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Study of Structural and Thermodynamic Properties for Polychlorinated Dibenzothiophenes by Density Functional Theory

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Standard enthalpy, standard Gibbs energy, standard entropies, and standard heat capacities at constant volume for 136 polychlorinated dibenzothiophenes (PCDTs) in the gaseous state at 298.15 K and 101.325 kPa have been computed using the density functional theory (B3LYP/6-31G*) with Gaussian 98. On the basis of the output data of Gaussian, isodesmic reactions were employed to calculate the standard enthalpy of formation and the standard Gibbs energy of formation of the 136 PCDTs in the gaseous state at 298.15 K and 101.325 kPa. The correlation equations between the standard entropy, standard heat capacity at constant volume, the standard enthalpy, the standard Gibbs energy, and the position of Cl substitution (N_{PCS}) were obtained, where all R^2 values are larger than 0.98. On the basis of the magnitude of the relative standard Gibbs energy of formation, the relative stability of PCDT isomers was theoretically proposed in this work and compared with that of polychlorinated dibenzofurans (PCDFs). In addition, the correlations between structural parameters and the position of Cl substitution (N_{PCS}) were discussed. The good correlations were found between molecular average polarizability, energy of the highest occupied molecular orbital, energy of the lowest unoccupied molecular orbital, molecular volume, and N_{PCS}, and all R^2 values are larger than 0.97.

Introduction

Polychlorinated dibenzothiophenes (PCDTs), the sulfur analogues of polychlorinated dibenzofurans (PCDFs), were first reported to occur in environmental samples in 1988[1] (the structure and atomic numbering of the parent is illustrated in Figure 1). An overview of these and subsequent samples and their origins is given in ref 2. Sielex et al.[3] have predicted gas chromatographic retention indices of PCDTs on nonpolar columns, and Puzyn et al.[4] have predicted environmental partition coefficients and Henry's law constants of 135 PCDT congeners. However, thermodynamic data of PCDT have not been reported.

Zeng et al.[5] and Li et al.[6] have researched the thermodynamic properties of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-*p*-dioxins (PBDDs) by B3LYP/6-31G*, respectively. We have calculated thermodynamic data of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorodibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), and polybrominated naphthalenes (PBNs),[7−11] and the data evaluated via the first principles are greatly different from those of AM1 and PM3.[12] Moreover, we have found that the isomers with low free energy have a high ratio of formation; i.e., the ratio of formation for isomers are consistent with their relative stabilities. At the same time, we have found that thermodynamic properties of these compounds have good relations with the position of Cl substitution (N_{PCS}).

In this study, the thermodynamic properties (standard entropy (S^{θ}), standard heat capacities at constant pressure (C^{θ}_P), the standard enthalpies (H^{θ}), and the standard Gibbs energies (G^{θ})) in the gaseous state at 298.15 K and 101.325 kPa were computed for all 136 PCDTs using density functional theory (DFT) with Gaussian 98 programs.[13] With the design of isodemic reactions, the standard enthalpies of formation ($\Delta_f H^{\theta}$) and the standard Gibbs energies of formation ($\Delta_f G^{\theta}$) of PCDTs were obtained. The purpose of this study is to discuss the correlations of structural and thermodynamic properties with N_{PCS}. In addition, according to the magnitude of the relative standard Gibbs energies of formation, the theoretic relative stability orders of the isomers are discussed. At the same time, we have discussed the correlations between structural parameters and the position of Cl substitution (N_{PCS}).

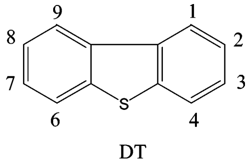

Figure 1. Numbering of carbon atoms in DT.

Like PCDDs and PCDFs, PCDTs have a variable number of chlorines attached to two phenyl rings. In this study, dibenzothiophene (DT) attached to from one to eight chlorine atom(s) was defined MCDT (monochlodibenzothiophenes), DCDT (dichlodibenzothiophenes), tri-CDT (trichlodibenzothiophenes), TCDT (tetrachlodibenzothiophenes), penta-CDT (pentachlodibenzothiophenes), hexa-CDT (hexachlodibenzothiophenes), hepta-CDT (heptachlodibenzothiophenes), and OCDT (octachlodibenzothiophenes), respectively.

Computational Methods

Becke's three-parameter hybrid function combined with the gradient-correlation functional of Lee, Yang, and Parr (LYP), denoted B3LYP, was employed in the computations using DFT. The all-electron 6-31G* basis set was employed. Geometries

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were optimized using analytic gradient techniques, that is, the Berny algorithm with redundant internal coordinates. The stationary points on the potential energy surface were characterized by calculations of vibrational frequencies, which were done analytically at DFT levels. Following the geometry optimization, frequencies were calculated using the same method at a stationary point. Throughout this paper, all calculations for PCDTs were carried out with B3LYP/6-31G* Opt Freq.

The equations used for computing thermochemical data in Gaussian programs are derived from statistical thermodynamics. Two key ideas of statistical thermodynamics are the Boltzmann distribution and the partition function. The partition function is like a thermodynamic wave function, in the sense that it contains all thermodynamic information about the system, just as the quantum mechanical wave function contains all dynamic information.

Entropy and Heat Capacity. The entropy and heat capacity can be directly obtained from the output of Gaussian programs. The equations used for computing thermochemical data in the programs are equivalent to those given in statistical mechanics texts.[14,15]

Enthalpy and Gibbs Energy of Formation. In this study, reaction 1, which is similar to the isodesmic reaction used to calculate thermodynamic data for the PBDDs[6] and PBDEs,[16] served as the basis for calculating $\Delta_f H^\theta$ and $\Delta_f G^\theta$ for the PCDTs.

$$\text{dibenzothiophene} + n\cdot\text{chlorobenzene} = \text{PCDT} + n\cdot\text{benzene} \quad (1)$$

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

$$\Delta_r H^\theta = [H^\theta{}_{\text{PCDT}} + nH^\theta{}_{\text{benzene}}] - [H^\theta{}_{\text{DT}} + nH^\theta{}_{\text{chlorobenzene}}] \quad (2)$$

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

$$\Delta_r H^\theta = [\Delta_f H^\theta{}_{\text{PCDT}} + n\Delta_f H^\theta{}_{\text{benzene}}] - [\Delta_f H^\theta{}_{\text{DT}} + n\Delta_f H^\theta{}_{\text{chlorobenzene}}] \quad (3)$$

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

$$\Delta_f H^\theta{}_{\text{PCDT}} = H^\theta{}_{\text{PCDT}} + nH^\theta{}_{\text{benzene}} - nH^\theta{}_{\text{chlorobenzene}} - H^\theta{}_{\text{DT}} - n\Delta_f H^\theta{}_{\text{benzene}} + n\Delta_f H^\theta{}_{\text{chlorobenzene}} + \Delta_f H^\theta{}_{\text{DT}} \quad (4)$$

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

$$\Delta_f G^\theta{}_{\text{PCDT}} = G^\theta{}_{\text{PCDT}} + nG^\theta{}_{\text{benzene}} - nG^\theta{}_{\text{chlorobenzene}} - G^\theta{}_{\text{DT}} - n\Delta_f G^\theta{}_{\text{benzene}} + n\Delta_f G^\theta{}_{\text{chlorobenzene}} + \Delta_f G^\theta{}_{\text{DT}} \quad (5)$$

The experimental values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ for dibenzothiophene, chlorobenzene, and benzene taken from the literature[17,18] are listed in Table 1, which also lists the values of H^θ and G^θ calculated at the B3LYP/6-31G* level for these compounds.

