichlorobenzene	24.6	24.8	0.2	336.7	345.4	8.7	77.2	72.9	−4.3
6	1,1′-biphenyl	182.1			392.7	385.9	−6.8	280.1	280.3	0.2
7	2,2′-DCB	126.8	141.6	14.8		448.4			239.7	
8	4,4′-DCB	120.1	121.5	1.4		444.9			220.6	
9	benzenethiol	111.5			336.7	333.6	−3.1	147.6		

[a] Taken from ref 15.

Table 3. Calculation Data of $S_{T,m}$, $C_{p,m}$, $\Delta_0{}^T H_m/T$, and $\Delta_0{}^T G_m/T$ for Some Compounds[a]

		$C_{p,m}$			$S_{T,m}$			$\Delta_0{}^T H_m/T$			$\Delta_0{}^T G_m/T$		
	T	calcd[b]	calcd[c]	diff.	calcd[b]	calcd[c]	diff.	calcd[b]	calcd[c]	diff.	calcd[b]	calcd[c]	diff.
molecule	K	$J \cdot mol^{-1} \cdot K^{-1}$											
1-bromonaphthalene	298.15	153.85	153.33	0.52	389.14	388.50	0.64	84.99	84.07	0.92	304.15	304.46	−0.31
	300.00	154.72	154.24	0.48	390.10	389.45	0.65	85.35	84.47	0.88	304.75	304.99	−0.24
	400.00	200.00	200.57	−0.57	440.98	440.35	0.63	108.49	107.85	0.64	332.49	332.49	0.00
	500.00	237.40	238.50	−1.10	489.76	489.34	0.42	130.67	130.34	0.33	359.09	359.00	0.09
	600.00	267.19	268.44	−1.25	535.79	535.57	0.22	151.04	150.97	0.07	384.75	384.61	0.14
	700.00	290.91	292.16	−1.25	578.84	578.80	0.04	169.41	169.50	−0.09	409.43	409.30	0.13
	800.00	310.16	311.30	−1.14	618.97	619.11	−0.14	185.81	186.08	−0.27	433.16	433.04	0.12
	900.00	325.98	326.99	−1.01	656.45	656.71	−0.26	200.54	200.89	−0.35	455.91	455.82	0.09
	1000.00	339.11	340.04	−0.93	691.52	691.85	−0.33	213.76	214.17	−0.41	477.76	477.69	0.07
2-bromonaphthalene	298.15	154.26	153.75	0.51	388.05	390.07	−2.02	84.60	84.43	0.17	303.45	305.65	−2.20
	300.00	155.14	154.67	0.47	389.01	391.03	−2.02	85.02	84.87	0.15	303.99	306.18	−2.19
	400.00	200.37	200.92	−0.55	440.02	442.03	−2.01	108.37	108.25	0.12	331.65	333.79	−2.14
	500.00	237.65	238.78	−1.13	488.88	491.09	−2.21	130.62	130.70	−0.08	358.26	360.38	−2.12
	600.00	267.23	268.66	−1.43	534.91	537.37	−2.46	151.04	151.32	−0.28	383.87	386.06	−2.19
	700.00	290.83	292.35	−1.52	577.96	580.63	−2.67	169.37	169.83	−0.46	408.59	410.80	−2.21
	800.00	309.91	311.46	−1.55	618.09	620.96	−2.87	185.77	186.38	−0.61	432.32	434.58	−2.26
	900.00	325.60	327.13	−1.53	655.53	658.58	−3.05	200.46	201.18	−0.72	455.07	457.40	−2.33
	1000.00	338.65	340.17	−1.52	690.51	693.74	−3.23	213.68	214.44	−0.76	476.83	479.30	−2.47
2,3-dibromonaphthalene	298.15	170.58	170.47	0.11	421.65	429.61	−7.96	96.11	97.52	−1.41	325.54	332.11	−6.57
	300.00	171.46	171.37	0.09	422.74	430.66	−7.92	96.57	97.93	−1.36	326.17	332.72	−6.55
	400.00	215.86	216.27	−0.41	478.30	486.30	−8.00	121.00	122.08	−1.08	357.30	364.22	−6.92
	500.00	251.96	252.68	−0.72	530.52	538.62	−8.10	143.72	144.70	−0.98	386.80	393.92	−7.12
	600.00	280.37	281.23	−0.86	579.05	587.32	−8.27	164.22	165.17	−0.95	414.83	422.15	−7.32
	700.00	302.84	303.72	−0.88	624.03	632.43	−8.40	182.46	183.41	−0.95	441.57	449.01	−7.44
	800.00	320.87	321.72	−0.85	665.70	674.20	−8.50	198.70	199.63	−0.93	467.00	474.58	−7.58
	900.00	335.60	336.39	−0.79	704.36	712.97	−8.61	213.13	214.03	−0.90	491.23	498.94	−7.71
	1000.00	347.77	348.51	−0.74	740.39	749.06	−8.67	225.98	226.89	−0.91	514.41	522.16	−7.75

[a] $S_{T,m}$ is molar entropy at T. $C_{p,m}$ is the molar heat capacity at constant pressure. $\Delta_0{}^T H_m/T$ is an average thermal correction to molar enthalpy between 0 and T. $\Delta_0{}^T G_m/T$ is an average thermal correction to molar Gibbs energy between 0 and T. [b] Taken from literature.[19] [c] Taken from in this work.

for frequency = 0.95) and compared the calculation data with literature one.[19] Where $S_{T,m}$ is molar entropy at T K, $C_{p,m}$ is molar heat capacity at constant pressure, $\Delta_0{}^T H_m/T$ the specific thermal correction to molar enthalpy, and $\Delta_0{}^T G_m/T$ the specific thermal correction to molar Gibbs energy. The data are listed in Table 3, which indicate that the calculation data in this work match well with those reported in the literature, while in our other study[8] we found that the calculated data of S^θ are in agreement with the experiment for 1,2-, 1,3-, and 1,4-dichlorobenzene at 298.15 K, which indicated that our calculation method is feasible.

Using a statistical thermodynamics calculation program,[12] ideal-gas thermodynamic functions such as molar entropy, heat capacity, and enthalpy can be computed easily from the molecular partition function. All of the necessary information is usually included in the output file from a vibrational frequency calculation executed using the quantum chemistry software from Gaussian, Inc. The statistical thermodynamics calculation

Table 4. Comparison of ΔE_R Calculated at Different Levels for DCAQN

	ΔE_R		
	$\mathrm{kJ \cdot mol^{-1}}$		
molecule	BHandHLYP/ 6-31G*	BHandHLYP/ 6-311^{+2}G**	B3LYP/ 6-311G**
12	47.50	46.67	45.89
13	33.75	32.91	32.47
14	70.11	67.49	67.65
15	61.38	59.48	59.16
16	31.20	30.63	30.04
17	31.12	30.54	29.93
18	62.73	60.33	60.76
23	12.92	12.46	12.72
26	0.00	0.00	0.00
27	0.10	0.11	0.13

program will automatically extract the essential data from the Gaussian output file and compute thermodynamic functions at several temperatures. The theoretical foundation of this C_p calculation is the partition function and its relationship with thermodynamic parameters in physical chemistry. The expression of C_V in physical chemistry is as follows:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_{V,N}\right]_V \tag{11}$$

$$C_{p,m} = C_{V,m} + R = = \frac{\partial}{\partial T}\left[NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_{V,N}\right]_V + R \tag{12}$$

As is known, C_V and C_p are functions of T for ideal gas, and $C_{p,m} - C_{V,m} = R$. So, the values of $C_{p,m}$ at (200 to 1000) K for PCAQN congeners were calculated on its basis.

