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Density Functional Theory Studies on the Thermodynamic Properties of Polychlorinated Diphenyl Sulfides

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Thermodynamic properties, including entropy (S^{θ}), heat capacity at constant volume ($C^{\theta}{}_{v}$), enthalpy (H^{θ}), and Gibbs energy (G^{θ}) for 209 polychlorinated diphenyl sulfides (PCDPSs) 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 energy of formation ($\Delta_f G^{\theta}$) were obtained by designing isodesmic reactions. The relations of S^{θ}, $C^{\theta}{}_{v}$, $\Delta_f H^{\theta}$, and $\Delta_f G^{\theta}$ with the number and position of chlorine substitution (N_{PCS}) are discussed. It suggested that S^{θ}, $C^{\theta}{}_{v}$, $\Delta_f H^{\theta}$, and $\Delta_f G^{\theta}$ of PCDPSs vary greatly with N_{PCS}. The values of heat capacity at constant pressure ($C^{\theta}{}_{p}$) at temperatures from (200 to 1800) K for PCDPS congeners were calculated using a statistical thermodynamics calculation program based on Gaussian output files, and their temperature dependencies were obtained using the least-squares method. On the basis of the magnitude of the relative standard Gibbs energy of formation ($\Delta_{R,f}G^{\theta}$), the relative stability of PCDPS isomers is theoretically proposed and compared with that of the polychlorinated diphenyl ether (PCDE) isomers.

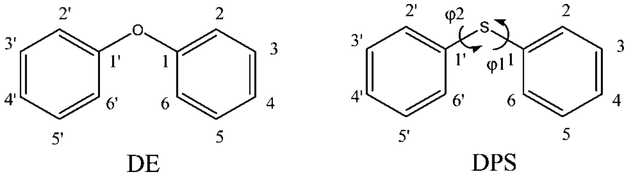

Figure 1. Molecular structures and atomic numbering of diphenyl ether (DE) and diphenyl sulfide (DPS).

Introduction

Polychlorinated diphenyl ethers (PCDEs), a group of halogenated aromatic compounds, are a subfamily of persistent organic pollutants (POPs) and have been detected in a wide range of environmental samples.[1,2] Polychlorinated diphenyl sulfides (PCDPSs), sulfur analogues of PCDEs, are also environmentally interesting compounds, and the detection of trichlorinated diphenyl sulfides (tri-CDPSs) and tetrachlorinated diphenyl sulfides (TCDPSs) in stack gas and bleached pulp mill effluent samples has been reported.[3,4] The structures and atom numbering of diphenyl ether (DE) and diphenyl sulfide (DPS) are shown in Figure 1.

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

In this study, the thermodynamic properties (entropy (S^{θ}), heat capacity at constant volume ($C^{\theta}{}_{v}$), heat capacity at constant pressure ($C^{\theta}{}_{p}$), enthalpy of formation ($\Delta_f H^{\theta}$), and Gibbs energy of formation ($\Delta_f G^{\theta}$) in the ideal gas state at 298.15 K and 101.325 kPa) were computed for all 209 PCDPSs using DFT. The purpose of this study was to obtain a set of thermodynamic values for PCDPSs and to discuss the correlation between these thermodynamic properties and the number and position of chlorine substitution (N_{PCS}) and the temperature dependence of their heat capacities at constant pressure ($C^{\theta}{}_{p}$). Furthermore, based on the magnitude of the relative standard Gibbs energy of formation ($\Delta_{R,f}G^{\theta}$), the theoretical relative stability order of the isomers is proposed.

Computational Method

We have calculated the values of $\Delta_r H^{\theta}$ for the two reactions 2 diphenyl sulfide → thianthrene + 2 benzene and 2 chlorobenzene → 1,2-dichlorobenzene + benzene at B3LYP/6-31G* and B3LYP/6-311G** levels and compared them with experimental ones to test the feasibility of our method. The calculated values of $\Delta_r H^{\theta}$ are (−9.96 and 14.52) kJ·mol^{-1} at the B3LYP/6-31G* level and (−9.05 and 14.88) kJ·mol^{-1} at the B3LYP/6-311G** level, respectively, while the corresponding experimental values (obtained from $\Delta_f H^{\theta}$ of diphenyl sulfide, thianthrene, benzene, chlorobenzene, and 1,2-dichlorobenzene) are (−6.14 and 9.45) kJ·mol^{-1}, respectively. It can be seen that the discrepancies between calculated values and experimental ones for $\Delta_r H^{\theta}$ are all less than 6 kJ·mol^{-1}, and the differences between the results at two different calculation levels are less than 1 kJ·mol^{-1},

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Table 1. Thermodynamic Data Used to Calculate $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of PCDPSs[a]

compound	$\Delta_f H^\theta$ kJ·mol^{-1}	$\Delta_f G^\theta$ kJ·mol^{-1}	H^θ hartree	G^θ hartree
diphenyl sulfide	165.03[b]	280.84[b]	−861.29078[d]	−861.34063[d]
benzene	82.93[c]	129.73[c]	−232.14258[d]	−232.17302[d]
chlorobenzene	51.84[c]	99.23[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 energy of formation of the compound. H^θ is the standard enthalpy, and G^θ is the standard Gibbs energy. [b] Taken from ref 11. [c] Taken from ref 13. [d] Obtained from B3LYP/6-31G* calculations.

which show that DFT B3LYP/6-31G* calculation is suitable for our study. So throughout this paper, geometry optimizations and energy calculations for all 209 PCDPS molecules were performed at the B3LYP/6-31G* level with the Gaussian 98 program.[12] Frequency calculations were then carried out for all of the possible geometries to ensure they are minima on the potential energy surface. In this paper, PCDPS congeners with one to ten chlorine atoms are represented by the notation MCDPS, DCDPS, tri-CDPS, TCDPS, penta-CDPS, hexa-CDPS, hepta-CDPS, octa-CDPS, nona-CDPS, and deca-CDPS, respectively. Prefix numbers represent the positions (see Figure 1) of chlorine substitution. (e.g., 2,3,4,5-TCDPS).

Isodesmic reactions were used successfully to obtain thermodynamic data for PCDEs[9] and PBDEs[8] in previous studies. Similarly, isodesmic reaction 1 was designed to calculate $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of PCDPSs in this study.

$$\text{diphenyl sulfide} + n\text{chlorobenzene} = \text{PCDPS} + n\text{benzene} \tag{1}$$

The standard enthalpy of 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

$$\Delta_r H^\theta = [H^\theta{}_{\text{PCDPS}} + nH^\theta{}_{\text{benzene}}] - [H^\theta{}_{\text{diphenyl sulfide}} + nH^\theta{}_{\text{chlorobenzene}}] \tag{2}$$

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

$$\Delta_r H^\theta = [\Delta_f H^\theta{}_{\text{PCDPS}} + n\Delta_f H^\theta{}_{\text{benzene}}] - [\Delta_f H^\theta{}_{\text{diphenyl sulfide}} + n\Delta_f H^\theta{}_{\text{chlorobenzene}}] \tag{3}$$

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

$$\Delta_f H^\theta{}_{\text{PCDPS}} = H^\theta{}_{\text{PCDPS}} + nH^\theta{}_{\text{benzene}} - nH^\theta{}_{\text{chlorobenzene}} - H^\theta{}_{\text{diphenyl sulfide}} - n\Delta_f H^\theta{}_{\text{benzene}} + n\Delta_f H^\theta{}_{\text{chlorobenzene}} + \Delta_f H^\theta{}_{\text{diphenyl sulfide}} \tag{4}$$

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

$$\Delta_f G^\theta{}_{\text{PCDPS}} = G^\theta{}_{\text{PCDPS}} + nG^\theta{}_{\text{benzene}} - nG^\theta{}_{\text{chlorobenzene}} - G^\theta{}_{\text{diphenyl sulfide}} - n\Delta_f G^\theta{}_{\text{benzene}} + n\Delta_f G^\theta{}_{\text{chlorobenzene}} + \Delta_f G^\theta{}_{\text{diphenyl sulfide}} \tag{5}$$

The experimental values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ for diphenyl sulfide, chlorobenzene, and benzene taken from the literature[11,13] 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.

The number and position of Cl substitution (N_{PCS}) includes the number of Cl atoms on the different positions of the parent compound and the number of relative position for these Cl atoms. The number and position of Cl substitution are defined as follows: the numbers of chlorine atoms at positions 2 (6, 2′, 6′), 3 (5, 3′, 5′), and 4 (4′) are defined as $N_{2(6)}$, $N_{3(5)}$, and N_4, and the numbers of relative ortho, meta, and para positions between two chlorine atoms on the same phenyl ring for all chlorines on two phenyl rings are symbolized as N_o, N_m, and N_p, respectively. For example, $N_{2(6)}$, $N_{3(5)}$, N_4, N_o, N_m, and N_p equal 2, 2, 1, 4, 4, and 2 for 2,3,4,5,6-penta-CDPS and equal 4, 4, 2, 8, 8, and 4 for 2,3,4,5,6,2′,3′,4′,5′,6′-deca-CDPS, respectively. Moreover, the parameters mentioned above are defined as a general designation N_{PCS} and listed in Table 2.

Using the SPSS 12.0 for Windows statistic analysis program, the values of N_{PCS} 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

The values of thermodynamic quantities (S^θ, $C^\theta{}_v$, H^θ, and G^θ) calculated for 209 PCDPSs 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.

Conformational Isomers of PCDPS Congeners. There exist two C−S single bonds in PCDPS congeners about which the two phenyl rings can rotate. So each PCDPS congener can have several stable conformations. The conformations of diphenyl sulfide and PCDPS congeners are described by the torsional angles ($\varphi 1$ and $\varphi 2$) between the C−S−C plane and planes of the phenyl rings. The angles are defined as positive when the rotation is clockwise looking down the C4−C1 and C4′−C1′ axes toward the sulfur (see Figure 1). Theoretically, there are four possible types of conformations of diphenyl sulfide: planar ($\varphi 1 = \varphi 2 = 0°$), butterfly ($\varphi 1 = \varphi 2 = 90°$), skew ($\varphi 1 = 0°$, $\varphi 2 = 90°$), and twist ($\varphi 1$, $\varphi 2 > 0°$). Obviously, planar conformation is certainly not stable due to steric repulsion of the *ortho*-hydrogen atoms. However, chemical intuition cannot decide which of the remaining conformations is favored. Considering CPU time, it would be impractical to find all of the possible stable conformations for each of the 209 PCDPS congeners. So diphenyl sulfide and 20 PCDPS congeners (2-MCDPS, 3-MCDPS, 4-MCDPS, 2,6-DCDPS, 2,2′-DCDPS, 3,3′-DCDPS, 3,5,4′-tri-CDPS, 2,3,6-tri-CDPS, 3,5,3′,5′-TCDPS, 2,3,5,6,-TCDPS, 2,4,5,3′,5′-penta-CDPS, 2,3,4,5,6-penta-CDPS, 2,4,5,2′,4′,5′-hexa-CDPS, 2,3,4,5,6,2′-hexa-CDPS, 2,3,4,5,2′,4′,5′-hepta-CDPS, 2,3,4,5,6,2′,6′-hepta-CDPS, 2,3,4,5,2′,3′,4′,5′-octa-CDPS, 2,3,4,5,6,2′,3′,6′-octa-CDPS, 2,3,4,5,6,2′,3′,4′,5′-nona-CDPS, and 2,3,4,5,6,2′,3′,5′,6′-nona-CDPS) were selected for conformation study.