The basic requirement of an isodesmic reaction is that the number of each type of bond is conserved in products and reactants. The method of isodesmic reactions relies on the similarity of the bonding environments in the reactants and products that leads to partial cancellation of systematic errors in the density functional and ab initio molecular orbital calculations.[15] The results of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ from eqs 4 and 5 for PCDTs are listed in Table 2. At the B3LYP/6-31G* level, the mean absolute deviation of calculated thermochemical quantities from experiment for a variety of compounds is 33.05 kJ·mol^{-1} and the standard deviation is 39.75 kJ·mol^{-1}.[19] Because all the values are from theoretical calculations, variables can be exactly repeatable.

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

	$\Delta_f H^\theta$	$\Delta_f G^\theta$	H^θ	G^θ
compound	kJ·mol^{-1}	kJ·mol^{-1}	hartree	hartree
benzene	82.92[b]	129.66[b]	−232.14258	−232.17302
chlorobenzene	51.1[b]	98.5[b]	−691.74731	−691.78288
benzothiophene	149.04[c]	243.29[c]	−860.13514	−860.17980

[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 17. [c]Taken from ref 18. Other data obtained from B3LYP/6-31G* calculations.

Structural Parameters. Structural properties such as the dipole moment of the molecules (μ), energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), the most negative atomic net charges of the molecule (q^-), the most positive atomic net charges of the molecule on the hydrogen ($q\text{H}^+$), molecular volume (V_i), and molecular average polarizability (α) were also obtained from the output of Gaussian programs.

Correlations between Structural and Thermodynamic Properties and Cl Substitution Positions. If the numbers of chlorine atoms at positions 1 or 9 are defined as N_1, the numbers of chlorine atoms at positions 2 or 8 are defined as N_2; the numbers of chlorine atoms at positions 3 or 7 are defined as N_3; the numbers of chlorine atoms at positions 4 or 6 are defined as N_4; the numbers of chlorine atoms at ortho, meta, and para positions are symbolized as N_o, N_m, and N_p; and the numbers of dichlorine atoms at positions 1 and 9 are $N_{1,9}$, respectively. Ortho, meta, and para positions indicate two chlorine atoms substituent to ortho, meta, and para positions, respectively. For 1,2,3,4,6,9-hexa-CDT, the N_1, N_2, N_3, N_4, N_o, N_m, N_p, and $N_{1,9}$ equals 2, 1, 1, 2, 3, 2, 2, and 1, respectively. Using the GQSARF2.0 program,[20] N_{PCS} were taken as theoretical descriptors to establish the correlation equations. These equations with large R^2 values show that structural and thermodynamic properties have good relations with N_{PCS} for PCDTs.

Results and Discussion

All of the energies and other thermodynamic quantities calculated for 136 PCDTs of the ideal gaseous state at 298.15 K are listed in Table 2.

Relations of Thermodynamic Properties and N_{PCS}. The dependence of PCDTs' thermodynamic properties on the number of chlorines was investigated. The correlations of S^θ, $C^\theta{}_P$, H^θ, and G^θ with N_{PCS} for PCDTs can be described as follows (eqs 6 to 9) using the GQSARF2.0 program

$$S^\theta/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 394.28 + 27.84N_1 + 29.89N_2 + 30.26N_3 + 29.14N_4 - 1.67N_o \quad (6)$$

$$R^2 = 0.9997 \quad \text{SE} = 0.676$$

$$C^\theta{}_P/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 168.86 + 15.86N_1 + 15.87N_2 + 15.86N_3 + 15.79N_4 \quad (7)$$