In previous reports, Grabda et al. have predicted the gas phase thermodynamic properties of 209 PBDEs, 209 PBBs, 19 PBPs, HBCD, and TBBPA using the DFT method.[20] They assessed the quality of the DFT predictions obtained by comparison of the calculated data with certain experimentally measured properties of brominated arenes available in the literature. The results showed that the average standard deviations calculated for these comparisons amount to (2.6 and 12.7) $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ for $C_{p,m}$ and S^θ, respectively, and 7.5 $\mathrm{kJ \cdot mol^{-1}}$ for $\Delta_f H^\theta$. It follows that the parameters obtained by DFT calculations at only a moderate level of the theoretical depth are accurate, and the absolute enthalpy (H^θ) and Gibbs energy (G^θ) functions applied for estimating the $\Delta_f H^\theta$ and $\Delta_f G^\theta$ afford high quality results.

In addition, the values of E for DCAQNs were also calculated at two levels of B3LYP/6-311G** and BHandHLYP/6-311^{+2}G**. With the lowest value of E at each level defined as zero, the ΔE_R was obtained by the values of others minus the lowest value and also listed in Table 4. Comparing ΔE_R as shown in Table 4, it was found that ΔE_R of 1,4-DCAQN calculated using three methods is the maximum, and that of 2,6-DCAQN is the minimum. The discrepancies of ΔE_R between the two compounds, by B3LYP/6-311G**, BHandHLYP/6-311^{+2}G**, and BHandHLYP/6-311G**, are (67.65, 67.49, and 70.11) $\mathrm{kJ \cdot mol^{-1}}$, respectively. The values of E calculated using three methods are different, but the order of the relative magnitude and the change tendency of ΔE_R are accordant. So, the relative stability order of DCAQN congeners proposed at the BHandHLYP/6-311G** level was feasible theoretically. In addition, calculation at the B3LYP/6-311G** and BHandHLYP/6-311++G** levels would cost more computer time, so the BHandHLYP/6-311G** calculation for all 76 PCAQNs was chosen in the present study.

Results and Discussion

The calculated values of thermodynamic properties for all of the 76 PCAQNs in the gaseous state are listed in Table 5.

Relation of the Numbers and Positions of Chlorine Substitute (N_{PCS}) to S^θ. We have used the multiple linear regression method of the SPSS 12.0 for Windows program to obtain the relation between N_{PCS} and S^θ as can be seen in eq 13. From eq 13, it has been shown that S^θ increases with the increasing number of chlorine atoms substituted for hydrogen increasing. Equation 13 has a large squared regression coefficient R^2 (0.993) and small standard error SE (3.49), which shows that there exist good correlations between the values obtained from Gaussian 03 program and N_{PCS}, and each S^θ can be predicted with reasonable accuracy from the N_{PCS} of PCAQNs. Figure 2 shows plots of the values obtained from the correlations versus the corresponding DFT results and their deviations.

$$S^\theta/\mathrm{J \cdot mol^{-1} \cdot K^{-1}} = 438.34 + 27.05N$$
$$R^2 = 0.993 \qquad \mathrm{SE} = 3.49 \qquad F = 10587.763 \tag{13}$$

Calculated Results of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ Values and the Relative Stability of Isomer Groups. With the design of isodesmic reactions, $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of PCAQNs were obtained and are presented in Table 5. Using the multiple linear regression method, the correlation expressions of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ to N_{PCS} are presented in eqs 14 and 15. Equations 14 and 15 clearly demonstrate that the substitute number and position of chlorine atoms influence the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ clearly. From eqs 14 and 15, conclusions can be obtained: (I) The values of $\Delta_f H^\theta$ increase with the substitute number of chlorine atoms at positions α, while they decrease with the substitute number of chlorine atoms at positions β, and the effect of N_β is more important. When N_β increases by 1, the value of $\Delta_f H^\theta$ decreases to 26.332 $\mathrm{kJ \cdot mol^{-1}}$. (II) The values of $\Delta_f G^\theta$ also increase with the substitute number of chlorine atoms at positions N_α, while they decrease with the substitute number of chlorine atoms at positions N_β, and the effect of N_β is more important too. (III) N_o, N_m, and N_p have great effects on the values of $\Delta_f H^\theta$, as well as $\Delta_f G^\theta$, with the following order: $N_o > N_p > N_m$, which indicates that the chlorine atom located at position ortho significantly decreases the stability of the congeners. The lower stability of the ortho substituted PCAQNs certainly results from epulsive force between the chlorine atoms. (IV) The squared correlation coefficients R^2 of eqs 14 and 15 are 0.985 and 0.986, respectively. Thus, the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ can be predicted by the N_{PCS} of the PCAQNs obtained. The difference between the $\Delta_f G^\theta$ values calculated at the BHandHLYP/6-31G* level and predicted by eq 15 is very small. The plots of the values obtained from the correlations versus the corresponding DFT results and their deviations were also shown in Figure 2.

$$\Delta_f H^\theta/\mathrm{kJ \cdot mol^{-1}} = -117.534 + 3.534N_\alpha - 26.332N_\beta + 15.341N_o + 3.350N_m + 3.395N_p$$
$$R^2 = 0.985 \qquad \mathrm{SE} = 2.764 \qquad F = 910.177 \tag{14}$$

$$\Delta_f G^\theta/\mathrm{kJ \cdot mol^{-1}} = -5.967 + 4.539N_\alpha - 25.745N_\beta + 15.882N_o + 3.365N_m + 3.668N_p$$
$$R_2 = 0.986 \qquad \mathrm{SE} = 2.641 \qquad F = 1073.306 \tag{15}$$

Relative Stability of Isomer Groups and Comparison with PCDDs. Supposing that the lowest $\Delta_f G^\theta$ of the isomers with the same numbers of substituent chlorine atoms is zero, the

Table 5. Thermodynamic Parameters of PCAQNs Computed at the BHandHLYP/6-311G Level and N_{PCS}[a]**

