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A Gaussian-3X Prediction on the Enthalpies of Formation of Chlorinated Phenols and Dibenzo-*p*-dioxins

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The standard gas-phase enthalpies of formation of chlorinated benzenes, phenols and dibenzo-*p*-dioxins have been predicted using G3X and/or G3XMP2 model chemistries coupled with isodesmic reactions and compared to the previous theoretical and experimental values. A set of values for chlorinated benzenes are first suggested based on experimental measurements and the closed agreed G3X calculations with different isodesmic reactions. The results on polychlorinated dibenzo-*p*-dioxins (PCDDs) show a large difference between G3XMP2 and previous experimental measurements and predictions using group additivity methods, semiempirical quantum chemistry, and DFT calculations, especially for highly chlorinated species. Using the well-balanced isodesmic reactions (IR3 and IR5), the discrepancies between G3XMP2 and DFT predictions on PCDDs can be reduced to within 16 kJ/mol. The relative stability of PCDD isomers can be rationalized by the positional interactions, and the overestimation by DFT with less balanced isodesmic reactions is due to the overestimation of the *ortho*-Cl−Cl repulsive interactions when comparing with G3XMP2. Our calculations suggest further experimental measurements, especially on highly chlorinated phenols and PCDDs.

I. Introduction

Chlorinated organic pollutants are widely distributed in the environment.[1,2] Of these compounds, the chlorinated aromatics are of interest for their high toxicity, bioaccumulation, and persistence in the environment, such as chlorinated benzenes (ClBzs), phenols (ClPhs), polychlorinated naphthalenes (PCNs), dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), etc. With the regulations on the industrial production of certain chlorinated compounds, recent interest focuses on the formation and reduction of PCDD/DFs in municipal waste incineration processes. All these compounds have been detected in the thermal and/or incineration processes of chlorine-containing wastes and materials,[3−8] where the thermodynamic properties of these compounds are important in understanding their formation mechanisms and isomer distributions.[9−13] The modeling studies on gas-phase PCDD/DF formation mechanism have used crudely estimated kinetic and thermodynamic parameters.[9,14,15] One striking fact is that PCDD/DF isomer distributions within homologues are similar across various waste incineration fly ashes. This implies a controlling factor from the thermodynamic properties of the products, even though attempts to correlate the PCDD/DF isomer distribution with the thermodynamic properties have generally failed and the kinetics are considered as the more likely controlling factor.[3,14−18] Yet, a correlation between accurate thermodynamic properties and isomer distributions is required.

The experimental determinations of the enthalpy and entropy of chlorinated aromatics have been hampered by the incomplete combustion of chlorine,[19,20] the impurity of the sample,[21] the lack of molecular structures and vibrational frequencies, and the uncertainty in the enthalpy change measurements for phase transitions.[22] Calorimetric measurements have been performed on benzenes,[19,23−27] and a few phenols[28] and dibenzo-*p*-dioxins.[21,29−33] The results often carry large uncertainties, and the agreement between different measurements, if they exist, is poor, e.g., $\Delta_f H_{298K}^\circ$ (*g*, 1,2,4-$C_6H_3Cl_3$) from two groups differ by as much as 13 kJ/mol.[25,27] Alternately, predictions of the enthalpies of formation of these compounds have used the group additivity method,[34−37] semiempirical PM3[11,38] and MNDO,[39,40] density functional theory (DFT) methods,[12,41−47] and recently G3X calculations on ClBzs[44,48] and G3MP2 on several phenols and phenoxy radicals.[49] DFT and *ab initio* predictions are often coupled with isodesmic reactions to gain better reliability, and close agreement with the experimental and compiled values has been obtained for Di-ClBzs[12,41,44] and Di-ClPhs.[50] However, discrepancies increase gradually with the degree of chlorination, to ∼30 kJ/mol for C_6Cl_6 from DFT prediction, even though the experiments are equally uncertain. $\Delta_f H_{298K}^\circ$ (*g*) of ClBzs obtained from G3X and G3XMP2 atomization energies are also systematically lower than the experiments, by *ca.* 20 kJ/mol for C_6Cl_6,[44,48] rendering the necessary utilization of isodesmic reactions. The purpose of the present study is on the prediction of enthalpies of formation for ClPhs and PCDDs at G3X and/or G3XMP2 levels[51−53] using isodesmic reactions.

II. Quantum Chemistry Methods

DFT and *ab initio* calculations are performed using G03 suite of programs.[54] The geometries of ClBzs and ClPhs are optimized at B3LYP level with the 6-31G(2df,p) and 6-311+G(3df,2p) basis sets, and those of PCDDs with the 6-31G(2df,p) basis set only. The B3LYP/6-31G(2df,p) vibrational frequencies are scaled by 0.9854 for evaluation of zero-point energy (ZPE) corrections. The electronic energies are calculated using the G3X and/or G3XMP2 model chemistries[51−53] to approximate electron correlation levels of QCISD(T,Full) and QCISD(T,FC)/

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TABLE 1: Zero-Point Energies (ZPE), G3X and G3XMP2 Electronic Energies (*E*), and Thermal Corrections at 298 K ($H^T - H^0$) for Chlorinated Benzenes and Phenols (All in Hartrees)

molecules	ZPE	$H^T - H^0$	*E*(G3X)[a]	*E*(G3X)[b]	*E*(G3XMP2)[a]
C_6H_6	0.09869	0.00535	−232.15433	−232.15436	−231.93235
C_6H_5Cl	0.08944	0.00644	−691.61399	−691.61397	−691.08792
1,2-$C_6H_2Cl_4$	0.08007	0.00759	−1151.07028	−1151.07019	−1150.24013
1,3-$C_6H_2Cl_4$	0.08005	0.00761	−1151.07241	−1151.07228	−1150.24224
1,4-$C_6H_2Cl_4$	0.08005	0.00763	−1151.07230	−1151.07223	−1150.24214
1,2,3-$C_6H_3Cl_3$	0.07060	0.00879	−1610.52572	−1610.52557	−1609.39149
1,2,4-$C_6H_3Cl_3$	0.07060	0.00882	−1610.52780	−1610.52767	−1609.39355
1,3,5-$C_6H_3Cl_3$	0.07055	0.00884	−1610.52978	−1610.52967	−1609.39548
1,2,3,4-$C_6H_2Cl_4$	0.06110	0.01002	−2069.98040	−2069.98019	−2068.54210
1,2,3,5-$C_6H_2Cl_4$	0.06109	0.01005	−2069.98250	−2069.98230	−2068.54414
1,2,4,5-$C_6H_2Cl_4$	0.06114	0.01006	−2069.98268	−2069.98250	−2068.54433
C_6HCl_5	0.05158	0.01128	−2529.43451	−2529.43422	−2527.69211
C_6Cl_6	0.04201	0.01250	−2988.88588	−2988.88553	−2986.83942
C_6H_5OH	0.10296	0.00644	−307.35192	−307.35194	−307.08788
2-C_6H_4ClOH	0.09384	0.00751	−766.81391		−766.24576
3-C_6H_4ClOH	0.09365	0.00759	−766.81132		−766.24312
4-C_6H_4ClOH	0.09364	0.00761	−766.81054		−766.24239
5-C_6H_4ClOH	0.09362	0.00759	−766.81124		−766.24306
6-C_6H_4ClOH	0.09369	0.00759	−766.80876		−766.24060
2,3-$C_6H_3Cl_2OH$	0.08447	0.00869	−1226.27025	−1226.27010	−1225.39798
2,4-$C_6H_3Cl_2OH$	0.08444	0.00873	−1226.27142	−1226.27128	−1225.39917
2,5-$C_6H_3Cl_2OH$	0.08442	0.00872	−1226.27212	−1226.27198	−1225.39983
2,6-$C_6H_3Cl_2OH$	0.08449	0.00871	−1226.26989	−1226.26974	−1225.39762
3,4-$C_6H_3Cl_2OH$	0.08426	0.00879	−1226.26678	−1226.26666	−1225.39451
3,5-$C_6H_3Cl_2OH$	0.08421	0.00880	−1226.26942	−1226.26929	−1225.39707
3,6-$C_6H_3Cl_2OH$	0.08430	0.00880	−1226.26708		−1225.39477
4,5-$C_6H_3Cl_2OH$	0.08423	0.00879	−1226.26663		−1225.39437
4,6-$C_6H_3Cl_2OH$	0.08428	0.00881	−1226.26636		−1225.39410
5,6-$C_6H_3Cl_2OH$	0.08427	0.00877	−1226.26492		−1225.39265
2,3,4-$C_6H_2Cl_3OH$	0.07498	0.00993	−1685.72500		−1684.54865
2,3,5-$C_6H_2Cl_3OH$	0.07497	0.00994	−1685.72762		−1684.55119
2,3,6-$C_6H_2Cl_3OH$	0.07505	0.00993	−1685.72554		−1684.54913
2,4,5-$C_6H_2Cl_3OH$	0.07497	0.00996	−1685.72674		−1684.55038
2,4,6-$C_6H_2Cl_3OH$	0.07501	0.00997	−1685.72649		−1684.55010
2,5,6-$C_6H_2Cl_3OH$	0.07503	0.00993	−1685.72535		−1684.54895
3,4,5-$C_6H_2Cl_3OH$	0.07477	0.01002	−1685.72196		−1684.54556
3,4,6-$C_6H_2Cl_3OH$	0.07485	0.01004	−1685.72189		−1684.54548
3,5,6-$C_6H_2Cl_3OH$	0.07481	0.01003	−1685.72240		−1684.54596
4,5,6-$C_6H_2Cl_3OH$	0.07481	0.01000	−1685.71970		−1684.54334
2,3,4,5-C_6HCl_4OH	0.06548	0.01117	−2145.17986		−2143.69899
2,3,4,6-C_6HCl_4OH	0.06554	0.01120	−2145.17997		−2143.69907
2,3,5,6-C_6HCl_4OH	0.06556	0.01118	−2145.18064		−2143.69970
2,4,5,6-C_6HCl_4OH	0.06551	0.01120	−2145.17962		−2143.69874
3,4,5,6-C_6HCl_4OH	0.06533	0.01125	−2145.17475		−2143.69385
C_6Cl_5OH	0.05602	0.01242	−2604.63151		−2602.84689

