

Thermochemical Properties, $\Delta_f H^\circ(298.15\text{ K})$, $S^\circ(298.15\text{ K})$, and $C_p^\circ(T)$, of 1,4-Dioxin, 2,3-Benzodioxin, Furan, 2,3-Benzofuran, and Twelve Monochloro and Dichloro Dibenzo-*p*-dioxins and Dibenzofurans

Li Zhu and Joseph W. Bozzelli^{a)}

Department of Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, New Jersey 07102

(Received 24 June 2002; revised manuscript received 3 December 2002; accepted 17 February 2003; published 24 November 2003)

Values for $\Delta_f H^\circ(298.15\text{ K})$, $S^\circ(298.15\text{ K})$, and $C_p^\circ(T)$ ($5 \leq T/\text{K} \leq 6000$) are computed by density functional B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p) calculation methods for 12 monochloro and dichloro dibenzo-*p*-dioxins and dibenzofurans: 1-chloro dibenzo-*p*-dioxin, 2-chloro dibenzo-*p*-dioxin, 1,6-dichloro dibenzo-*p*-dioxin, 1,8-dichloro dibenzo-*p*-dioxin, 1,9-dichloro dibenzo-*p*-dioxin, 2,8-dichloro dibenzo-*p*-dioxin, 3-chloro dibenzofuran, 4-chloro dibenzofuran, 1,6-dichloro dibenzofuran, 3,6-dichloro dibenzofuran, 3,7-dichloro dibenzofuran, and 4,6-dichloro dibenzofuran. Molecular structures and vibration frequencies are determined at the B3LYP/6-31G(d,p) level of theory. Isodesmic reactions are utilized at each calculation level to determine the enthalpy of formation of each species. Contributions to the entropy and the heat capacity from translation, vibration, and external rotations are calculated using the rigid-rotor-harmonic-oscillator approximation based on the B3LYP/6-31G(d,p) structures. The enthalpies of formation for 1,4-dioxin, furan, 2,3-benzodioxin, 2,3-benzofuran, dibenzo-*p*-dioxin, and dibenzofuran are also calculated. Thermochemical properties of two composite central atom groups and four interaction groups are derived for use in a group additivity scheme to calculate these thermochemical properties of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. © 2003 American Institute of Physics.
[DOI: 10.1063/1.1571057]

Key words: B3LYP; chlorinated compounds; density functional calculation; dioxin; enthalpy; entropy; furan; gas-phase; heat capacity; isodesmic reactions; thermochemical properties.

Contents

1. Introduction.....	1714
2. Methodology.....	1715
2.1. $\Delta_f H^\circ(298.15\text{ K})$	1716
2.2. $S^\circ(298.15\text{ K})$ and $C_p^\circ(T)$ ($5 \leq T/\text{K} \leq 6000$)...	1717
3. Results and Discussion.....	1718
3.1. Geometries.....	1718
3.2. $\Delta_f H^\circ(298.15\text{ K})$	1718
3.3. $S^\circ(298.15\text{ K})$ and $C_p^\circ(T)$ ($5 \leq T/\text{K} \leq 6000$)...	1721
3.4. Group Values.....	1721
3.4.1. DD and DF.....	1723
3.4.2. ORT/CI/DD, ORT/CI/DF, MET/CI/	
DD, MET/CI/DF.....	1723
3.4.3. Comparison of Results from Group	
Additivity with Recommended	
Calculated Data.....	1723
4. Summary.....	1726
5. Acknowledgments.....	1726

6. References.....	1726
7. Appendix: List of Supplemental Materials.....	1728

List of Tables

1. Abbreviations and given numbers of the species and groups studied in this work.....	1716
2. Calculated total energies at 298.15 K.....	1718
3. Calculated $\Delta_{\text{rxn}} H^\circ(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$ of isodesmic reactions.....	1719
4. Enthalpies of formation for reference species (and literature citations).....	1720
5. Comparison of calculated $\Delta_f H^\circ(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$ for selected chlorobenzenes and chlorophenols with literature data.....	1720
6. Calculated $\Delta_f H^\circ(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$ using isodesmic reactions.....	1721
7. Ideal gas phase enthalpies of formation: $\Delta_f H^\circ(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	1722
8. Ideal gas phase entropies: $S^\circ(298.15\text{ K})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	1723
9. Ideal gas phase heat capacities: $C_p^\circ(T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	1724
10. Group values for PCDD/F.....	1725

^{a)}Author to whom correspondence should be addressed; electronic mail: bozzelli@njit.edu
© 2003 American Institute of Physics.