$$R^2 = 0.9999 \quad \text{SE} = 0.28$$

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

molecule	V_i cm^3·mol^{-1}	a 10^{-30} esu	qH$^+$ e	q^+ e	q^- e	μ debye	H^θ hartree	C^θ_P J·mol^{-1}·K^{-1}	S^θ J·mol^{-1}·K^{-1}	$\Delta_fH^{\theta a}$ kJ·mol^{-1}	$\Delta_fG^{\theta b}$ kJ·mol^{-1}	relative Δ_fG^θ kJ·mol^{-1}	N_1	N_2	N_3	N_4	N_o	N_m	N_p	$N_{1.9}$
DT	135.6	137.9	0.1423	0.2104	−0.1825	0.901	−860.13514	168.25	393.21	149.04	243.29		0	0	0	0	0	0	0	0
MCDT																				
1	144.3	149.4	0.1596	0.2215	−0.1826	0.808	−1319.73548	184.20	422.09	128.75	222.34	9.32	1	0	0	0	0	0	0	0
2	141.3	151.9	0.1574	0.2214	−0.1816	1.717	−1319.73880	184.57	423.34	120.03	213.26	0.23	0	1	0	0	0	0	0	0
3	149.2	153.7	0.1661	0.2243	−0.1820	2.448	−1319.73886	184.57	423.56	119.87	213.02	0.00	0	0	1	0	0	0	0	0
4	145.0	150.2	0.1549	0.2492	−0.1842	2.565	−1319.73810	184.23	422.63	121.85	215.29	2.27	0	0	0	1	0	0	0	0
DCDT																				
1,2	161.2	163.0	0.1640	0.2291	−0.1820	2.168	−1779.33313	200.08	450.98	198.43	208.44	24.60	1	1	0	0	1	0	0	0
1,3	159.2	165.3	0.1771	0.2344	−0.1824	1.980	−1779.33783	200.52	452.37	186.09	195.69	11.85	1	0	1	0	0	1	0	0
1,4	161.4	162.2	0.1634	0.2591	−0.1843	1.041	−1779.33720	200.21	451.72	187.74	197.54	13.70	1	0	0	1	0	0	1	0
1,6	159.0	161.7	0.1641	0.2597	−0.1812	1.308	−1779.33811	200.20	451.65	185.36	195.17	11.34	1	0	0	1	0	0	0	0
1,7	156.3	165.3	0.1683	0.2349	−0.1847	2.325	−1779.33913	200.51	452.31	182.67	192.28	8.44	1	0	1	0	0	0	0	0
1,8	158.5	163.0	0.1823	0.2317	−0.1807	2.823	−1779.33869	200.45	452.18	183.82	193.48	9.64	1	1	0	0	0	0	0	0
1,9	157.1	161.2	0.1582	0.2346	−0.1786	2.202	−1779.31914	200.47	450.32	235.16	245.37	61.54	2	0	0	0	0	0	0	1
2,3	159.0	167.1	0.1721	0.2317	−0.1844	3.196	−1779.33714	200.46	452.36	187.91	197.51	13.67	0	1	1	0	1	0	0	0
2,4	160.2	164.5	0.1769	0.2579	−0.1833	2.622	−1779.34042	200.59	452.71	179.29	188.79	4.95	0	1	0	1	0	1	0	0
2,6	155.2	164.3	0.1601	0.2592	−0.1819	0.980	−1779.34136	200.56	452.82	176.81	186.27	2.44	0	1	0	1	0	0	0	0
2,7	157.7	168.0	0.1686	0.2346	−0.1834	0.673	−1779.34214	200.85	453.50	174.77	184.03	0.19	0	1	1	0	0	0	0	0
2,8	160.5	165.8	0.1613	0.2318	−0.1792	2.093	−1779.34194	200.91	453.66	175.31	184.52	0.69	0	2	0	0	0	0	0	0
3,4	161.4	167.1	0.1721	0.2317	−0.1844	3.196	−1779.33714	200.46	452.36	187.91	197.51	13.67	0	0	1	1	1	0	0	0
3,6	157.2	166.1	0.1694	0.2620	−0.1860	2.771	−1779.34147	200.58	452.87	176.54	185.99	2.15	0	0	1	1	0	0	0	0
3,7	157.6	170.1	0.1686	0.2376	−0.1839	1.341	−1779.34219	200.87	453.70	174.64	183.84	0.00	0	0	2	0	0	0	0	0
4,6	157.3	162.2	0.1576	0.2872	−0.1579	3.723	−1779.34059	200.27	452.05	178.84	188.53	4.69	0	0	0	2	0	0	0	0
tri-CDT																				
1,2,3	169.4	178.4	0.1756	0.2390	−0.1801	3.049	−2238.93015	215.97	479.68	269.76	196.24	35.78	1	1	1	0	2	1	0	0
1,2,4	170.5	176.2	0.1827	0.2652	−0.1836	2.119	−2238.93384	216.15	480.46	260.08	186.34	25.87	1	1	0	1	1	1	1	0
1,2,6	173.2	175.6	0.1666	0.2666	−0.1772	0.401	−2238.93554	216.00	480.04	255.62	182.00	21.53	1	1	0	1	1	0	0	0
1,2,7	171.1	179.4	0.1687	0.2420	−0.1841	1.681	−2238.93654	216.39	481.24	253.01	179.03	18.56	1	1	1	0	1	0	0	0
1,2,8	171.9	176.8	0.1821	0.2392	−0.1798	3.152	−2238.93606	216.41	481.25	254.27	180.28	19.82	1	2	0	0	1	0	0	0
1,2,9	169.7	174.8	0.1659	0.2425	−0.1779	3.373	−2238.91618	216.35	477.85	306.45	233.48	73.02	2	1	0	0	1	0	0	1
1,3,4	171.9	177.6	0.1822	0.2671	−0.1840	2.485	−2238.93500	216.09	480.40	257.03	183.30	22.83	1	0	1	1	1	1	1	0
1,3,6	174.8	178.0	0.1791	0.2716	−0.1831	1.360	−2238.94016	216.47	481.68	243.49	169.38	8.91	1	0	1	1	0	1	0	0
1,3,7	175.1	182.1	0.1793	0.2470	−0.1847	0.258	−2238.94114	216.75	482.34	240.93	166.62	6.15	1	0	2	0	0	1	0	0
1,3,8	172.3	179.5	0.1828	0.2441	−0.1806	1.865	−2238.94074	216.82	482.37	241.96	167.64	7.18	1	1	1	0	0	1	0	0
1,3,9	173.4	177.4	0.1799	0.2469	−0.1801	2.713	−2238.92152	216.74	480.31	292.43	218.73	58.27	2	0	1	0	0	1	0	1
1,4,6	171.5	174.5	0.1657	0.2964	−0.1580	2.071	−2238.93943	216.16	480.83	245.42	171.56	11.09	1	0	0	2	0	0	1	0
1,4,7	171.0	178.5	0.1700	0.2712	−0.1866	1.598	−2238.94055	216.49	481.76	242.47	168.34	7.87	1	0	1	1	0	0	1	0
1,4,8	170.8	176.2	0.1831	0.2683	−0.1820	1.112	−2238.94014	216.45	481.34	243.55	169.53	9.07	1	1	0	1	0	0	1	0
1,4,9	169.7	174.2	0.1661	0.2713	−0.1803	1.157	−2238.92064	216.43	479.39	294.73	221.30	60.84	2	0	0	1	0	0	1	1
1,6,7	171.5	177.0	0.1710	0.2674	−0.1811	2.819	−2238.93693	216.03	480.15	251.97	178.32	17.85	1	0	1	1	1	0	0	0
1,6,8	167.5	175.8	0.1855	0.2674	−0.1806	2.710	−2238.94005	216.51	481.65	243.79	169.69	9.22	1	1	0	1	0	1	0	0
1,7,8	169.8	178.5	0.1877	0.2413	−0.1849	3.728	−2238.93708	216.33	481.14	251.57	177.62	17.16	1	1	1	0	1	0	0	0
2,3,4	169.9	179.0	0.1667	0.2643	−0.1834	3.743	−2238.93402	216.08	479.82	259.61	186.05	25.58	0	1	1	1	2	1	0	0
2,3,6	167.4	179.9	0.1752	0.2686	−0.1862	2.447	−2238.93947	216.42	481.58	245.31	171.22	10.76	0	1	1	1	1	0	0	0
2,3,7	171.9	184.0	0.1744	0.2445	−0.1839	1.037	−2238.94018	216.74	482.50	243.43	169.08	8.61	0	1	2	0	1	0	0	0
2,3,8	170.6	181.5	0.1745	0.2415	−0.1834	2.268	−2238.94001	216.72	482.41	243.90	169.57	9.10	0	2	1	0	1	0	0	0
2,4,6	170.7	176.9	0.1792	0.2949	−0.1564	2.615	−2238.94258	216.59	482.09	237.13	162.89	2.43	0	1	0	2	0	1	0	0
2,4,7	169.3	181.0	0.1792	0.2703	−0.1853	1.083	−2238.94342	216.87	482.83	234.92	160.46	0.00	0	1	1	1	0	1	0	0
2,4,8	171.3	178.8	0.1796	0.2676	−0.1808	1.126	−2238.94322	216.95	483.12	235.47	160.93	0.46	0	2	0	1	0	1	0	0
2,6,7	167.2	180.0	0.1657	0.2672	−0.1815	1.305	−2238.93991	216.37	481.29	244.16	170.16	9.70	0	1	1	1	1	0	0	0
3,4,6	170.9	177.7	0.1646	0.2947	−0.1576	3.969	−2238.93916	216.14	480.70	246.11	172.29	11.83	0	0	1	2	1	0	0	0
3,4,7	169.6	182.1	0.1710	0.2700	−0.1857	2.513	−2238.94000	216.38	481.34	243.90	169.89	9.43	0	0	2	1	1	0	0	0