Our B3LYP/6-31G* calculation showed that diphenyl sulfide has a twist conformation in which both $\varphi 1$ and $\varphi 2$ are 46.5°. For 20 selected PCDPS congeners, only skew or twist conformations can be optimized as an energy minimum, while the butterfly conformation is always a saddle point on the potential energy surface. Our calculations have also indicated that if a PCDPS congener has the C2 symmetry of both rings (for example, 4-MCDPS, 2,6-DCDPS, 3,5,4′-tri-CDPS, etc.) it has only one stable conformation, and this conformation is in twist structure generally. Contrarily, if a PCDPS congener has only one or has no ring with C2 symmetry (for example, 2-MCDPS, 2,2′-DCDPS, 2,4,5,3′,5′-penta-CDPS, etc.), it has two or more

Table 2. Thermodynamic Properties of PCDPSs from DFT Calculations and N_{pcs}

molecule	S^{θ} $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	C^{θ}_{v} $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	H^{θ} hartree	G^{θ} hartree	$\Delta_{\mathrm{f}}H^{\theta}$ $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{\mathrm{f}}G^{\theta}$ $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{\mathrm{R,f}}G^{\theta}$ $\mathrm{kJ \cdot mol^{-1}}$	$N_{2(6)}$	$N_{3(5)}$	N_4	N_{o}	N_{m}	N_{p}
DPS	438.96	174.70	−861.29078	−861.34063				0	0	0	0	0	0
MCDP													
2	470.07	190.58	−1320.89242	−1320.94585	142.04	262.57	9.39	1	0	0	0	0	0
3	479.07	190.99	−1320.89498	−1320.94943	135.32	253.18	0.00	0	1	0	0	0	0
4	476.03	190.87	−1320.89488	−1320.94899	135.58	254.33	1.15	0	0	1	0	0	0
DCDPS													
2,2′	497.13	206.72	−1780.49194	−1780.54840	124.63	251.32	20.64	2	0	0	0	0	0
2,3′	504.93	206.83	−1780.49560	−1780.55299	115.02	239.27	8.59	1	1	0	0	0	0
2,4′	505.01	206.76	−1780.49603	−1780.55344	113.89	238.09	7.41	1	0	1	0	0	0
3,3′	507.95	207.40	−1780.49839	−1780.55593	107.70	231.55	0.87	0	2	0	0	0	0
3,4′	507.30	207.11	−1780.49860	−1780.55626	107.15	230.68	0.00	0	1	1	0	0	0
4,4′	500.73	207.04	−1780.49865	−1780.55558	107.01	232.47	1.79	0	0	2	0	0	0
2,3	495.76	206.37	−1780.49132	−1780.54767	126.26	253.24	22.56	1	1	0	1	0	0
2,4	508.28	206.86	−1780.49536	−1780.55314	115.65	238.87	8.19	1	0	1	0	1	0
2,5	500.18	206.83	−1780.49588	−1780.55273	114.29	239.95	9.27	1	1	0	0	0	1
2,6	498.23	206.73	−1780.48816	−1780.54480	134.56	260.77	30.09	2	0	0	0	1	0
3,4	514.41	206.70	−1780.49390	−1780.55237	119.49	240.90	10.22	0	1	1	1	0	0
3,5	505.86	207.19	−1780.49776	−1780.55526	109.35	233.31	2.63	0	2	0	0	1	0
tri-CDPS													
2,3,2′	518.53	222.19	−2240.08812	−2240.14706	115.99	250.28	41.64	2	1	0	1	0	0
2,3,3′	529.10	222.58	−2240.09427	−2240.15441	99.84	230.98	22.34	1	2	0	1	0	0
2,3,4′	528.23	222.53	−2240.09473	−2240.15478	98.63	230.01	21.37	1	1	1	1	0	0
2,4,2′	520.96	222.51	−2240.09274	−2240.15196	103.86	237.41	28.77	2	0	1	0	1	0
2,4,3′	532.97	223.04	−2240.09828	−2240.15886	89.31	219.30	10.66	1	1	1	0	1	0
2,4,4′	530.45	222.90	−2240.09875	−2240.15904	88.08	218.82	10.18	1	0	2	0	1	0
2,6,4′	530.05	222.87	−2240.09213	−2240.15238	105.46	236.31	27.67	2	0	1	0	1	0
2,5,2′	526.12	222.76	−2240.09522	−2240.15502	97.35	229.38	20.74	2	1	0	0	0	1
2,5,3′	532.44	223.07	−2240.09870	−2240.15922	88.21	218.35	9.71	1	2	0	0	0	1
2,5,4′	530.04	222.96	−2240.09920	−2240.15944	86.90	217.77	9.13	1	1	1	0	0	1
2,6,2′	515.61	222.58	−2240.08693	−2240.14554	119.11	254.27	45.63	3	0	0	0	1	0
2,6,3′	528.74	222.95	−2240.09213	−2240.15223	105.46	236.70	28.06	2	1	0	0	1	0
3,4,2′	527.39	222.44	−2240.09362	−2240.15357	101.55	233.19	24.55	1	1	1	1	0	0
3,4,3′	537.43	222.92	−2240.09695	−2240.15804	92.81	221.45	12.81	0	2	1	1	0	0
3,4,4′	539.15	222.84	−2240.09728	−2240.15857	91.94	220.06	11.42	0	1	2	1	0	0
3,5,2′	529.51	222.99	−2240.09734	−2240.15752	91.78	222.82	14.18	1	2	0	0	1	0
3,5,3′	536.53	223.36	−2240.10063	−2240.16162	83.14	212.05	3.41	0	3	0	0	1	0
3,5,4′	544.57	223.36	−2240.10102	−2240.16292	82.12	208.64	0.00	0	2	1	0	1	0
2,3,4	533.79	222.27	−2240.08909	−2240.14976	113.44	243.19	34.55	1	1	1	2	1	0
2,3,5	525.19	222.65	−2240.09362	−2240.15332	101.55	233.84	25.20	1	2	0	1	1	1
2,3,6	525.88	222.56	−2240.08549	−2240.14529	122.89	254.92	46.28	2	1	0	1	1	1
2,4,5	526.79	222.50	−2240.09386	−2240.15374	100.92	232.74	24.10	1	1	1	1	1	1
2,4,6	527.60	222.93	−2240.08975	−2240.14972	111.71	243.29	34.65	2	0	1	0	3	0
3,4,5	538.01	222.50	−2240.09157	−2240.15272	106.93	235.42	26.78	0	2	1	2	1	0
TCDPS													
2,3,2′,3′	551.86	238.17	−2699.68841	−2699.75114	96.56	235.01	39.65	2	2	0	2	0	0
2,3,2′,4′	553.15	238.48	−2699.69299	−2699.75587	84.53	222.59	27.23	2	1	1	1	1	0
2,3,2′,5′	553.31	238.57	−2699.69265	−2699.75554	85.42	223.45	28.09	2	2	0	1	0	1
2,3,2′,6′	558.56	238.36	−2699.68796	−2699.75145	97.74	234.19	38.83	3	1	0	1	1	0
2,3,3′,4′	560.08	238.36	−2699.69272	−2699.75638	85.24	221.25	25.89	1	2	1	2	0	0
2,3,3′,5′	559.63	238.87	−2699.69583	−2699.75944	77.08	213.21	17.85	1	3	0	1	1	0
2,4,2′,4′	555.44	238.81	−2699.69701	−2699.76014	73.98	211.38	16.02	2	0	2	0	2	0
2,4,2′,5′	555.12	238.91	−2699.69740	−2699.76050	72.95	210.43	15.07	2	1	1	0	1	1
2,4,2′,6′	564.63	238.78	−2699.69192	−2699.75610	87.34	221.98	26.62	3	0	1	0	2	0
2,4,3′,4′	562.20	238.73	−2699.69666	−2699.76057	74.90	210.25	14.89	1	1	2	1	1	0
2,4,3′,5′	566.31	239.27	−2699.69978	−2699.76416	66.70	200.82	5.46	1	2	1	0	2	0
2,5,2′,5′	556.29	238.98	−2699.69706	−2699.76029	73.85	210.98	15.62	2	2	0	0	0	2
2,5,2′,6′	564.53	238.86	−2699.69240	−2699.75657	86.08	220.75	25.39	3	1	0	0	1	1
2,5,3′,4′	563.12	238.82	−2699.69704	−2699.76105	73.90	208.99	13.63	1	2	1	1	0	1
2,5,3′,5′	561.32	239.30	−2699.70017	−2699.76397	65.68	201.32	5.96	1	3	0	0	1	1
2,6,2′,6′	536.01	238.67	−2699.68426	−2699.74519	107.45	250.63	55.27	4	0	0	0	2	0
2,6,3′,4′	557.08	238.65	−2699.69077	−2699.75409	90.36	227.26	31.90	2	1	1	1	1	0
2,6,3′,5′	559.41	239.14	−2699.69453	−2699.75812	80.49	216.68	21.32	2	2	0	0	2	0
3,4,3′,4′	563.57	238.59	−2699.69554	−2699.75960	77.84	212.79	17.43	0	2	2	2	0	0
3,4,3′,5′	565.32	239.10	−2699.69911	−2699.76337	68.46	202.90	7.54	0	3	1	1	1	0
3,5,3′,5′	561.51	239.67	−2699.70241	−2699.76624	59.80	195.36	0.00	0	4	0	0	2	0
2,3,4,2′	550.75	238.08	−2699.68842	−2699.75102	96.53	235.32	39.96	2	1	1	2	1	0
2,3,4,3′	560.95	238.44	−2699.69185	−2699.75561	87.53	223.27	27.91	1	2	1	2	1	0
2,3,4,4′	554.98	238.29	−2699.69236	−2699.75544	86.19	223.72	28.36	1	1	2	2	1	0
2,3,5,2′	552.22	238.53	−2699.69283	−2699.75560	84.95	223.30	27.94	2	2	0	1	1	1
2,3,5,3′	560.36	238.91	−2699.69622	−2699.75991	76.05	211.98	16.62	1	3	0	1	1	1
2,3,5,4′	556.29	238.78	−2699.69676	−2699.75999	74.63	211.77	16.41	1	2	1	1	1	1
2,3,6,2′	554.56	238.52	−2699.68625	−2699.74928	102.23	239.89	44.53	3	1	0	1	1	1
2,3,6,3′	555.50	238.76	−2699.68908	−2699.75222	94.80	232.17	36.81	2	2	0	1	1	1
2,3,6,4′	557.00	238.68	−2699.68923	−2699.75254	94.40	231.33	35.97	2	1	1	1	1	1
2,4,5,2′	552.28	238.54	−2699.69283	−2699.75560	84.95	223.30	27.94	2	1	1	1	1	1