[a] Electronic energies based on B3LYP/6-311+G(3df,2p) geometries. [b] Electronic energies based on B3LYP/6-31G(2df,p) geometries from Dorofeeva et al.[48]

G3ExtraLarge, respectively. The calculations are based on B3LYP/6-311+G(3df,2p) geometries for ClBzs and ClPhs and B3LYP/6-31G(2df,p) ones for PCDDs. B3LYP/6-311++G-(3df,3pd) calculations have also been carried out on ClBzs and PCDDs using the NWChem 5.0 package.[55,56]

There have been several discussions on the thermal corrections of the low-frequency vibration modes. Leon et al.[41] treated all modes below 260 cm^{-1} as the internal rotations (more properly pseudorotations) and assigned a thermal correction of RT/2 at 298 K, following the suggestion of Nicolaides et al.,[57] while Zhu et al.[12] stated that vibrational frequency is not the deciding issue and treated all as harmonic oscillators. Careful examination on the low-frequency modes of the present systems reveals their natures of internal rotations (along the C−O bond in phenols) and out-of-plane-large-amplitude modes (C−Cl bonds), etc. The out-of-plane modes with extremely low vibrational frequencies, e.g., the butterfly motions of the two benzene rings along (approximately) the O−O axis (16 cm^{-1} for Octa-CDD and 38 cm^{-1} for DD), should be described as oscillators with potentials of mixed quadratic (q^2) and quartic (q^4) terms. When these out-of-plane oscillators are treated as harmonic oscillators, the ZPE corrections are usually underestimated, and in contrast the thermal corrections are overestimated (pure quadratic = RT and pure quartic = 0.75 RT when $h\nu/kT \rightarrow 0$).[58] For simplicity, these out-of-plane modes will be treated as harmonic oscillators because of the error cancellation of ZPE and thermal correction. This would introduce a relatively larger error in the calculations of entropies (and thereafter ΔG), and the errors are prone to increase with the degree of chlorination, even though it is difficult to evaluate exactly the uncertainties. Small errors can be inferred from the calculation on the entropy of dibenzofuran, which has found deviations up to 3.5 J K^{-1} mol^{-1} compared to the experiment for temperatures less than 720 K.[42]

III. Results and Discussion

The ZPE corrections and G3X(MP2) electronic energies of chlorinated benzenes and phenols are listed in Table 1, and the G3XMP2 electronic energies of PCDDs in Table 2. The G3X electronic energies of chlorinated benzenes and phenols in the present study are slightly lower by 0.1−0.4 mHartree than those

TABLE 2: Order Number (no.), Zero-Point Energies (ZPE), G3XMP2 Electronic Energies (*E*), and Thermal Corrections at 298 K ($H^T - H^0$) for PCDDs (in Hartrees)

no.	PCDD	ZPE	$H^T - H^0$	E(G3XMP2)
0	none	0.16515	0.01052	−611.75482
1	1-	0.15575	0.01180	−1070.90743
2	2-	0.15572	0.01178	−1070.90921
3	1,2-	0.14625	0.01307	−1530.05862
4	1,3-	0.14622	0.01311	−1530.06037
5	1,4-	0.14631	0.01310	−1530.05886
6	1,6-	0.14631	0.01309	−1530.05938
7	1,7-	0.14626	0.01308	−1530.06114
8	1,8-	0.14625	0.01308	−1530.06099
9	1,9-	0.14630	0.01309	−1530.05908
10	2,3-	0.14625	0.01306	−1530.06030
11	2,7-	0.14622	0.01307	−1530.06284
12	2,8-	0.14622	0.01307	−1530.06286
13	1,2,3-	0.13675	0.01436	−1989.20892
14	1,2,4-	0.13680	0.01440	−1989.20937
15	1,2,6-	0.13683	0.01436	−1989.21045
16	1,2,7-	0.13674	0.01436	−1989.21218
17	1,2,8-	0.13675	0.01436	−1989.21207
18	1,2,9-	0.13681	0.01437	−1989.21015
19	1,3,6-	0.13678	0.01440	−1989.21207
20	1,3,7-	0.13671	0.01439	−1989.21386
21	1,3,8-	0.13672	0.01439	−1989.21382
22	1,3,9-	0.13677	0.01440	−1989.21196
23	1,4,6-	0.13681	0.01442	−1989.21037
24	1,4,7-	0.13681	0.01439	−1989.21222
25	2,3,6-	0.13678	0.01435	−1989.21193
26	2,3,7-	0.13673	0.01434	−1989.21371
27	1,2,3,4-	0.12727	0.01566	−2448.35713
28	1,2,3,6-	0.12730	0.01565	−2448.36054
29	1,2,3,7-	0.12721	0.01565	−2448.36227
30	1,2,3,8-	0.12723	0.01564	−2448.36223
31	1,2,3,9-	0.12726	0.01566	−2448.36042
32	1,2,4,6-	0.12728	0.01572	−2448.36076
33	1,2,4,7-	0.12733	0.01567	−2448.36258
34	1,2,4,8-	0.12728	0.01568	−2448.36255
35	1,2,4,9-	0.12731	0.01570	−2448.36075
36	1,2,6,7-	0.12731	0.01564	−2448.36132
37	1,2,6,8-	0.12728	0.01567	−2448.36297
38	1,2,6,9-	0.12734	0.01568	−2448.36132
39	1,2,7,8-	0.12728	0.01562	−2448.36283
40	1,2,7,9-	0.12726	0.01567	−2448.36288
41	1,2,8,9-	0.12729	0.01564	−2448.36109
42	1,3,6,8-	0.12725	0.01571	−2448.36468
43	1,3,6,9-	0.12729	0.01572	−2448.36299
44	1,3,7,8-	0.12724	0.01566	−2448.36456
45	1,3,7,9-	0.12724	0.01571	−2448.36460
46	1,4,6,9-	0.12735	0.01573	−2448.36134
47	1,4,7,8-	0.12732	0.01566	−2448.36295
48	2,3,7,8-	0.12726	0.01562	−2448.36446
49	1,2,3,4,6-	0.11777	0.01697	−2907.50846
50	1,2,3,4,7-	0.11773	0.01695	−2907.51022
51	1,2,3,6,7-	0.11774	0.01695	−2907.51136
52	1,2,3,6,8-	0.11771	0.01698	−2907.51294
53	1,2,3,6,9-	0.11780	0.01697	−2907.51133
54	1,2,3,7,8-	0.11772	0.01693	−2907.51284
55	1,2,3,7,9-	0.11771	0.01698	−2907.51289
56	1,2,3,8,9-	0.11776	0.01693	−2907.51125
57	1,2,4,6,7-	0.11778	0.01699	−2907.51162
58	1,2,4,6,8-	0.11773	0.01703	−2907.51324
59	1,2,4,6,9-	0.11778	0.01705	−2907.51163
60	1,2,4,7,8-	0.11776	0.01697	−2907.51252
61	1,2,4,7,9-	0.11775	0.01702	−2907.51325
62	1,2,4,8,9-	0.11779	0.01698	−2907.51159
63	1,2,3,4,6,7-	0.10824	0.01825	−3366.65923
64	1,2,3,4,6,8-	0.10824	0.01828	−3366.46157
65	1,2,3,4,6,9-	0.10826	0.01830	−3366.65927
66	1,2,3,4,7,8-	0.10823	0.01824	−3366.66077
67	1,2,3,6,7,8-	0.10822	0.01823	−3366.66117
68	1,2,3,6,7,9-	0.10824	0.01828	−3366.46204
69	1,2,3,6,8,9-	0.10823	0.01829	−3366.46204
70	1,2,3,7,8,9-	0.10822	0.01823	−3366.66120
71	1,2,4,6,7,9-	0.10827	0.01833	−3366.66184
72	1,2,4,6,8,9-	0.10826	0.01833	−3366.66173
73	1,2,3,4,6,7,8-	0.09869	0.01955	−3825.80906
74	1,2,3,4,6,7,9-	0.09869	0.01961	−3825.60046
75	Octa-	0.08915	0.02088	−4284.95694

by Dorofeeva et al.[48] because the improved geometries of B3LYP/6-311+G(3df,2p) are used here for G3X electronic energy calculation.