Table 2. (Continued)

molecule	V_i cm^3·mol^{-1}	a 10^{-30} esu	qH^+ e	q^+ e	q^- e	μ debye	H^θ hartree	C^θ_P J·mol^{-1}·K^{-1}	S^θ J·mol^{-1}·K^{-1}	$\Delta_f H^{\theta a}$ kJ·mol^{-1}	$\Delta_f G^{\theta b}$ kJ·mol^{-1}	relative $\Delta_f G^\theta$ kJ·mol^{-1}	N_1	N_2	N_3	N_4	N_o	N_m	N_p	$N_{1.9}$
TCDT																				
1,2,3,4	180.8	190.8	0.1614	0.2714	−0.1839	3.161	−2698.52622	231.56	507.40	343.60	186.85	48.41	1	1	1	1	3	2	1	0
1,2,3,6	185.8	191.3	0.1786	0.2757	−0.1821	1.792	−2698.53232	231.91	508.81	327.58	170.41	31.97	1	1	1	1	2	1	0	0
1,2,3,7	180.5	195.6	0.1777	0.2513	−0.1844	1.144	−2698.53334	232.21	509.39	324.91	167.56	29.12	1	1	2	0	2	1	0	0
1,2,3,8	182.1	192.7	0.1826	0.2484	−0.1799	2.830	−2698.53287	232.24	509.43	326.15	168.80	30.35	1	2	1	0	2	1	0	0
1,2,3,9	180.5	190.5	0.1768	0.2519	−0.1783	3.828	−2698.51324	232.25	506.33	377.69	221.26	82.81	2	1	1	0	2	1	0	1
1,2,4,6	180.7	188.7	0.1848	0.3017	−0.1576	1.539	−2698.53587	232.10	509.64	318.28	160.86	22.41	1	1	0	2	1	1	1	0
1,2,4,7	182.8	193.0	0.1848	0.2771	−0.1859	0.053	−2698.53696	232.38	510.33	315.41	157.78	19.34	1	1	1	1	1	1	1	0
1,2,4,8	182.6	190.3	0.1831	0.2742	−0.1814	1.771	−2698.53648	232.42	510.34	316.67	159.05	20.60	1	2	0	1	1	1	1	0
1,2,4,9	183.8	188.2	0.1843	0.2772	−0.1796	2.724	−2698.51666	232.34	507.01	368.70	212.07	73.62	2	1	0	1	1	1	1	1
1,2,6,7	186.5	191.5	0.1710	0.2745	−0.1769	1.367	−2698.53419	231.90	508.94	322.70	165.48	27.04	1	1	1	1	2	0	0	0
1,2,6,8	187.1	189.9	0.1853	0.2745	−0.1764	2.076	−2698.53717	232.36	510.23	314.87	157.27	18.83	1	2	0	1	1	1	0	0
1,2,6,9	182.1	188.1	0.1683	0.2783	−0.1760	1.708	−2698.51746	232.31	506.98	366.62	209.99	71.55	2	1	0	1	1	0	1	1
1,2,7,8	182.6	192.8	0.1875	0.2487	−0.1843	3.248	−2698.53427	232.19	509.55	322.48	165.09	26.64	1	2	1	0	2	0	0	0
1,2,7,9	184.6	191.5	0.1818	0.2545	−0.1793	2.745	−2698.51832	232.61	507.89	364.35	207.46	69.01	2	1	1	0	1	1	0	1
1,2,8,9	178.0	188.5	0.1678	0.2502	−0.1735	3.897	−2698.51300	232.28	505.75	378.33	222.07	83.62	2	2	0	0	2	0	0	1
1,3,4,6	178.4	190.1	0.1841	0.3034	−0.1578	2.486	−2698.53706	232.02	509.39	315.14	157.80	19.36	1	0	1	2	1	1	1	0
1,3,4,7	181.2	194.6	0.1843	0.2786	−0.1862	0.985	−2698.53813	232.36	510.44	312.34	154.68	16.24	1	0	2	1	1	1	1	0
1,3,4,8	180.3	192.1	0.1847	0.2760	−0.1817	1.038	−2698.53769	232.36	510.27	313.49	155.88	17.44	1	1	1	1	1	1	1	0
1,3,4,9	181.3	189.8	0.1850	0.2786	−0.1802	2.537	−2698.51856	232.28	508.08	363.73	206.78	68.33	2	0	1	1	1	1	1	1
1,3,6,7	178.5	194.1	0.1807	0.2789	−0.1831	1.191	−2698.53876	232.33	510.35	310.69	153.06	14.62	1	0	2	1	1	1	0	0
1,3,6,8	183.1	192.6	0.1860	0.2791	−0.1826	0.725	−2698.54183	232.75	511.62	302.62	144.61	6.17	1	1	1	1	0	2	0	0
1,3,6,9	180.4	190.8	0.1817	0.2825	−0.1818	1.172	−2698.52276	232.67	509.34	352.68	195.35	56.91	2	0	1	1	0	1	1	1
1,3,7,8	179.1	195.8	0.1882	0.2535	−0.1846	1.861	−2698.53888	232.63	511.04	310.36	152.52	14.08	1	1	2	0	1	1	0	0
1,3,7,9	179.9	194.5	0.1818	0.2588	−0.1802	1.428	−2698.52359	233.01	510.41	350.52	192.87	54.43	2	0	2	0	0	2	0	1
1,4,6,7	181.4	190.1	0.1722	0.3033	−0.1524	2.685	−2698.53808	231.99	509.24	312.46	155.16	16.72	1	0	1	2	1	0	1	0
1,4,6,8	181.8	188.9	0.1865	0.3034	−0.1576	1.773	−2698.54110	232.49	510.65	304.54	146.82	8.38	1	1	0	2	0	1	1	0
1,4,6,9	180.4	187.2	0.1681	0.3071	−0.1419	0.668	−2698.52173	232.36	508.34	355.40	198.37	59.93	2	0	0	2	0	0	2	1
1,4,7,8	182.3	192.0	0.1887	0.2774	−0.1866	2.352	−2698.53827	232.34	510.15	311.97	154.39	15.95	1	1	1	1	1	0	1	0
2,3,4,9	185.7	190.5	0.1901	0.2738	−0.1808	3.749	−2698.53374	231.90	508.43	323.86	166.81	28.36	1	1	1	1	2	1	0	0
2,3,4,6	182.4	191.8	0.1680	0.3011	−0.1561	3.430	−2698.53603	232.10	509.39	317.84	160.50	22.05	0	1	1	2	2	1	0	0
2,3,4,7	181.0	196.2	0.1727	0.2764	−0.1853	1.879	−2698.53684	232.32	509.94	315.73	158.22	19.78	0	1	2	1	2	1	0	0
2,3,4,8	185.5	193.7	0.1702	0.2735	−0.1810	2.075	−2698.53666	232.29	509.67	316.20	158.77	20.32	0	2	1	1	2	1	0	0
2,3,6,7	176.6	196.2	0.1767	0.2764	−0.1859	1.253	−2698.53778	232.25	510.21	313.26	155.67	17.23	0	1	2	1	2	0	0	0
2,3,6,8	187.2	194.8	0.1811	0.2766	−0.1854	0.681	−2698.54105	232.71	511.62	304.68	146.67	8.23	0	2	1	1	1	1	0	0
2,3,7,8	186.1	198.0	0.1762	0.2512	−0.1834	1.200	−2698.53785	232.51	511.06	313.08	155.23	16.79	0	2	2	0	2	0	0	0
2,4,6,7	184.7	192.8	0.1807	0.3024	−0.1559	2.094	−2698.54090	232.45	510.75	305.06	147.30	8.86	0	1	1	2	1	1	0	0
2,4,6,8	180.3	191.6	0.1815	0.3024	−0.1549	0.691	−2698.54411	232.89	512.21	296.63	138.44	0.00	0	2	0	2	0	2	0	0
3,4,6,7	191.9	192.8	0.1807	0.3024	−0.1559	2.094	−2698.54090	232.45	510.75	305.06	147.30	8.86	0	0	2	2	2	0	0	0