Table 2 Continued

	S^θ	C^θ_v	H^θ	G^θ	$\Delta_f H^\theta$	$\Delta_f G^\theta$	$\Delta_{R,f} G^\theta$						
molecule	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	hartree	hartree	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$N_{2(6)}$	$N_{3(5)}$	N_4	N_o	N_m	N_p
2,4,5,3′	560.53	238.91	−2699.69622	−2699.75993	76.05	211.93	16.57	1	2	1	1	1	1
2,4,5,4′	561.72	238.74	−2699.69698	−2699.76082	74.06	209.59	14.23	1	1	2	1	1	1
2,4,6,2′	562.12	238.79	−2699.69058	−2699.75448	90.86	226.24	30.88	3	0	1	0	3	0
2,4,6,3′	558.19	239.10	−2699.69332	−2699.75677	83.67	220.22	24.86	2	1	1	0	3	0
2,4,6,4′	558.82	239.04	−2699.69346	−2699.75699	83.30	219.65	24.29	2	0	2	0	3	0
3,4,5,2′	557.27	238.32	−2699.69111	−2699.75446	89.47	226.29	30.93	1	2	1	2	1	0
3,4,5,3′	563.77	238.72	−2699.69436	−2699.75844	80.94	215.84	20.48	0	3	1	2	1	0
3,4,5,4′	563.85	238.62	−2699.69473	−2699.75882	79.96	214.84	19.48	0	2	2	2	1	0
2,3,4,5	559.48	238.11	−2699.68639	−2699.74998	101.86	238.05	42.69	1	2	1	3	2	1
2,3,4,6	553.67	238.36	−2699.68202	−2699.74496	113.33	251.23	55.87	2	1	1	2	3	1
2,3,5,6	553.65	238.42	−2699.68180	−2699.74473	113.91	251.84	56.48	2	2	0	2	2	2
penta-CDPS													
2,3,4,2′,3′	575.51	253.82	−3159.28361	−3159.34902	90.49	236.01	43.21	2	2	1	3	1	0
2,3,4,2′,4′	577.10	254.07	−3159.28825	−3159.35385	78.31	223.33	30.53	2	1	2	2	2	0
2,3,4,2′,5′	576.94	254.14	−3159.28803	−3159.35361	78.88	223.96	31.16	2	2	1	2	1	1
2,3,4,2′,6′	571.57	254.09	−3159.28264	−3159.34761	93.03	239.71	46.91	3	1	1	2	2	0
2,3,4,3′,4′	585.06	254.04	−3159.28857	−3159.35507	77.47	220.13	27.33	1	2	2	3	1	0
2,3,4,3′,5′	587.37	254.63	−3159.29325	−3159.36001	65.18	207.16	14.36	1	3	1	2	2	0
2,3,5,2′,3′	576.60	254.23	−3159.28742	−3159.35296	80.48	225.67	32.87	2	3	0	2	1	1
2,3,5,2′,4′	578.31	254.56	−3159.29202	−3159.35776	68.41	213.06	20.26	2	2	1	1	2	1
2,3,5,2′,5′	578.65	254.62	−3159.29180	−3159.35757	68.98	213.56	20.76	2	3	0	1	1	2
2,3,5,2′,6′	574.06	254.63	−3159.28648	−3159.35173	82.95	228.90	36.10	3	2	0	1	2	1
2,3,5,3′,5′	586.92	255.08	−3159.29587	−3159.36259	58.30	200.38	7.58	1	4	0	1	2	1
2,3,6,2′,4′	573.47	254.49	−3159.28678	−3159.35196	82.16	228.29	35.49	3	1	1	1	2	1
2,3,6,2′,5′	574.26	254.60	−3159.28657	−3159.35185	82.72	228.58	35.78	3	2	0	1	1	2
2,3,6,3′,4′	585.24	254.48	−3159.28774	−3159.35426	79.64	222.25	29.45	2	2	1	2	1	1
2,4,5,2′,4′	579.05	254.45	−3159.29302	−3159.35884	65.78	210.23	17.43	2	1	2	1	2	1
2,4,5,2′,5′	580.05	254.53	−3159.29280	−3159.35873	66.36	210.52	17.72	2	2	1	1	1	2
2,3,5,3′,4′	590.65	254.64	−3159.29446	−3159.36160	62.00	202.98	10.18	1	3	1	2	1	1
2,4,5,3′,4′	590.32	254.48	−3159.29472	−3159.36182	61.32	202.41	9.61	1	2	2	2	1	1
2,4,5,3′,5′	595.96	255.09	−3159.29774	−3159.36548	53.39	192.80	0.00	1	3	1	1	2	1
2,4,6,2′,3′	573.58	254.55	−3159.28650	−3159.35170	82.90	228.98	36.18	3	1	1	1	3	0
2,4,6,2′,4′	575.13	254.88	−3159.29105	−3159.35643	70.95	216.56	23.76	3	0	2	0	4	0
2,4,6,2′,5′	576.42	254.99	−3159.29086	−3159.35638	71.45	216.69	23.89	3	1	1	0	3	1
2,4,6,2′,6′	571.72	254.86	−3159.28574	−3159.35073	84.90	231.52	38.72	4	0	1	0	4	0
2,4,6,3′,4′	587.12	254.80	−3159.29199	−3159.35873	68.49	210.52	17.72	2	1	2	1	3	0
2,4,6,3′,5′	587.68	255.32	−3159.29560	−3159.36240	59.01	200.88	8.08	2	2	1	0	4	0
3,4,5,2′,3′	583.32	254.09	−3159.28867	−3159.35498	77.20	220.36	27.56	1	3	1	3	1	0
3,4,5,2′,4′	586.22	254.46	−3159.29317	−3159.35981	65.39	207.68	14.88	1	2	2	2	2	0
2,4,5,2′,6′	574.30	254.49	−3159.28742	−3159.35270	80.48	226.35	33.55	3	1	1	1	2	1
3,4,5,3′,4′	593.28	254.41	−3159.29269	−3159.36012	66.65	206.87	14.07	0	3	2	3	1	0
3,4,6,2′,3′	577.56	254.14	−3159.28838	−3159.35403	77.96	222.86	30.06	2	2	1	2	1	1
2,3,4,5,2′	580.46	253.93	−3159.28553	−3159.35151	85.45	229.47	36.67	2	2	1	3	2	1
2,3,4,5,3′	584.97	254.23	−3159.28891	−3159.35540	76.57	219.26	26.46	1	3	1	3	2	1
2,3,4,5,4′	583.22	254.10	−3159.28651	−3159.35280	82.87	226.09	33.29	1	2	2	3	2	1
2,3,4,6,2′	572.11	254.14	−3159.28090	−3159.34593	97.60	244.12	51.32	3	1	1	2	3	1
2,3,4,6,3′	585.20	254.53	−3159.28558	−3159.35210	85.32	227.93	35.13	2	2	1	2	3	1
2,3,4,6,4′	584.69	254.43	−3159.28569	−3159.35215	85.03	227.79	34.99	2	1	2	2	3	1
2,3,5,6,2′	572.25	254.24	−3159.28057	−3159.34562	98.47	244.94	52.14	3	2	0	2	2	2
2,3,5,6,3′	584.10	254.62	−3159.28520	−3159.35160	86.31	229.24	36.44	2	3	0	2	2	2
2,3,5,6,4′	585.33	254.52	−3159.28534	−3159.35188	85.95	228.50	35.70	2	2	1	2	2	2
2,3,4,5,6	579.53	253.76	−3159.27306	−3159.33893	118.19	262.50	69.70	2	2	1	4	4	2
3,4,5,2′,6′	585.77	254.48	−3159.28824	−3159.35482	78.33	220.78	27.98	2	2	1	2	2	0
2,3,6,2′,3′	572.05	254.22	−3159.28218	−3159.34720	94.24	240.79	47.99	3	2	0	2	1	1
2,3,6,2′,6′	570.09	254.50	−3159.28149	−3159.34629	96.05	243.18	50.38	4	1	0	1	2	1
2,3,6,3′,5′	585.33	254.97	−3159.29134	−3159.35787	70.19	212.78	19.98	2	3	0	1	2	1
3,4,5,2′,5′	590.04	254.63	−3159.29370	−3159.36077	64.00	205.16	12.36	1	3	1	2	1	1
3,4,5,3′,5′	594.66	254.94	−3159.29596	−3159.36355	58.06	197.86	5.06	0	4	1	2	2	0
hexa-CDPS													
2,3,4,2′,3′,4′	607.83	269.67	−3618.88309	−3618.95219	73.18	223.13	25.52	2	2	2	4	2	0
2,3,4,2′,3′,5′	611.50	270.21	−3618.88665	−3618.95616	63.83	212.71	15.10	2	3	1	3	2	1
2,3,4,2′,3′,6′	616.72	270.07	−3618.88219	−3618.95229	75.54	222.87	25.26	3	2	1	3	2	1
2,3,4,2′,4′,6′	616.07	270.27	−3618.88657	−3618.95660	64.04	211.55	13.94	3	1	2	2	4	0
2,3,4,3′,4′,5′	614.20	269.96	−3618.88678	−3618.95659	63.49	211.58	13.97	1	3	2	4	2	0
2,3,5,2′,3′,5′	611.91	270.63	−3618.89087	−3618.96042	52.76	201.52	3.91	2	4	0	2	2	2
2,3,5,2′,3′,6′	601.72	270.43	−3618.88339	−3618.95179	72.39	224.18	26.57	3	3	0	2	2	2
2,3,5,6,3′,4′	587.31	262.09	−3618.88378	−3618.95054	71.37	227.46	29.85	2	3	1	3	2	2
2,3,5,2′,4′,6′	603.62	270.77	−3618.88771	−3618.95632	61.05	212.29	14.68	3	2	1	1	4	1
2,3,5,3′,4′,5′	612.89	270.31	−3618.88946	−3618.95913	56.46	204.91	7.30	1	4	1	3	2	1
2,3,4,6,3′,4′	613.32	270.46	−3618.88405	−3618.95370	70.66	219.16	21.55	2	2	2	3	3	1
2,3,6,2′,3′,6′	598.52	270.34	−3618.87850	−3618.94654	85.23	237.96	40.35	4	2	0	2	2	2
2,3,6,3′,4′,5′	614.02	270.28	−3618.88495	−3618.95475	68.30	216.41	18.80	2	3	1	3	2	1
2,3,4,2′,4′,5′	610.23	270.00	−3618.88768	−3618.95705	61.13	210.37	12.76	2	2	2	3	2	1
2,3,5,2′,4′,5′	612.09	270.54	−3618.89116	−3618.96074	51.99	200.68	3.07	2	3	1	2	2	2
2,3,6,2′,4′,5′	602.53	270.32	−3618.88436	−3618.95285	69.85	221.40	23.79	3	2	1	2	2	2

