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DFT Calculation on the Thermodynamic Properties of Polychlorinated Dibenzo-*p*-dioxins: Intramolecular Cl−Cl Repulsion Effects and Their Thermochemical Implications

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Polychlorinated dibenzo-*p*-dioxins (PCDDs) are one of the most intensively studied chemical pollutants. However, the absence of reliable thermodynamic data on PCDDs seriously limits quantitative understanding of their formation and distribution at combustion sources. By carrying out a DFT calculation (B3LYP/6-31G**) for thermodynamic properties of 75 PCDD congeners, we find that previous thermodynamic estimations on the gas-phase enthalpies of formation (ΔH_f) and Gibbs free energy of PCDDs were seriously misestimated, particularly for highly chlorinated congeners, largely as a result of underestimating the intramolecular Cl−Cl repulsion energy. The disagreement between the DFT calculation and other methods becomes progressively larger with increasing chlorine substitution. Octachlorodibenzo-*p*-dioxin (OCDD) that has been considered as the most thermodynamically stable congener in previous calculations turns out to be much less stable. The differences in calculated ΔH_f values between OCDD and the most toxic congener, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, or other laterally chlorinated (2,3,7,8-substituted) toxic congeners are within 1 kcal/mol. Most ΔH_f values for congeners with five to eight chlorines differ by only 1−2 kcal/mol, since the decreasing electronic energies with increasing the number of chlorines in PCDDs are counterbalanced by increasing Cl−Cl repulsion energy. The intramolecular chlorine repulsion effects in PCDDs are systematically analyzed by using isodesmic reactions.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) have attracted much interests from not only scientists but also the general public because of their extreme toxicity and ubiquitous contamination in the global environment through atmospheric transport.[1,2] Since most PCDDs are emitted from combustion sources, knowledge about their thermodynamic properties (e.g., enthalpy of formation, ΔH_f, and Gibbs free energy of formation, ΔG_f) is invaluable for quantitative prediction of their formation and the relative congener distribution at emission sources.[3] The thermodynamic data are also important in the studies of dioxin dechlorination and destruction processes.[4−7] However, experimental values of ΔH_f are available for only three of 75 PCDD congeners (1-monochlorodibenzo-*p*-dioxin,[8] 2-monochlorodibenzo-*p*-dioxin[9] and 2,3-dichlorodibenzo-*p*-dioxin[10]), mainly because of experimental difficulties. In addition, experimental ΔH_f values for chlorinated organic compounds may have significant uncertainties, because their combustion reactions in calorimetric measurements are often incomplete. Therefore, there have been a number of reports that estimated PCDDs' thermodynamic properties theoretically using AM1,[11] MNDO,[11−13] PM3,[14] group additivity method (GAM),[12,15−18] and DFT calculation.[19] However, the previous thermodynamic calculations on PCDDs showed significant discrepancies, depending on the calculation method used. The published calculated ΔH_f values for a PCDD congener often showed differences over 30 kcal/mol.[12] Therefore, there is no reliable standard thermodynamic data on PCDDs, although it is critically important in various aspects of dioxin research.

Here, we report the first consistent and reliable thermodynamic data of PCDDs by performing DFTcalculations for 75 congeners and systematically analyze the origin of disagreements between different calculations. In this study, we find that the literature thermodynamic data of PCDDs are seriously misestimated, particularly for highly chlorinated congeners, and that the relative order of stability among PCDD congeners is significantly changed. This discrepancy mainly results from the fact that previous calculations underestimated the intramolecular Cl−Cl repulsion effect on ΔH_f and ΔG_f of PCDDs. The present dioxin thermodynamic data set should serve as a more reliable source in predicting equilibrium congener distribution from combustion sources, understanding the formation, and estimating the fate of PCDDs in the environment.

Computational Methods

To estimate ΔH_f and ΔG_f of PCDDs, we have carried out DFT calculations at the level of hybrid B3LYP density functional theory with 6-31G** basis sets using a Gaussian 98 suite of programs,[20] as described in our previous works.[21,22] We also performed additional calculation of the single-point energies for the most stable isomers in the PCDD homologues and seven

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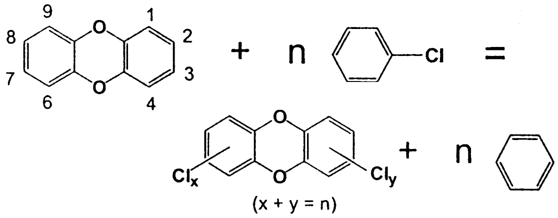
toxic congeners at the B3LYP/6-311G** and B3LYP/cc-pVTZ levels, on the basis of the geometry optimized at B3LYP/6-31G**. The electronic energy (E_e) and thermal energy (E_T = ZPE (zero point E) + E_{vib} + E_{rot} + E_{trans}) were calculated to get H (= E_e + E_T + RT) at 298 K and 1 atm for benzene (Bz), chlorobenzene (CB), dibenzo-*p*-dioxin (DD), and 75 PCDD congeners with rigid rotor and harmonic oscillator approximation. In the low vibrational frequency region (<260 cm^{-1}), the dioxin molecule has the torsional modes of two benzene rings. These torsional frequencies contribute to thermal enthalpy and entropy.[23] Although their contribution to E_T was not calculated, these errors should be canceled out in isodesmic reaction[24] like eq 1. As for the notation in this paper, PCDD congeners with one to eight chlorines are represented by MCDD, DCDD, TrCDD, TCDD, PeCDD, HxCDD, HpCDD, and OCDD, respectively. Prefix numbers represent the positions (see eq 1) of chlorine substitution (e.g., 2,3,7,8-TCDD or simply 2,3,7,8-T).