Table 2. (Continued)

molecule	V_i	a	$q\mathrm{H}^+$	q^+	q^-	μ	H^θ	C^θ_p	S^θ	$\Delta_\mathrm{f}H^{\theta\mathrm{a}}$	$\Delta_\mathrm{f}G^{\theta\mathrm{b}}$	relative $\Delta_\mathrm{f}G^\theta$	N_1	N_2	N_3	N_4	N_o	N_m	N_p	$N_{1,9}$
	$\mathrm{cm^3{\cdot}mol^{-1}}$	10^{-30} esu	e	e	e	debye	hartree	$\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$	$\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$	$\mathrm{kJ{\cdot}mol^{-1}}$	$\mathrm{kJ{\cdot}mol^{-1}}$	$\mathrm{kJ{\cdot}mol^{-1}}$								
penta-CDT																				
1,2,3,4,6	195.8	203.6	0.1656	0.3073	−0.1576	2.490	−3158.12812	247.50	536.15	402.15	161.86	28.27	1	1	1	2	3	2	1	0
1,2,3,4,7	194.7	208.3	0.1725	0.2828	−0.1860	1.060	−3158.12920	247.85	537.19	399.31	158.70	25.11	1	1	2	1	3	2	1	0
1,2,3,4,8	194.7	205.4	0.1832	0.2801	−0.1815	2.118	−3158.12871	247.82	537.10	400.58	160.00	26.41	1	2	1	1	3	2	1	0
1,2,3,4,9	192.9	203.0	0.1636	0.2831	−0.1799	3.522	−3158.10918	247.78	533.55	451.87	212.34	78.75	2	1	1	1	3	2	1	1
1,2,3,6,7	197.6	207.8	0.1800	0.2831	−0.1819	0.253	−3158.13082	247.77	537.37	395.06	154.40	20.81	1	1	2	1	3	1	0	0
1,2,3,6,8	195.4	206.0	0.1857	0.2830	−0.1813	1.200	−3158.13376	248.28	538.83	387.33	146.24	12.65	1	2	1	1	2	2	0	0
1,2,3,6,9	192.2	204.1	0.1797	0.2868	−0.1802	2.251	−3158.11431	248.17	535.36	438.39	198.33	64.74	2	1	1	1	2	1	1	1
1,2,3,7,8	194.9	209.3	0.1879	0.2576	−0.1799	2.151	−3158.13088	248.05	538.13	394.88	154.00	20.41	1	2	2	0	3	1	0	0
1,2,3,7,9	192.0	208.0	0.1833	0.2633	−0.1797	2.307	−3158.11515	248.53	536.48	436.19	195.80	62.21	2	1	2	0	2	2	0	1
1,2,3,8,9	198.2	204.7	0.1784	0.2591	−0.1775	3.661	−3158.10987	248.12	534.08	450.05	210.38	76.79	2	2	1	0	3	1	0	1
1,2,4,6,7	188.5	204.9	0.1862	0.3088	−0.1521	1.142	−3158.13434	247.91	537.93	385.81	144.99	11.40	1	1	1	2	2	1	1	0
1,2,4,6,8	195.7	203.3	0.1869	0.3088	−0.1575	0.511	−3158.13727	248.33	539.15	378.11	136.92	3.33	1	2	0	2	1	2	1	0
1,2,4,6,9	196.7	201.4	0.1862	0.3125	−0.1409	1.319	−3158.11758	248.29	536.04	429.81	189.55	55.96	2	1	0	2	1	1	2	1
1,2,4,7,8	197.1	206.6	0.1883	0.2828	−0.1861	1.625	−3158.13450	248.19	538.74	385.39	144.33	10.74	1	2	1	1	2	1	1	0
1,2,4,7,9	194.4	205.2	0.1862	0.2883	−0.1809	1.280	−3158.11856	248.60	537.03	427.24	186.68	53.09	2	1	1	1	1	2	1	1
1,2,4,8,9	197.5	202.2	0.1860	0.2843	−0.1751	2.599	−3158.11327	248.24	534.82	441.14	201.24	67.65	2	2	0	1	2	1	1	1
1,2,6,7,8	190.7	205.0	0.1898	0.2804	−0.1767	2.751	−3158.13078	247.76	537.10	395.16	154.58	20.99	1	2	1	1	3	1	0	0
1,2,6,7,9	194.8	204.2	0.1868	0.2855	−0.1758	1.888	−3158.11521	248.15	535.62	436.04	195.90	62.31	2	1	1	1	2	1	1	1
1,3,4,6,7	198.2	206.5	0.1855	0.3103	−0.1518	2.029	−3158.13551	247.84	537.86	382.75	141.94	8.35	1	0	2	2	2	1	1	0
1,3,4,6,8	200.0	205.0	0.1866	0.3103	−0.1575	0.653	−3158.13853	248.33	539.29	374.82	133.59	0.00	1	1	1	2	1	2	1	0
1,3,4,6,9	191.9	203.1	0.1867	0.3137	−0.1465	1.685	−3158.11948	248.22	536.93	424.81	184.29	50.70	2	0	1	2	1	1	2	1
1,3,4,7,8	191.9	208.5	0.1889	0.2845	−0.1865	0.831	−3158.13568	248.12	538.65	382.29	141.25	7.66	1	1	2	1	2	1	1	0
1,3,4,7,9	191.7	207.1	0.1868	0.2894	−0.1818	0.548	−3158.12045	248.53	538.06	422.27	181.41	47.82	2	0	2	1	1	2	1	1
1,3,6,7,8	194.9	208.0	0.1905	0.2847	−0.1829	1.696	−3158.13536	248.19	538.50	383.14	142.15	8.56	1	1	2	1	2	2	0	0
1,4,6,7,8	193.8	203.9	0.1910	0.3090	−0.1570	2.840	−3158.13468	247.92	537.82	384.93	144.14	10.55	1	1	1	2	2	1	1	0
2,3,4,6,7	193.7	208.3	0.1688	0.3078	−0.1548	2.402	−3158.13425	247.87	537.57	386.04	145.32	11.73	0	1	2	2	3	1	0	0