A. Enthalpies of Formation of Chlorobenzenes. The available experimental determinations of the enthalpies of formation of chlorobenzenes includes the calorimetry measurements by Platonov et al.,[23−26] by Yan et al. on trichlorobenzenes,[27] and by Sinke and Stull on C_6Cl_6,[59] etc. The values have been critically evaluated in several data compilations by Stull et al.,[60] Cox and Pilcher,[61] and Pedley.[62,63] For the two sets of data on $C_6H_3Cl_3$, agreement is observed on 1,2,3-$C_6H_3Cl_3$ only, while the difference for 1,2,4-$C_6H_3Cl_3$ is as large as 13 kJ/mol. A mistake is found in Platonov et al.'s study[25] on 1,3,5-$C_6H_3Cl_3$ where $\Delta_{fus}H_{298K}° = 11.4$ kJ/mol was left out in converting $\Delta_f H_{298K}°$ (*s*) to $\Delta_f H_{298K}°$ (*g*). The corrected $\Delta_f H_{298K}°$ (1,3,5-$C_6H_3Cl_3$, *g*) $= -1.9$ kJ/mol is in agreement with the value of -2.6 ± 1.4 kJ/mol by Yan et al., which in turn can be further adjusted to -3.5 kJ/mol with the new enthalpy of sublimation by Rahac et al.[64]

It is noticed that the $\Delta_f H_{298K}°$ obtained from G3X atomization energies agree with the experimental values from Pedley[62] for $C_6H_4Cl_2$, from Yan et al.[27] for $C_6H_3Cl_3$, and from Platonov et al.[23−26] with the recently measured enthalpies of sublimation[64] for $C_6H_2Cl_4$ and C_6HCl_5 (Table 3). The maximum deviation does not exceed 6.5 kJ/mol, with G3X predictions being lower for $C_6H_4Cl_2$ and $C_6H_3Cl_3$ and higher for $C_6H_2Cl_4$ and C_6HCl_5 than the experiments. The G3X deviations from the experiments can be reduced to within 3.2 kJ/mol for Di- and Tri-ClBzs using the following isodesmic reactions IR1 with $\Delta_f H_{298K}°$ of C_6H_6 and C_6H_5Cl from Pedley:[62]

$$C_6H_{6-n}Cl_n + (n-1)C_6H_6 \rightarrow nC_6H_5Cl \qquad \text{(IR1)}$$

However, the G3X predictions for $C_6H_2Cl_4$ and C_6HCl_5 using IR1 are much higher than the experimental values. Alternatively, Dorofeeva et al.[48] have employed isodesmic reactions involving Di- and Tri-ClBzs, together with C_6H_5Cl, which are used to predict the enthalpies of formation for Tetra-, Penta-, and Hexa-ClBzs. The values are still much higher than the experiments as indicated in Table 3. Dorofeeva et al.,[48] however, insisted on the experimental values from the agreement on the enthalpy changes of the following reactions from experiments and G3X, arguing that these reactions are better balanced on the Cl−Cl interactions:

$$\text{1,2,3,4-}C_6H_2Cl_4 + \text{1,3-}C_6H_4Cl_2 \rightarrow \text{1,2,3,5-}C_6H_2Cl_4 + \text{1,2-}C_6H_4Cl_2 \qquad \text{(R26)}$$

$$\text{1,2,3,5-}C_6H_2Cl_4 + \text{1,2-}C_6H_4Cl_2 \rightarrow \text{1,2,3,4-}C_6H_2Cl_4 + \text{1,3-}C_6H_4Cl_2 \qquad \text{(R27)}$$

$$\text{1,2,4,5-}C_6H_2Cl_4 + \text{1,2-}C_6H_4Cl_2 \rightarrow \text{1,2,3,5-}C_6H_2Cl_4 + \text{1,3-}C_6H_4Cl_2 \qquad \text{(R28a)}$$

$$C_6HCl_5 + C_6H_5Cl \rightarrow \text{1,2,3,4-}C_6H_2Cl_4 + \text{1,2-}C_6H_4Cl_2 \qquad \text{(R29)}$$

TABLE 3: Enthalpies of Formation of Chlorobenzenes from Atomization (AR) and Isodesmic Reactions (IR) at the G3X Level, along with Other Values (in kJ/mol)

	AR				
chlorobenzenes	G3X	G3X MP2	isodesmic reactions	G3X//IR	others
C_6H_6	84.7	78.0			**82.6 ± 0.7**[b]
C_6H_5Cl	51.3	43.7			**52.0 ± 1.3**[b]
1,2-$C_6H_4Cl_2$	26.5	18.0	$C_6H_4Cl_2 + C_6H_6 \rightarrow 2C_6H_5Cl$	30.0	**30.2 ± 2.1**[b]
1,3-$C_6H_2Cl_4$	20.9	12.5	$C_6H_4Cl_2 + C_6H_6 \rightarrow 2C_6H_5Cl$	24.4	**25.7 ± 2.1**[b]
1,4-$C_6H_2Cl_4$	21.2	12.8	$C_6H_4Cl_2 + C_6H_6 \rightarrow 2C_6H_5Cl$	24.8	**22.5 ± 1.5**[b]
1,2,3-$C_6H_3Cl_3$	3.8	−5.5	$C_6H_3Cl_3 + 2C_6H_6 \rightarrow 3C_6H_5Cl$	10.2	**8.2 ± 1.8**[c]
1,2,4-$C_6H_3Cl_3$	−1.6	−10.9	$C_6H_3Cl_3 + 2C_6H_6 \rightarrow 3C_6H_5Cl$	4.8	**4.9 ± 1.6**[c]
1,3,5-$C_6H_3Cl_3$	−6.9	−16.0	$C_6H_3Cl_3 + 2C_6H_6 \rightarrow 3C_6H_5Cl$	−0.4	**−3.5 ± 1.4**[c]
1,2,3,4-$C_6H_2Cl_4$	−16.9	−27.2	$C_6H_2Cl_4 + 3C_6H_6 \rightarrow 4C_6H_5Cl$	−7.6	−25.4 ± 1.0[b,d]
			$C_6H_2Cl_4 + C_6H_4Cl_2 \rightarrow 2C_6H_3Cl_3$[a]	−10.6	−20.4[e]
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 2(1,3\text{-}C_6H_4Cl_2)$	−5.0	
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 2(1,2\text{-}C_6H_4Cl_2)$	−7.4	
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 1,2\text{-}C_6H_4Cl_2 + 1,4\text{-}C_6H_4Cl_2$	−9.9	
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 1,2,3\text{-}C_6H_3Cl_3 + C_6H_5Cl$	−9.7	
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 1,2,4\text{-}C_6H_3Cl_3 + C_6H_5Cl$	−7.6	
			average	**−8.3**	
1,2,3,5-$C_6H_2Cl_4$	−22.3	−32.4	$C_6H_2Cl_4 + 3C_6H_6 \rightarrow 4C_6H_5Cl$	−13.1	−34.9 ± 1.0[b,d]
			$C_6H_2Cl_4 + C_6H_4Cl_2 \rightarrow 2C_6H_3Cl_3$[a]	−16.0	−27.7[e]
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 1,2\text{-}C_6H_4Cl_2 + 1,3\text{-}C_6H_4Cl_2$	−11.7	
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 1,3\text{-}C_6H_4Cl_2 + 1,4\text{-}C_6H_4Cl_2$	−14.2	
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 1,2,3\text{-}C_6H_3Cl_3 + C_6H_5Cl$	−15.7	
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 1,2,4\text{-}C_6H_3Cl_3 + C_6H_5Cl$	−13.0	
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 1,3,5\text{-}C_6H_3Cl_3 + C_6H_5Cl$	−16.1	
			average	**−14.3**	
1,2,4,5-$C_6H_2Cl_4$	−22.7	−32.8	$C_6H_2Cl_4 + 3C_6H_6 \rightarrow 4C_6H_5Cl$	−13.4	−32.6 ± 0.8[b,d]
			$C_6H_2Cl_4 + C_6H_4Cl_2 \rightarrow 2C_6H_3Cl_3$[a]	−16.4	−27.0[e]
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 2(1,2\text{-}C_6H_4Cl_2)$	−13.2	
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 2(1,3\text{-}C_6H_4Cl_2)$	−11.0	
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 2(1,4\text{-}C_6H_4Cl_2)$	−18.2	
			$C_6H_2Cl_4 + C_6H_6 \rightarrow 1,2,4\text{-}C_6H_3Cl_3 + C_6H_5Cl$	−13.4	
			average	**−14.3**	
C_6HCl_5	−36.0	−47.1	$C_6HCl_5 + 4C_6H_6 \rightarrow 4C_6H_5Cl$	−24.0	−40.0 ± 8.7[b,d]
			$C_6HCl_5 + C_6H_6 + C_6H_5Cl \rightarrow 3C_6H_4Cl_2$[a]	−25.5	−37.3[e]
			$C_6HCl_5 + C_6H_5Cl \rightarrow 2C_6H_3Cl_3$[a]	−27.2	
			$C_6HCl_5 + C_6H_6 \rightarrow C_6H_4Cl_2 + C_6H_3Cl_3$[a]	−25.7	
			average	**−25.6**	
C_6Cl_6	−48.2	−60.3	$C_6Cl_6 + 5C_6H_6 \rightarrow 6C_6H_5Cl$	−33.3	−44.7 ± 8.5[d]
			$C_6Cl_6 + 2C_6H_6 \rightarrow 3C_6H_4Cl_2$[a]	−34.4	−35.5 ± 9.3[b]
			$C_6Cl_6 + C_6H_6 \rightarrow 2C_6H_3Cl_3$[a]	−36.5	−36.0 ± 9.6[f]
			average	**−34.7**	−33.89[g]