The calculated H of PCDDs and literature values of ΔH_f and ΔG_f of Bz, CB, and DD were used in estimating the gas-phase ΔH_f and ΔG_f of PCDDs on the basis of the following isodesmic reaction.



(1)

$$\Delta H_r = [H\,(\text{PCDD}) + nH\,(\text{Bz})] - [H\,(\text{DD}) + nH\,(\text{CB})] \tag{2}$$

$$\Delta H_r = [\Delta H_f\,(\text{PCDD}) + n\Delta H_f\,(\text{Bz})] - [\Delta H_f\,(\text{DD}) + n\Delta H_f\,(\text{CB})] \tag{3}$$

The value of ΔH_r calculated from eq 2 was substituted into eq 3 to yield the ΔH_f of PCDDs,

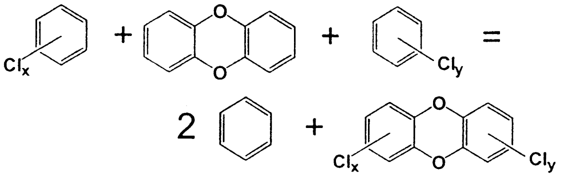
$$\Delta H_f\,(\text{PCDD}) = \Delta H_r - n\Delta H_f\,(\text{Bz}) + \Delta H_f\,(\text{DD}) + n\Delta H_f\,(\text{CB}) \tag{4}$$

where ΔH_f (Bz) = 19.8 kcal/mol,[25] ΔH_f (CB) = 12.4 kcal/mol,[25] and ΔH_f (DD) = −14.2 kcal/mol.[26] ΔG_f values of PCDDs were calculated in the same way after getting the total entropy (S_{tot} = S_{trans} + S_{vib} + S_{rot}).[24,27,28] The experimental value of ΔG_f (CB) was not available and was calculated from eq 5 to be 23.77 kcal/mol (S_{CB} = 74.86 cal/mol·K from our calculation and S_{elemt} from ref 12).

$$\Delta G_f = \Delta H_f - T[S_{CB} - \Sigma S_{elemt}] \tag{5}$$

The ΔG_f values for Bz and DD were 31.0 kcal/mol[25] and 14.13 kcal/mol,[18] respectively. The numerical values of E_e, ZPE, E_T, ΔH_f, ΔG_f, and S_{tot} for all PCDD congeners are listed in Table 1. The present DFT results of ΔH_f for 1-MCDD, 2-MCDD, and 2,3-DCDD showed agreements within ~3 kcal/mol with the reported experimental values, which were ΔH_f = −(21.1 ± 1.1) kcal/mol for 1-MCDD,[8] −(17.7 ± 0.8) kcal/mol for 2-MCDD[9], and −(26.7 ± 1.6) kcal/mol for 2,3-DCDD.[10]

Isodesmic reactions other than reaction 1 could also be used for the evaluation of thermodynamic properties. For example, Leon et al.[19] employed isodesmic reaction 6 that used polychlorinated benzenes (PCBs) as references to obtain calculated ΔH_f values of PCDDs.



(6)

Since the reference compounds, PCBs, are structurally more similar to PCDDs than CB, using reaction 6 seems to be more balanced and reliable in evaluating accurate enthalpies of formation of PCDDs than using reaction 1. However, it should be noted that isodesmic calculations are based on the experimental ΔH_f values of references (CB or PCBs in this case). Although the experimental ΔH_f value of CB is reliable, those of PCBs are highly uncertain and questionable, especially for highly chlorinated benzenes. For example, the reported experimental ΔH_f values of 1,2,4-trichlorobenzene are −8.1[29] and 4.9 kJ/mol;[30] ΔH_f values of 1,2,3-trichlorobenzene are 3.8[31] and 8.2 kJ/mol,[30] depending on the literature source. Therefore, the isodesmic calculation that uses the experimental ΔH_f of PCBs is not reliable at all. It is well-known that experimental ΔH_f for chlorinated organic compounds is often subjected to considerable uncertainties, and PCBs are the case.[32] Therefore, we preferred isodesmic reaction 1 to reaction 6 in this calculation. Isodesmic calculations based on reaction 6 were also performed and compared with those based on reaction 1. The isodesmic reaction based on CB (reaction 1) has an additional merit in that it does not include any intramolecular Cl−Cl interaction energy in it. Since one of the main purposes of this calculation is to analyze the chlorine repulsion energies in PCDD molecules, using reaction 1 enables us to derive the chlorine repulsion energy for a specific chlorination pattern from the calculated ΔH_r. The use of isodesmic reaction 6 is not proper for this purpose, because the intramolecular chlorine repulsion energies are already contained in the values of ΔH_f (PCBs) and are not equivalent to those of PCDDs.

Results and Discussion

Comparison between DFT and Other Results. Figure 1 compares the ΔH_f and ΔG_f values calculated from this work with those of previous estimations. The results based on the semiempirical and GA calculation predicted that the enthalpies of formation decreased with increasing the degree of chlorination and that ΔH_f of OCDD was the lowest of all PCDDs. Whereas PM3,[14] GAM(2),[12] and GAM(3)[16] calculations indicated that ΔH_f decreased quite linearly with increasing the number of chlorine, MNDO[12] and GAM(1)[15] predicted that the slope of decreasing ΔH_f was reduced with highly chlorinated congeners. On the other hand, the present DFT results using the B3LYP/6-31G** basis set show only a little variation in ΔH_f from tetra- to octachlorination. Many congeners of tetra- to heptachlorinated dioxins have slightly more negative values of ΔH_f than OCDD. In terms of ΔG_f, OCDD is the least stable (6.65 kcal/mol) among all congeners with the number of Cl ≥ 3 (except 1,2,3-TrCDD and 1,2,3,4-TCDD), and 1,3,6,8-TCDD is the most stable (−0.39 kcal/mol) among the 75 congeners. The disagreement between DFT and other methods becomes progressively larger with increasing chlorine substitution.