Table 2 Continued

molecule	S^θ $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	C^θ_v $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	H^θ hartree	G^θ hartree	$\Delta_f H^\theta$ $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_f G^\theta$ $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_{R,f} G^\theta$ $\mathrm{kJ \cdot mol^{-1}}$	$N_{2(6)}$	$N_{3(5)}$	N_4	N_o	N_m	N_p
2,4,5,2′,4′,5′	613.14	270.40	−3618.89221	−3618.96191	49.24	197.61	0.00	2	2	2	2	2	2
2,4,5,2′,4′,6′	604.09	270.63	−3618.88865	−3618.95732	58.58	209.66	12.05	3	1	2	1	4	1
2,4,5,3′,4′,5′	613.10	270.18	−3618.89045	−3618.96014	53.86	202.26	4.65	1	3	2	3	2	1
2,3,6,2′,4′,6′	599.40	270.64	−3618.88279	−3618.95092	73.97	226.46	28.85	4	1	1	1	4	1
2,4,6,2′,4′,6′	596.04	271.02	−3618.88706	−3618.95482	62.76	216.22	18.61	4	0	2	0	6	0
2,4,6,3′,4′,5′	616.23	270.65	−3618.88919	−3618.95924	57.17	204.62	7.01	2	2	2	2	4	0
3,4,5,3′,4′,5′	613.87	270.26	−3618.88945	−3618.95923	56.48	204.65	7.04	0	4	2	4	2	0
2,3,4,5,2′,3′	608.24	269.75	−3618.88289	−3618.95203	73.71	223.55	25.94	2	3	1	4	2	1
2,3,4,5,2′,4′	609.28	270.01	−3618.88747	−3618.95672	61.68	211.24	13.63	2	2	2	3	3	1
2,3,4,5,2′,5′	609.38	270.12	−3618.88709	−3618.95636	62.68	212.18	14.57	2	3	1	3	2	2
2,3,4,5,2′,6′	620.37	270.06	−3618.88259	−3618.95310	74.49	220.74	23.13	3	2	1	3	3	1
2,3,4,5,3′,4′	616.43	269.94	−3618.88705	−3618.95712	62.78	210.19	12.58	1	3	2	4	2	1
2,3,4,5,3′,5′	615.64	270.47	−3618.89005	−3618.96003	54.91	202.54	4.93	1	4	1	3	3	1
2,3,4,6,2′,3′	600.28	269.97	−3618.87872	−3618.94695	84.66	236.89	39.28	3	2	1	3	3	1
2,3,4,6,2′,4′	601.48	270.26	−3618.88330	−3618.95167	72.63	224.49	26.88	3	1	2	2	4	1
2,3,4,6,2′,5′	602.25	270.33	−3618.88309	−3618.95155	73.18	224.81	27.20	3	2	1	2	3	2
2,3,4,6,2′,6′	598.50	270.26	−3618.87807	−3618.94610	86.36	239.12	41.51	4	1	1	2	4	1
2,3,4,6,3′,5′	614.09	270.71	−3618.88761	−3618.95742	61.31	209.40	11.79	2	3	1	2	4	1
2,3,5,6,2′,3′	600.47	270.06	−3618.87836	−3618.94661	85.60	237.78	40.17	3	3	0	3	2	2
2,3,5,6,2′,4′	602.10	270.37	−3618.88291	−3618.95135	73.65	225.33	27.72	3	2	1	2	3	2
2,3,5,6,2′,5′	602.10	270.43	−3618.88273	−3618.95117	74.13	225.81	28.20	3	3	0	2	2	3
2,3,5,6,2′,6′	598.49	270.37	−3618.87774	−3618.94577	87.23	239.98	42.37	4	2	0	2	3	2
2,3,5,6,3′,5′	612.66	270.80	−3618.88722	−3618.95686	62.34	210.87	13.26	2	4	0	2	3	2
2,3,4,5,6,2′	618.61	269.95	−3618.87345	−3618.94370	98.49	245.42	47.81	3	2	1	4	4	2
2,3,4,5,6,3′	609.11	269.93	−3618.87636	−3618.94560	90.85	240.43	42.82	2	3	1	4	4	2
2,3,4,5,6,4′	612.12	269.91	−3618.87650	−3618.94608	90.48	239.17	41.56	2	2	2	4	4	2
hepta-CDPS													
2,3,4,5,2′,3′,4′	637.27	285.52	−4078.47989	−4078.55233	62.91	218.20	12.42	2	3	2	5	3	1
2,3,4,5,2′,3′,5′	638.23	285.99	−4078.48341	−4078.55596	53.67	208.67	2.89	2	4	1	4	3	2
2,3,4,5,2′,3′,6′	645.05	285.83	−4078.47907	−4078.55239	65.06	218.04	12.26	3	3	1	4	3	2
2,3,4,5,2′,4′,5′	638.68	285.81	−4078.48446	−4078.55706	50.91	205.78	0.00	2	3	2	4	3	2
2,3,4,5,2′,4′,6′	643.30	286.08	−4078.48344	−4078.55657	53.59	207.07	1.29	3	2	2	3	5	1
2,3,4,5,3′,4′,5′	641.51	285.75	−4078.48349	−4078.55641	53.46	207.49	1.71	1	4	2	5	3	1
2,3,4,6,2′,3′,4′	628.25	285.69	−4078.47601	−4078.54742	73.10	231.09	25.31	3	2	2	4	4	1
2,3,4,6,2′,3′,5′	630.54	286.18	−4078.47976	−4078.55143	63.25	220.56	14.78	3	3	1	3	4	2
2,3,4,6,2′,3′,6′	627.04	286.10	−4078.47493	−4078.54621	75.93	234.27	28.49	4	2	1	3	4	2
2,3,4,6,2′,4′,5′	631.12	286.07	−4078.48073	−4078.55247	60.71	217.83	12.05	3	2	2	3	4	2
2,3,4,6,2′,4′,6′	628.63	286.43	−4078.47923	−4078.55069	64.64	222.51	16.73	4	1	2	2	6	1
2,3,4,6,3′,4′,5′	641.37	286.02	−4078.48116	−4078.55406	59.58	213.66	7.88	2	3	2	4	4	1
2,3,5,6,2′,3′,4′	628.65	285.81	−4078.47563	−4078.54709	74.10	231.96	26.18	3	3	1	4	3	2
2,3,5,6,2′,3′,5′	630.00	286.26	−4078.47945	−4078.55106	64.07	221.54	15.76	3	4	0	3	3	3
2,3,5,6,2′,3′,6′	626.49	286.16	−4078.47463	−4078.54584	76.72	235.24	29.46	4	3	0	3	3	3
2,3,5,6,2′,4′,5′	630.83	286.15	−4078.48042	−4078.55212	61.52	218.75	12.97	3	3	1	3	3	3
2,3,5,6,2′,4′,6′	628.37	286.52	−4078.47892	−4078.55034	65.46	223.43	17.65	4	2	1	2	5	2
2,3,5,6,3′,4′,5′	640.90	286.12	−4078.48077	−4078.55362	60.60	214.81	9.03	2	4	1	4	3	2
2,3,4,5,6,2′,3′	627.11	285.40	−4078.46955	−4078.54083	90.06	248.39	42.61	3	3	1	5	4	2
2,3,4,5,6,2′,4′	628.30	285.70	−4078.47410	−4078.54552	78.11	236.08	30.30	3	2	2	4	5	2
2,3,4,5,6,2′,5′	628.41	285.74	−4078.47390	−4078.54533	78.64	236.58	30.80	3	3	1	4	4	3
2,3,4,5,6,2′,6′	624.91	285.69	−4078.46898	−4078.54002	91.56	250.52	44.74	4	2	1	4	5	2
2,3,4,5,6,3′,4′	640.66	285.64	−4078.47474	−4078.54756	76.43	230.72	24.94	2	3	2	5	4	2
2,3,4,5,6,3′,5′	639.98	286.14	−4078.47827	−4078.55102	67.17	221.64	15.86	2	4	1	4	5	2
octa-CDPS													
2,3,4,5,6,2′,3′,4′	655.11	301.13	−4538.06677	−4538.14123	78.69	242.78	26.72	3	3	2	6	5	2
2,3,4,5,6,2′,3′,6′	653.97	301.79	−4538.06580	−4538.14007	81.23	245.83	29.77	4	3	1	5	5	3
2,3,4,5,6,2′,4′,5′	657.35	301.46	−4538.07151	−4538.14623	66.24	229.66	13.60	3	3	2	5	5	3
2,3,4,5,6,2′,4′,6′	655.04	301.85	−4538.07004	−4538.14450	70.10	234.20	18.14	4	2	2	4	7	2
2,3,4,5,6,3′,4′,5′	667.01	301.45	−4538.07174	−4538.14756	65.64	226.16	10.10	2	4	2	6	5	2
2,3,4,5,6,2′,3′,5′	675.51	301.69	−4538.07326	−4538.15004	61.65	219.65	3.59	3	4	1	5	5	3
2,3,4,5,2′,3′,4′5′	665.24	301.32	−4538.07580	−4538.15141	54.98	216.06	0.00	2	4	2	6	4	2
2,3,4,5,2′,3′,4′6′	656.54	301.46	−4538.07238	−4538.14701	63.96	227.61	11.55	3	3	2	5	5	2
2,3,4,5,2′,3′,5′6′	656.69	301.60	−4538.07199	−4538.14664	64.98	228.58	12.52	3	4	1	5	4	3
2,3,4,6,2′,3′,4′6′	655.41	301.83	−4538.07131	−4538.14581	66.77	230.76	14.70	4	2	2	4	6	2
2,3,4,6,2′,3′,5′6′	654.76	301.91	−4538.07097	−4538.14540	67.66	231.84	15.78	4	3	1	4	5	3
2,3,5,6,2′,3′,5′6′	649.43	301.99	−4538.07061	−4538.14444	68.61	234.36	18.30	4	4	0	4	4	4
nona-CDPS													
2,3,4,5,6,2′,3′,4′,5′	699.19	317.29	−4997.66570	−4997.74510	62.82	228.06	0.00	3	4	2	7	6	3
2,3,4,5,6,2′,3′,4′,6′	681.18	317.23	−4997.66207	−4997.73950	72.36	242.77	14.71	4	3	2	6	7	3
2,3,4,5,6,2′,3′,5′,6′	681.38	317.34	−4997.66170	−4997.73916	73.33	243.66	15.60	4	4	1	6	6	4
deca-CDPS													
2,3,4,5,6,2′,3′,4′,5′6′	702.65	332.68	−5457.25274	−5457.33261	78.18	256.30		4	4	2	8	8	4

stable conformations in general, which imply that most PCDPS congeners have two or more conformational isomers. Furthermore, if both skew and twist conformations exist for the same PCDPS congener, the former is always more stable than the latter, and the energy difference between these two conformations is much larger than that between two twist conformations.