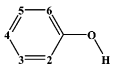
[a] $C_6H_4Cl_2$ and $C_6H_3Cl_3$ are the average of each three isomers. *b*From Pedley.[62] [c] From Yan et al.[27] with new enthalpies of sublimation.[65] [d] From Platonov et al.[23,25] [e] From Platonov et al.[23,25] with new enthalpies of sublimation.[65] [f] From Cox and Pilcher.[61] [g] From Stull.[60]

However, each of these reactions contains two species with undefined enthalpy of formation (Tetra- and Penta-ClBzs in these cases), and there is a danger of circular reference. Thereafter, we have employed isodesmic reactions involving C_6H_6, C_6H_5Cl, $C_6H_4Cl_2$, and $C_3H_3Cl_3$ to predict $\Delta_f H_{298K}°$ for $C_6H_2Cl_4$, C_6HCl_5, and C_6Cl_6, with the relatively well-established values (in boldface in Table 3) for C_6H_5Cl and $C_6H_4Cl_2$ from Pedley[62] and for $C_6H_3Cl_3$ from Yan et al.[27] Agreement within 7 kJ/mol is observed across different isodesmic reactions (Table 3). In these isodesmic reactions, nonspecified $C_6H_4Cl_2$ and $C_6H_3Cl_3$ represent the average of each three isomers. Equal weighting factor is assumed for each isodesmic reaction, since no preference can be assigned to certain reactions or species. The preferred values for $C_6H_2Cl_4$, C_6HCl_5 and C_6Cl_6 are taken as the simple averages across all the reactions for each species, and are used later for chlorophenols and PCDDs.

The averaged G3X results from isodesmic reactions are −8.3, −14.3, −14.3, −25.6, and −34.7 kJ/mol for 1,2,3,4-, 1,2,3,5-, 1,2,4,5-$C_6H_2Cl_4$, C_6HCl_5, and C_6Cl_6, respectively, being higher than the experimental determinations of −25.4, −34.9, −32.6, −40.0, and −44.7 kJ/mol by Plantonov et al.,[23,25,26] even after the corrections to −20.4, −27.7, −27.0, and −37.3 kJ/mol for $C_6H_2Cl_4$ and C_6HCl_5 with the new enthalpies of sublimation by Sabbah et al.[65] On the other hand, G3X $\Delta_f H_{298K}°$ (C_6Cl_6, *g*) = −34.7 kJ/mol agrees with the values of −35.9 ± 9.6 kJ/mol listed by Cox and Pilcher,[61] −33.89 kJ/mol by Stull,[60] and −35.5 ± 9.3 kJ/mol by Pedley.[62] These values are based on the combustion measurement by Sinke and Stull[59] and the estimated $\Delta_f H_{sub}°$ of 92.0 ± 8.4 kJ/mol by Sears et al.[66] Using the later $\Delta_f H_{sub}°$ of 90.5 ± 0.8 kJ/mol[65] or 96.8 ± 0.5 kJ/mol,[67] $\Delta_f H_{298K}°$ (*g*) from Cox and Picher is adjusted to −37.4 ± 9.6 or −31.1 ± 9.6 kJ/mol, both agreeing with G3X prediction.

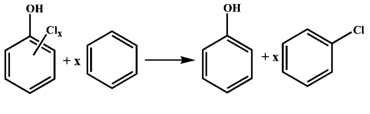
Judging from the standard deviation of the average over different isodesmic reactions, the propagation of errors from $C_6H_{6-n}Cl_n$ ($n = 0-3$), and the accuracy of G3X on the enthalpy changes of reactions, an approximate confidence range of ±5 kJ/mol is assigned to current G3X enthalpies of formation for $C_6H_2Cl_4$, C_6HCl_5 and C_6Cl_6 using isodesmic reactions. A similar confidence range is also expected for G3XMP2 using the same set of isodesmic reactions, where agreement with G3X within 0.2 kJ/mol is observed for chlorobenzenes using isodesmic reactions IR1.

B. Enthalpies of Formation of Chlorinated Phenols. For chlorinated phenols, calculations discriminate the Cl-substitutions on two *ortho* (2 and 6) and two *meta* (3 and 5) positions:

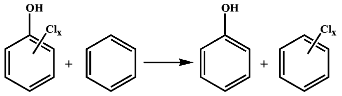


The substitution on site 2 is stabilized by the intramolecular hydrogen bond, e.g., 2-Mono-ClPh is lower than 6-Mono-ClPh by *ca.* 13 kJ/mol; while the substitutions on sites 3 and 5 result are about equal in stability, differing by only 0.1 kJ/mol between 3-Mono-ClPh and 5-Mono-ClPh. A similar difference of ~13 kJ/mol has also been found at the G3B3 level between 2,4-Di-ClPh and 4,6-Di-ClPh.[68] The strength of the hydrogen bond remains almost constant within 0.5 kJ/mol with further chlorination, in accordance with previous DFT studies.[69] The substitutions on sites 2/6 and/or 3/5 are connected by internal rotation along the C−OH bond. The barrier heights are ~11 kJ/mol for phenol and Cl-substitutions on sites 3, 4, and 5 only. The intramolecular hydrogen bonding with substitution on one of the *ortho*-positions increases the energy barriers by ~12 kJ/mol, while substitution on both *ortho*-sites slightly reduces it by *ca.* 2−3 kJ/mol relative to one *ortho*-substitution. The barriers of 10−11 and 19−23 kJ/mol for ClPhs with and without Cl-substitution on *ortho*-sites imply the plausibility to treat the C−OH internal rotations as harmonic oscillator under room temperature, and the employment of isodesmic reaction can further reduce the error.

The enthalpies of chlorinated phenols are obtained from the G3X atomization reaction and the following isodesmic reactions:



IR2



IR3

where the IR3 reactions are considered being better balanced for Cl−Cl interactions. The results are listed in Table 4 as G3X//AR, G3X//IR2, and G3X//IR3, respectively. $\Delta_f H_{298K}°$ (C_6H_5-OH) = −96.4 kJ/mol is taken from NIST evaluation.[70] The values for Di-ClPhs obtained from G3X//IR3 are identical to those by Dorofeeva et al.[48] The values obtained from both isodesmic reactions agree within 4 kJ/mol, and the differences between G3X and G3XMP2 are within 2 kJ/mol (Table 4). The calculated enthalpies of formation here show that the group additivity method has large disagreement with the present predictions, e.g., it underestimates by *ca.* 27 kJ/mol for 2,3-, 2,4-, and 2,5-Di-ClPhs and by 17 kJ/mol for 2,4,5-Tri-ClPh, and overestimated by *ca.* 40 kJ/mol for 2,6-Di-ClPh.[34]

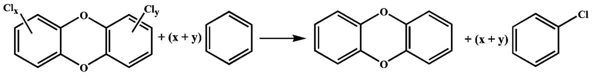
Janoschek et al.[49] have obtained $\Delta_f H_{298K}°$ = −138.4, −167.1, and −189.1 kJ/mol for 2-Mono-ClPh, 2,4-Di-ClPh, and 2,4,6-Tri-ClPh, respectively, using G3MP2B3 atomization energies with ZPEs at the B3LYP/6-31G(d) level, and Burcat et al.[68] improved the values to −130.9 and −158.0 kJ/mol for 2-Mono-ClPh and 2,4-Di-ClPh using G3B3 atomization energies. With improved B3LYP/6-31G(2df,p) ZPEs and further improved B3LYP/6-311+G(3df,2p) geometries in the present study, the values are −137.0, −165.7, and −188.0 kJ/mol from G3XMP2//AR, −132.2, −160.0, and −181.5 kJ/mol from G3X//AR, and −132.8, −156.6, and −180.5 kJ/mol from G3X//IR3.