11. Comparison of thermochemical properties from group additivity with the recommended values. 1725
12. Comparison of thermochemical properties of 23DCDD and 2378TCDD from group additivity with literature values. 1726

List of Figures

1. PCDD/F formation from chlorophenols 1715

1. Introduction

Multisubstituted aromatic or polyaromatic molecules such as chlorinated dioxins and furans are often observed in the effluent streams from combustors or incinerators. These species are also found in a wide number of environmentally sensitive reservoirs including lakes, streams, and airborne particulates. These compounds are thought to be hazardous and toxic and, as a consequence, are undesirable products of incomplete combustion. The global distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans has been studied by Wagrowski and Hites.¹

The formation or presence of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in combustion processes containing chlorinated organic materials has been frequently studied.^{2–18} Fly ash, acting as a heterogeneous catalyst, plays a crucial role in the formation of PCDD/Fs in the afterburning zone of municipal waste incinerators. Precursors for PCDD/Fs are considered to be aromatic structures like toluene or phenol.¹⁷

The motivation for this study on the PCDD/Fs is the need for the thermochemical data as a function of temperature for use in the kinetic modeling of the pyrolysis and the oxidation of chlorinated aromatic species (Fig. 1). Important products detected in the pyrolysis and oxidation of chlorinated phenols and anisole include dibenzo-*p*-dioxin, 1-chlorodibenzo-*p*-dioxin (1CDD), 1,9-dichlorodibenzo-*p*-dioxin (19DCDD), dibenzofuran, 4-chlorodibenzofuran (4CDF), and 4,6-dichlorodibenzofuran (46DCDF).¹⁹

Three fundamental thermochemical properties— $\Delta_f H^\circ(298.15\text{ K})$, $S^\circ(298.15\text{ K})$, $C_p^\circ(T)$ —provide a basis for understanding and predicting the formation and degradation of PCDD/Fs.

There are a number of studies on the estimation of thermochemical properties of (chlorinated or nonchlorinated) dibenzo-*p*-dioxins and dibenzofurans. Most of them use group additivity (GA) methods, such as Shaub,^{21,22} Wu *et al.*,²³ Thompson,²⁴ and Dorofeeva and Gurvich.²⁵ There are also a few results from semiempirical calculations: the enthalpy of formation for 2,3,7,8-TCDD by Fokin *et al.*,²⁶ and the enthalpies of formation for tetra, penta, hexa, hepta, and octa-chlorinated dibenzo-*p*-dioxins and dibenzofurans by Koester and Hites,²⁷ both of which used the modified neglect of diatomic differential overlap (MNDO) method in Molecular Orbital PACKage (MOPAC). Saito and Fuwa²⁸ have utilized the Parametric Method number 3 (PM3) method for the

enthalpies, entropies, and heat capacities of chlorinated benzenes and phenols, PCDD/Fs, PCBs, and Co-PCB (coplanar-PCB).

The enthalpy of formation of gas-phase dibenzofuran has been reviewed by Cox and Pilcher²⁹ ($83.3 \pm 5.0\text{ kJ}\cdot\text{mol}^{-1}$) and by Pedley *et al.*³⁰ ($83.4 \pm 4.7\text{ kJ}\cdot\text{mol}^{-1}$), while two experimental values have been determined by Sabbah³¹ ($47.3 \pm 4.8\text{ kJ}\cdot\text{mol}^{-1}$) and Chirico *et al.*³² ($55.3 \pm 0.3\text{ kJ}\cdot\text{mol}^{-1}$). The value of Chirico *et al.*³² is supported by Thompson²⁴ and Dorofeeva *et al.*³³ Recently, Notario *et al.*³⁴ obtained an average value of $51.9 \pm 6.7\text{ kJ}\cdot\text{mol}^{-1}$ from isodesmic reactions and separately by an atomization reaction calculated at the G3(MP2)//B3LYP level and corrected by bond additivity with ring correction.

There is less experimental data on the enthalpy of formation for dibenzo-*p*-dioxin. Shaub²¹ estimated a value by first obtaining $\Delta_f H^\circ(298.15\text{ K})$ (dibenzo-*p*-dioxin) = $-62.8\text{ kJ}\cdot\text{mol}^{-1}$ from enthalpy comparisons of 9,10-dihydroanthracene and dibenzopyran. Next he compared the enthalpy of benzene, phenol, and varied chlorobenzenes and chlorophenols. Lastly, he then estimated the enthalpies of formation for various chlorinated dioxins, using observed trends and differences. A detailed examination for the entropy of dioxin and some chlorinated dioxins based on adjustment of vibrational frequencies, moments of inertia, and other properties of benzene, chlorinated benzenes, and anthracenes, was also carried out by Shaub.²¹