The dependence of the calculation results on the basis set was investigated. Table 2 compares the calculated ΔH_f values obtained at the level of (a) B3LYP/6-31G**, (b) B3LYP/6-

TABLE 1: B3LYP/6-31G Calculated E_e (Hartree), ΔE_e^{rel} (kcal/mol), ZPE (kcal/mol), ΔE_T (kcal/mol), S_{tot} (cal/mol·K), ΔH_f (kcal/mol), and ΔG_f (kcal/mol) (at 298.15 K and 1 atm) of PCDDs**

congener	E_e	ΔE_e^{rel}	ZPE	$E_{T=298}$	$S_{tot,298}$	$\Delta H^\circ_{f,298}$	$\Delta G^\circ_{f,298}$
DD	−612.54018	-	105.44	111.48	94.37	−14.15	14.13
2-M	−1072.13315	0.00	99.36	106.20	104.23	−20.41	8.27
1-M	−1072.13034	1.76	99.41	106.25	104.42	−18.60	10.03
2,7-D	−1531.72563	0.00	93.22	100.88	110.24	−26.42	3.82
2,8-D	−1531.72563	0.00	93.24	100.89	110.17	−26.41	3.85
1,7-D	−1531.72290	1.72	93.29	100.94	111.61	−24.64	5.19
1,8-D	−1531.72280	1.78	93.28	100.94	111.68	−24.58	5.23
1,3-D	−1531.72191	2.34	93.27	100.94	111.65	−24.02	5.79
2,3-D	−1531.72104	2.88	93.27	100.91	109.82	−23.50	6.86
1,6-D	−1531.72021	3.40	93.35	101.02	110.27	−22.88	7.35
1,4-D	−1531.71960	3.79	93.35	101.01	110.08	−22.49	7.79
1,9-D	−1531.71956	3.81	93.35	101.01	110.07	−22.47	7.81
1,2-D	−1531.71836	4.57	93.31	100.96	111.31	−21.77	8.15
1,3,7-Tr	−1991.31407	0.00	87.14	95.63	119.00	−29.81	1.15
1,3,8-Tr	−1991.31405	0.01	87.14	95.63	118.95	−29.79	1.19
2,3,7-Tr	−1991.31327	0.50	87.14	95.60	118.55	−29.34	1.77
1,4,7-Tr	−1991.31176	1.45	87.23	95.71	118.67	−28.28	2.78
1,3,6-Tr	−1991.31138	1.69	87.21	95.70	118.90	−28.04	2.95
1,3,9-Tr	−1991.31083	2.03	87.20	95.69	118.83	−27.71	3.31
1,2,7-Tr	−1991.31063	2.16	87.19	95.65	118.51	−27.63	3.48
1,2,8-Tr	−1991.31053	2.22	87.19	95.65	118.56	−27.57	3.53
1,7,8-Tr	−1991.31050	2.24	87.21	95.66	118.35	−27.53	3.63
1,4,6-Tr	−1991.30851	3.49	87.26	95.76	118.87	−26.19	4.81
1,2,6-Tr	−1991.30798	3.82	87.27	95.73	118.35	−25.89	5.27
1,2,9-Tr	−1991.30729	4.25	87.25	95.71	118.49	−25.47	5.64
1,2,4-Tr	−1991.30646	4.78	87.22	95.71	118.63	−24.95	6.13
1,2,3-Tr	−1991.30502	5.68	87.21	95.66	118.11	−24.10	7.13
1,3,6,8-T	−2450.90225	0.00	81.06	90.38	124.59	−33.03	−0.39
1,3,7,9-T	−2450.90181	0.27	81.06	90.38	124.45	−32.77	−0.08
1,3,7,8-T	−2450.90145	0.50	81.06	90.34	125.56	−32.57	−0.22
2,3,7,8-T	−2450.90069	0.98	81.06	90.32	122.63	−32.12	1.10
1,3,6,9-T	−2450.89942	1.77	81.12	90.44	126.03	−31.20	1.01
1,4,7,8-T	−2450.89911	1.97	81.13	90.42	124.17	−31.03	1.74
1,2,6,8-T	−2450.89889	2.10	81.12	90.41	125.55	−30.91	1.45
1,2,4,7-T	−2450.89849	2.36	81.12	90.42	125.46	−30.64	1.74
1,2,4,8-T	−2450.89841	2.41	81.11	90.40	125.61	−30.61	1.73
1,2,7,9-T	−2450.89837	2.43	81.11	90.40	125.51	−30.59	1.78
1,2,7,8-T	−2450.89801	2.66	81.09	90.36	125.36	−30.40	2.01
1,2,3,7-T	−2450.89702	3.28	81.07	90.34	125.39	−29.79	2.61
1,2,3,8-T	−2450.89699	3.30	81.08	90.35	125.23	−29.77	2.68
1,4,6,9-T	−2450.89662	3.53	81.19	90.51	123.05	−29.38	3.73
1,2,6,9-T	−2450.89605	3.89	81.16	90.46	125.83	−29.06	3.21
1,2,6,7-T	−2450.89559	4.18	81.16	90.43	123.92	−28.82	4.03
1,2,4,9-T	−2450.89518	4.43	81.16	90.47	125.59	−28.52	3.83
1,2,4,6-T	−2450.89517	4.44	81.13	90.45	125.93	−28.53	3.72
1,2,8,9-T	−2450.89486	4.64	81.15	90.42	123.82	−28.37	4.51
1,2,3,6-T	−2450.89435	4.96	81.14	90.42	125.35	−28.04	4.38
1,2,3,9-T	−2450.89376	5.33	81.13	90.41	125.19	−27.69	4.78
1,2,3,4-T	−2450.88835	8.72	81.15	90.42	123.39	−24.27	8.72
1,2,4,7,9-Pe	−2910.48591	0.00	75.01	85.15	132.75	−33.42	0.13
1,2,4,6,8-Pe	−2910.48586	0.03	74.97	85.13	133.11	−33.41	0.04
1,2,4,7,8-Pe	−2910.48558	0.21	74.99	85.10	132.55	−33.26	0.36
1,2,3,6,8-Pe	−2910.48498	0.59	74.97	85.09	132.59	−32.89	0.71
1,2,3,7,9-Pe	−2910.48456	0.85	74.98	85.09	132.43	−32.63	1.02
1,2,3,7,8-Pe	−2910.48422	1.06	74.96	85.05	132.21	−32.46	1.25
1,2,4,6,9-Pe	−2910.48306	1.79	75.04	85.20	133.17	−31.58	1.85
1,2,4,6,7-Pe	−2910.48262	2.06	75.05	85.16	132.61	−31.34	2.26
1,2,4,8,9-Pe	−2910.48250	2.14	75.03	85.16	132.72	−31.27	2.29
1,2,3,6,9-Pe	−2910.48225	2.30	75.05	85.16	132.28	−31.11	2.59
1,2,3,6,7-Pe	−2910.48168	2.65	75.02	85.11	132.26	−30.80	2.89
1,2,3,8,9-Pe	−2910.48115	2.99	75.03	85.11	132.01	−30.47	3.30
1,2,3,4,7-Pe	−2910.48011	3.64	75.01	85.10	132.04	−29.82	3.94
1,2,3,4,6-Pe	−2910.47690	5.66	75.06	85.16	132.09	−27.75	6.00
1,2,4,6,8,9-Hx	−3370.06947	0.00	68.94	79.91	138.17	−33.74	1.54
1,2,4,6,7,9-Hx	−3370.06945	0.00	68.93	79.90	138.44	−33.73	1.47
1,2,3,6,7,9-Hx	−3370.06860	0.54	68.92	79.85	139.25	−33.25	1.71
1,2,3,6,8,9-Hx	−3370.06854	0.58	68.91	79.85	139.44	−33.22	1.69
1,2,3,6,7,8-Hx	−3370.06774	1.08	68.91	79.81	137.43	−32.76	2.74
1,2,3,4,6,8-Hx	−3370.06752	1.22	68.91	79.84	139.16	32.58	2.41
1,2,3,7,8,9-Hx	−3370.06725	1.38	68.90	79.80	137.47	−32.45	3.03
1,2,3,4,7,8-Hx	−3370.06714	1.46	68.91	79.81	137.55	−32.37	3.09
1,2,3,4,6,9-Hx	−3370.06471	2.98	68.97	79.91	137.73	−30.75	4.66
1,2,3,4,6,7-Hx	−3370.06415	3.33	68.95	79.86	138.97	−30.45	4.59
1,2,3,4,6,7,9-Hp	−3829.65089	0.00	62.81	74.58	146.32	−32.80	3.39
1,2,3,4,6,7,8-Hp	−3829.65007	0.51	62.81	74.54	145.73	−32.33	4.04
OCDD	−4289.23236	-	56.73	69.29	149.73	−31.87	6.65