Ribeiro da Silva et al. have measured the enthalpies of formation of 3- and 4-Mono-ClPh and six Di-ClPh isomers.[28] The values are obtained from the measured heat of combustion of their solid states and the enthalpies of sublimation, where the latter are extrapolated from the values at 364 K. The measured $\Delta_{Sub} H_{298K}°$ differ significantly by 3−8 kJ/mol from the recent study,[67] and the simplified extrapolation procedure is criticized. The gas-phase enthalpies of formation with the same $\Delta_f H_{298K}°$ (*s*) and both sets of $\Delta_{Sub} H_{298K}°$ are listed in Table 4 and compared to G3X predictions. The agreement between experiment and theory is improved for 3- and 4-Mono-ClPh and for 3,4-Di-ClPh only with the new sublimation enthalpies. On the other hand, the better agreement of the values from Ribeiro da Silva et al. with DFT-B3LYP/6-311++G(2df,2p)[50] and G3X//IR3 predictions on Di-ClPhs does not necessarily guarantee their high reliability on the measured enthalpies of sublimation over that of Verevkin et al.[67] because of the possible uncertainty on the measured heat of combustion on their solid states.

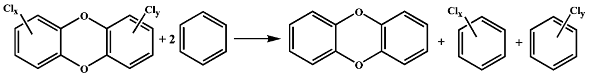
$\Delta_f H_{298K}°$ (C_6Cl_5OH, *g*) = −203.8 ± 3.0 kJ/mol can be obtained from $\Delta_f H_{298K}°$ (*s*) of −295.4 ± 2.9 kJ/mol from the combustion study by Sinke and Stull[59] as reanalyzed by Cox and Pilcher[61] and the recently determined heat of sublimation of 91.6 ± 0.4 kJ/mol by Verevkin et al.[67] A much lower value of −228 ± 3.6 kJ/mol can also be obtained using the heat of sublimation of 67.4 ± 2.1 kJ/mol given by Cox and Pilcher.[61] The value with new heat of sublimation is in excellent agreement with our G3X//IR3 prediction of −202.5 kJ/mol.

No experimental or theoretical study is available for other chlorophenols, and current calculations represent a systematic attempt. Until further experimental measurement on the heats of combustion and sublimation, we would recommend our G3X//IR3 predictions for further modeling study.

C. Enthalpies of Formation of Polychlorinated Dibenzo-*p*-dioxins. Enthalpies of formation of PCDDs can be obtained in principle from G3XMP2 atomization directly; however, the deviations are large as evidenced by chlorophenols. It is necessary to employ isodesmic reactions. Two reactions have been used here:



IR4



IR5

where IR5 is preferred with the conservation of intra-ring Cl−Cl interactions to reduce the electron correlation errors,[41,44,48] even though Lee et al. have insisted on IR4, arguing that the enthalpies of formation for Tri-ClBzs and Tetra-ClBzs are highly uncertain.[43]

A reliable value for $\Delta_f H_{298K}°$ (DD) is required before the application of isodesmic reactions for PCDDs. Two measurements on the enthalpies of formation of DD have been performed by the same group, giving values of −59.2 ± 4.4 kJ/mol in 1997[29] and −50.1 ± 2.2 kJ/mol in 2002,[21] with the later value being preferred by those authors. Both values have been used in previous DFT calculations on PCDDs using isodesmic reactions.[11,41−44,46] Direct estimations have resulted −62.8,[34] −61.9,[35] −55,[36] and −70[42] kJ/mol by the group additivity method, −40.2 and −94.1 kJ/mol by semiempirical PM3[38] and MNDO calculations,[40,71] and −61.3,[41] −51.8,[12] and −50.33 kJ/mol[44] by DFT-B3LYP/6-311+G(3df,2p) calculations using different isodesmic reactions. Following the experimental preference[21] and recent DFT estimations,[12,44] we shall use $\Delta_f H_{298K}°$ (DD) = −50.1 ± 2.2 kJ/mol, even though further experimental measurement and/or high-level theoretical prediction are desirable for confirmation.

Table 5 lists the enthalpies of formation of PCDDs predicted from G3XMP2//IR4 and //IR5, and values from B3LYP//IR4 using 6-31G(2df,p) and 6-311++G(3df,3pd) basis set are given in the Supporting Information. At the G3XMP2 level, results

TABLE 4: Barrier Heights of Ph−OH Internal Rotations at the G3XMP2 Level, and Enthalpies of Formation of Chlorophenols at 298 K (in kJ/mol) Obtained from Atomization (//AR) and Isodesmic Reactions IR1 and IR2 (//IR1 and //IR2) at the G3X and G3XMP2 Levels (All in kJ/mol)[a]

		$\Delta_f H_{298K}^\circ$ (kJ/mol)						
		AR		IR2		IR3		
phenols	BH (kJ/mol) G3XMP2	G3X	G3XMP2	G3X	G3XMP2	G3X	G3XMP2	other studies
phenol	10.9	−92.9	−96.9					**−96.4**[b]
2-	22.4	−132.2	−137.0	−132.8	−132.8	**−132.8**	−132.8	−130.9[c]
3-	11.3	−125.7	−130.4	−126.3	−126.2	**−126.3**	−126.2	−137.0 ± 8.6[d] −129.5,[e] −138.3[f]
4-	10.2	−123.6	−128.4	−124.2	−124.2	**−124.2**	−124.2	−128.2 ± 8.6[d] −120.6[e]
5-		−125.5	−130.3	−126.1	−126.1	**−126.1**	−126.1	
6-		−118.9	−123.7	−119.5	−119.5	**−119.5**	−119.5	−117.8[c]
2,3-	23.3	−157.0	−162.6	−154.8	−154.7	**−154.7**	−154.5	−151.6 ± 2.5[d] −146.4[e]
2,4-	21.5	−160.0	−165.7	−157.9	−157.8	**−156.6**	−156.6	−156.3 ± 1.9[d] −148.4,[e] −167.0[f] −158.0[c]
2,5-	22.6	−162.0	−167.5	−159.8	−159.6	**−162.2**	−161.9	−158.4 ± 2.4[d] −154.7[e]
2,6-	19.7	−156.0	−161.6	−153.8	−153.7	**−152.6**	−152.5	−146.3 ± 1.5[d] −142.8[e]
3,4-	10.8	−148.2	−153.8	−146.0	−145.9	**−145.9**	−145.7	−150.3 ± 2.5[d] −141.8[e]
3,5-	11.8	−155.2	−160.6	−153.1	−152.7	**−151.8**	−151.5	−148.2 ± 1.5[d] −141.7[e]
3,6-		−148.8	−154.3	−146.7	−146.4	**−149.1**	−148.7	
4,5-		−147.9	−153.5	−145.7	−145.6	**−145.6**	−145.4	
4,6-		−147.0	−152.6	−144.8	−144.7	**−143.4**	−143.5	−145.4[c]
5,6-		−143.3	−148.9	−141.2	−141.0	**−141.1**	−140.9	
2,3,4-	22.6	−177.8	−184.3	−172.8	−172.7	**−174.8**	−174.7	
2,3,5-	23.5	−184.7	−191.0	−179.7	−179.4	**−179.6**	−179.3	
2,3,6-	20.5	−179.0	−185.4	−174.0	−173.8	**−173.9**	−173.7	
2,4,5-	21.5	−182.4	−188.8	−177.4	−177.2	**−177.3**	−177.1	
2,4,6-	18.8	−181.5	−188.0	−176.5	−176.3	**−180.5**	−179.7	−143.4,[e] −189.0[f]
3,4,5-	11.0	−170.2	−176.5	−165.1	−164.9	**−167.2**	−166.9	
3,4,6-		−169.7	−176.1	−164.7	−165.5	**−164.6**	−165.2	
3,5,6-		−171.2	−177.4	−166.2	−165.8	**−166.1**	−165.7	
4,5,6-		−164.2	−170.6	−159.2	−159.0	**−161.2**	−161.0	
2,3,4,5-	22.5	−198.9	−205.2	−191.1	−189.8	**−191.7**	−190.4	
2,3,4,6-	19.9	−199.0	−205.2	−191.2	−189.8	**−192.4**	−191.2	
2,3,5,6-	20.7	-200.8	−206.8	−192.9	−191.5	**−193.8**	−192.4	
2,4,5,6-		−198.2	−204.4	−190.4	−189.0	**−191.6**	−190.4	
3,4,5,6-		−185.7	−191.9	−177.9	−176.5	**−178.5**	−177.1	
2,3,4,5,6-	20.0	−211.5	−219.5	-200.8	-200.5	**−202.5**	−201.9	−203.8 ± 3.0[g] −228. ± 3.6[h]