Thompson²⁴ estimated $\Delta_f H^\circ(298.15\text{ K})$ = $-55.0\text{ kJ}\cdot\text{mol}^{-1}$ for dibenzo-*p*-dioxin from the observed trend in the enthalpies of formation of several series of cyclic species. In 1999, Kolesov *et al.*³⁵ published $\Delta_f H^\circ(298.15\text{ K})$ = $-59.2 \pm 4.4\text{ kJ}\cdot\text{mol}^{-1}$ for dibenzo-*p*-dioxin, based on a rotating-bomb calorimeter experiment; this value, $-59.2 \pm 3.8\text{ kJ}\cdot\text{mol}^{-1}$, was adopted by Dorofeeva *et al.*³³ In a recent article by Pimenova *et al.*,³⁶ coauthored with Kolesov, a redetermined value, $\Delta_f H^\circ(298.15\text{ K})$ = $-50.1 \pm 2.2\text{ kJ}\cdot\text{mol}^{-1}$, for dibenzo-*p*-dioxin was reported. Here they indicated that low purity caused the different results in their earlier experiments. We also calculate the $\Delta_f H^\circ(298.15\text{ K})$ of dibenzofuran and dibenzo-*p*-dioxin in this study as they are important species; a comparison of our calculated values with experimental data serves as a test of our working reaction calculation method. For PCDD/Fs, Thompson²⁴ evaluated the available data on chlorobenzenes, chlorophenols, and chlorohydroquinones. He recommended an additivity method where a value of $-29.5\text{ kJ}\cdot\text{mol}^{-1}$ is added for each chlorine substitution in dibenzo-*p*-dioxins or dibenzofurans. An additional correction of $+7.5\text{ kJ}\cdot\text{mol}^{-1}$ is applied for each ortho/Cl/Cl interaction, and $+2.5\text{ kJ}\cdot\text{mol}^{-1}$ correction for each meta/Cl/Cl interaction. Chlorination of one ring was considered to have no influence on the other ring.

Kolesov *et al.*³⁵ measured the enthalpies of formation of 1-chloro dibenzo-*p*-dioxin ($88.2 \pm 4.8\text{ kJ}\cdot\text{mol}^{-1}$), 2-chloro dibenzo-*p*-dioxin ($-74.1 \pm 3.3\text{ kJ}\cdot\text{mol}^{-1}$), and 2,3-dichloro dibenzo-*p*-dioxin ($-111.9 \pm 6.9\text{ kJ}\cdot\text{mol}^{-1}$), using a rotating-bomb calorimeter. Their results showed large differences

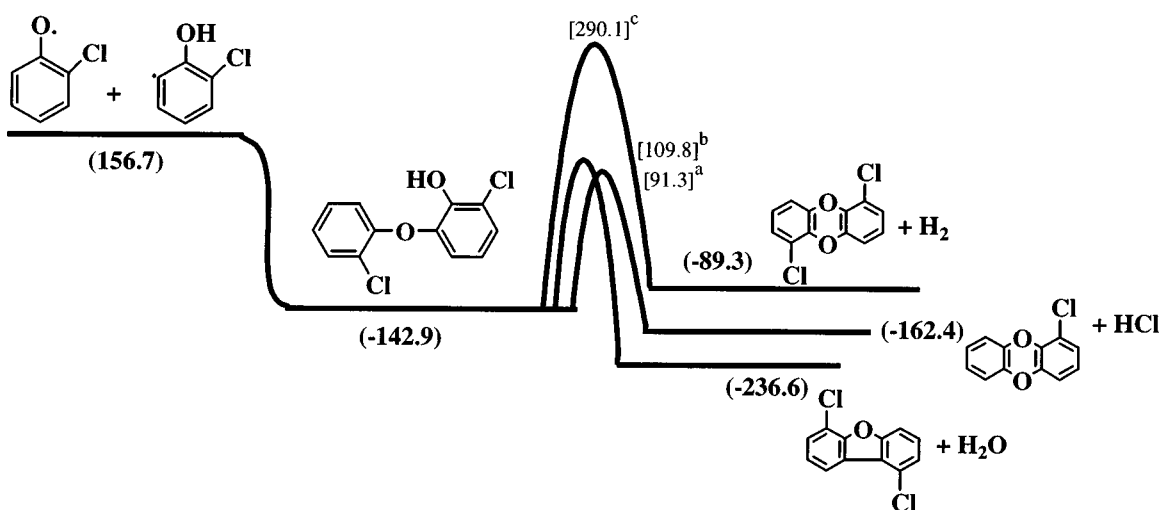


Fig. 1. PCDD/F Formation from chlorophenols ($\text{kJ}\cdot\text{mol}^{-1}$). (a) Estimated from calculation on *o,o'*-biphenol \rightarrow dibenzofuran + H_2O at B3LYP/6-31G(d,p) level. (b) Calculated at B3LYP/6-31G(d,p) level. (c) Estimated from Okamoto and Tomonari²⁰ at B3LYP/6-311++G(2d,2p)//B3LYP/6-31G(d',p').

with values of Shaub²² (-95.0 , -137.7 , and -204.0 $\text{kJ}\cdot\text{mol}^{-1}$) and close agreements with values of Thompson²⁴ (-84.5 , -84.5 , -106.5 $\text{kJ}\cdot\text{mol}^{-1}$), respectively. The effect of chlorination estimated from 1CDD on the enthalpy of formation by Kolesov *et al.*³⁵ is -29.0 $\text{kJ}\cdot\text{mol}^{-1}$, and the interaction between oxygen and chlorine is unclear; but is reported as less than 2 $\text{kJ}\cdot\text{mol}^{-1}$.