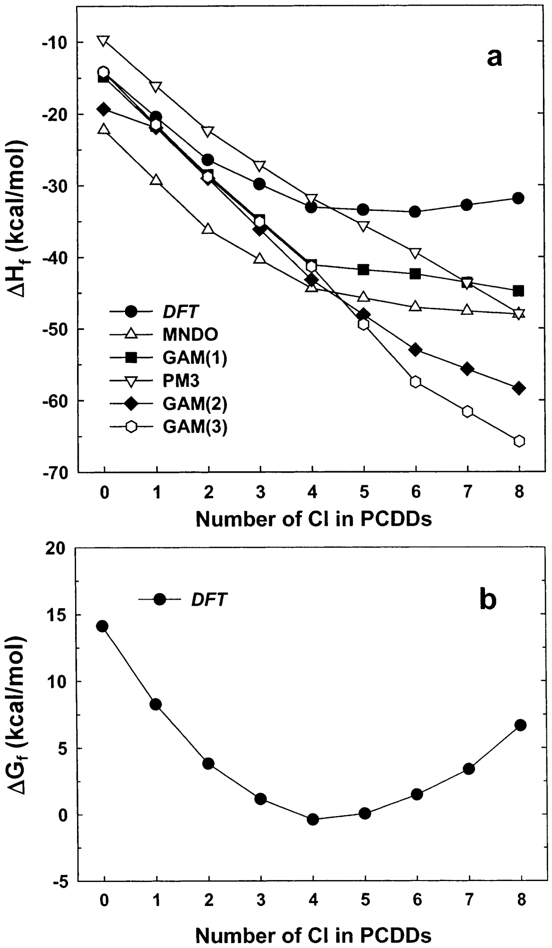


Figure 1. (a) ΔH_f and (b) ΔG_f (at 298 K and 1 atm) of PCDD congeners (non- to octachlorinated) that are calculated by DFT at the level of B3LYP/6-31G** (this work), MNDO, PM3, and GAMs are compared for the most thermodynamically stable isomers within homologues (i.e., DD, 2-MCDD, 2,7-DCDD, 1,3,7-TrCDD, 1,3,6,8-TCDD, 1,2,4,6,8-PeCDD, 1,2,4,6,7,9-HxCDD, 1,2,3,4,6,7,9-HpCDD, and OCDD).