[a] Calculations are based on B3LYP/6-31G(2df,p) ZPE corrections and B3LYP/6-311+G(3df,2p) geometries. [b] Experimental value taken from NIST webbook.[70] [c] Theoretical calculations from G3B3 atomization energies.[68] [d] Experimental values from Ribeiro da Silva et al.[28] [e] Experimental values from Ribeiro da Silva et al.[28] with enthalpies of sublimation from Verevkin et al.[67] [f] G3MP2 calculations by atomization energy procedure from Janoschek et al.[49] [g] Experimental value from Sinke and Stull[59] with enthalpies of sublimation from Verevkin et al.[67] [h] Experimental value from Sinke and Stull[59] with enthalpies of sublimation from Cox and Pilcher.[61]

using IR4 and IR5 agree closely, with only three of the discrepancies being larger than 4 kJ/mol. Previous DFT calculations have observed large discrepancies on the predicted enthalpy of formation using IR4 and IR5 for higher PCDDs, up to 60 kJ/mol for Octa-CDD.[41] While our B3LYP/6-31G(2df,p)//IR4 calculations agree closely with previous B3LYP/6-31G(d,p) ones,[43] e.g., −125.5 kJ/mol *versus* −124.0 kJ/mol for Octa-CDD, a significantly systematic underestimation by DFT-B3LYP//IR4 can be found when compared to G3XMP2//IR4. The DFT $\Delta_r H_{298K}^\circ$ (IR5) are also in close agreement with previous calculations, e.g., −63.2 kJ/mol from B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p)[48] *versus* −61.9 kJ/mol from the present B3LYP/6-311++G(3df,3pd)/6-31G(2df,p) calculation, both being lower than −46.2 kJ/mol from G3XMP2. Increasing size of basis set for DFT-B3LYP calculations improves its agreement with G3XMP2 only slightly, e.g., $\Delta_f H_{298K}^\circ$ (Octa-CDD) = −125.5, −139.4, and −184.5 kJ/mol from B3LYP/6-31G(2df,p), B3LYP/6-311++G(3df,3pd), and G3XMP2 using IR4. On the other hand, agreement between G3XMP2 and B3LYP is improved significantly to within 16 kJ/mol when IR5 is used, e.g., $\Delta_f H_{298K}^\circ$ (Octa-CDD) = −170.0 and −185.6 kJ/mol from B3LYP/6-311++G(3df,3pd) and G3XMP2, respectively. The values at the B3LYP/6-311++G(3df,3pd)//IR5 level are listed in Table 5.

Enthalpies of formation have been determined by bomb calorimetry for 1-Mono-CDD (−88.3 ± 4.6 kJ/mol[30]), 2-Mono-CDD (−74.1 ± 3.3[31] or −90.7 ± 3.8 kJ/mol redetermined and preferred by the same research group[32]), and 2,3-Di-CDD (−111.9 ± 6.9 kJ/mol[33]), being lower systematically by 13−16 kJ/mol than the G3XMP2//IR5 predictions of −72.9, −77.6, and −96.4, respectively, while the relative stability between two Mono-CDDs is in accordance within the experimental and

TABLE 5: Enthalpies of Formation at 298 K from G3XMP2 Atomization Energies (//AR) and Isodesmic Reactions (//IR4 and //IR5) (All in kJ/mol)[a]

	G3XMP2			DFT
PCDDs	//AR	//IR4	//IR5	//IR5
0-	−68.3	−50.1	**−50.1**	−50.1
Mono-CDD				
1-	−94.7	−72.9	**−72.9**	−69.1
2-	−99.5	−77.6	**−77.6**	−76.4
Di-CDD				
1,2-	−117.7	−92.1	**−91.9**	−87.9
1,3-	−122.3	−96.7	**−95.5**	−91.7
1,4-	−118.1	−92.5	**−94.8**	−88.0
1,6-	−119.5	−93.9	**−93.9**	−87.5
1,7-	−124.3	−98.7	**−98.7**	−94.8
1,8-	−124.0	−98.4	**−98.4**	−94.6
1,9-	−118.8	−93.2	**−93.2**	−86.2
2,3-	−122.2	−96.6	**−96.4**	−95.2
2,7-	−128.9	−103.3	**−103.3**	−102.4
2,8-	−129.0	−103.4	**−103.4**	−102.2
Tri-CDD				
1,2,3-	−138.4	−109.1	**−111.1**	−107.3
1,2,4-	−139.3	−110.0	**−109.9**	−102.9
1,2,6-	−142.2	−112.9	**−112.7**	−105.9
1,2,7-	−146.9	−117.6	**−117.4**	−113.2
1,2,8-	−146.7	−117.4	**−117.2**	−112.8
1,2,9-	−141.4	−112.1	**−111.9**	−104.6
1,3,6-	−146.5	−117.2	**−116.0**	−109.3
1,3,7-	−151.4	−122.1	**−120.9**	−116.8
1,3,8-	−151.2	−121.9	**−120.7**	−116.5
1,3,9-	−146.2	−116.9	**−115.7**	−108.4
1,4,6-	−141.9	−112.6	**−114.9**	−104.7
1,4,7-	−146.8	−117.5	**−119.8**	−112.9
2,3,6-	−146.2	−116.9	**−116.7**	−112.9
2,3,7-	−151.1	−121.8	**−121.6**	−120.3
Tetra-CDD				
1,2,3,4-	−153.4	−120.4	**−120.7**	−13.9
1,2,3,6-	−162.3	−129.3	**−131.3**	−124.7
1,2,3,7-	−167.1	−134.1	**−136.1**	−132.0
1,2,3,8-	−167.0	−134.0	**−136.0**	−131.7
1,2,3,9-	−162.1	−129.1	**−131.1**	−123.6
1,2,4,6-	−162.8	−129.8	**−129.7**	−119.3
1,2,4,7-	−167.6	−134.5	**−134.5**	−127.4
1,2,4,8-	−167.6	−134.6	**−134.5**	−127.3
1,2,4,9-	−162.7	−129.7	**−129.6**	−119.1
1,2,6,7-	−164.4	−131.4	**−131.0**	−123.9
1,2,6,8-	−168.7	−135.7	**−134.3**	−127.2
1,2,6,9-	−164.2	−131.2	**−133.5**	−122.6
1,2,7,8-	−168.5	−135.5	**−135.1**	−130.8
1,2,7,9-	−168.5	−135.5	**−134.1**	−126.3
1,2,8,9-	−163.8	−130.8	**−130.4**	−122.4
1,3,6,8-	−172.3	−140.2	**−136.9**	−130.6
1,3,6,9-	−168.6	−135.6	**−136.7**	−126.1
1,3,7,8-	−173.0	−140.0	**−138.6**	−134.4
1,3,7,9-	−173.0	−140.0	**−137.6**	−129.9
1,4,6,9-	−164.1	−131.1	**−135.7**	−121.4
1,4,7,8-	−168.6	−135.6	**−137.9**	−130.6
2,3,7,8-	−172.8	−139.8	**−139.4**	−138.2
Penta-CDD				
1,2,3,4,6-	−176.7	−140.0	**−141.5**	−130.0
1,2,3,4,7-	−181.5	−144.8	**−146.3**	−138.1
1,2,3,6,7-	−184.5	−147.7	**−152.1**	−142.4
1,2,3,6,8-	−188.6	−151.9	**−152.7**	−145.6
1,2,3,6,9-	−184.2	−147.4	**−151.8**	−141.1
1,2,3,7,8-	−188.5	−151.7	**−153.6**	−149.4
1,2,3,7,9-	−188.5	−151.7	**−152.6**	−144.8
1,2,3,8,9-	−184.2	−147.4	**−149.3**	−141.2
1,2,4,6,7-	−184.9	−148.2	**−147.9**	−136.9
1,2,4,6,8-	−189.2	−152.5	**−151.2**	−140.2
1,2,4,6,9-	−184.8	−148.1	**−150.3**	−135.7
1,2,4,7,8-	−187.4	−150.7	**−150.4**	−144.7
1,2,4,7,9-	−189.2	−152.5	**−151.2**	−140.1
1,2,4,8,9-	−184.8	−148.1	**−147.8**	−136.6
Hexa-CDD				
1,2,3,4,6,7-	−198.6	−158.2	**−158.5**	−147.4
1,2,3,4,6,8-	−202.8	−162.4	**−161.7**	−150.6
1,2,3,4,6,9-	−198.5	−158.2	**−160.9**	−146.2
1,2,3,4,7,8-	−202.7	−162.3	**−162.6**	−155.2
1,2,3,6,7,8-	−203.8	−163.4	**−167.4**	−160.4
1,2,3,6,7,9-	−204.5	−164.8	**−166.0**	−154.9
1,2,3,6,8,9-	−204.5	−164.8	**−166.0**	−154.8
1,2,3,7,8,9-	−203.9	−163.5	**−167.5**	−159.5
1,2,4,6,7,9-	−205.1	−164.8	**−164.5**	−149.4
1,2,4,6,8,9-	−204.9	−164.5	**−164.3**	−149.3
Hepta-CDD				
1,2,3,4,6,7,8-	−218.1	−174.0	**−176.5**	−165.3
1,2,3,4,6,7,9-	−218.9	−174.7	**−175.2**	−159.8
Octa-CDD				
1,2,3,4,6,7,8,9-	−232.4	−184.5	**−185.6**	−170.0

[a] DFT calculations are based on B3LYP/6-311++G(3df,3pd) electronic energies and B3LYP/6-31G(2df,p) ZPE corrections.

theoretical uncertainties. At the G3XMP2/IR5 level, the lowering of enthalpy of formation from DD to Mono-CDD is 22.8 and 27.5 kJ/mol for 1- and 2-Mono-CDDs, respectively, being similar to those changes of 22.5 and 29.2 kJ/mol from phenol to 6- and 5-C_6H_4ClOH, respectively. In Shaub's estimation of enthalpies of formation for PCDD/Fs using the group additivity method,[34] the primary Cl-substitution effects were estimated from the differences between phenol and chlorophenols. However, this would lead to low substitution effects especially for α-positions because of the hydrogen bond in 2-Mono-ClPh; thereafter, their final results tend to be low, e.g., the value of −407 kJ/mol for Octa-CDD by Shaub is greatly lower than our G3XMP2//IR5 prediction of −185.6 kJ/mol.