	V_m	S^θ	$\Delta_f H^\theta$	$\Delta_f G^\theta$	$\Delta_f G^\theta_R$	$C_{p,m}$(J·mol^{-1}·K^{-1})											
molecule	Å^3	J·mol^{-1}·K^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	constant	10^{-3} T	10^5 T^{-1}	10^7 T^{-2}	R^2	SE	N_α	N_β	N_o	N_m	N_p	$N_{1,8}$
AQN	245.97	429.91	−119.40	−6.26		550.86	52.54	−1.60	1.49	1.000	1.51	0	0	0	0	0	0
Mono-CAQN																	
1	262.61	464.67	−115.07	−2.95	29.43	564.23	44.96	−1.56	1.44	1.000	1.46	1	0	0	0	0	0
2	267.37	459.33	−146.09	−32.38	0.00	563.85	45.15	−1.56	1.44	1.000	1.46	0	1	0	0	0	0
Di-CAQN																	
1,2	287.38	496.22	−125.02	−12.96	44.73	577.63	37.50	−1.53	1.39	1.000	1.40	1	1	1	0	0	0
1,3	281.30	493.47	−138.73	−25.86	31.83	577.40	37.55	−1.53	1.39	1.000	1.40	1	1	0	1	0	0
1,4	291.27	493.43	−102.93	9.95	67.64	577.59	37.40	−1.53	1.38	1.000	1.39	2	0	0	0	1	0
1,5	287.43	493.54	−111.34	1.51	59.20	577.60	37.42	−1.53	1.38	1.000	1.40	2	0	0	0	0	0
1,6	288.08	493.81	−141.22	−28.45	29.24	577.25	37.58	−1.53	1.38	1.000	1.40	1	1	0	0	0	0
1,7	285.45	493.72	−141.30	−28.51	29.19	577.27	37.57	−1.53	1.38	1.000	1.40	1	1	0	0	0	0
1,8	286.40	488.13	−109.94	4.52	62.21	577.41	37.55	−1.53	1.38	1.000	1.40	2	0	0	0	0	1
2,3	288.53	486.73	−159.01	−44.12	13.57	576.53	38.19	−1.53	1.39	1.000	1.42	0	2	1	0	0	0
2,6	279.67	488.29	−172.11	−57.69	0.00	576.78	37.84	−1.53	1.38	1.000	1.40	0	2	0	0	0	0
2,7	289.02	488.25	−171.95	−57.51	0.18	576.75	37.86	−1.53	1.38	1.000	1.41	0	2	0	0	0	0
Tri-CAQN																	
1,2,3	298.83	525.04	−134.46	−21.66	47.13	591.06	30.11	−1.50	1.34	1.000	1.35	1	2	2	1	0	0
1,2,4	320.53	520.17	−110.39	3.87	72.66	591.14	29.90	−1.50	1.34	1.000	1.34	2	1	1	1	1	0
1,2,5	313.65	519.81	−121.54	−7.18	61.61	590.84	30.06	−1.50	1.33	1.000	1.35	2	1	1	0	0	0
1,2,6	304.81	524.78	−150.64	−37.76	31.03	590.56	30.18	−1.50	1.33	1.000	1.35	1	2	1	0	0	0
1,2,7	309.75	525.85	−150.64	−38.08	30.71	590.69	30.10	−1.50	1.33	1.000	1.35	1	2	1	0	0	0
1,2,8	309.25	514.93	−120.64	−4.82	63.97	590.64	30.20	−1.50	1.33	1.000	1.35	2	1	1	0	0	1
1,3,5	308.21	524.81	−134.58	−21.71	47.08	590.83	29.99	−1.50	1.33	1.000	1.35	2	1	0	1	0	0
1,3,6	300.74	522.49	−164.11	−50.55	18.24	590.41	30.20	−1.50	1.33	1.000	1.35	1	2	0	1	0	0
1,3,7	311.03	522.53	−164.36	−50.81	17.98	590.54	30.11	−1.50	1.33	1.000	1.34	1	2	0	1	0	0
1,3,8	305.88	517.41	−132.95	−17.87	50.92	590.58	30.15	−1.50	1.33	1.000	1.35	2	1	0	1	0	1
1,4,5	303.73	516.72	−103.27	12.02	80.81	590.39	30.20	−1.49	1.33	1.000	1.34	3	0	0	0	1	1
1,4,6	312.23	522.96	−128.68	−15.25	53.54	590.56	30.06	−1.50	1.33	1.000	1.34	2	1	0	0	1	0
2,3,5	310.78	520.92	−153.75	−39.72	29.07	590.01	30.57	−1.50	1.33	1.000	1.36	1	2	1	0	0	0
2,3,6	311.35	516.11	−184.25	−68.79	0.00	589.49	30.86	−1.50	1.33	1.000	1.36	0	3	1	0	0	0
TCAQN																	
1,2,3,4	325.63	545.27	−101.52	14.59	94.15	605.40	22.10	−1.47	1.29	1.000	1.29	2	2	3	2	1	0
1,2,3,5	327.91	548.17	−130.62	−15.37	64.18	604.31	22.66	−1.47	1.29	1.000	1.30	2	2	2	1	0	0
1,2,3,6	324.99	552.20	−159.51	−45.47	34.09	604.04	22.77	−1.47	1.29	1.000	1.29	1	3	2	1	0	0
1,2,3,7	325.52	551.87	−159.72	−45.57	33.98	604.07	22.76	−1.47	1.29	1.000	1.30	1	3	2	1	0	0
1,2,3,8	330.72	542.50	−129.55	−12.61	66.94	603.87	22.93	−1.47	1.29	1.000	1.30	2	2	2	1	0	1
1,2,4,5	326.78	544.25	−110.76	5.66	85.21	603.84	22.77	−1.47	1.28	1.000	1.29	3	1	1	1	1	1
1,2,4,6	320.21	549.74	−135.52	−20.74	58.82	604.13	22.57	−1.47	1.28	1.000	1.29	2	2	1	1	1	0
1,2,4,7	336.22	549.60	−135.45	−20.63	58.93	604.09	22.59	−1.47	1.28	1.000	1.29	2	2	1	1	1	0
1,2,4,8	333.20	544.20	−111.38	5.06	84.61	603.71	22.86	−1.46	1.28	1.000	1.29	3	1	1	1	1	1
1,2,5,6	321.13	546.63	−131.37	−15.66	63.90	604.05	22.74	−1.47	1.28	1.000	1.29	2	2	2	0	0	0
1,2,5,7	322.32	550.03	−144.14	−29.44	50.11	604.16	22.58	−1.47	1.28	1.000	1.29	2	2	1	1	0	0
1,2,5,8	331.84	544.51	−114.00	2.35	81.90	603.44	22.97	−1.46	1.28	1.000	1.29	3	1	1	0	1	1
1,2,6,7	330.53	551.75	−162.70	−48.52	31.04	603.49	23.07	−1.47	1.28	1.000	1.30	1	3	2	0	0	0
1,2,6,8	327.52	544.25	−143.01	−26.59	52.96	603.79	22.83	−1.47	1.28	1.000	1.30	2	2	1	1	0	1
1,2,7,8	324.98	542.22	−130.95	−13.93	65.62	603.70	22.96	−1.47	1.28	1.000	1.30	2	2	2	0	0	1
1,3,5,7	324.56	555.35	−157.22	−44.11	35.44	604.16	22.51	−1.47	1.29	1.000	1.29	2	2	0	2	0	0
1,3,5,8	329.27	546.55	−125.45	−9.71	69.84	603.54	22.82	−1.46	1.28	1.000	1.29	3	1	0	1	1	1
1,3,6,7	334.71	549.47	−176.24	−61.38	18.17	603.21	23.16	−1.47	1.28	1.000	1.30	1	3	1	1	0	0
1,3,6,8	322.58	546.88	−155.05	−39.42	40.13	603.69	22.81	−1.47	1.28	1.000	1.29	2	2	0	2	0	1
1,4,5,8	331.61	544.65	−100.11	16.19	95.74	602.94	23.15	−1.46	1.27	1.000	1.29	4	0	0	0	2	2
1,4,6,7	332.09	551.71	−140.64	−26.45	53.11	603.39	23.00	−1.46	1.28	1.000	1.29	2	2	1	0	1	0
2,3,6,7	328.22	543.46	−196.21	−79.55	0.00	602.33	23.79	−1.47	1.29	1.000	1.32	0	4	2	0	0	0
Penta-CAQN																	
1,2,3,4,5	354.02	570.29	−103.17	14.83	70.88	617.87	15.12	−1.44	1.24	1.000	1.24	3	2	3	2	1	1
1,2,3,4,6	344.19	574.62	−126.23	−9.52	46.52	618.40	14.76	−1.44	1.24	1.000	1.23	2	3	3	2	1	0
1,2,3,5,6	345.82	574.82	−140.06	−23.41	32.64	617.59	15.28	−1.44	1.24	1.000	1.25	2	3	3	1	0	0
1,2,3,5,7	358.04	577.31	−152.88	−36.98	19.07	617.58	15.23	−1.44	1.24	1.000	1.24	2	3	2	2	0	0
1,2,3,5,8	356.91	571.77	−122.55	−4.99	51.06	616.82	15.62	−1.43	1.23	1.000	1.25	3	2	2	1	1	1
1,2,3,6,7	351.44	579.32	−171.35	−56.05	0.00	616.89	15.71	−1.44	1.24	1.000	1.25	1	4	3	1	0	0
1,2,3,6,8	354.43	571.82	−151.31	−33.77	22.28	617.18	15.47	−1.44	1.24	1.000	1.25	2	3	2	2	0	1
1,2,3,7,8	350.80	569.63	−139.51	−21.32	34.73	617.09	15.59	−1.44	1.24	1.000	1.25	2	3	3	1	0	1
1,2,4,5,6	340.65	572.06	−121.20	−3.72	52.33	616.85	15.57	−1.43	1.23	1.000	1.24	3	2	2	1	1	1
1,2,4,5,7	353.14	573.77	−132.58	−15.62	40.43	617.06	15.36	−1.43	1.23	1.000	1.24	3	2	1	2	1	1
1,2,4,5,8	349.62	571.99	−108.30	9.18	65.23	616.19	15.84	−1.43	1.23	1.000	1.24	4	1	1	1	2	2
1,2,4,6,7	340.52	577.84	−147.06	−31.32	24.73	616.97	15.52	−1.44	1.23	1.000	1.24	2	3	2	1	1	0
1,2,4,6,8	352.63	573.49	−133.22	−16.17	39.88	616.94	15.44	−1.43	1.23	1.000	1.24	3	2	1	2	1	1
1,2,4,7,8	350.26	571.67	−121.96	−4.37	51.68	616.83	15.59	−1.43	1.23	1.000	1.24	3	2	2	1	1	1
Hexa-CAQN																	
1,2,3,4,5,6	365.76	597.77	−113.59	5.56	36.24	630.91	7.91	−1.41	1.19	1.000	1.19	3	3	4	2	1	1
1,2,3,4,5,7	372.64	599.78	−124.60	−6.05	24.63	631.12	7.69	−1.41	1.19	1.000	1.18	3	3	3	3	1	1
1,2,3,4,5,8	362.55	597.93	−101.19	17.91	48.60	630.22	8.19	−1.40	1.18	1.000	1.19	4	2	3	2	2	2
1,2,3,4,6,7	370.34	603.22	−137.46	−19.93	10.75	631.22	7.71	−1.41	1.19	1.000	1.19	2	4	4	2	1	0
1,2,3,5,6,7	371.82	602.17	−148.52	−30.68	0.00	631.04	7.90	−1.41	1.19	1.000	1.20	2	4	4	2	0	0
1,2,3,5,6,8	355.24	599.41	−129.37	−10.71	19.97	630.29	8.19	−1.40	1.19	1.000	1.19	3	3	3	2	1	1
1,2,3,5,7,8	369.66	599.47	−130.04	−11.40	19.28	630.28	8.19	−1.41	1.19	1.000	1.19	3	3	3	2	1	1
1,2,3,6,7,8	370.89	597.45	−147.54	−28.29	2.39	630.56	8.19	−1.41	1.19	1.000	1.20	2	4	4	2	0	1
1,2,4,5,6,8	368.35	599.52	−116.09	2.53	33.22	629.53	8.50	−1.40	1.18	1.000	1.19	4	2	2	2	2	2
1,2,4,5,7,8	371.27	599.62	−116.19	2.40	33.08	629.55	8.48	−1.40	1.18	1.000	1.19	4	2	2	2	2	2