Table 3. Values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ for Some Representative PCDPS Congeners and the Values of $\Delta_{R,f} G^\theta$ for Three MCDPS Congeners at the B3LYP/6-31G* and B3LYP/6-311G Levels**

molecule	$\Delta_f H^\theta$/kJ·mol^{-1}		$\Delta_f G^\theta$/kJ·mol^{-1}		$\Delta_{R,f} G^\theta$/kJ·mol^{-1}	
2-MCDPS	142.04[a]	141.84[b]	262.57[a]	263.90[b]	9.39[a]	9.63[b]
3-MCDPS	135.32[a]	134.98[b]	253.18[a]	254.27[b]	0.00[a]	0.00[b]
4-MCDPS	135.58[a]	135.51[b]	254.33[a]	254.57[b]	1.15[a]	0.30[b]
3,4′-DCDPS	107.15[a]	106.98[b]	230.68[a]	231.63[b]		
3,5,4′-tri-CDPS	82.12[a]	81.73[b]	208.64[a]	211.69[b]		
3,5,3′,5′-TCDPS	59.80[a]	59.78[b]	195.36[a]	195.64[b]		
2,4,5,3′,5′-penta-CDPS	53.39[a]	53.87[b]	192.80[a]	194.71[b]		
2,4,5,2′,4′,5′-hexa-CDPS	49.24[a]	49.96[b]	197.61[a]	198.97[b]		
2,3,4,5,2′,4′,5′-hepta-CDPS	50.91[a]	52.40[b]	205.78[a]	207.66[b]		
2,3,4,5,2′,3′,4′,5′-octa-CDPS	54.98[a]	57.07[b]	216.06[a]	218.45[b]		
2,3,4,5,6,2′,3′,4′,5′-nona-CDPS	62.82[a]	65.02[b]	228.06[a]	230.87[b]		
2,3,4,5,6,2′,3′,4′,5′6′-deca-CDPS	78.18[a]	78.95[b]	256.30[a]	257.35[b]		

[a] Calculated at the B3LYP/6-31G* level. [b] Calculated at the B3LYP/6-311G** level

Table 4. Most Stable and Least Stable Isomers in Different Isomer Groups for PCDPSs and PCDEs and the Differences of $\Delta_f G^\theta$, $\Delta_f H^\theta$, and TS^θ ($\Delta(\Delta_f G^\theta)$, $\Delta(\Delta_f H^\theta)$, and $\Delta(TS^\theta)$) between the Most Stable and Least Stable Isomers for PCDPSs

substance	most stable isomer	least stable isomer	$\Delta(\Delta_f G^\theta)$/kJ·mol^{-1}	$\Delta(\Delta_f H^\theta)$/kJ·mol^{-1}	$\Delta(TS^\theta)$/kJ·mol^{-1}
MCDPS	3-	2-	9.39	6.72	2.67
DCDPS	3,4′-	2,6-	30.09	27.41	2.68
tri-CDPS	3,5,4′-	2,3,6-	46.36	40.77	5.59
TCDPS	3,5,3′,5′-	2,3,5,6-	56.48	54.11	2.37
penta-CDPS	2,4,5,3′,5′-	2,3,4,5,6-	69.70	64.80	4.90
hexa-CDPS	2,4,5,2′,4′,5′-	2,3,4,5,6,2′-	47.81	49.25	1.44
hepta-CDPS	2,3,4,5,2′,4′,5′-	2,3,4,5,6,2′,6′-	44.74	40.65	4.09
octa-CDPS	2,3,4,5,2′,3′,4′,5′-	2,3,4,5,6,2′,3′,6′-	29.77	26.25	3.52
nona-CDPS	2,3,4,5,6,2′,3′,4′,5′-	2,3,4,5,6,2′,3′,5′6′-	15.60	10.51	5.09
MCDE	3-	2-			
DCDE	3,3′-	2,2′-			
tri-CDE	3,5,4′-	2,3,2′-			
TCDE	3,5,3′,5′-	2,6,2′,6′-			
penta-CDE	2,4,5,3′,5′-	2,3,4,5,6-			
hexa-CDE	2,4,5,2′,4′,5′-	2,3,4,5,6,2′-			
hepta-CDE	2,3,4,5,2′,4′,5′-	2,3,4,5,6,2′,3′-			
octa-CDE	2,3,4,5,2′,3′,4′,5′-	2,3,4,5,6,2′,3′,4′-			
nona-CDE	2,3,4,5,6,2′,3′,5′,6′-	2,3,4,5,6,2′,3′,4′,5′-			

For example, skew conformation of 2-MCDPS is 5.39 kJ·mol^{-1} more stable than the twist one, while the difference of $\Delta_f G^\theta$ between two twist conformations for 2,3,6-tri-CDPS is only 0.06 kJ·mol^{-1}. So, for the other 189 PCDPS congeners, we always select skew conformation as the initial input to optimize their geometries.

As for the interconversion between two different conformations for the same PCDPS congener, it was found that the interconversion via a butterfly transition state has a higher barrier than that via a skew one generally. However, most of these barriers are less than 15 kJ·mol^{-1}, which imply that the interconversion between different conformations for PCDPS congeners is relatively free at room temperature. So the thermodynamic data of the various conformations should be weighted in accordance with their relative abundances, and the weighted averages of thermodynamic data, for a congener, can be calculated according to the conversion equilibrium constant. For example, 2,2′-DCDPS has two conformations: one has approximate skew structure, and another is in twist structure with C_2 symmetry. The values of $\Delta_f G^\theta$ for two conformations are (251.32 and 260.04) kJ·mol^{-1}, respectively, and the calculated weighted average is 251.57 kJ·mol^{-1}, which indicates that the weighted average is very close to the value for a more stable skew conformation. Two stable twist conformations for 2,3,6-tri-CDPS were located for which the values of $\Delta_f G^\theta$ are (254.92 and 254.98) kJ·mol^{-1}, respectively, and the calculated weighted average is 254.95 kJ·mol^{-1}, which shows that the weighted average is actually the same as values for both twist conformations. So for PCDPS congeners with two or more conformations, only the more or the most stable one is considered.

Comparison between Calculation Results at Different Levels. The dependence of the calculation results on the basis set was investigated. Table 3 compares the calculated $\Delta_f H^\theta$ and $\Delta_f G^\theta$ values for 3 MCDPS congeners and most stable isomers in the other congener group and $\Delta_{R,f} G^\theta$ values for 3 MCDPS congeners obtained at the level of (a) B3LYP/6-31G* and (b) B3LYP/6-311G**. The calculated $\Delta_f H^\theta$ and $\Delta_f G^\theta$ values exhibit negligible dependence on the basis set and do not deviate by more than 3 kJ·mol^{-1}. Moreover, the relative stability of the studied isomers is little affected by the level of the basis set. So, for other PCDPS congeners, only the calculations at the B3LYP/6-31G* level are performed to save CPU time.

Relative Stability of Isomer Groups. It has been known that the isomers with higher Gibbs energies are less stable than those with lower Gibbs energies. On the basis of the lowest $\Delta_f G^\theta$ in each PCDPS isomer group, the relative standard Gibbs energies of formation ($\Delta_{R,f} G^\theta$) of PCDPSs were obtained and are also listed in Table 2. For comparison of these parameters, the most stable and the least stable isomers in the nine categories of congeners are summarized and listed in Table 4. It is obvious that the relative thermodynamic stability of PCDPSs with the same degree of chlorination is determined by the different position of the chlorine atom and the relative position between chlorine atoms on the same phenyl ring. In other words, the relative stability of PCDPSs is determined by the repulsion interaction between S and Cl atoms and the repulsion interaction between two Cl atoms on the same phenyl ring. In addition, the interaction between Cl atoms at different phenyl rings may have a significant effect on the relative stability of PCDPS congeners.