$\Delta_f H_{298K}^\circ$ (2,3,7,8-Tetra-CDD) = −164.6 kJ/mol[33] has also been estimated as $\Delta_f H_{298K}^\circ$ (2,3-Di-CDD, −111.9 ± 6.9) + [$\Delta_f H_{298K}^\circ$ (2,3-Di-CDD) − $\Delta_f H_{298K}^\circ$ (DD, −59.2)]. The value can be adjusted to −173.7 kJ/mol with the new experimental value of −50.1 kJ/mol for DD. Both are significantly lower than the G3XMP2//R5 value of −139.4 kJ/mol, even though $\Delta_f H_{298K}^\circ$ (2,3,7,8-Tetra-CDD) − $\Delta_f H_{298K}^\circ$ (2,3-Di-CDD) ≈ $\Delta_f H_{298K}^\circ$ (2,3-Di-CDD) − $\Delta_f H_{298K}^\circ$ (CDD) is valid at the G3XMP2 level.

The relative stability of PCDD isomers can be rationalized by the so-called positional interactions:[34] the primary effects (χ_α and χ_β) of replacing H-atom with Cl-atom, and the secondary effects of Cl−Cl interaction, which can be detailed as intra-benzene-ring ones as 1−2, 1−3, 1−4, and 2−3, and inter-ring ones as 1−6, 1−7, 1−9, 2−7, 2−8, and alike. The three- and four-body Cl−Cl interactions considered in previous group additivity estimation[35,42] are not considered here. The enthalpies of formation are then expressed as the summation of these terms, e.g.:

$$\begin{aligned}\Delta_f H_{298K}^\circ \text{ (1,2,3,6,7,9-Hexa-CDD)} &= h_0 + 3\chi_\alpha + 3\chi_\beta + \\ &2\mathrm{ClCl}_{1,2} + 2\mathrm{ClCl}_{1,3} + \mathrm{ClCl}_{1,4} + \mathrm{ClCl}_{2,3} + \mathrm{ClCl}_{1,6} + \\ &3\mathrm{ClCl}_{1,7} + 2\mathrm{ClCl}_{1,8} + \mathrm{ClCl}_{1,9} + \mathrm{ClCl}_{2,7} + \mathrm{ClCl}_{2,8}\end{aligned}$$

where $\mathrm{ClCl}_{m,n}$ represents the Cl−Cl interactions at sites m and n. The parameters obtained from the regression analysis of the enthalpies of formation are listed in Table 6. As expected, the parameters obtained from atomization energy and isodesmic reaction schemes differ only on the primary effect of substitution, e.g., −25.56 kJ/mol of χ_α from G3XMP2//AR to −21.85 kJ/mol from G3XMP2//IR4, while the $\mathrm{ClCl}_{m,n}$ interactions

TABLE 6: The Positional Interactions for PCDDs (All in kJ/mol)[a]

	G3XMP2 //AR	G3XMP2 //IR4	G3MP2 //IR4	DFT//B1 //IR4	DFT//B2 //IR4	G3XMP2 //IR5	DFT//B2 //IR5
h_0	−70.86	−52.72	−52.63	−51.70	−51.07	−52.34	−51.42
χ_α	−25.56	−21.85	−21.89	−19.47	−20.25	−22.09	−20.29
χ_β	−27.91	−24.19	−24.23	−23.00	−23.94	−24.15	−23.12
$ClCl_{12}$	6.22	6.22	6.34	11.81	11.09	5.98	6.26
$ClCl_{13}$	1.76	1.77	1.83	2.84	2.59	2.76	2.72
$ClCl_{14}$	2.41	2.42	2.33	3.21	3.09	1.73	2.69
$ClCl_{23}$	5.75	5.75	5.86	10.76	9.84	3.86	2.88
$ClCl_{16}$	0.93	0.93	1.04	1.69	1.62	0.36	1.35
$ClCl_{17}$	0.21	0.21	0.17	0.32	0.24	0.10	0.20
$ClCl_{18}$	0.38	0.38	0.33	0.54	0.50	0.53	0.51
$ClCl_{19}$	1.27	1.26	1.39	3.13	2.68	1.24	2.43
$ClCl_{27}$	−0.37	−0.37	−0.37	−0.53	−0.60	0.22	−0.54
$ClCl_{28}$	−0.29	−0.30	−0.30	−0.43	−0.52	−0.27	−0.44

[a] Electronic energies: DFT//B1 = B3LYP/6-31G(2df,p), DFT//B2 = B3LYP/6-311++G(3df,3pd).

remain unchanged from G3XMP2//AR to G3XMP2//IR4. The regression shows that the *ortho*-ClCl interactions ($ClCl_{12}$ and $ClCl_{23}$) are much higher than the other ones, while the inter-benzene-ring interactions are of minor importance except those between sites 1 and 9 or 6. From the positional parameters, the stable isomers tend to have more substitutions on β-sites, to distribute Cl-substitution on different rings, and to avoid neighboring substitutions. For example of Tetra-CDDs, the most stable isomer is 2,3,7,8-Tetra-CDD. The regression also shows that the B3LYP method with the less balanced isodesmic reactions IR4 overpredict significantly the *ortho*-ClCl interactions than G3XMP2; while the differences between G3XMP2 and B3LYP with the well-balanced IR5 are relatively small. This would explain the overestimation of the DFT method on the enthalpies of formation of PCDDs and ClBzs using IR4.[12]

IV. Conclusion

The enthalpies of formation have been predicted at the G3X level for chlorinated benzenes and phenols and at the G3XMP2 level for dibenzo-*p*-dioxins using isodesmic reactions. The results from different isodesmic reactions agree closely at the G3X(MP2) level, rendering their reliability. The best estimations are listed boldface in Tables 3−5. The G3XMP2 results for PCDDs are considerably different from previous experiments and DFT calculations, especially for highly chlorinated compounds. The failure of DFT using the less balanced isodesmic reaction is due largely to the overestimated *ortho*-Cl−Cl repulsive interactions.

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Supporting Information Available: The rotational constants and vibrational frequencies of PCDDs at the B3LYP/6-31G-(2df,p) level. The electronic energies and the enthalpies of formation derived using isodesmic reactions IR4 at the B3LYP level with the 6-31G(2df,p) and 6-311++G(3df,3pd) basis sets. The file is in Microsoft Excel format. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ramamoorthy, S.; Ramamoorthy, S. *Chlorinated Organic Compounds in the Environment: Regulatory and Monitoring Assessment*; CRC Press LLC: Boca Raton, 1997.

(2) Eisler, R. *Handbook of Chemical Risk Assessment: Health Hazards to Humans, Plants, and Animals*; CRC Press LLC: Boca Raton, 2000; Vol. 2. Organics.

(3) Shaub, W. M.; Tsang, W. *Environ. Sci. Technol.* **1983**, *17*, 721.

(4) Tuppurainen, K.; Asikainen, A.; Ruokojarvi, P.; Ruuskanen, J. *Acc. Chem. Res.* **2003**, *36*, 652.

(5) Froese, K. L.; Hutzinger, O. *Environ. Sci. Technol.* **1996**, *30*, 1009.

(6) Froese, K. L.; Hutzinger, O. *Environ. Sci. Technol.* **1996**, *30*, 998.

(7) Kanters, M. J.; Van Nispen, R.; Louw, R.; Mulder, P. *Environ. Sci. Technol.* **1996**, *30*, 2121.

(8) Wiater-Protas, I.; Louw, R. *Eur. J. Org. Chem.* **2001**, 3945.

(9) Tan, P.; Hurtado, I.; Neuschutz, D.; Eriksson, G. *Environ. Sci. Technol.* **2001**, *35*, 1867.

(10) Okamoto, Y.; Tomonari, M. *J. Phys. Chem. A* **1999**, *103*, 7686.

(11) Burcat, A.; Khachatryan, L.; Dellinger, B. L. *J. Phys. Chem. Ref. Data* **2003**, *32*, 443.

(12) Zhu, L.; Bozzelli, J. W. *J. Phys. Chem. Ref. Data* **2003**, *32*, 1713.

(13) Murabayashi, M.; Moesta, H. *Environ. Sci. Technol.* **1992**, *26*, 797.

(14) Khachatryan, L.; Asatryan, R.; Dellinger, B. L. *Chemosphere* **2003**, *52*, 695.