The geometry and vibration frequencies of 2,3,7,8-TCDD have been recently calculated by Liu *et al.*³⁷ at PM3, MP2/6-31G*, and B3LYP/6-311G* levels. The same authors also estimated the entropy and the heat capacity from 298 to 1500 K plus the energy differences between E_{HOMO} and E_{LUMO} .

The entropy of dibenzofuran, $S^\circ(298.15\text{ K}) = 374.4$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, was experimentally determined by Chirico *et al.*³² Dorofeeva *et al.*³³ estimated this value using statistical thermodynamics based on experimental and calculated vibrational frequencies, and their result, $S^\circ(298.15\text{ K}) = 375.9$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, is close to the value of Chirico *et al.*,³² within 1.5 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

For dibenzo-*p*-dioxin, Thompson²⁴ estimated $S^\circ(298.15\text{ K}) = 296.0$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ from Benson's group additivity using a "CHETAH³⁸ computer database" (with carbonyl group is used for $\text{C}_\text{B}/\text{O}$ group). He found this value was significantly different from the similar compound, dibenzofuran (see above), so he suggested use the value of Shaub²¹ (388.0 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) as more accurate. Dorofeeva *et al.*³³ calculated $S^\circ(298.15\text{ K}) = 396.5$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Thompson²⁴ suggested adding an entropy correction of 22.6 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for each chlorine substituted in place of a H atom. He suggested no interaction term for repulsive interaction between multiple Cl's for the entropies of chlorinated dibenzo-*p*-dioxins and dibenzofurans. A set of groups and a series of interaction groups were developed by Wu *et al.*²³ in 1993 to improve the accuracy of thermodynamic properties of multisubstituted aromatic compounds. Com-

parison of this group additivity estimation with literature values also shows good agreement.

Dorofeeva *et al.*³³ developed a more straightforward estimation method than Wu *et al.*,²³ involving ten groups for GA estimation of $\Delta_f H^\circ(298.15\text{ K})$, $S^\circ(298.15\text{ K})$, and $C_p^\circ(T)$ (300 – 1500 K) of 75 PCDDs and 135 PCDFs. They used experimental enthalpy of formation values from a few polychlorinated chlorobenzenes, as well as dibenzo-*p*-dioxin and dibenzofuran, in deriving the groups. They also assumed that (i) Cl/Cl interaction on the same ring of PCDD/F is the same as that in polychlorinated benzene, and (ii) chlorination on one side of benzo ring of PCDD/F has no influence on the other side.

This study estimates the fundamental thermochemical properties— $\Delta_f H^\circ(298.15\text{ K})$, $S^\circ(298.15\text{ K})$, and $C_p^\circ(T)$ —using density functional calculation methods for dibenzo-*p*-dioxin, dibenzofuran, and 12 monochlorinated or dichlorinated dibenzo-*p*-dioxins and dibenzofurans, 1CDD, 2CDD, 16DCDD, 18DCDD, 19DCDD, 28DCDD, 3CDF, 4CDF, 16DCDF, 36DCDF, 37DCDF, and 46DCDF (Table 1). The enthalpy of formation of each species is obtained at each calculation level using isodesmic working reactions, and the data are compared with available literature. We also use MOPAC6/PM3 to calculate $\Delta_f H^\circ(298.15\text{ K})$, $S^\circ(298.15\text{ K})$, and $C_p^\circ(T)$ of these species; these serve as reference data because a number of the early studies, noted above, used MOPAC6.

2. Methodology

All calculations are performed using the GAUSSIAN94³⁹ program suite. The structure of each species is fully optimized at density functional B3LYP/6-31G(d,p) level of theory. Harmonic vibration frequencies and zero-point vibrational energies (ZPVE) are computed at the same level. Then

TABLE I. Abbreviations and given numbers of the species and groups studied in this work

Species	Abbreviation	Number
1,4-Dioxin		1
2,3-Benzodioxin		2
Dibenzo- <i>p</i> -dioxin		3
1-Chloro dibenzo- <i>p</i> -dioxin	1CDD	4
2-Chloro dibenzo- <i>p</i> -dioxin	2CDD	5
1,6-Dichloro dibenzo- <i>p</i> -dioxin	16DCDD	6
1,8-Dichloro dibenzo- <i>p</i> -dioxin	18DCDD	7
1,9-Dichloro dibenzo- <i>p</i> -dioxin	19DCDD	8
2,8-Dichloro dibenzo- <i>p</i> -dioxin	28DCDD	9
Furan		10
2,3-Benzofuran		11
Dibenzofuran		12
3-Chloro dibenzofuran	3CDF	13
4-Chloro dibenzofuran	4CDF	14
1,6-Dichlorodibenzofuran	16DCDF	15
3,6-Dichlorodibenzofuran	36DCDF	16
3,7-Dichlorodibenzofuran	37DCDF	17
4,6-Dichlorodibenzofuran	46DCDF	18
Polychlorinated dibenzo- <i>p</i> -dioxins and dibenzofurans	PCDD/Fs	
Additivity groups		
Skeletons of dioxin, C ₄ O ₂ , no H's	DD	
Skeletons of furan, C ₄ O, no H's	DF	
<i>Ortho</i> interaction between Cl and dibenzo- <i>p</i> -dioxin structure	ORT/Cl/DD	
<i>Meta</i> interaction between Cl and dibenzo- <i>p</i> -dioxin structure	MET/Cl/DD	
<i>Ortho</i> interaction between Cl and dibenzofuran structure	ORT/Cl/DF	
<i>Meta</i> interaction between Cl and dibenzofuran structure	MET/Cl/DF	