2,3,4,6,8	193.4	206.8	0.1825	0.3079	−0.1546	1.350	−3158.13746	248.30	538.92	377.61	136.49	2.90	0	2	1	2	2	2	0	0
2,3,4,7,8	194.2	210.4	0.1783	0.2826	−0.1854	0.468	−3158.13436	248.12	538.39	385.75	144.78	11.20	0	2	2	1	3	1	0	0
hexa-CDT																				
1,2,3,4,6,7	210.2	220.4	0.1722	0.3140	−0.1520	1.343	−3617.72650	263.33	564.96	469.90	146.05	14.70	1	1	2	2	4	2	1	0
1,2,3,4,6,8	209.3	218.6	0.1862	0.3141	−0.1577	0.637	−3617.72936	263.83	566.30	462.39	138.13	6.79	1	2	1	2	3	3	1	0
1,2,3,4,6,9	202.7	216.5	0.1711	0.3177	−0.1408	2.308	−3617.70999	263.74	562.63	513.26	190.10	58.75	2	1	1	2	3	2	2	1
1,2,3,4,7,8	205.3	222.2	0.1884	0.2884	−0.1861	1.033	−3617.72664	263.63	565.40	469.55	145.56	14.22	1	2	2	1	4	2	1	0
1,2,3,4,7,9	208.1	220.7	0.1844	0.2938	−0.1814	1.616	−3617.71092	264.06	563.62	510.83	187.37	56.02	2	1	2	1	3	3	1	1
1,2,3,4,8,9	204.3	217.4	0.1710	0.2898	−0.1754	2.905	−3617.70568	263.67	561.38	524.58	201.78	70.44	2	2	1	1	4	2	1	1
1,2,3,6,7,8	201.6	221.8	0.1901	0.2885	−0.1817	1.299	−3617.72726	263.64	565.51	467.90	143.88	12.54	1	2	2	1	4	2	0	0
1,2,3,6,7,9	205.9	220.8	0.1881	0.2936	−0.1802	1.136	−3617.71191	264.02	563.94	508.21	184.66	53.31	2	1	2	1	3	2	1	1
1,2,3,6,8,9	210.0	221.5	0.1799	0.2679	−0.1779	2.817	−3617.70661	264.00	562.42	522.13	199.03	67.68	2	2	1	1	3	2	1	1
1,2,3,7,8,9	207.7	218.7	0.1905	0.3140	−0.1570	1.459	−3617.73074	263.79	566.25	458.78	134.53	3.19	2	2	2	0	4	2	0	1
1,2,4,6,7,8	204.1	217.7	0.1884	0.3188	−0.1453	0.365	−3617.71518	264.12	564.53	499.63	175.90	44.56	1	2	1	2	3	2	1	0
1,2,4,6,7,9	212.8	215.7	0.1877	0.3177	−0.1378	1.106	−3617.71320	264.21	563.88	504.83	181.30	49.95	2	1	1	2	2	2	2	1
1,2,4,6,8,9	211.2	218.6	0.1874	0.2925	−0.1793	2.055	−3617.70997	264.09	563.12	513.32	190.02	58.67	2	2	0	2	2	2	2	1
1,3,4,6,7,8	208.9	220.6	0.1911	0.3155	−0.1566	1.435	−3617.73196	263.78	566.20	455.57	131.35	0.00	1	1	2	2	3	2	1	0
1,3,4,6,7,9	204.7	219.6	0.1879	0.3200	−0.1463	0.741	−3617.71707	264.04	565.48	494.66	170.65	39.30	2	0	2	2	2	2	2	1
2,3,4,6,7,8	204.7	222.6	0.1719	0.3135	−0.1533	0.943	−3617.73066	263.76	565.91	458.98	134.84	3.49	0	2	2	2	4	2	0	0
hepta-CDT																				
1,2,3,4,6,7,8	214.6	234.5	0.1905	0.3191	−0.1570	0.436	−4077.32282	279.22	592.98	543.10	135.92	0.00	1	2	2	2	5	3	1	0
1,2,3,4,6,7,9	221.2	233.4	0.1892	0.3237	−0.1453	0.798	−4077.30749	279.60	591.30	583.35	176.67	40.75	2	1	2	2	4	3	2	1
1,2,3,4,6,8,9	213.6	231.2	0.1885	0.3227	−0.1388	1.350	−4077.30553	279.66	590.44	588.50	182.07	46.16	2	2	1	2	4	3	2	1
1,2,3,4,7,8,9	215.2	234.4	0.1820	0.2977	−0.1796	1.776	−4077.30228	279.51	589.64	597.01	190.83	54.91	2	2	2	1	5	3	1	1
OCDT																				
1,2,3,4,6,7,8,9	232.7	247.2	0.0000	0.3277	−0.1346	0.692	−4536.89778	295.11	617.01	672.35	183.04	–	2	2	2	2	6	4	2	1

$$H^{\theta}/\text{hartree} = -860.14948 - 459.58776N_1 - 459.59679N_2 - 459.59816N_3 - 459.59835N_4 \quad (8)$$

$$R^2 = 1.0000 \quad \text{SE} = 0.00564$$

$$G^{\theta}/\text{hartree} = -860.19454 - 459.59083N_1 - 459.60000N_2 - 459.60141N_3 - 459.60156N_4 \quad (9)$$

$$R^2 = 1.0000 \quad \text{SE} = 0.00577$$

where R^2 is the squared correlation coefficient and SE is the standard error. From eqs 6 and 7, the conclusion can be obtained that S^{θ} decreases with an increase of N_o, whereas C^{θ}_P is not related to the number of relative positions for these Cl atoms. Similarly, in view of eqs 8 and 9, it suggests that the H^{θ} and G^{θ} of PCDTs obviously vary with the chlorine substitute at different positions, in which the order of increase of the H^{θ} and G^{θ} values is position 4 > position 3 > position 2 > position 1.