Table 5. Correlation Equations of Thermodynamic Properties with N_{PCS}, the Squared Correlation Coefficient (R^2), the Standard Error (SE), the Statistical Test Value (F), and the Significance Level (p) of the Correlation Equations

equation	R^2	SE	F	p
$S^\theta/\mathrm{J\cdot mol^{-1}\cdot K^{-1}} = 452.721 + 22.721N_{2(6)} + 27.950(N_{3(5)} + N_4)$	0.989	4.80	8918.554	0.000
$C^\theta{}_v/\mathrm{J\cdot mol^{-1}\cdot K^{-1}} = 175.494 + 15.791N_{2(6)} + 15.767(N_{3(5)} + N_4)$	0.999	0.65	179670.4	0.000
$\Delta_f H^\theta/\mathrm{kJ\cdot mol^{-1}} = 158.643 - 15.636N_{2(6)} - 27.813(N_{3(5)} + N_4) + 12.823N_o + 3.716(N_m + N_p)$	0.969	3.37	1577.9	0.000
$\Delta_f G^\theta/\mathrm{kJ\cdot mol^{-1}} = 270.832 - 8.406N_{2(6)} - 22.349(N_{3(5)} + N_4) + 13.183N_o + 3.658(N_m + N_p)$	0.922	4.09	604.755	0.000

It can be seen from Tables 2 and 4 that the isomers with chlorine atoms substituted at positions 2 (6, 2′, 6′) and with chlorine located on near positions are not stable. On the contrary, the isomers with chlorine atoms substituted at positions 3 (5, 3′, 5′) and 4 (4′) and with chlorine located far away from each other are relatively stable. For MCDPSs, the 2-MCDPS isomer is less stable than 3-MCDPS and 4-MCDPS by an amount of (9.39 and 8.24) kJ·mol^{-1}, respectively. This is because the Cl−S distance in 2-MCDPS (3.146 Å) is much shorter than those in 3-MCDPS (5.524 Å) and 4-MCDPS (6.339 Å), so the Cl−S repulsion interaction in the former is much stronger than those in the latter two. For DCDPSs, the 3,4′-DCDPS is the most stable, while the 2,6-DCDPS is the least stable with a difference of 30.09 kJ·mol^{-1} in their values of Gibbs energy. Similarly, the 3,5,4′-, 3,5,3′,5′-, 2,4,5,3′,5′-, 2,4,5,2′,4′,5′-, 2,3,4,5,2′,4′,5′-, 2,3,4,5,2′,3′,4′,5′-, and 2,3,4,5,6,2′,3′,4′,5′- are the most stable isomers with differences of (46.36, 56.48, 69.70, 47.81, 44.74, 29.77, and 15.60) kJ·mol^{-1} to the least stable isomers 2,3,6-, 2,3,5,6-, 2,3,4,5,6-, 2,3,4,5,6,2′-, 2,3,4,5,6,2′,6′-, 2,3,4,5,6,2′,3′,6′-, and 2,3,4,5,6,2′,3′,5′,6′- for tri-CDPSs, TCDPSs, penta-CDPSs, hexa-CDPSs, hepta-CDPSs, octa-CDPSs, and nona-CDPSs, respectively. Moreover, our calculations indicate that the interaction between Cl atoms at different phenyl rings may be significant. For example, 2,6,2′,6′-TCDPS is 10.74 kJ·mol^{-1} less stable than 2,3,6,2′-TCPDS. The possible reason is that in the former the two shortest Cl−Cl distances between chlorine on two phenyl rings are both 3.886 Å, while for the latter, the shortest Cl−Cl distance between the two rings is longer than 5 Å. In addition, it was found that the differences of $\Delta_f G^\theta$ in each PCDPS isomer group are mainly due to the differences of $\Delta_f H^\theta$, since the differences of $\Delta_f H^\theta$ between the most stable and least stable isomers in MCDPSs, DCDPSs, tri-CDPSs, TCDPSs, penta-CDPSs, hexa-CDPSs, hepta-CDPSs, octa-CDPSs, and nona-CDPSs are (6.72, 27.41, 40.77, 54.11, 64.80, 49.25, 40.65, 26.25, and 10.51) kJ·mol^{-1}, respectively, while the corresponding differences of TS^θ in these isomer groups are only (2.67, 2.68, 5.59, 2.37, 4.90, 1.44, 4.09, 3.52, and 5.09) kJ·mol^{-1}, respectively. The differences of $\Delta_f G^\theta$, $\Delta_f H^\theta$, and TS^θ are all listed in Table 4 for comparison.

Relations of Thermodynamic Properties with N_{PCS}. The correlation equations of S^θ, $C^\theta{}_v$, $\Delta_f H^\theta$, and $\Delta_f G^\theta$ with N_{PCS} were obtained using the SPSS 12.0 for Windows program and are indicated in Table 5 where R^2 is the squared correlation coefficient; SE is the standard error; F is the statistical test F-value; and p is the p-value. Plots of estimated $\Delta_f H^\theta$ and $\Delta_f G^\theta$ values from the correlations versus those calculated by DFT are shown in Figures 2 and 3, respectively. To examine the quality of the generated correlation equations, a test of the null hypothesis (F test) was performed. The F-values for these correlation equations greatly exceed the critical F-value (3.040 or 2.416) at a 95 % confidence level, which suggests that these regressions are highly significant and satisfactory. From Table 5, the following conclusions can be drawn: (1) the correlations between S^θ or $C^\theta{}_v$ and N_{PCS} is good since the corresponding R^2 values are close to 1.000, which clearly represent the influence of the number and position of chlorine substitution on these values. Furthermore, Cl substitution on the positions 3 (5, 3′, 5′) and 4 (4′) affects the values of S^θ more significantly than substitution on the positions 2 (6, 2′, 6′), while Cl substitution on the different positions has approximately the same effect on the values of $C^\theta{}_v$. (2) Although the correlations between $\Delta_f H^\theta$ or $\Delta_f G^\theta$ and N_{pcs} are not good, the trend is obvious; i.e., both the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ decrease with an increase of $N_{2(6)}$, $N_{3(5)}$, and N_4 and increase with an increase of N_o, N_m, and N_p. (3) Cl substitution on the positions 3 (5, 3′, 5′) and 4 (4′) affects the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ more significantly than substitution on the positions 2 (6, 2′, 6′), since the decreasing electronic energies with increasing number of chlorines are counteracted partly by repulsion interaction between the S atom and Cl atoms at positions 2 (6, 2′, 6′). (4) Although the number of relative positions has only a negligible influence on the values of S^θ and $C_v{}^\theta$ for PCDPS congeners, it affects the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ significantly. For example, if N_o is increased by one, the increase of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ is (12.82 and 13.18) kJ·mol^{-1},

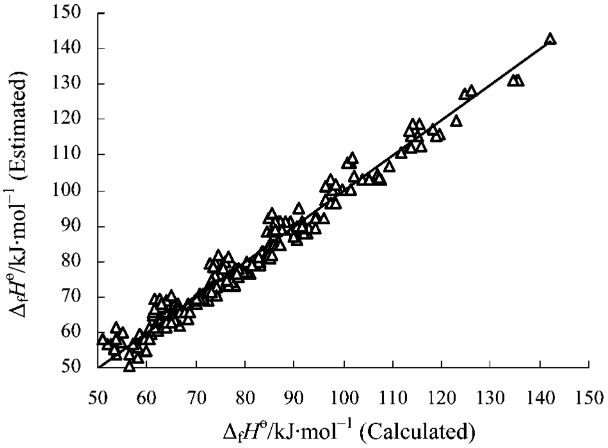

Figure 2. Plot of estimated $\Delta_f H^\theta$ values from the correlation versus those calculated by DFT.

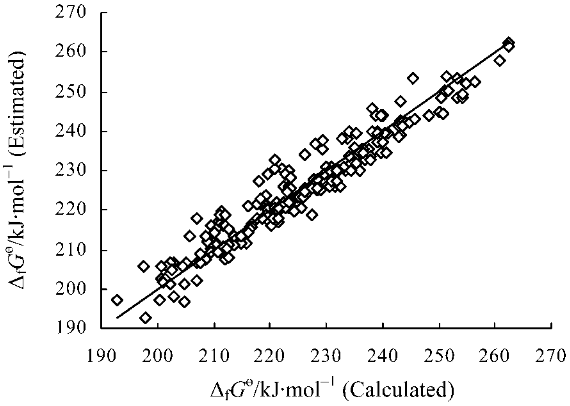

Figure 3. Plot of estimated $\Delta_f G^\theta$ values from the correlation versus those calculated by DFT.

Table 6. Regression Parameter (*A*, *B*, *C*, and *D*) and Standard Error (SE) of the Correlation Equations between Heat Capacity at Constant Pressure (C^{θ}_{p}) and Temperature

molecule	$A/\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$B/\mathrm{J \cdot mol^{-1} \cdot K^{-2}}$	$C/10^5\ \mathrm{J \cdot mol^{-1}}$	$D/10^7\ \mathrm{J \cdot mol^{-1} \cdot K}$	SE
DPS	570.59	0.014244	−1.6850	1.6032	1.94
MCDPS					
2	577.69	0.010569	−1.6276	1.5219	1.74
3	577.47	0.010612	−1.6251	1.5198	1.73
4	577.47	0.010612	−1.6251	1.5198	1.73
DCDPS					
2,2′	585.11	0.006796	−1.5717	1.4419	1.53
2,3′	584.61	0.006949	−1.5683	1.4397	1.53
2,4′	584.54	0.006981	−1.5680	1.4384	1.54
3,3′	584.36	0.007012	−1.5658	1.4375	1.53
3,4′	584.31	0.007044	−1.5659	1.4371	1.54
4,4′	584.23	0.007099	−1.5662	1.4377	1.55
2,3	585.06	0.006855	−1.5732	1.4462	1.55
2,4	584.68	0.006966	−1.5701	1.4440	1.55
2,5	584.64	0.006964	−1.5695	1.4425	1.54
2,6	585.22	0.006747	−1.5710	1.4420	1.53
3,4	584.71	0.007000	−1.5714	1.4460	1.56
3,5	584.54	0.006966	−1.5679	1.4419	1.54
tri-CDPS					
2,3,2′	592.55	0.003050	−1.5173	1.3658	1.35
2,3,3′	592.55	0.003050	−1.5173	1.3658	1.35
2,3,4′	591.96	0.003252	−1.5139	1.3632	1.35
2,4,2′	592.18	0.003152	−1.5145	1.3631	1.34
2,4,3′	591.61	0.003352	−1.5111	1.3619	1.35
2,4,4′	591.56	0.003375	−1.5111	1.3611	1.36
2,6,4′	592.00	0.003204	−1.5117	1.3597	1.34
2,5,2′	591.83	0.003280	−1.5120	1.3608	1.35
2,5,3′	591.64	0.003317	−1.5105	1.3604	1.35
2,5,4′	591.57	0.003349	−1.5102	1.3592	1.35
2,6,2′	592.44	0.003052	−1.5144	1.3618	1.34
2,6,3′	592.06	0.003158	−1.5116	1.3595	1.33
3,4,2′	592.04	0.003268	−1.5155	1.3659	1.37
3,4,3′	591.70	0.003346	−1.5121	1.3629	1.36
3,4,4′	591.63	0.003393	−1.5122	1.3628	1.37
3,5,2′	591.86	0.003245	−1.5119	1.3621	1.34
3,5,3′	591.53	0.003333	−1.5094	1.3604	1.34
3,5,4′	591.45	0.003360	−1.5086	1.3588	1.34
2,3,4	592.59	0.003116	−1.5205	1.3746	1.37
2,3,5	592.25	0.003185	−1.5170	1.3707	1.36
2,3,6	592.77	0.002992	−1.5178	1.3687	1.35
2,4,5	592.16	0.003266	−1.5181	1.3728	1.38
2,4,6	592.48	0.003059	−1.5155	1.3674	1.34
3,4,5	592.31	0.003222	−1.5191	1.3747	1.38
TCDPS					
2,3,2′,3′	599.73	−0.000586	−1.4616	1.2891	1.17
2,3,2′,4′	599.38	−0.000498	−1.4586	1.2858	1.17
2,3,2′,5′	599.34	−0.000473	−1.4584	1.2862	1.17
2,3,2′,6′	599.65	−0.000597	−1.4593	1.2852	1.16
2,3,3′,4′	599.41	−0.000473	−1.4601	1.2886	1.18
2,3,3′,5′	599.19	−0.000461	−1.4573	1.2866	1.16
2,4,2′,4′	598.98	−0.000374	−1.4559	1.2837	1.17
2,4,2′,5′	598.99	−0.000395	−1.4549	1.2818	1.16
2,4,2′,6′	599.24	−0.000473	−1.4564	1.2831	1.16
2,4,3′,4′	599.01	−0.000349	−1.4573	1.2865	1.18
2,4,3′,5′	598.79	−0.000338	−1.4543	1.2843	1.16
2,5,2′,5′	598.90	−0.000354	−1.4547	1.2823	1.17
2,5,2′,6′	599.25	−0.000502	−1.4554	1.2811	1.15
2,5,3′,4′	599.01	−0.000368	−1.4564	1.2848	1.17
2,5,3′,5′	598.83	−0.000372	−1.4537	1.2829	1.16
2,6,2′,6′	599.81	−0.000707	−1.4578	1.2824	1.14
2,6,3′,4′	599.44	−0.000514	−1.4582	1.2858	1.17
2,6,3′,5′	599.22	−0.000519	−1.4548	1.2820	1.14
3,4,3′,4′	599.13	−0.000347	−1.4589	1.2888	1.19
3,4,3′,5′	598.96	−0.000373	−1.4557	1.2857	1.17
3,5,3′,5′	598.75	−0.000364	−1.4524	1.2828	1.15
2,3,4,2′	599.82	−0.000577	−1.4638	1.2936	1.18
2,3,4,3′	599.56	−0.000517	−1.4617	1.2927	1.18
2,3,4,4′	599.50	−0.000484	−1.4617	1.2917	1.18
2,3,5,2′	599.46	−0.000501	−1.4601	1.2899	1.17
2,3,5,3′	599.28	−0.000473	−1.4583	1.2892	1.17
2,3,5,4′	599.21	−0.000444	−1.4581	1.2879	1.17
2,3,6,2′	599.80	−0.000641	−1.4598	1.2868	1.16
2,3,6,3′	599.69	−0.000627	−1.4588	1.2866	1.15
2,3,6,4′	599.60	−0.000581	−1.4588	1.2863	1.16
2,4,5,2′	599.47	−0.000505	−1.4601	1.2899	1.17