Table 5. Continued

molecule	V_m Å^3	S^θ J·mol^{-1}·K^{-1}	$\Delta_f H^\theta$ kJ·mol^{-1}	$\Delta_f G^\theta$ kJ·mol^{-1}	$\Delta_f G^\theta_R$ kJ·mol^{-1}	$C_{p,m}$(J·mol^{-1}·K^{-1}) constant	10^{-3} T	10^5 T^{-1}	10^7 T^{-2}	R^2	SE	N_α	N_β	N_o	N_m	N_p	$N_{1,8}$
						Hepta-CAQN											
1,2,3,4,5,6,7	396.36	625.36	−121.49	−1.22	0.00	644.31	0.54	−1.38	1.14	1.000	1.14	3	4	5	3	1	1
1,2,3,4,5,6,8	390.38	625.23	−109.04	11.26	12.48	643.48	0.89	−1.37	1.14	1.000	1.14	4	3	4	3	2	2
						OCAQN											
1,2,3,4,5,6,7,8	414.73	650.95	−101.81	20.17		657.42	−6.71	−1.35	1.09	1.000	1.09	4	4	6	4	2	2

[a] V_m is the molecular volume. S^θ is standard entropy. $\Delta_f H^\theta$ is the standard enthalpy of formation of the compound. $\Delta_f G^\theta$ is the standard Gibbs energy of formation of the compound. $\Delta_f G^\theta_R$ is the relative magnitude of the standard Gibbs energy of formation. $C^\theta_{p,m}$ is the molar heat capacity at constant pressure. N is the number of Cl atom substitutions, and the subscript PCS indicates the positions.