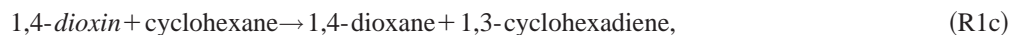
B3LYP/6-31G(d,p)-optimized geometrical parameters are used to obtain the total electronic energies in B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p) single-point calculations. Curtiss *et al.*⁴⁰ report that B3LYP/6-31g(d,p) provides a highly accurate structure for compounds with elements up to atomic number 10. Durant^{41,42} has compared density functional calculations BHandH and B3LYP with MP2 and Hartree–Fock methods for the geometry and vibration frequencies. He reported that these density functional methods provided an improved geometry and vibration frequencies, relative to MP2 at reduced computation expense. Petersson⁴³ recommended use of B3LYP or BLYP for the geometry and the vibrational frequencies in several of his CBS calculation methods. Wong and Radom⁴⁴ showed that the less expensive B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) procedure performs quite well for the calculation of barriers (transition states) of methyl radical addition to alkenes, with a mean absolute deviation of about 5.4 kJ·mol⁻¹ from experimental values.

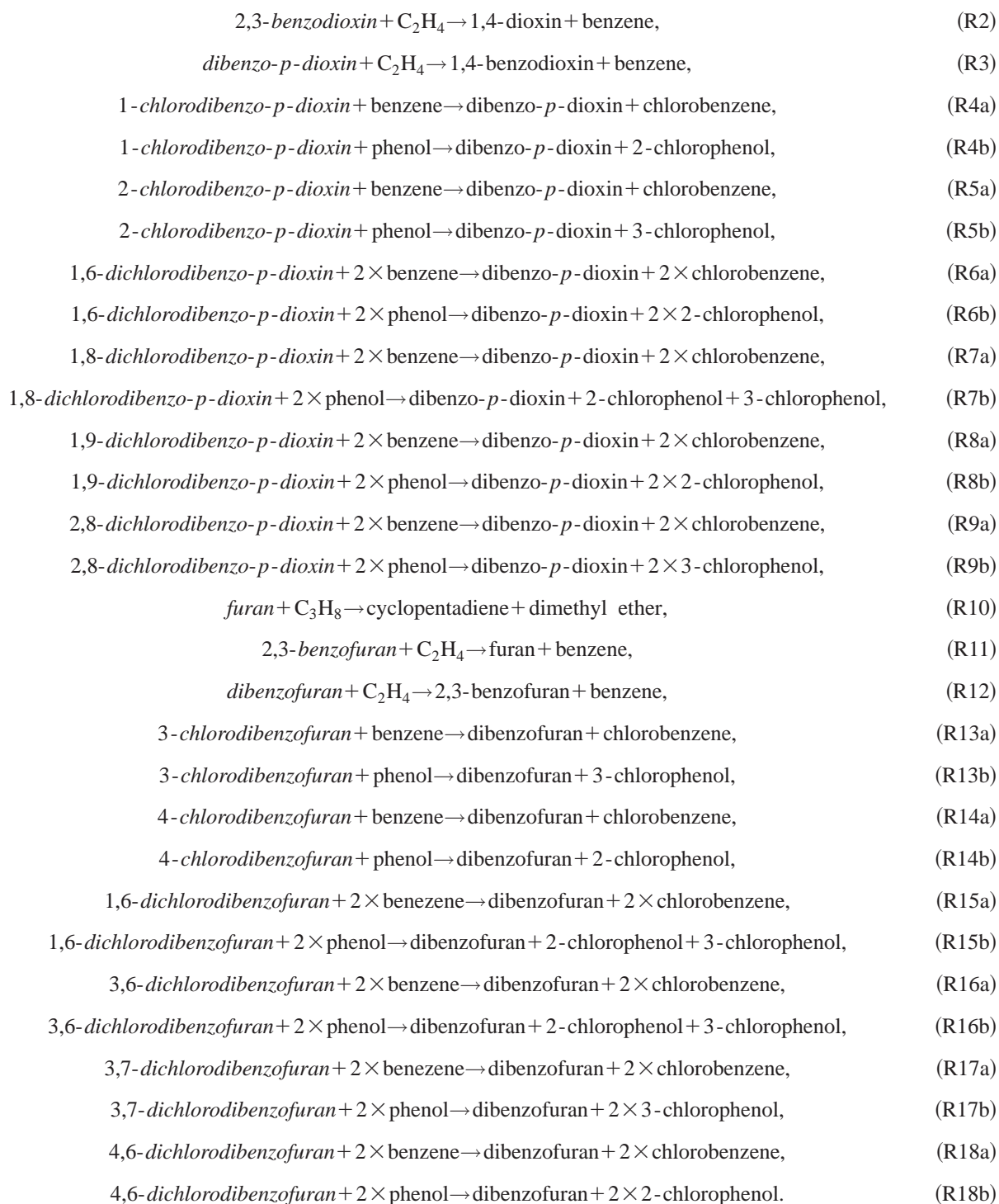
2.1. $\Delta_f H^\circ$ (298.15 K)