TABLE 2: ΔH_f (kcal/mol) of the Most Stable and Toxic Congeners Calculated Using Isodesmic Reaction 1 and B3LYP/6-31G,[a] B3LYP/6-311G**//B3LYP/6-31G**,[b] and B3LYP/cc-pVTZ//B3LYP/6-31G**[c]**

	$\Delta H_f^{a,d}$	$\Delta H_f^{b,d}$	$\Delta H_f^{c,d}$
2-M	−20.41	−20.55	−20.53
	(−1072.133 15)	(−1072.304 25)	(−1072.372 16)
2,7-D	−26.42	−26.43	−26.62
	(−1531.725 63)	(−1531.924 89)	(−1532.001 98)
1,3,7-Tr	−29.81	−29.74	−30.11
	(−1991.314 07)	(−1991.541 52)	(−1991.627 75)
1,3,6,8-T	−33.03	−32.89	−33.63
	(−2450.902 25)	(−2451.157 91)	(−2451.253 59)
1,2,4,7,9-Pe	−33.42	−32.81	−34.06
	(−2910.485 91)	(−2910.769 17)	(−2910.874 52)
1,2,4,6,8,9-Hx	−33.74	−32.99	−34.73
	(−3370.069 47)	(−3370.380 85)	(−3370.495 83)
1,2,3,4,6,7,9-Hp	−32.80	−32.23	−34.40
	(−3829.650 89)	(−3829.990 87)	(−3830.115 40)
		Toxic Congeners)	
2,3,7,8-T	−32.12	−31.92	−32.92
	(−2450.900 69)	(−2451.156 27)	(−2451.252 37)
1,2,3,7,8-Pe	−32.46	−32.04	−33.41
	(−2910.484 22)	(−2910.767 79)	(−2910.873 32)
1,2,3,6,7,8-Hx	−32.76	−32.46	−34.09
	(−3370.067 74)	(−3370.379 84)	(−3370.494 64)
1,2,3,7,8,9-Hx	−32.45	−31.86	−33.78
	(−3370.067 25)	(−3370.378 88)	(−3370.494 15)
1,2,3,4,7,8-Hx	−32.37	−31.81	−33.69
	(−3370.067 14)	(−3370.378 81)	(−3370.494 01)
1,2,3,4,6,7,8-Hp	−32.33	−31.53	−33.87
	(−3829.650 07)	(−3829.989 70)	(−3830.114 50)
OCDD	−31.87	−30.86	−33.79
	(−4289.232 36)	(−4289.599 99)	(−4289.734 57)

[d] The calculated electronic energies, E_e (Hartree), are given in parentheses.

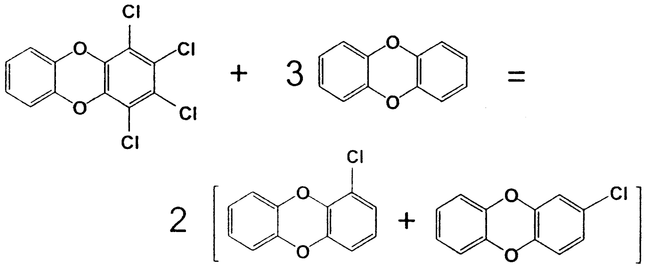
311G**//B3LYP/6-31G**, and (c) B3LYP/cc-pVTZ//B3LYP/6-31G**. The calculated ΔH_f values exhibit negligible dependence on the basis set for less chlorinated congeners (Cl $\leq$ 4) and show a slight dependence for highly chlorinated congeners, but do not deviate by more than 3 kcal/mol (for OCDD), at most. The general trend of ΔH_f variation as a function of chlorination shown in Figure 1a is little affected by the level of the basis set.

The DFT results based on isodesmic reaction 6 and two different basis sets are listed in Table 3. Since the experimental enthalpy values of PCBs carry significant uncertainties, the results obtained from using the calculated[19] enthalpies of PCBs are compared (i.e., ΔH_f (exp) vs ΔH_f (calc) in Table 3). The differences between the two sets of ΔH_f (PCDDs) progressively increase with the number of chlorines, which implies that the experimental ΔH_f (PCBs) values are unreliable for highly chlorinated PCBs. The results obtained from isodesmic reaction 1 (Table 2) are compared, as well. It is noted that the ΔH_f (PCDDs) values evaluated from using isodesmic reaction 6 and the calculated enthalpies of PCBs are close to those from isodesmic reaction 1 and not exceeding 1.2 kcal/mol. It is not surprising, considering that isodesmic reaction 6 combined with the calculated ΔH_f (PCBs) values, which are based on the experimental ΔH_f of Bz and CB, is practically identical to isodesmic reaction 1. Therefore, what seems to be critical in evaluating accurate ΔH_f (PCDDs) is not whether we use isodesmic reaction 1 or 6, but whether reliable experimental enthalpies of formation of reference compounds are available. In a recent study of DFT calculation on PCDDs, Leon et al.[19] derived a similar conclusion and considered using isodesmic reaction 1 to be more reliable than using reaction 6.