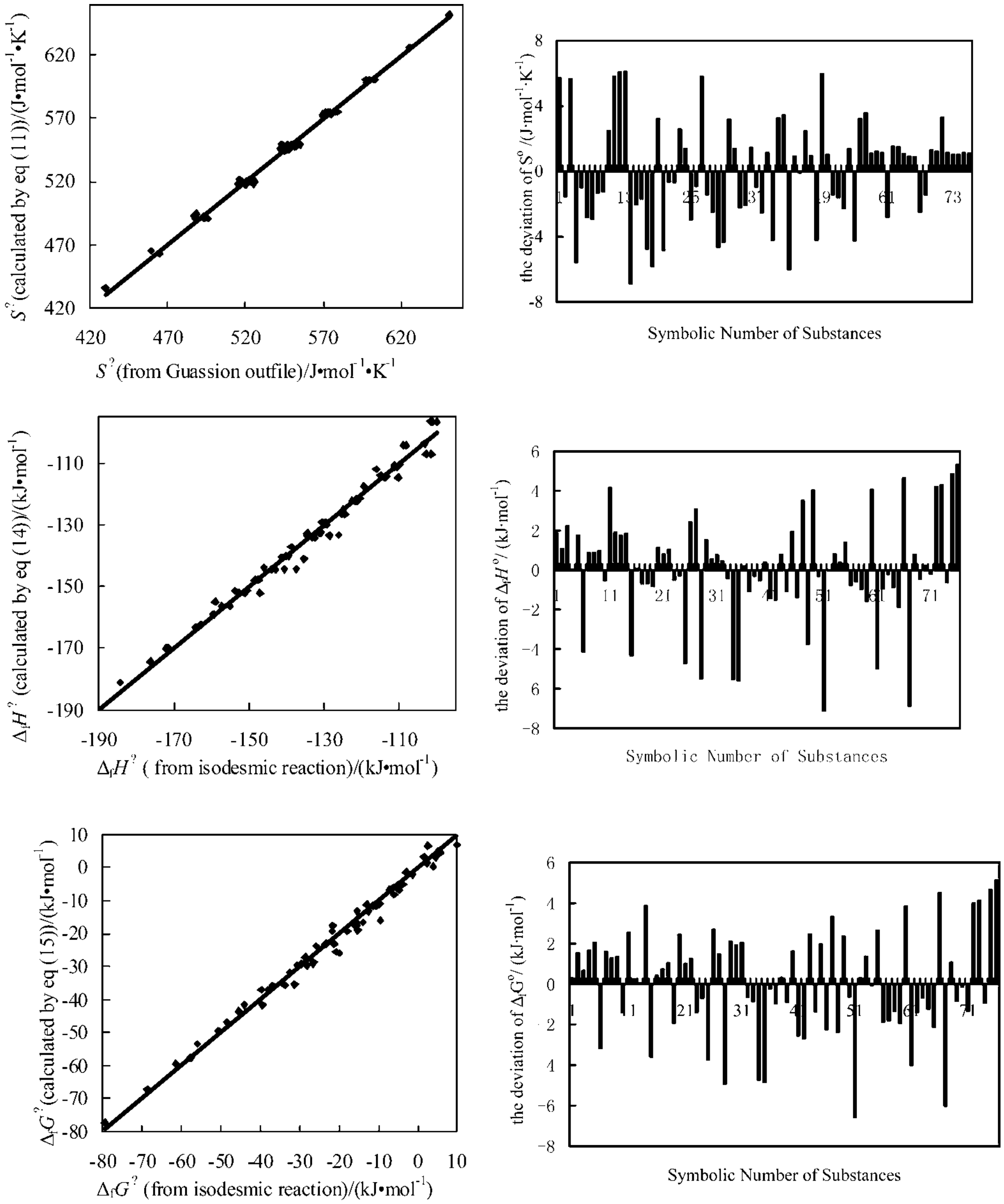
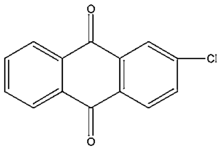
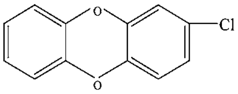
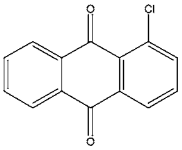
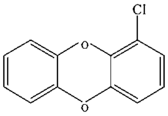
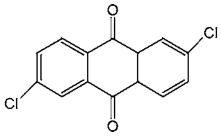
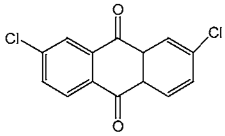
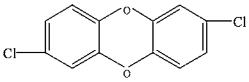
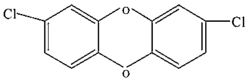
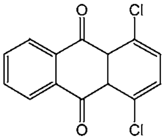
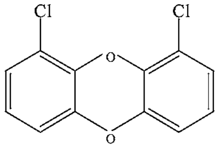
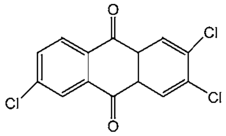
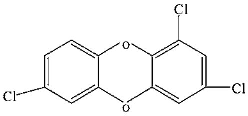
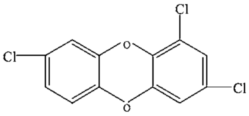
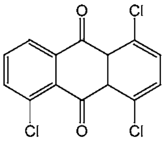
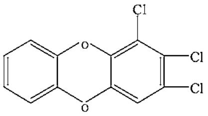
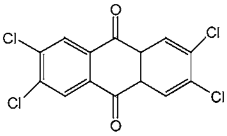
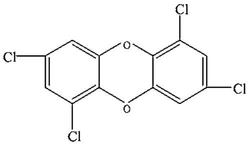
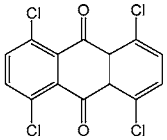
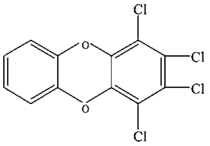
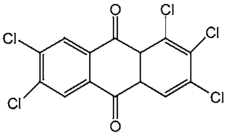
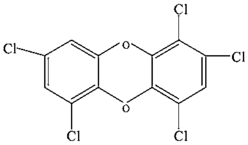
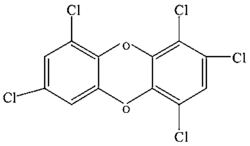
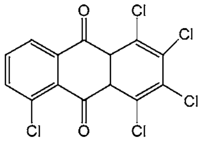
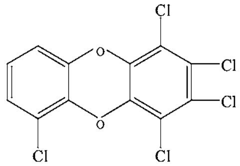
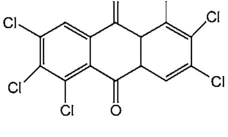
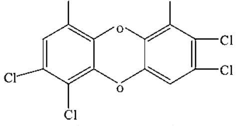
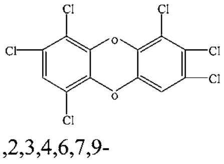
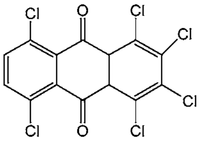
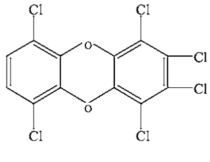
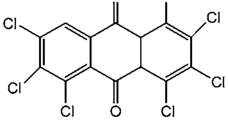
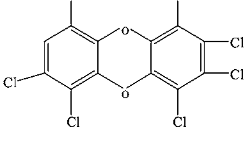
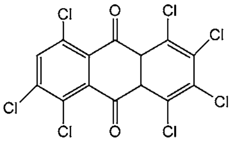
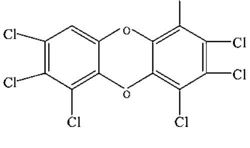