The standard enthalpies of formation are obtained using total energies obtained by the B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p) calculation methods and generic

isodesmic reactions; this working reaction analysis allows us to achieve an important cancellation of errors in the calculation results. The total energies is corrected by the ZPVE, which is scaled by 0.9806, as recommended by Scott and Radom.⁴⁵ Thermal corrections from 0 to 298.15 K are calculated to estimate total energies at 298.15 K.⁴⁶ 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.⁴⁶ Redfern *et al.*⁴⁷ compared the deviation of enthalpies of formation from experimental data for C₁–C₁₆ *n*-alkanes using the B3LYP method. They showed that use of a bond isodesmic working reaction or a homodesmotic working reaction with B3LYP calculations significantly improves the absolute accuracy in the calculations. Chen and Bozzelli⁴⁸ also showed that the B3LYP method results in good agreement to the values obtained with high level composite methods, CBSQ and G3(MP2), for up to 5 carbon ethers and ether radicals.

The following isodesmic reactions are selected to determine $\Delta_f H^\circ$ (298.15 K) of the target (*italic*) species:





The number of each bond type is conserved in reactions (R1)–(R18). As an example, there are two C–C, two C=C, four C–O, and 16 C–H in the reactants and products of (R1), so (R1) is an isodesmic reaction.

2.2. $S^\circ(298.15 \text{ K})$ and $C_p^\circ(T)$ ($5 \leq T/\text{K} \leq 6000$)

Contributions to $S^\circ(298.15 \text{ K})$ and $C_p^\circ(T)$ from translation, vibration, and external rotation (TVR) of each

MCDD/F or DCDD/F are obtained using the rigid-rotor-harmonic-oscillator approximation for the frequencies, along with moments of inertia based on the optimized B3LYP/6-31G(d,p) structure. The SMCPS computer program⁴⁹ is used for this calculation.

The low frequencies of chlorinated dibenzo-*p*-dioxins and polychlorinated benzenes below 260 cm^{-1} , corresponding to the ring bending modes, were treated as internal rotators by

TABLE 2. Calculated total energies at 298.15 K^{a,b}

Species	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)	ZPVE ^{c,d}	$H_{298}-H_0^d$
1,4-Dioxin (1)	-305.122 6158	-305.233 0512	190.7	15.3
2,3-Benzodioxin (2)	-458.744 5484	-458.895 5508	312.0	21.3
Dibenzo- <i>p</i> -dioxin (3)	-612.364 8265	-612.556 2978	432.5	27.8
1CDD (4)	-1071.963 1576	-1072.188 3174	407.8	31.1
2CDD (5)	-1071.965 9911	-1072.191 0159	407.6	31.1
16DCDD (6)	-1531.561 1775	-1531.820 0451	383.0	34.5
18DCDD (7)	-1531.563 8853	-1531.822 7356	382.8	34.5
19DCDD (8)	-1531.560 5090	-1531.819 5715	383.0	34.5
28DCDD (9)	-1531.566 7702	-1531.825 5776	382.5	34.5
Furan (10)	-229.953 9102	-230.031 9813	180.6	12.2
2,3-Benzofuran (11)	-383.560 9708	-383.680 3428	302.5	18.1
Dibenzofuran (12)	-537.170 9796	-537.331 5606	423.6	24.8
3CDF (13)	-996.772 6770	-996.966 8849	398.6	28.2
4CDF (14)	-996.770 0590	-996.964 3403	398.9	28.2
16DCDF (15)	-1456.371 4972	-1456.599 4433	374.3	31.5
36DCDF (16)	-1456.371 2859	-1456.599 3147	373.8	31.6
37DCDF (17)	-1456.373 9666	-1456.601 9466	373.5	31.5
46DCDF (18)	-1456.368 3240	-1456.596 5887	374.1	31.6

^aAll calculations are based on B3LYP/6-31G(d,p) optimized structures.

^bTotal energies (ZPVE and thermal corrections are included) in hartree, 1 hartree = 627.51 kcal·mol⁻¹ = 2625.5 kJ·mol⁻¹.