(15) Khachatryan, L.; Burcat, A.; Dellinger, B. L. *Combust. Flame* **2003**, *132*, 406.

(16) Mulholland, J. A.; Akki, U.; Yang, Y.; Ryu, J.-Y. *Chemosphere* **2001**, *42*, 719.

(17) Wiesenhahn, D. F.; Li, C. P.; Penner, S. S. *Energy* **1988**, *13*, 225.

(18) Altwicker, E. R.; Konduri, R. K. N. V.; Milligan, M. S. *Chemosphere* **1990**, *20*, 1935.

(19) Hubbard, W. N.; Knowlton, J. W.; Huffman, H. M. *J. Phys. Chem.* **1954**, *58*, 396.

(20) Manion, J. A. *J. Phys. Chem. Ref. Data* **2002**, *31*, 123.

(21) Pimenova, S. M.; Melkhanova, S. V.; Kolesov, V. P.; Demyanov, P. I.; Fedotov, A. N.; Vorobieva, V. P. *J. Chem. Thermodyn.* **2002**, *34*, 385.

(22) Mader, B. T.; Pankow, J. F. *Atmos. Environ.* **2003**, *37*, 3103.

(23) Platonov, V. A.; Simulin, Y. N. *Russ. J. Phys. Chem.* **1983**, *57*, 840.

(24) Platonov, V. A.; Simulin, Y. N. *Russ. J. Phys. Chem.* **1984**, *58*, 1630.

(25) Platonov, V. A.; Simulin, Y. N. *Russ. J. Phys. Chem.* **1985**, *59*, 179.

(26) Platonov, V. A.; Simulin, Y. N.; Rozenberg, M. M. *Russ. J. Phys. Chem.* **1985**, *59*, 814.

(27) Yan, H.; Gu, J.; An, X. W.; Hu, R. *Huaxue Xuebao* **1987**, *45*, 1184.

(28) Ribeiro da Silva, M. A. V.; Ferrao, M. L. C. C. H.; Fang, J. *J. Chem. Thermodyn.* **1994**, *26*, 839.

(29) Lukyanova, V. A.; Kolesov, V. P.; Avramenko, N. V.; Vorobiera, V. P.; Golovkov, V. F. *Russ. J. Phys. Chem. (Engl. Transl.)* **1997**, *71*, 338.

(30) Papina, T. S.; Lukyanova, V. A.; Kolesov, V. P.; Golovkov, V. F.; Chernov, C. A.; Vorobiera, V. P. *Zh. Fiz. Khim.* **1998**, *72*, 1.

(31) Papina, T. S.; Kolesov, V. P.; Vorobiera, V. P.; Folovkov, V. F. *J. Chem. Thermodyn.* **1996**, *28*, 307.

(32) Lukyanova, V. A.; Papina, T. S.; Kolesov, V. P.; Fedotov, A. N.; Dem'yanov, P. I.; Avramenko, N. V. *J. Chem. Thermodyn.* **2003**, *35*, 1507.

(33) Papina, T. S.; Kolesov, V. P.; Lukyanova, V. A.; Golovkov, V. F.; Chernov, C. A.; Vorobiera, V. P. *J. Chem. Thermodyn.* **1998**, *30*, 431.

(34) Shaub, W. M. *Thermochim. Acta* **1982**, *55*, 59.

(35) Thompson, D. *Chemosphere* **1994**, *29*, 2583.

(36) Thompson, D. *Thermochim. Acta* **1995**, *261*, 7.

(37) Shaub, W. M. *Thermochim. Acta* **1982**, *58*, 11.

(38) Saito, N.; Fuwa, A. *Chemosphere* **2000**, *40*, 131.

(39) Koester, C. J.; Hites, R. A. *Chemospherre* **1988**, *17*, 2355.

(40) Unsworth, J.-F.; Dorans, H. *Chemosphere* **1993**, *27*, 351.

(41) Leon, L. A.; Notario, R.; Quijano, J.; Sanchez, C. *J. Phys. Chem.* A **2002**, *106*, 6618.

(42) Dorofeeva, O. V.; Iorish, V. S.; Moiseeva, N. F. *J. Chem. Eng. Data* **1999**, *44*, 516.

(43) Lee, J. E.; Choi, W.; Mhin, B. J. *J. Phys. Chem. A* **2003**, *107*, 2693.

(44) Dorofeeva, O. V.; Yungman, V. S. *J. Phys. Chem. A* **2003**, *107*, 2848.

(45) Wang, Z.-Y.; Zhai, Z.-C.; Wang, L.-S.; Chen, J.-L.; Kikichi, O.; Watanabe, T. *J. Mol. Struct. (THEOCHEM)* **2004**, *672*, 97.

(46) Zhai, Z.-C.; Wang, Z.-Y. *J. Mol. Struct. (THEOCHEM)* **2005**, *724*, 221.

(47) Thompson, D.; Ewan, B. C. *J. Phys. Chem. A* **2007**, *111*, 5043.

(48) Dorofeeva, O. V.; Vishnevskiy, Y. V.; Moiseeva, N. F. *Struct. Chem.* **2006**, *17*, 383.

(49) Janoschek, R.; Fabian, W. M. F. *J. Mol. Struct.* **2003**, *661*−*662*, 635.

(50) Gomes, J. R. B.; Ribeiro da Silva, M. A. V. *J. Phys. Chem. A* **2003**, *107*, 869.

(51) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(52) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.

(53) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 108.

(54) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.05; Gaussian, Inc.: Wallingford, CT, 2004.

(55) Bylaska, E. J.; de Jong, W. A.; Kowalski, K.; Straatsma, T. P.; Valiev, M.; Wang, D.; Apra, E.; Windus, T. L.; Hirata, S.; Hackler, M. T.; Zhao, Y.; Fan, P.-D.; Harrison, R. J.; Dupuis, M.; Smith, D. M. A.; Nieplocha, J.; Tipparaju, V.; Krishnan, M.; Auer, A. A.; Nooijen, M.; Brown, E.; Cisneros, G.; Fann, G. I.; Fruchtl, H.; Garza, J.; Hirao, K.; Kendall, R.; Nichols, J. A.; Tsemekhman, K.; Wolinski, K.; Anchell, J.; Bernholdt, D.; Borowski, P.; Clark, T.; Clerc, D.; Dachsel, H.; Deegan, M.; Dyall, K.; Elwood, D.; Glendening, E.; Gutowski, M.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; Kobayashi, R.; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; Nakajima, T.; Niu, S.; Pollack, L.; Rosing, M.; Sandrone, G.; Stave, M.; Taylor, H.; Thomas, G.; van Lenthe, J.; Wong, A.; Zhang, Z. *NWChem, A Computational Chemistry Package for Parallel Computers*, version 5.0; Pacific Northwest National Laboratory: Richland, WA, 2006.

(56) Kendall, R. A.; Apra, E.; Bernholdt, D. E.; Bylaska, E. J.; Dupuis, M.; Fann, G. I.; Harrison, R. J.; Ju, J.; Nichols, J. A.; Nieplocha, J.; Straatsma, T. P.; Windus, T. L.; Wong, A. T. *Comput. Phys. Commun.* **2000**, *128*, 260.

(57) Nicolaides, L. A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460.

(58) Cottrell, T. L. *Trans. Faraday Soc.* **1948**, 716.

(59) Sinke, G. C.; Stull, D. R. *J. Phys. Chem.* **1958**, *62*, 397.

(60) Stull, D. R.; Westrum, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley and Son: New York, 1969.

(61) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(62) Pedley, J. B. *Thermochemical Data and Structures of Organic and Organometallic Compounds*; Texas 1994; Vol. 1.

(63) Pedley, J. B.; Naylor, R. O.; Kirby, S. P. *Thermodynamic Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London 1986.

(64) Rahac, V.; Ruzicka, V.; Ruzicka, K.; Polednicek, M.; Aim, K.; Jose, J.; Zabransky, M. *Fluid Phase Equilib.* **1999**, *157*, 121.

(65) Sabbah, R.; An, X. W. *Thermochim. Acta* **1991**, *179*, 81.

(66) Sears, G. W.; Hopke, E. R. *J. Am. Chem. Soc.* **1949**, *71*, 1632.

(67) Verevkin, S. P.; Emel'yanenko, V. N.; Klamt, A. *J. Chem. Eng. Data* **2007**, *52*, 499.

(68) Burcat, A.; Ruscic, B. Ideal Gas Thermochemical Database with Updates from Active Thermochemical Tables <ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics/BURCAT.THR>.

(69) Han, J.; Deming, R. L.; Tao, F.-M. *J. Phys. Chem. A* **2004**, *108*, 7736.

(70) *Neutral Thermochemical Data*; Afeefy, H. Y., Liebman, J. F., Stein, S. E., Eds.; Gaitherburg, MD (http://webbook.nist.gov), 2003.

(71) Fokin, A. V.; Vorobieva, N. P.; Raevskii, N. I.; Vborison, Y. A.; Kolomiets, A. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 2544.