Figure 2. Plots of the values obtained from the correlations versus the corresponding DFT results.

relative standard Gibbs energies of formation ($\Delta_f G^\theta_R$) were obtained by $\Delta_f G^\theta$ of other isomers minus the lowest $\Delta_f G^\theta$ of isomers with the same substituent numbers. These values are also listed in Table 5. From Table 5, it can be found that the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ are varied between isomers with the same number of chlorine atoms. For example, among the 22 isomers of TCAQNs, 2,3,6,7-TCAQN possesses the lowest value of $\Delta_f G^\theta$, and 1,4,5,8-TCAQN possesses the highest corresponding value, where their discrepancy ($\Delta_f G^\theta_R$) is 95.47 kJ·mol^{-1}. In the same way, the $\Delta_f G^\theta_R$ of 1,2,3,6,7-penta-CAQN is lower than those of the other 14 isomers, and 1,2,3,4,5-penta-CAQN is higher than those of the others, where their discrepancy ($\Delta_f G^\theta_R$) is 70.78 kJ·mol^{-1}.

In each group of isomers, the most stable and unstable isomers as indicated by the Gibbs energy of formation can be obtained and are listed in Table 6. From Table 6, when AQN is substituted by one, two, and three chlorine atoms, the most stable and unstable isomers are similar to PCDDs, while to the other isomers, the results are different (see Table 6). This is because, for PCAQNs, the value of the $\Delta_f G^\theta$ chlorine substituting

Table 6. Most Stable and Least Stable Isomers in Different Isomer Groups

Mono-				
Di-	2,6- 2,7-  	2,7- 2,8-  	1,4- 	1,9- 
Tri-	2,3,6- 	1,3,7- 1,3,8-  	1,4,5- 	1,2,3- 
Tetra-	2,3,6,7- 	1,3,6,8- 	1,4,5,8- 	1,2,3,4- 
Penta-	1,2,3,6,7- 	1,2,4,6,8- 1,2,4,7,9-  	1,2,3,4,5- 	1,2,3,4,6- 
Hexa-	1,2,3,5,6,7- 	1,2,3,6,7,9- 1,2,3,6,8,9-  	1,2,3,4,5,8- 	1,2,3,4,6,9- 
Hepta-	1,2,3,4,5,6,7- 	1,2,3,4,6,7,9- 	1,2,3,4,5,6,8- 	1,2,3,4,6,7,8- 

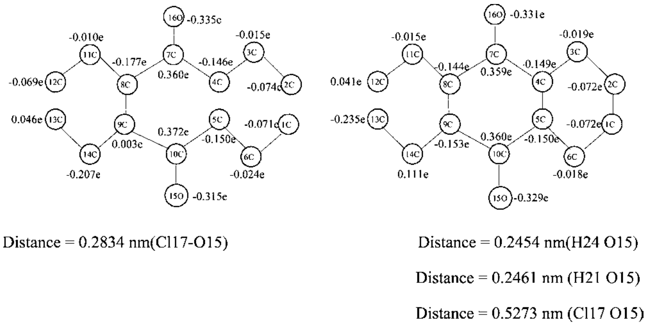


Figure 3. Actual molecular structures obtained in the DFT optimization of 1-MCAQN and 2-MCAQN.

position α is 30.284 kJ·mol^{-1} larger than the chlorine substituting position β (see eq 15), while the value of $\Delta_f G^{\theta}$ increases to 15.882 kJ·mol^{-1} when the pair numbers of the chlorine substituting position ortho is increased by 1, so the isomer chlorine substituting position ortho is more stable than the chlorine substituting position α. As for PCDDs, the correlation expressions of $\Delta_f G^{\theta}$ to N_{PCS} are presented in eq 16. When the value of the $\Delta_f G^{\theta}$ chlorine substituting position α is 8.340 kJ·mol^{-1} larger than the chlorine substituting position β, the value of $\Delta_f G^{\theta}$ increases to 14.321 kJ·mol^{-1} when the pair numbers of chlorine substituting position ortho is increased by 1, that is, the isomer chlorine substituting position α is more stable than the chlorine substituting position ortho for PCDD isomers. Because of the differences between two class compounds, when the number of chlorine atoms substituted for hydrogen is larger than 3, the chlorine atom replaces as much as possible at position β for the most stable isomers of PCAQNs, and the more chlorine atoms replaced at position α, the more unstable the isomer is. However, for PCDDs, the chlorine atoms replace as far as possible away from the position ortho of other chlorine atom in the most stable isomer; the more chlorine atoms replace on the same benzene ring, and the number of positions ortho is more in the most unstable isomers. These results can be used to examine if the most stable isomers are the most abundant in the environment.

$$\Delta_f G^{\theta}_{PCDD}/\text{kJ}\cdot\text{mol}^{-1} = 63.002 - 5.818N_{\alpha} - 14.158N_{\beta} + 14.321N_{o} + 2.542N_{m} + 3.701N_{p}$$

$$R_2 = 0.956 \qquad \text{SE} = 2.478 \qquad F = 301.434 \tag{16}$$

From the discussion above, the reasons those compounds with chlorines attached at the position α are most unstable may be the following: (i) The distance between the Cl atom replaced at the positions α and the O atom is nearer than that between the Cl atom replaced at positions β and the O atom, so the repulsive force between the chlorine and the oxygen atoms is obviously stronger than that of the latter. (ii) Cl and O atoms possess negative charges, while the H atom has a positive charge. So, the higher stability of PCAQNs, with chlorines being attached at positions β, certainly results from intramolecular hydrogen bonding occurring between the hydrogen and the negative regions of the O atom. Taking MCAQNs as an example, on the basis of Gaussian output files, these data can be found as shown in Figure 3: the distance (between the Cl at positions α and the O atom) and charge are 0.2834 nm, −0.0310 e (Cl), and −0.3147 e (O) for Cl at positions α, respectively, and 0.5273 nm, −0.0534 e (Cl), −0.3288 (O), and 0.141 e (H) for Cl at positions β, respectively.