^cScaled by 0.9806 as recommended by Scott and Random.⁴⁵

^dIn units of kJ·mol⁻¹.

León *et al.*⁵⁰ in the evaluation of the thermal correction to the enthalpies. This is a result from studies on molecules with internal rotors where the harmonic oscillator model fails to describe internal rotors adequately when the barrier to rotation is close to or below the thermal energy. In the limit of high temperatures or low frequencies, a harmonic oscillator contributes RT but a free rotor only contributes $(1/2)RT$ to heat capacities. Nicolaides *et al.*⁵¹ recommended that internal rotations with frequencies below 260 cm⁻¹ be treated as free rotors rather than as harmonic oscillators in the evaluation of $\Delta H(T)$ at 298.15 K. In these chlorinated dibenzo-*p*-dioxin and dibenzofuran systems the low frequency modes are not internal rotations; they are a ring (or multi-ring) bending or distortion. We feel the frequency of the vibration is not the deciding issue. The important feature is whether the average potential energy increases with the excitation energy of a degree of freedom (as in an oscillator) or remains constant (as in translational motion or a free rotor). We suggest the ring bending vibrations in PCDD/Fs are probably between $(1/2)RT$ to RT . We concur these vibrations are not harmonic, but the scale of the anharmonicity effects are undetermined here. We choose to use the corresponding calculated vibration frequencies in our estimation of entropy, heat capacity, and ZPVE.

3. Results and Discussion

3.1. Geometries

The geometries for the 12 mono- or di-chlorinated dibenzo-*p*-dioxins or dibenzofurans from the fully optimization at the density functional theory (DFT) B3LYP/6-31G(d,p) level are shown in the Appendix (Supplemental Materials 1). For each species, the optimized geometry shows a planar structure. The C–C bond is ~ 1.39 Å on the

benzo ring, ~ 1.40 Å on the furan or dioxin ring, whereas the C–O bond is in the range of 1.37–1.38 Å. All C–H and C–Cl bonds are in the ranges of 1.08–1.09 and 1.74–1.75 Å, respectively.

Harmonic vibrational frequencies and moments of inertia calculated at the B3LYP/6-31G(d,p) level on the basis of optimized geometries at this same level of theory are listed in the Appendix (Supplemental Materials 2).

3.2. $\Delta_f H^\circ(298.15 \text{ K})$

The enthalpies of formation for all target species are obtained using the isodesmic reaction method at two different DFT levels of theory.

The total energies at 298.15 K (Table 2) are used to obtain the enthalpy changes of the isodesmic reactions (Table 3). The enthalpies of formation for the reference species used in the isodesmic reactions are summarized in Table 4.

We have used the isodesmic reactions and total energies at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) to calculate the enthalpies of formation, $\Delta_f H^\circ(298.15 \text{ K})$, for all chlorobenzenes and chlorophenols. Details on these results are discussed by Zhu *et al.*⁵² and some results on chlorobenzenes and chlorophenols are listed in Table 5. Comparisons of our results with available literature data show good agreement for dichlorobenzenes and monochlorophenols, some of which are used as reference species in this study. These data also provide some indication on the accuracy of our methods for estimation enthalpies. The largest discrepancy, -42 kJ·mol⁻¹, is in the $\Delta_f H^\circ(298.15 \text{ K})$ of hexachlorobenzene from our calculation and the experiment by Platonov and Simulin⁵³ in 1985. Additional experiments and calculations by the scientific community are needed to resolve this discrepancy in enthalpy values.

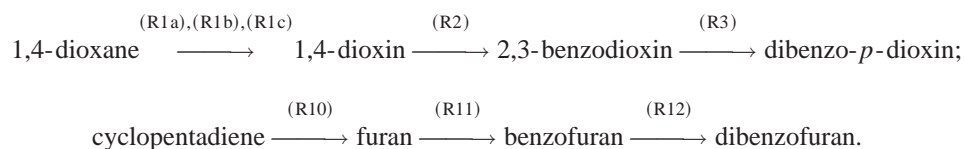
THERMOCHEMICAL PROPERTIES OF CHLORINATED DIBENZODIOXINS AND DIBENZOFURANS 1719

TABLE 3. Calculated $\Delta_{\text{rxn}}H$ (298.15 K)/kJ·mol⁻¹ of isodesmic reactions^a