Calculation Results of $\Delta_f H^{\theta}$ and $\Delta_f G^{\theta}$ and Relative Stability of Isomer Groups. With the design of isodemic reactions, $\Delta_f H^{\theta}$ and $\Delta_f G^{\theta}$ of PCDTs were obtained. On the basis of the lowest $\Delta_f G^{\theta}$ of isomers with the same numbers of substituents, the obtained relative standard Gibbs energies of formation are also listed in Table 2. Table 2 shows that the values of $\Delta_f H^{\theta}$ and $\Delta_f G^{\theta}$ are different from each other because their substituent positions of chlorine are different. Among 28 isomers of penta-CDTs, 1,3,4,6,8-penta-CDT possesses the lowest value of $\Delta_f G^{\theta}$, and 1,2,3,4,9-penta-CDT possesses the highest corresponding value, where the discrepancy of them is 78.75 kJ·mol^{-1}. In the same way, the $\Delta_f G^{\theta}$ of 2,4,6,8-TCDT is lower than those of the other 37 isomers, whereas 1,2,8,9-TCDT is higher than those of the other 37 isomers, where the discrepancy of them is 83.62 kJ·mol^{-1}.

Table 3. Most Stable and Unstable Isomer in Different Isomer Groups for PCDTs and PCDFs

substance	most stable isomer	most unstable isomer
MCDT	2-; 3-	1-
DCDT	2,7-; 3,7-	1,9-
tri-CDT	2,4,7-	1,2,9-
TCDT	2,4,6,8-	1,2,8,9-
penta-CDT	1,3,4,6,8-	1,2,3,4,9-
hexa-CDT	1,3,4,6,7,8-	1,2,3,4,8,9-
hepta-CDT	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
MCDF	2-; 3-	4-
DCDF	1,7-	1,9-
tri-CDF	1,3,7-	1,2,9-
TCDF	1,3,6,8-	1,2,8,9-
penta-CDF	1,3,4,6,8-	1,2,3,4,9-
hexa-CDF	1,2,4,6,7,8-	1,2,3,4,8,9-
hepta-CDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-

For the PCDT compounds in each isomer group, the isomer with the lower relative standard Gibbs energy of formation is relatively stable, whereas that with the higher relative standard Gibbs energy of formation is unstable. Thus, the relative stability of each isomer group can be determined, and the most stable isomer and most unstable one are listed in Table 3.

As can be seen from Table 3, the most unstable isomers in MCDTs, DCDTs, tri-CDTs, TCDTs, penta-CDTs, hexa-CDTs, and hepta-CDTs are all those with chlorine being attached to 1,9 simultaneously. On the contrary, the chlorine atoms in the most stable isomers are distributed at two aromatic rings, and the substituent groups are relatively far away from each other. For MCDTs, the 3-MCDT is the most stable, whereas the 1-MCDT is the least stable with a difference of 9.32 kJ·mol^{-1} in their energy values. The 2- and 4-MCDT isomers are less stable than the 3-MCDT isomer by an amount of 0.23 and 2.27 kJ·mol^{-1}, respectively. For DCDTs, the 3,7-DCDT is the most stable, whereas the 1,9-DCDT is the least stable with a difference of 61.54 kJ·mol^{-1}. Similarly, the 2,4,7-, 2,4,6,8-, 1,3,4,6,8-, 1,3,4,6,7,8-, and 1,2,3,4,6,7,8- are the most stable isomers with differences of 73.02, 83.62, 78.75, 70.44, and 54.91 kJ·mol^{-1} to the least stable isomers 1,2,9-, 1,2,8,9-, 1,2,3,4,9-, 1,2,3,4,8,9-, and 1,2,3,4,7,8,9- for tri-CDTs, TCDTs, penta-CDTs, hexa-CDTs, and hepta-CDTs, respectively. The chlorine substituent at positions 1 and 9 synchronously seems to destabilize the isomers, and the resulting steric effect may be one of the important sources of the relative instabilities of the PCDTs apart from the associated electrostatic effects.

In addition, we have compared the most stable and unstable isomer of PCDTs with those of PCDFs (listed in Table 3). From Table 3, the conclusion can be obtained that the most unstable isomers are consistent in two congeners except isomers with one chlorine atom, whereas the most stable isomers are consistent only for isomers with one, five, and seven chlorine atoms. This is because the radius of the sulfur atom for PCDTs is larger than that of the oxygen atom for PCDFs, which makes

Table 4. Calculation Data of $S_{\text{T,m}}$, $C_{p,\text{m}}$, $\Delta_0{}^{\text{T}}H_{\text{m}}/T$, and $\Delta_0{}^{\text{T}}G_{\text{m}}/T$ for MCDTs[a]

		J·mol^{-1}·K^{-1}						J·mol^{-1}·K^{-1}			
compound	temp	$C_{p,\text{m}}$	$S_{\text{T,m}}$	$\Delta_0{}^{\text{T}}H_{\text{m}}/T$	$\Delta_0{}^{\text{T}}G_{\text{m}}/T$	compound	temp	$C_{p,\text{m}}$	$S_{\text{T,m}}$	$\Delta_0{}^{\text{T}}H_{\text{m}}/T$	$\Delta_0{}^{\text{T}}G_{\text{m}}/T$
1-MCDT	200	132.09	365.77	290.59	445.72	3-MCDT	200	132.55	367.10	291.53	447.25
	300	194.35	431.20	326.58	430.01		300	194.71	432.69	327.68	431.50
	400	249.39	494.90	360.75	438.32		400	249.60	496.47	361.96	439.82
	500	293.55	555.49	393.70	455.75		500	293.65	557.10	394.98	457.27
	600	327.92	612.18	425.44	477.15		600	327.97	613.80	426.78	478.69
	700	354.84	664.83	455.92	500.25		700	354.87	666.45	457.30	501.80
	800	376.31	713.66	485.12	523.91		800	376.34	715.29	486.54	525.47
	900	393.75	759.02	513.07	547.54		900	393.78	760.66	514.50	549.11
	1000	408.13	801.28	539.80	570.83		1000	408.16	802.91	541.26	572.40
2-MCDT	200	132.56	366.88	291.42	447.03	4-MCDT	200	132.31	366.26	290.69	446.26
	300	194.70	432.48	327.54	431.28		300	194.36	431.74	326.83	430.54
	400	249.57	496.24	361.80	439.60		400	249.27	495.41	361.06	438.85
	500	293.61	556.86	394.81	457.05		500	293.38	555.97	394.05	456.28
	600	327.93	613.56	426.59	478.46		600	327.75	612.63	425.81	477.67
	700	354.84	666.21	457.11	501.57		700	354.70	665.26	456.30	500.75
	800	376.31	715.04	486.34	525.24		800	376.21	714.07	485.51	524.40
	900	393.76	760.40	514.30	548.88		900	393.68	759.43	513.46	548.03
	1000	408.14	802.66	541.04	572.17		1000	408.09	801.67	540.19	571.30

[a] Where $S_{\text{T,m}}$ is molar entropy at T; $C_{p,\text{m}}$ is molar heat capacity at constant pressure; $\Delta_0{}^{\text{T}}H_{\text{m}}/T$ is an average thermal correction to molar enthalpy between 0 and T; and $\Delta_0{}^{\text{T}}G_{\text{m}}/T$ is an average thermal correction to molar Gibbs energy between 0 and T.