Temperature Dependence of Molar Heat Capacity of PCAQNs at Constant Pressure. The values of molar heat capacity at constant pressure ($C_{p,m}$) for PCAQN congeners have not been reported. The values of $C_{p,m}$ (200 to 1000 K) have accordingly been calculated using a statistical thermodynamics calculation program based on Gaussian output files.

Using the calculated values of $C_{p,m}$ of PCAQNs at different temperatures (T), the relations between $C_{p,m}$ and temperature were obtained using the least-squares method, as in eq 17.

$$C_{p,m} = a + b(10^{-3}T) + c(10^{5}T^{-1}) + d(10^{7}T^{-2}) \tag{17}$$

Constant a and regression coefficients b, c, and d are listed in Table 5. The correlation coefficients (R^2) are all equal to 1.0, and all of the standard deviations (SD) are low.

To validate the precision of the method, we have calculated $C_{p,m}$ of some aromatic hydrocarbons at the temperatures between

Table 7. Differences between Calculated and Experimental Values of $C_{p,m}$

	$C_{p,m}$/J·mol^{-1}·K^{-1}											
	400 K			600 K			800 K			1000 K		
name	calcd[a]	exptl[b]	diff.	calcd[a]	exptl[b]	diff.	calcd[a]	exptl[b]	diff.	calcd[a]	exptl[b]	diff.
aniline	140.21	142.97	−2.76	190.77	192.84	−2.07	224.13	225.06	−0.93	247.55	247.61	−0.06
phenol	132.96	135.77	−2.81	180.47	182.17	−1.70	211.29	211.79	−0.50	232.57	232.17	0.40
benzenethiol	138.70	142.97	−4.27	184.99	192.84	−7.85	215.25	225.06	−9.81	236.20	247.61	−11.41
m-cresol	163.43	162.09	1.34	220.49	218.66	1.83	258.98	256.35	2.63	286.10	286.60	−0.50
p-cresol	163.47	161.71	1.76	220.47	217.99	2.48	258.96	255.68	3.28	286.10	290.70	−4.60
o-cresol	163.22	166.27	−3.05	220.36	220.79	−0.43	258.90	257.53	1.37	286.05	287.94	−1.89
biphenyl	220.10	221.04	−0.94	307.01	307.69	−0.68	363.49	363.67	−0.18	402.15	401.66	0.49
chlorobenzene	126.72	128.11	−1.39	170.54	172.21	−1.67	198.71	200.37	−1.66	217.93	219.58	−1.65
1,2-dichlorobenzene	141.49	142.76	−1.27	182.95	184.39	−1.44	208.99	210.37	−1.38	226.37	227.69	−1.32
1,3-dichlorobenzene	141.85	143.01	−1.16	183.18	184.47	−1.29	209.12	210.41	−1.29	226.43	227.69	−1.26
1,4-dichlorobenzene	141.81	143.26	−1.45	183.14	184.77	−1.63	209.09	210.66	−1.57	226.41	227.86	−1.45
perchlorobenzene	200.45	201.17	−0.72	232.75	233.38	−0.63	250.37	249.74	0.63	260.45	260.83	−0.38
1,2-difluorobenzene	135.54	137.07	−1.53	178.65	181.29	−2.64	205.94	209.70	−3.76	224.16	228.95	−4.79
1,3-difluorobenzene	135.82	136.90	−1.08	179.03	180.46	−1.43	206.21	207.82	−1.61	224.33	225.64	−1.31
1,4-difluorobenzene	135.87	137.40	−1.53	179.05	180.75	−1.70	206.23	207.86	−1.63	224.35	225.89	−1.54
perfluorobenzene	183.10	183.59	−0.49	218.90	219.87	−0.97	240.17	241.08	−0.91	252.93	253.68	−0.75
toluene	142.13	140.08	2.05	197.95	197.48	0.47	236.04	235.60	0.44	263.02	264.93	−1.91
ethylbenzene	168.91	170.54	−1.63	236.46	236.14	0.32	282.96	280.96	2.00	316.06	312.84	3.22

[a] Calculated using the statistical thermodynamics calculation program. [b] Taken from ref 21.

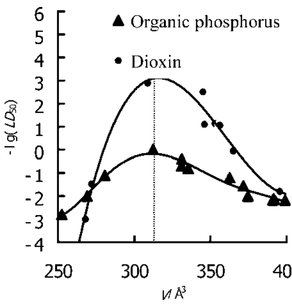


Figure 4. Relation of the molecular volume of dioxin and organic phosphorus compound over toxicity to a rat.

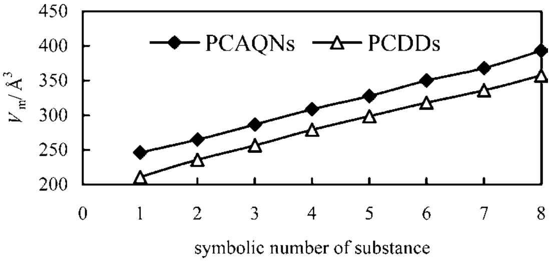


Figure 5. Calculated average V_m of PCAQNs and PCDDs.

(200 to 1000) K and compared them with the experimental data (seen Table 7). Table 7 shows that benzenethiol possesses the largest deviation of -11.41 J·mol^{-1}·K^{-1}, and the differences of calculated values and those from ref 21 for the other compounds are small, which indicates the method used in this study is of high precision.

Molecular Volume of PCAQNs and the Prediction of Toxicity. In this work, the molecular volume defined as the one inside a contour with charge density of 0.001 e/Bohr^3 was employed. In addition, the keyword "tight" was chosen so as to increase the precision of the volume, and the mean molecular volume V_i (Å^3) was obtained from the result of repeated computation of 10 times and is listed in Table 5. As reported,[22] in one series of compounds, molecular volumes are closely relative to biological toxicity; that is, (309 to 320) Å^3 of molecular volume is key for their high toxicity. The closer to this volume, the higher toxicity could be observed; that is, an inversed "V" type relationship could be found between effective concentration and molecular volume with its maximum being (309 to 320) Å^3 (see Figure 4). Figure 5 is drawn by using the molecular numbers as the *x*-axis and V_m of PCAQNs and PCDDs as the *y*-axis. As shown in Figure 5, with the increase of the chlorine substituted number, V_m of PCAQNs and PCDDs exhibits the same changing trend. For the isomers with the same chlorine substituted number, V_m of PCDDs is slightly smaller than that of PCAQNs. As shown in Table 5, all of the V_m of tri-CAQNs are almost (309 to 320) Å^3; that is, tri-CAQNs may be the most toxic for PCAQN congeners. When the chlorine-substituted number is above four, molecular volume will be larger than 320 Å^3, and ultimately, its toxicity will decrease. Meanwhile, for PCDDs, the congeners with four chlorine atoms (the volumes are (300 to 320) Å^3) possess the most toxicity.