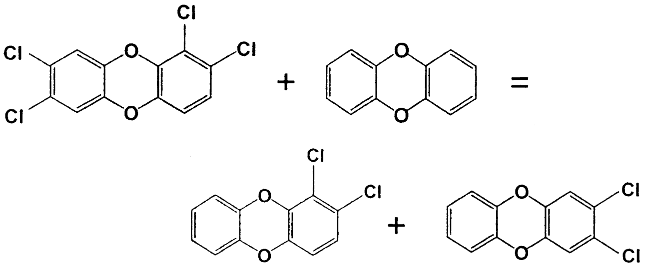
Origin of Discrepancy and Intramolecular Cl−Cl Repulsion. The origin of the discrepancies among the different sets of calculated ΔH_f (PCDDs) can be sought systematically by analyzing the effects of the intramolecular chlorine repulsion and the different chlorination positions, which are included in E_e. The E_T terms should make a negligible contribution (i.e., $\Delta H_r \sim \Delta E_e$), since they are mostly canceled out in eq 2. The isodesmic reaction energies, ΔH_r, are positive ($\leq$ 41.2 kcal/mol) for all PCDDs. The reaction energy consists of four components: (1) the difference energy (ΔE_1) of chlorination between the lateral (2, 3, 7, 8) and nonlateral (1, 4, 6, 9) positions, (2) intramolecular Cl−Cl repulsion (ΔE_2) within one benzene ring, (3) intramolecular Cl−Cl repulsion (ΔE_3) between two benzene rings, and (4) the difference of the C−Cl bond strength between CB and PCDD (ΔE_4).

$$\Delta E_r = \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 \tag{7}$$

Since 2-MCDD is more stable than 1-MCDD by 1.76 kcal/mol, ΔE_1 of a specific congener is calculated by multiplying 1.76 by the number of nonlateral chlorines. The Cl−Cl repulsion terms, ΔE_2 and ΔE_3, are evaluated by a simple additivity method using isodesmic reactions. For example, ΔE_2 (1,2,3,4-TCDD) and ΔE_3 (1,2,7,8-TCDD) are calculated as follows.



$$\Delta E_2\ (1,2,3,4\text{-T}) = E_e\ (1,2,3,4\text{-T}) + 3E_e\ (\text{DD}) - 2[E_e\ (1\text{-M}) + E_e\ (2\text{-M})] \quad (8)$$



$$\Delta E_3\ (1,2,7,8\text{-T}) = E_e\ (1,2,7,8\text{-T}) + E_e\ (\text{DD}) - E_e\ (1,2\text{-D}) - E_e\ (2,3\text{-D}) \quad (9)$$

In general, successive chlorination makes PCDD more stable. However, the accompanying intramolecular chlorine repulsion counterbalances or overcomes the stabilizing effect of chlorination when substituting more than three chlorines on one benzene ring. For example, although 1,2,3,4-TCDD is more chlorinated than 1,2,4-TrCDD, the former ($\Delta H_f = -24.3$ kcal/mol) is slightly less stable than the latter ($\Delta H_f = -25.0$ kcal/mol) as a result of the chlorine repulsion effect. The fourth term, ΔE_4, should be ascribed to the difference between ΔE_r and $\Delta E_1 + \Delta E_2 + \Delta E_3$. This extra energy term results from the fact that the C$-$Cl bond of CB is stronger than that of PCDD by 1.1 kcal/mol. Therefore, ΔE_4 turns out to be exactly proportional to the total number of chlorines (i.e., $\Delta E_4 = n \times 1.1$ kcal/mol), which indicates that the above analysis of ΔE terms is self-consistent and reliable. This self-consistency and predictability in the analysis of ΔE terms strongly supports that the ΔH_f (PCDDs) values that were calculated with using isodesmic reaction 1 are reliable, as well. These energy components, ΔE_1, ΔE_2, ΔE_3, and ΔE_4, for selected PCDD congeners are listed in Table 4.

On the other hand, it would be informative to compare the Cl$-$Cl repulsion energies (ΔE_2) between PCDDs and PCBs. The ΔE_2 terms in PCBs can be calculated by using simple isodesmic reactions. For example, ΔE_2 (1,2-DCB) = ΔH_f (Bz) + ΔH_f (1,2-DCB) $-$ 2ΔH_f (CB). The ΔE_2 terms in PCDDs and PCBs sharing the same chlorination pattern are compared in Table 5. The Cl$-$Cl repulsion energies in PCDDs and PCBs are very close to each other, and the differences do not exceed 0.6 kcal/mol.

The order of stability within homologues does not agree among different methods. For example, PM3[14] predicted that 2,3,7,8-TCDD was the most stable isomer among the TCDDs, while other methods showed 1,3,6,8-TCDD as the most stable. Thompson[32] showed that the equilibrium isomer distribution among TrCDDs depended on how the chlorine$-$chlorine interaction was taken into account. The most abundant TrCDD isomers were 1,3,7-TrCDD and 1,3,8-TrCDD when the Cl$-$Cl interactions at the ortho, meta, and para substitutions were considered on the basis of chlorinated benzoquinones, whereas 1,4,6-TrCDD and 1,4,7-TrCDD were the most abundant isomers when the Cl$-$Cl interactions at the ortho and meta substitutions (no para interaction) were derived from the enthalpies of formation of chlorinated benzenes. Therefore, a reliable estimation on the intramolecular chlorine repulsion is critical for quantitative predictions on PCDD formation. Figure 2 compares the structure of the most and least stable isomers within homologues according to the DFT(B3LYP/6-31G**) result. The MNDO method[12,13] showed the closest agreement with DFT calculation in predicting the most stable isomers within homologues. From Figure 2, it is obvious that the relative thermodynamic stability of PCDDs with the same degree of chlorination is determined by the intramolecular chlorine repulsion effect. The most stable isomers have no or the minimum number of nearest chlorines, whereas the least stable isomers have the maximum number of nearest chlorines. With OCDD, the intramolecular Cl$-$Cl repulsion energy (both ΔE_2 and ΔE_3) is maximized.