Table 5. Correlations of Structural Parameters with N_{PCS} for PCDTs[a]

eq	descriptor	constant	N_1	N_2	N_3	N_4	N_o	N_m	N_p	$N_{1,9}$	R^2	SE
11	V_i	134.58	11.89	12.11	11.84	12.11	–	–	–	–	0.9775	2.644
12	α	137.28	12.08	14.02	15.98	12. 70	–	–	–	–	0.9985	0.765
13	E_{HOMO}	−0.2165	−0.0025	−0.0048	−0.0077	−0.0049	0.0017		–	–	0.9789	0.0009
14	E_{LUMO}	−0.0399	−0.0057	−0.0073	−0.0062	−0.0065	–	–	–	−0.0051	0.9847	0.0013
15	μ	2.8380	–	−0.5673	−0.8033	–	0.5050	–	0.7223	–	0.2650	0.802
16	qH^+	0.1615	0.0064	0.0109	0.0107	–	−0.0087	–	–	–	0.1448	0.0166
17	q^+	0.2314	–	–	0.0100	0.0244	–	0.0076	–	–	0.4400	0.0266
18	q^-	-0.1899	–	–	–	0.0141	–	–	–	0.0069	0.5951	0.0088

[a] Where R^2 is the squared correlation coefficient and SE is the standard error.

the distances close between 1 and 9 carbon atoms for PCDTs. Consequently, the repulsion effects of Cl atom substituents at the 1 and 9 positions increase. So, the isomer with the 1 position substituted by the chlorine atom is more unstable than those with the 2, 3, and 4 positions substituted by the same atoms. For instance, the distance between the Cl atom substituent at the 1 position and the C atom at the 9 position is 3.295 Å^3 for 1-MCDT, which is shorter than that of 1-MCDF (3.531 Å^3). And the distance of the Cl atom substituent at the 1 position and the H atom substituent at the 9 position (2.569 Å^3) for 1-MCDT is also shorter than that of 1-MCDF (2.919 Å^3). In addition, the distance of Cl atoms (3.139 Å^3) for 1,9-DCDT is shorter than that of 1,9-DCDF (3.253 Å^3), whereas the distance of C atoms at the 1 and 9 positions is 3.458 Å^3 for 1,9-DCDT and is also shorter than that of 1,9-DCDF (3.632 Å^3).

Values of $C_{p,m}$, $S_{T,m}$, $\Delta_0{}^TH_m/T$, and $\Delta_0{}^TG_m/T$ for MCDTs at Various Temperatures. The values of $C_{p,m}$, $S_{T,m}$, $\Delta_0{}^TH_m/T$, and $\Delta_0{}^TG_m/T$ for MCDTs at various temperatures, to our knowledge, have not been reported. So, we have also calculated the values of $C_{p,m}$, $S_{T,m}$, $\Delta_0{}^TH_m/T$, and $\Delta_0{}^TG_m/T$ at (200 to 1000) K, which are listed in Table 4, where $S_{T,m}$ is molar entropy at T/K; $C_{p,m}$ is molar heat capacity at constant pressure; $\Delta_0{}^TH_m/T$ is specific thermal correction to molar enthalpy; and $\Delta_0{}^TG_m/T$ is specific thermal correction to molar Gibbs energy.

From Table 4, the following conclusions can be obtained: (1) For four isomers, 2-MCDT has the largest value of $C_{p,m}$ (132.56 J·mol^{-1}·K^{-1}) and 1-MCDT has the smallest value (132.09 J·mol^{-1}·K^{-1}) at 200 K, the difference of which is 0.47 J·mol^{-1}·K^{-1}; 3-MCDT has the largest value (408.16 J·mol^{-1}·K^{-1}) and 1-MCDT has the smallest value (408.09 J·mol^{-1}·K^{-1}) at 1000 K, the difference of which is only 0.07 J·mol^{-1}·K^{-1}. In general, the values of $C_{p,m}$ for four isomers are close at the same temperature. (2) From 200 to 1000 K, 3-MCDT has the largest values for $S_{T,m}$, $\Delta_0{}^TH_m/T$, and $\Delta_0{}^TG_m/T$ and 1-MCDT has the smallest values; the difference of both is (1.33, 0.94, and 1.53) J·mol^{-1}·K^{-1} at 200 K and (1.63, 1.46, and 1.57) J·mol^{-1}·K^{-1} at 1000 K, respectively. The values of the difference slightly increase as temperature increases.

Correlation Matrix of Parameters for PCDTs. Pairwise correlation between structural and thermodynamic parameters of 136 PCDT compounds was determined with the least-squares method. The results show that thermodynamic properties (H^θ, G^θ, C^θ_P, S^θ) have high correlations with V_i, E_{HOMO}, E_{LUMO}, and α, respectively (the absolute values of r are larger than 0.95); the correlations between q^+, q^-, and these thermodynamic properties are low (the absolute values of r are between 0.69 and 0.89, whereas the correlations between qH^+, μ, and them are lower; the absolute values of r are less than 0.50). As discussed above, the high correlations between thermodynamic properties and N_{PCS} were found, which suggest structural parameters may relate with N_{PCS}. So, we discuss the correlations in the following.

Relations of Structural Parameters and N_{PCS}. The dependence of PCDTs' structural parameters on the number of chlorines was also investigated. Using the GQSARF2.0 program, the correlations of structural parameters with N_{PCS} for PCDTs are shown in Table 5. As we anticipated, good correlations are found between some structural parameters (V_i, α, E_{HOMO}, E_{LUMO}) and N_{PCS}. As seen from Table 5, R^2 values of V_i, α, E_{HOMO}, and E_{LUMO} are larger than 0.97. Obviously, molecular volume increases with the increasing number of substituent chlorines; i.e., V_i is in direct ratio to N_{PCS}. α has a high correlation with V_i and is in direct ratio to V_i, which explains that α is in direct ratio to N_{PCS} (seen from Table 5). So, V_i, α, E_{HOMO}, E_{LUMO}, and thermodynamic parameters can be accurately calculated by N_{PCS} obtained from the molecular structure. At the same time, Table 5 also shows that the correlations between μ, qH^+, q^+, q^-, and N_{PCS} are low (all R^2 values are smaller than 0.6).

Conclusion

The fully optimized calculation of 136 PCDTs was carried out at the B3LYP/6-31G* level, and structural and thermodynamic parameters were obtained. By designing isodesmic reactions, the standard enthalpies of formation (Δ_fH^θ) and the standard Gibbs energies of formation (Δ_fG^θ) were also calculated. The correlations between structural and thermodynamic parameters (such as S^θ, C^θ_P, H^θ, G^θ, V_i, E_{HOMO}, E_{LUMO}, α, qH^+, q^+, q^-, and μ) and N_{PCS} were discussed. According to the relative standard Gibbs energies of formation, the relative stability of PCDT isomers was theoretically proposed in this work.

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