Table 6 Continued

molecule	A/J·mol^{-1}·K^{-1}	B/J·mol^{-1}·K^{-2}	C/10^5 J·mol^{-1}	D/10^7 J·mol^{-1}·K	SE
2,4,5,3′	599.27	−0.000468	−1.4582	1.2891	1.17
2,4,5,4′	599.03	−0.000334	−1.4583	1.2892	1.19
2,4,6,2′	599.55	−0.000583	−1.4579	1.2855	1.15
2,4,6,3′	599.43	−0.000565	−1.4567	1.2855	1.15
2,4,6,4′	599.35	−0.000523	−1.4566	1.2852	1.16
3,4,5,2′	599.68	−0.000529	−1.4629	1.2942	1.18
3,4,5,3′	599.39	−0.000456	−1.4605	1.2928	1.18
3,4,5,4′	599.30	−0.000415	−1.4601	1.2915	1.18
2,3,4,5	600.37	−0.000717	−1.4693	1.3053	1.19
2,3,4,6	600.60	−0.000858	−1.4671	1.2998	1.17
2,3,5,6	600.55	−0.000840	−1.4665	1.2991	1.17
penta-CDPS					
2,3,4,2′,3′	607.61	−0.004478	−1.4101	1.2168	0.99
2,3,4,2′,4′	607.29	−0.004391	−1.4077	1.2143	0.99
2,3,4,2′,5′	607.24	−0.004371	−1.4073	1.2142	0.99
2,3,4,2′,6′	607.51	−0.004472	−1.4078	1.2134	0.98
2,3,4,3′,4′	607.19	−0.004299	−1.4083	1.2164	1.00
2,3,4,3′,5′	606.79	−0.004215	−1.4052	1.2154	1.00
2,3,5,2′,3′	607.25	−0.004370	−1.4076	1.2157	0.99
2,3,5,2′,4′	606.92	−0.004287	−1.4048	1.2129	0.99
2,3,5,2′,5′	606.90	−0.004278	−1.4047	1.2132	0.99
2,3,5,2′,6′	607.12	−0.004371	−1.4046	1.2116	0.98
2,3,5,3′,5′	606.68	−0.004230	−1.4023	1.2118	0.98
2,3,6,2′,4′	607.12	−0.004364	−1.4046	1.2104	0.98
2,3,6,2′,5′	607.06	−0.004344	−1.4040	1.2101	0.98
2,3,6,3′,4′	607.00	−0.004279	−1.4049	1.2117	1.00
2,4,5,2′,4′	606.83	−0.004232	−1.4049	1.2127	1.00
2,4,5,2′,5′	606.75	−0.004199	−1.4045	1.2128	1.00
2,3,5,3′,4′	606.66	−0.004168	−1.4041	1.2133	1.00
2,4,5,3′,4′	606.52	−0.004068	−1.4049	1.2150	1.01
2,4,5,3′,5′	606.35	−0.004078	−1.4019	1.2128	1.00
2,4,6,2′,3′	607.18	−0.004393	−1.4049	1.2116	0.98
2,4,6,2′,4′	606.84	−0.004300	−1.4022	1.2089	0.97
2,4,6,2′,5′	606.78	−0.004277	−1.4017	1.2089	0.98
2,4,6,2′,6′	607.09	−0.004396	−1.4025	1.2081	0.97
2,4,6,3′,4′	606.75	−0.004223	−1.4029	1.2107	0.99
2,4,6,3′,5′	606.57	−0.004243	−1.3995	1.2071	0.97
3,4,5,2′,3′	607.19	−0.004293	−1.4090	1.2186	1.01
3,4,5,2′,4′	606.82	−0.004194	−1.4058	1.2153	1.00
2,4,5,2′,6′	607.06	−0.004315	−1.4052	1.2123	0.99
3,4,5,3′,4′	606.81	−0.004159	−1.4068	1.2175	1.02
3,4,6,2′,3′	607.15	−0.004312	−1.4078	1.2159	1.00
2,3,4,5,2′	607.56	−0.004387	−1.4125	1.2244	1.01
2,3,4,5,3′	607.35	−0.004345	−1.4108	1.2237	1.00
2,3,4,5,4′	607.59	−0.004432	−1.4113	1.2222	1.00
2,3,4,6,2′	607.82	−0.004546	−1.4108	1.2200	0.99
2,3,4,6,3′	607.48	−0.004459	−1.4078	1.2172	0.98
2,3,4,6,4′	607.45	−0.004432	−1.4082	1.2175	0.99
2,3,5,6,2′	607.78	−0.004541	−1.4101	1.2192	0.99
2,3,5,6,3′	607.45	−0.004449	−1.4074	1.2170	0.98
2,3,5,6,4′	607.42	−0.004424	−1.4077	1.2171	0.99
2,3,4,5,6	609.03	−0.004906	−1.4200	1.2339	0.99
3,4,5,2′,6′	607.03	−0.004290	−1.4057	1.2139	0.99
2,3,6,2′,3′	607.45	−0.004461	−1.4070	1.2127	0.98
2,3,6,2′,6′	607.39	−0.004480	−1.4048	1.2094	0.97
2,3,6,3′,5′	606.85	−0.004302	−1.4019	1.2089	0.97
3,4,5,2′,5′	606.71	−0.004185	−1.4042	1.2132	1.00
3,4,5,3′,5′	606.67	−0.004189	−1.4038	1.2147	0.99
hexa-CDPS					
2,3,4,2′,3′,4′	614.98	−0.008145	−1.3568	1.1445	0.84
2,3,4,2′,3′,5′	614.57	−0.008023	−1.3537	1.1430	0.84
2,3,4,2′,3′,6′	614.80	−0.008118	−1.3537	1.1405	0.84
2,3,4,2′,4′,6′	614.59	−0.008080	−1.3522	1.1395	0.83
2,3,4,3′,4′,5′	614.70	−0.008049	−1.3558	1.1458	0.85
2,3,5,2′,3′,5′	614.26	−0.007965	−1.3505	1.1397	0.83
2,3,5,2′,3′,6′	614.74	−0.008151	−1.3518	1.1385	0.82
2,3,5,6,3′,4′	614.80	−0.008112	−1.3539	1.1426	0.84
2,3,5,2′,4′,6′	614.48	−0.008088	−1.3497	1.1373	0.81
2,3,5,3′,4′,5′	614.54	−0.008013	−1.3538	1.1442	0.84
2,3,4,6,3′,4′	614.79	−0.008112	−1.3539	1.1406	0.84
2,3,6,2′,3′,6′	614.96	−0.008240	−1.3517	1.1362	0.81
2,3,6,3′,4′,5′	614.67	−0.008077	−1.3529	1.1408	0.83
2,3,4,2′,4′,5′	614.51	−0.007971	−1.3544	1.1435	0.85
2,3,5,2′,4′,5′	614.16	−0.007884	−1.3510	1.1410	0.85
2,3,6,2′,4′,5′	614.63	−0.008079	−1.3521	1.1391	0.83
2,4,5,2′,4′,5′	614.03	−0.007815	−1.3511	1.1408	0.86