TABLE 3: B3LYP/6-31G and B3LYP/cc-pVTZ Calculated ΔH_f (kcal/mol) of PCDDs Based on Isodesmic Reaction 6 and the Experimental or Calculated Values of ΔH_f (PCBs)**

	6-31G**		cc-pVTZ		
	ΔH_f (exptl)[a]	ΔH_f (calcd)[b]	ΔH_f (exptl)[a]	ΔH_f (calcd)[b]	ΔH_f (c)[c]
2-M	−20.44	−20.44	−20.53	−20.53	−20.53
2,7-D	−26.46	−26.46	−26.62	−26.62	−26.62
1,3,7-Tr	−29.86	−30.12	−29.97	−30.23	−30.11
1,3,6,8-T	−33.07	−33.60	−33.35	−33.87	−33.63
1,2,4,7,9-Pe	−35.23	−34.49	−35.22	−34.48	−34.06
1,2,4,6,8,9-Hx	−37.32	−35.31	−37.33	−35.33	−34.73
1,2,3,4,6,7,9-Hp	−43.75	−35.19	−43.85	−35.30	−34.40
		Toxic Congeners			
2,3,7,8-T	−34.83	−33.02	−35.18	−33.36	−32.92
1,2,3,7,8-Pe	−37.43	−33.89	−37.65	−34.11	−33.41
1,2,3,6,7,8-Hx	−39.98	−34.73	−40.31	−35.05	−34.09
1,2,3,7,8,9-Hx	−39.68	−34.42	−40.01	−34.75	−33.78
1,2,3,4,7,8-Hx	−42.89	−34.43	−42.96	−34.50	−33.69
1,2,3,4,6,7,8-Hp	−45.10	−34.92	−45.13	−34.95	−33.87
OCDD	−50.19	−35.08	−50.08	−34.98	−33.79

[a] Experimental ΔH_f (PCBs) values (kcal/mol) used are 7.22 (1,2-DCB),[25] 6.14 (1,3-DCB),[25] 5.38 (1,4-DCB),[25] 1.96 (1,2,3-TrCB),[30] 1.17 (1,2,4-TrCB),[30] and −6.07 (1,2,3,4-TCB).[29] [b] Calculated ΔH_f (PCBs) values (kcal/mol) used are[19] 8.13 (1,2-DCB), 5.88 (1,3-DCB), 5.93 (1,4-DCB), 4.59 (1,2,3-TrCB), 2.17 (1,2,4-TrCB), and 1.48 (1,2,3,4-TCB). [c] Values are based on isodesmic reaction 1 (from Table 2, the fourth column) for comparison.

TABLE 4: Energy Terms (kcal/mol) of Reaction 7 for Selected PCDD Congeners

congener	ΔE_r	ΔE_1	ΔE_2	ΔE_3	ΔE_4
2-M	1.11	0.00	0.00	0.00	1.11
1-M	2.86	1.76	0.00	0.00	1.11
1,2-D	7.08	1.76	3.11	0.00	2.21
1,3-D	4.85	1.76	0.88	0.00	2.21
1,4-D	6.30	3.52	0.57	0.00	2.21
2,3-D	5.39	0.00	3.18	0.00	2.21
2,7-D	2.51	0.00	0.00	0.30	2.21
1,9-D	6.32	3.52	0.00	0.59	2.21
2,3,7-Tr	6.96	0.00	3.18	0.46	3.32
1,4,6-Tr	9.94	5.28	0.57	0.78	3.32
1,2,4-Tr	11.24	3.52	4.40	0.00	3.32
1,2,3-Tr	12.14	1.76	7.06	0.00	3.32
1,3,6,8-T	10.57	3.52	1.75	0.88	4.42
2,3,7,8-T	11.55	0.00	6.37	0.76	4.42
1,2,7,8-T	13.23	1.76	6.29	0.76	4.42
1,4,6,9-T	14.10	7.04	1.14	1.50	4.42
1,2,3,4-T	19.29	3.52	11.35	0.00	4.42
1,2,3,7,8-Pe	18.57	1.76	10.24	1.04	5.53
1,2,4,6,9-Pe	19.30	7.04	4.97	1.76	5.53
1,2,3,6,7,8-Hx	25.61	3.52	14.12	1.33	6.63
1,2,3,7,8,9-Hx	25.91	3.52	14.12	1.64	6.63
1,2,3,4,7,8-Hx	25.98	3.52	14.53	1.30	6.63
1,2,3,4,6,7,8-Hp	33.39	5.28	18.41	1.96	7.74
OCDD	41.19	7.04	22.70	2.61	8.84

TABLE 5: Cl-Cl Repulsion Energy (ΔE_2) Terms (kcal/mol) in PCBs and PCDDs with the Same Chlorination Pattern

	ΔE_2 (PCB)[a]	ΔE_2 (PCB)[b]	ΔE_2 (PCDD)[c]
1,2-D	3.36	3.13	3.11
1,3-D	1.04	0.88	0.88
1,4-D	0.87	0.93	0.57
1,2,3-Tr	7.53	6.99	7.06
1,2,4-Tr	4.93	4.57	4.40
1,2,3,4-T	11.98	11.28	11.35

[a] Based on the B3LYP/cc-pVTZ calculated ΔH_f (PCBs) values. [b] Based on ΔH_f (PCBs) values from ref 19. [c] From Table 4.