Conclusions

76 PCAQNs were fully optimized at the BHandHLYP/6-311G** level, and thus their H^θ, S^θ, and G^θ were consequently obtained. In addition, $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of formation for each PCAQN molecule were calculated by isodesmic reactions. The results showed that all of these thermodynamic parameters have a close relationship with the numbers and positions of chlorine substituents (N_{PCS}). Thus, the enthalpies and Gibbs energies of formation for 76 PCAQN congeners should be valuable in further thermodynamic modeling studies. According to the relative magnitude of their $\Delta_f G^\theta$, the order of relative stability of PCAQN congeners was theoretically proposed. It is found that the most unstable isomers are those with chlorines attached at the same aromatic ring while being close to each other, while the most stable isomers are those with chlorines replaced at two aromatic rings if possible, so that the chlorines can be apart from each other. Moreover, it is determined that there is a very good relationship between $C_{p,m}$ and temperature for the PCAQN congeners. The relative stabilities and toxicity predicted of PCAQNs were also compared with those of PCDDs.

Literature Cited

(1) Seiji, T.; Niels-Ulrik, F.; Masamitsu, H.; Keizo, S.; Katsumi, M. Quenching of bacteriochlorophyll fluorescence in chlorosomes from chloroflexus aurantiacus by exogenous quinones. *Photochem. Photobiol.* **2000**, *72* (3), 345–350.

(2) Yen, J. H.; Lin, K. H.; Wang, Y. S. Acute lethal toxicity of environmental pollutants to aquatic organisms. *Ecotoxicol. Environ. Saf.* **2002**, *52*, 113–116.

(3) Bramble, L. A.; Boardman, G. D.; Bevan, D. R.; Dietrich, A. M. Rat liver mitochondrial and microsomal tests for the assessment of quinone toxicity. *Environ. Toxicol. Chem.* **1994**, *13* (2), 307–316.

(4) Thompson, D.; Ewan, B. C. R. A group additivity algorithm for polychlorinated dibenzofurans derived from selected DFT analyses. *J. Phys. Chem. A* **2007**, *111*, 5043–5047.

(5) Zeng, X.; Freeman, P. K.; Vasil'ev, Y. V.; Voinov, V. G.; Simonich, S. L.; Barofsky, D. F. Theoretical Calculation of Thermodynamic Properties of Polybrominated Diphenyl Ethers. *J. Chem. Eng. Data* **2005**, *50*, 1548–1556.

(6) Kroon, M. C.; Buijs, W.; Peters, C. J.; Witkamp, G. J. Quantum chemical aided prediction of the thermal decomposition mechanisms and temperatures of ionic liquids. *Thermochim. Acta* **2007**, *465*, 40–47.

(7) Larowe, D. E.; Helgeson, H. C. The energetics of metabolism in hydrothermal systems: Calculation of the standard molal thermodynamic properties of magnesium-complexed adenosine nucleotides and NAD and NADP at elevated temperatures and pressures. *Thermochim. Acta* **2006**, *448*, 82–106.

(8) Wang, Z. Y.; Zhai, Z. C.; Wang, L. S.; Chen, J. L.; Kikuchi, O.; Watanabe, T. Prediction of gas phase thermodynamic function of polychlorinated dibenzo-*p*-dioxins using DFT. *J. Mol. Struct.: THEOCHEM* **2004**, *672* (1−3), 97–104.

(9) Wang, Z. Y.; Wu, Y. C.; Kikuchi, O.; Watanabe, T. DFT study of tetrachlorinated dibenzo-p-dioxins. *Acta Chim. Sin.* **2003**, *61*, 840–845.

(10) Wang, Z. Y.; Han, X. Y.; Zhai, Z. C.; Wang, L. S. Study on the thermodynamic property and relative stability of a series of polychlorinated biphenyls by density functional theory. *Acta Chim. Sin.* **2005**, *63*, 964–972.

(11) Wei, X. Y.; Liu, H.; Wang, Z. Y.; Zhu, J. J. Computational note on thermodynamic function of Polychlorinated Phenoxathiins (PCPTs). *J. Mol. Struct.: THEOCHEM* **2008**, *857*, 126–127.

(12) Irikura, K. K. *THERMO.PL*; National Institute of Standards and Technology: Gaithersburg, MD, 2002.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 03 (Revision A.1)*; Gaussian, Inc.: Pittsburgh, PA, 2003.

(14) Lee, J. E.; Choi, W.; Mhin, B. J. DFT calculation on the thermodynamic properties of polychlorinated dibenzo-p-dioxins: intramolecular Cl-Cl repulsion effects and their thermochemical implications. *J. Phys. Chem. A.* **2003**, *107*, 2693–2699.

(15) Dean, J. A., Ed.; *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1991.

(16) Foresman, J. B.; Frisch, A. *Exploring chemistry with electronic structure methods*; 2nd ed.; Gaussian Inc.: Pittsburgh, PA, 1996.
(17) Liu, H. X.; Yang, G. Y.; Wang, Z. Y.; Wang, L. S. Study of stability and thermodynamic properties for polychlorinated dihydrophezines by density functional theory. *Can. J. Chem. Eng.*, in press.
(18) Yuan, L. X.; Yu, J.; Wang, Z. Y.; Liu, H. X.; Ju, X. H. Thermodynamic property and relative stability of 76 polybrominated naphthalene by density functional theory. *J. Chem. Eng. Data* **2006**, *51*, 2032–2037.
(19) Frenkel, M.; Marsh, K. N.; Kabo, G. J.; Wilhoit, R. C.; Roganov, G. N. *Thermodynamics of organic in the gas state*; CRC press: Boca Raton, FL, 1994.
(20) Grabda, M.; Kudlak, S. O.; Shibata, E.; Nakamura, T. Gas phase thermodynamic properties of PBDEs, PBBs, PBPs, HBCD and TBBPA predicted using DFT method. *J. Mol. Struct.: THEOCHEM* **2007**, *822*, 38–44.
(21) Yao, Y. B.; Xie, T.; Gao, Y. M. *Handbook of Physics and Chemistry*; Shanghai Science and Technology Press: Shanghai, 1985; pp 912−1015.
(22) Wang, Z. Y.; Han, X. Y.; Wang, L. S.; Zhai, Z. C. The relationship between the toxicity and the molecular volume for dioxins, organic phosphorus and straight-chain fatty alcohol. *Chin. Sci. Bull.* **2004**, *49*, 1431–1436.

Received for review April 15, 2009. Accepted September 11, 2009. Financially supported by the National Natural Science Foundation of China (20737001) and the Zhejiang Provincial Natural Science Foundation of China (2008Y507280).

JE9003564