Table 6 Continued

molecule	A/J·mol^{-1}·K^{-1}	B/J·mol^{-1}·K^{-2}	C/10^5 J·mol^{-1}	D/10^7 J·mol^{-1}·K	SE
2,4,5,2′,4′,6′	614.37	−0.008017	−1.3501	1.1380	0.83
2,4,5,3′,4′,5′	614.41	−0.007937	−1.3539	1.1444	0.85
2,3,6,2′,4′,6′	614.70	−0.008179	−1.3499	1.1353	0.81
2,4,6,2′,4′,6′	614.39	−0.008094	−1.3474	1.1339	0.8
2,4,6,3′,4′,5′	614.41	−0.008020	−1.3506	1.1393	0.83
3,4,5,3′,4′,5′	614.49	−0.007969	−1.3545	1.1459	0.85
2,3,4,5,2′,3′	615.04	−0.008146	−1.3581	1.1483	0.85
2,3,4,5,2′,4′	614.72	−0.008064	−1.3556	1.1457	0.84
2,3,4,5,2′,5′	614.66	−0.008032	−1.3553	1.1459	0.85
2,3,4,5,2′,6′	614.96	−0.008161	−1.3557	1.1446	0.84
2,3,4,5,3′,4′	614.76	−0.008048	−1.3569	1.1481	0.85
2,3,4,5,3′,5′	614.57	−0.008043	−1.3541	1.1464	0.84
2,3,4,6,2′,3′	615.29	−0.008303	−1.3564	1.1438	0.82
2,3,4,6,2′,4′	614.94	−0.008202	−1.3538	1.1413	0.82
2,3,4,6,2′,5′	614.90	−0.008187	−1.3535	1.1414	0.82
2,3,4,6,2′,6′	615.21	−0.008315	−1.3542	1.1408	0.81
2,3,4,6,3′,5′	614.69	−0.008153	−1.3513	1.1398	0.81
2,3,5,6,2′,3′	615.28	−0.008305	−1.3560	1.1435	0.82
2,3,5,6,2′,4′	614.87	−0.008183	−1.3530	1.1406	0.82
2,3,5,6,2′,5′	614.85	−0.008171	−1.3529	1.1409	0.82
2,3,5,6,2′,6′	615.14	−0.008293	−1.3533	1.1397	0.81
2,3,5,6,3′,5′	614.65	−0.008135	−1.3509	1.1398	0.81
2,3,4,5,6,2′	616.25	−0.008597	−1.3635	1.1540	0.82
2,3,4,5,6,3′	615.96	−0.008521	−1.3610	1.1515	0.82
2,3,4,5,6,4′	615.88	−0.008481	−1.3607	1.1510	0.83
hepta-CDPS					
2,3,4,5,2′,3′,4′	622.76	−0.011980	−1.3055	1.0750	0.70
2,3,4,5,2′,3′,5′	622.36	−0.011852	−1.3029	1.0741	0.70
2,3,4,5,2′,3′,6′	622.58	−0.011937	−1.3030	1.0717	0.70
2,3,4,5,2′,4′,5′	622.29	−0.011798	−1.3035	1.0746	0.71
2,3,4,5,2′,4′,6′	622.36	−0.011894	−1.3012	1.0705	0.69
2,3,4,5,3′,4′,5′	622.48	−0.011869	−1.3049	1.0767	0.71
2,3,4,6,2′,3′,4′	622.94	−0.012090	−1.3041	1.0714	0.69
2,3,4,6,2′,3′,5′	622.59	−0.011998	−1.3013	1.0700	0.68
2,3,4,6,2′,3′,6′	622.80	−0.012084	−1.3012	1.0678	0.68
2,3,4,6,2′,4′,5′	622.47	−0.011927	−1.3015	1.0703	0.69
2,3,4,6,2′,4′,6′	622.51	−0.012006	−1.2991	1.0665	0.67
2,3,4,6,3′,4′,5′	622.57	−0.011953	−1.3024	1.0717	0.69
2,3,5,6,2′,3′,4′	622.88	−0.012076	−1.3033	1.0704	0.68
2,3,5,6,2′,3′,5′	622.54	−0.011984	−1.3006	1.0689	0.68
2,3,5,6,2′,3′,6′	622.75	−0.012072	−1.3006	1.0668	0.67
2,3,5,6,2′,4′,5′	622.44	−0.011916	−1.3009	1.0696	0.69
2,3,5,6,2′,4′,6′	622.49	−0.012009	−1.2984	1.0657	0.67
2,3,5,6,3′,4′,5′	622.55	−0.011949	−1.3020	1.0715	0.69
2,3,4,5,6,2′,3′	623.71	−0.012344	−1.3092	1.0779	0.68
2,3,4,5,6,2′,4′	623.37	−0.012252	−1.3065	1.0753	0.68
2,3,4,5,6,2′,5′	623.34	−0.012231	−1.3066	1.0758	0.68
2,3,4,5,6,2′,6′	623.61	−0.012347	−1.3069	1.0748	0.67
2,3,4,5,6,3′,4′	623.34	−0.012205	−1.3073	1.0770	0.69
2,3,4,5,6,3′,5′	623.15	−0.012212	−1.3042	1.0740	0.67
octa-CDPS					
2,3,4,5,6,2′,3′,4′	631.38	−0.016148	−1.2569	1.0052	0.58
2,3,4,5,6,2′,3′,6′	631.24	−0.016135	−1.2541	1.0016	0.57
2,3,4,5,6,2′,4′,5′	630.95	−0.015990	−1.2546	1.0044	0.59
2,3,4,5,6,2′,4′,6′	630.94	−0.016055	−1.2519	1.0005	0.57
2,3,4,5,6,3′,4′,5′	631.02	−0.016004	−1.2553	1.0058	0.58
2,3,4,5,6,2′,3′,5′	630.78	−0.015968	−1.2523	1.0013	0.57
2,3,4,5,2′,3′,4′5′	630.54	−0.015795	−1.2547	1.0061	0.60
2,3,4,5,2′,3′,4′6′	630.79	−0.015942	−1.2536	1.0028	0.59
2,3,4,5,2′,3′,5′6′	630.68	−0.015903	−1.2526	1.0018	0.58
2,3,4,6,2′,3′,4′6′	630.62	−0.015917	−1.2506	0.9990	0.58
2,3,4,6,2′,3′,5′6′	630.60	−0.015919	−1.2501	0.9981	0.58
2,3,5,6,2′,3′,5′6′	630.58	−0.015913	−1.2497	0.9979	0.57
nona-CDPS					
2,3,4,5,6,2′,3′,4′,5′	639.20	−0.019980	−1.2061	0.9365	0.54
2,3,4,5,6,2′,3′,4′,6′	639.09	−0.019982	−1.2036	0.9328	0.53
2,3,4,5,6,2′,3′,5′,6′	639.03	−0.019965	−1.2030	0.9323	0.53
deca-CDPS					
2,3,4,5,6,2′,3′,4′,5′6′	647.52	−0.024025	−1.1565	0.8673	0.57

respectively. Obviously, this is because the repulsion interaction between neighboring Cl atoms makes total energy and hence enthalpy (H^{θ}) and Gibbs energy (G^{θ}) of the PCDPS molecules increase.

Temperature Dependence of Heat Capacity at Constant Pressure (C^{θ}_{p}). To our knowledge, the values of C^{θ}_{p} at different temperature for PCDPS congeners have not been reported. On the basis of the Gaussian output files, the values of C^{θ}_{p} were calculated according to the statistical mechanical method of Herzberg[14] employing a self-compiled program at temperatures from (200 to 1800) K with an even temperature interval of 100 K. However, these C^{θ}_{p} values are not listed in the paper due to the length of the article and are given in the Supporting Information.

On the basis of the calculated values of C^{θ}_{p} of all PCDPSs at different temperatures, the relations between C^{θ}_{p} and temperature were obtained using the least-squares method and are given in eq 6. Regression parameters (A, B, C, and D) are listed in Table 6. The following conclusions can be drawn: (1) There are very good relationships between C^{θ}_{p} and temperature (T, T^{-1}, and T^{-2}) for almost all PCDPS 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^{θ}_{p} values in this study can be used to predict C^{θ}_{p} of PCDPSs at different temperatures. Moreover, the standard error (SE) values decrease with an increase in the number of Cl atoms. (2) For the same isomer group, the C^{θ}_{p} values are close to each other at the same temperature because their regression parameters are close to each other.

$$C^{\theta}_{\text{p}} = A + BT + CT^{-1} + DT^{-2} \tag{6}$$

Comparison with PCDEs. In this work, the relative stabilities of isomer groups of PCDPSs are compared with that of isomer groups of PCDEs reported previously. Most stable isomers and least stable ones in each isomer group for PCDPSs and PCDEs are listed in Table 4. It was found that most stable isomers are consistent in two congeners except for the isomer group with two and nine chlorine atoms. However, the least stable isomers are not consistent in general except for isomer groups with one, five, and six chlorine atoms. One of the reasons might be the different size between S and O atoms. Careful observation of Table 4 indicates that in the least stable PCDPS isomers the interaction between the S atom and Cl atoms at positions 2 (6, 2′, 6′) is comparable with that between two Cl atoms on the same phenyl ring. For the least stable PCDE isomers, if the number of Cl atoms (n) is less than 5, the total interaction between the O atom and Cl atoms at positions 2 (6, 2′, 6′) and between two Cl atoms on two rings is perhaps more significant than the interaction between two Cl atoms on the same ring; however, when n is larger than 5, the latter may have a more significant effect. Furthermore, to study how differently chlorination affects diphenyl ether (DE) and diphenyl sulfide (DPS), the energetics of the 209 reactions of polychlorinated diphenyl ethers + diphenyl sulfide → diphenyl ether + polychlorinated diphenyl sulfides have been obtained theoretically. Although the largest absolute values of calculated $\Delta_{\text{r}}H^{\theta}$ and $\Delta_{\text{r}}G^{\theta}$ reach (17.75 and 18.18) $\text{kJ}\cdot\text{mol}^{-1}$, respectively, their mean absolute values in all isomer groups are only (3.53 and 3.63) $\text{kJ}\cdot\text{mol}^{-1}$, respectively, which indicates that chlorination affects DE and DPS to the approximately same extent.

Conclusion

Thermodynamic properties, including entropy (S^{θ}), heat capacity at constant volume (C^{θ}_{v}), enthalpy (H^{θ}), Gibbs energy (G^{θ}), the standard enthalpy of formation ($\Delta_{\text{f}}H^{\theta}$), and the standard Gibbs energy of formation ($\Delta_{\text{f}}G^{\theta}$) of 209 PCDPS molecules were obtained by performing DFT B3LYP/6-31G* calculations and by designing isodesmic reactions. The temperature dependence relation of heat capacity at constant pressure (C^{θ}_{p}) was also obtained. The results showed that S^{θ}, C^{θ}_{v}, $\Delta_{\text{f}}H^{\theta}$, and $\Delta_{\text{f}}G^{\theta}$ are all greatly dependent on the number and position of chlorine substitution (N_{PCS}). The relative thermodynamic stability of PCDPS congeners with the same degree of chlorination is mainly determined by the repulsion interaction between S and Cl atoms and between two Cl atoms on the same phenyl ring.

Supporting Information Available:

The values of C^{θ}_{p} at temperatures from (200 to 1800) K for PCDPS congeners. This material is available free of charge via the Internet at http://pubs.acs.org

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