The discrepancy in ΔH_f (PCDDs) between this work and previous calculations originated from neglect or misestimation of the above four factors. PM3 calculation seems to significantly underestimate the intramolecular chlorine repulsion effect. GA approaches that are often considered as the most reliable method[12] do not treat the intramolecular repulsion accurately, because they use chlorine-containing molecules (e.g., chlorinated benzenes, phenols, and benzoquinones) as a surrogate that only approximates the chlorine repulsion in PCDDs. All of the GA estimations on PCDDs assumed that the chlorination of one ring had no influence on the other ring in their thermodynamic properties (i.e., $\Delta E_3 = 0$). While ΔE_3 terms are usually much smaller than ΔE_2 (see Table 4), some congeners with adjacent nonlateral chlorines (e.g., 1,4,6-TrCDD; 1,4,6,9-TCDD) have $\Delta E_3 > \Delta E_2$. On the other hand, it is interesting to note that more recent GA calculation (GAM 1, 2, 3 in this chronological order) showed progressively larger deviation from DFT(B3LYP/6-31G**) results, as shown in Figure 1. This indicates that there has been no consensus on how much the intramolecular chlorine repulsion energy affects the thermodynamic stability of PCDDs.

Table 6 compares the four terms from the present study with those of GAMs. GAM(3)[16] significantly underestimated the chlorine repulsion effect in a fully chlorinated ring. While GAM-(1)[15] estimated the chlorine repulsion effect (ΔE_2) more closely to DFT results, it did not take ΔE_1, ΔE_3, and ΔE_4 terms into account at all. Table 6 also shows that the significant disagreement among three ΔH_f values of OCDD is mainly due to the difference in the sum of ΔE terms and that a similar ΔH_f value (∼70 kcal/mol) would have been obtained without considering ΔE terms ($\Delta H_f - \Sigma\Delta E_i$).

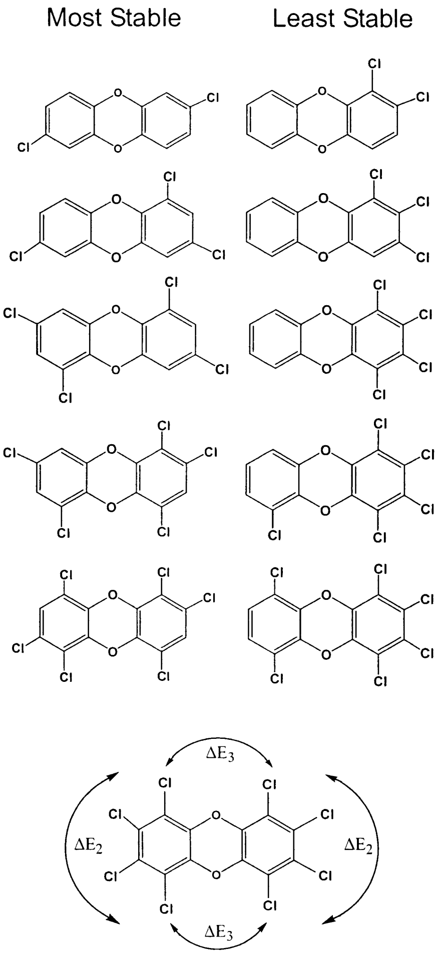


Figure 2. Most and least stable isomers of PCDDs within homologues of di- to hexachlorinated congeners on the basis of ΔG_f. The intramolecular Cl−Cl repulsion (ΔE_2 and ΔE_3) is schematically indicated on OCDD.

TABLE 6: Comparison of ΔE_1, ΔE_2, ΔE_3, ΔE_4 Terms (kcal/mol) between GAMs and DFT (B3LYP/6-31G) Calculation**

	GAM(3)[16]	GAM(1)[15]	DFT
ΔE_1	0	0	1.76 (7.04)[a]
ΔE_2 1,2-Cl_2	2.1	1.4	3.1
2,3-Cl_2	2.1	1.2	3.2
1,3-Cl_2	1.0	0.6	0.9
1,4-Cl_2	0.26	1.4	0.6
1,2,3-Cl_3	3.1	6.8	7.1
1,2,4-Cl_3	0.26	6.8	4.4
1,2,3,4-Cl_4	3.4 (6.8)[a]	12.4 (24.8)[a]	11.3 (22.6)
ΔE_3	0	0	0.3−2.6 (2.61)
ΔE_4	0	0	1.1 (8.8)
$\Sigma\Delta E_i$ (OCDD)	6.8	24.8	41.2
ΔH_f (OCDD)	−65.7	−44.8	−31.9
$\Delta H_f - \Sigma\Delta E_i$ (OCDD)	−72.5	−69.6	−73.1

[a] The number in parentheses is the corresponding value of OCDD.

Thermochemical Implications. Since biological toxicities[33] and many physicochemical properties of PCDDs[21,22] are strongly congener-specific, reliable thermodynamic data on a congener-by-congener basis are extremely important. Optimized conditions for minimizing the formation of toxic congeners at combustion sources should critically depend on their thermodynamic properties. The present DFT results predict that the enthalpies of formation of highly chlorinated dioxin congeners significantly increase as a result of the intramolecular chlorine repulsion effects. The DFT results successfully account for the observed PCDD distribution profiles in various combustion sources.[34−37] The amount of dioxins formed in de novo synthesis from carbon/fly ash,[34] wood burning,[35] and newspaper combustion[36] was in the order of TCDD ∼ PeCDD > HxCDD > HpCDD > OCDD, which is consistent with the profile of ΔH_f and ΔG_f in Figure 1. In addition, the predicted most stable isomers within homologues were found with highest concentrations: total TCDD isomers formed from the combustion of heavy oil composed of 35% of 1,3,6,8-TCDD.[36] The enthalpies and Gibbs free energies of formation for the complete set of 75 PCDDs that are provided by this work should be valuable in further thermodynamic modeling studies.

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Supporting Information Available: Tables of rotational constants, ΔE_1, ΔE_2, ΔE_3, and ΔE_4 for 75 PCDD congeners (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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