Isodesmic reactions	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)
	//B3LYP/6-31G(d,p)	
(R1a) 1,4-dioxin + 2 × C ₂ H ₆ → 1,4-dioxane + 2 × C ₂ H ₄	59.3	50.6
(R1b) 1,4-dioxin + cyclopentane → 1,4-dioxane + cyclopentadiene	-20.2	-22.2
(R1c) 1,4-dioxin + cyclohexane → 1,4-dioxane + 1,3-cyclohexadiene	-2.9	-6.4
(R2) 2,3-benzodioxin + C ₂ H ₄ → 1,4-dioxin + benzene	19.4	15.4
(R3) dibenzo- <i>p</i> -dioxin + C ₂ H ₄ → 2,3-benzodioxin + benzene	15.0	10.8
(R4a) 1 CDD + benzene → dibenzo- <i>p</i> -dioxin + chlorobenzene	-10.4	-9.9
(R4b) 1 CDD → dibenzo- <i>p</i> -dioxin + 2-chlorophenol	-15.7	-16.2
(R5a) 2 CDD + benzene → dibenzo- <i>p</i> -dioxin + chlorobenzene	-2.9	-2.8
(R5b) 2 CDD + phenol → dibenzo- <i>p</i> -dioxin + 3-chlorophenol	-3.8	-4.9
(R6a) 16DCDD + 2 × benzene → dibenzo- <i>p</i> -dioxin + 2 × chlorobenzene	-21.5	-20.5
(R6b) 16DCDD + 2 × phenol → dibenzo- <i>p</i> -dioxin + 2 × 2-chlorophenol	-32.3	-33.2
(R7a) 18DCDD + 2 × benzene → dibenzo- <i>p</i> -dioxin + 2 × chlorobenzene	-14.4	-13.4
(R7b) 18DCDD + 2 × phenol → Dibenzo- <i>p</i> -dioxin + 2-chlorophenol + 3-chlorophenol	-20.6	-21.9
(R8a) 19DCDD + 2 × benzene → dibenzo- <i>p</i> -dioxin + 2 × chlorobenzene	-23.3	-21.7
(R8b) 19DCDD + 2 × phenol → dibenzo- <i>p</i> -dioxin + 2 × 2-chlorophenol	-34.0	-34.4
(R9a) 28DCDD + 2 × benzene → dibenzo- <i>p</i> -dioxin + 2 × chlorobenzene	-6.9	-6.0
(R9b) 28DCDD + 2 × phenol → dibenzo- <i>p</i> -dioxin + 2 × 3-chlorophenol	-8.5	-10.2
(R10) furan + C ₃ H ₈ → cyclopentadiene + CH ₃ -O-CH ₃	99.9	91.3
(R11) 2,3-benzofuran + C ₂ H ₄ → furan + benzene	-19.7	-21.7
(R12) dibenzofuran + C ₂ H ₄ → 2,3-benzofuran + benzene	-11.9	-14.2
(R13a) 3CDF + benzene → dibenzofuran + chlorobenzene	-1.5	-1.2
(R13b) 3CDF + phenol → dibenzofuran + 3-chlorophenol	-2.4	-3.3
(R14a) 4CDF + benzene → dibenzofuran + chlorobenzene	-8.4	-7.9
(R14b) 4CDF + phenol → dibenzofuran + 2-chlorophenol	-13.8	-14.2
(R15a) 16DCDF + 2 × benzene → dibenzofuran + 2 × chlorobenzene	-10.6	-9.6
(R15b) 16DCDF + 2 × phenol → dibenzofuran + 2-chlorophenol + 3-chlorophenol	-16.8	-18.1
(R16a) 36DCDF + 2 × benzene → dibenzofuran + 2 × chlorobenzene	-11.2	-10.0
(R16b) 36DCDF + 2 × phenol → dibenzofuran + 2-chlorophenol + 3-chlorophenol	-17.4	-18.5
(R17a) 37DCDF + 2 × benzene → dibenzofuran + 2 × chlorobenzene	-4.1	-3.0
(R17b) 37DCDF + 2 × phenol → dibenzofuran + 2 × 3-chlorophenol	-5.8	-7.3
(R18a) 46DCDF + 2 × benzene → dibenzofuran + 2 × chlorobenzene	-18.9	-17.1
(R18b) 46DCDF + 2 × phenol → dibenzofuran + 2 × 2-chlorophenol	-29.7	-29.8

^aThe low values (near zero) of $\Delta_{\text{rxn}}H$ (298.15 K) indicate the similarity in energies on both sides of working reaction and suggest effective cancellation of errors if species structures are similar.

Dibenzo-*p*-dioxin and dibenzofuran are also important reference species used in calculation of $\Delta_f H^\circ$ (298.15 K) of all the mono- and di-chloro DD/Fs in this study. We start by calculating the $\Delta_f H^\circ$ (298.15 K) of these two species to show the accuracy of our calculation methods. We use several different working reactions (R1), (R2), (R3), (R10), (R11), and (R12) stepwise for this purpose:



The close agreement (precision) in the calculated $\Delta_f H^\circ$ (298.15 K) values of dibenzo-*p*-dioxin and dibenzofuran from these working reactions with the available literature values^{32,36} also serves to validate the literature values of dibenzo-*p*-dioxin and dibenzofuran.

The enthalpy of formation of 1,4-dioxin, $\Delta_f H^\circ$ (298.15 K) = -86.0 kJ·mol⁻¹, is calculated from reactions (R1a) to (R1c) and the literature values of

$\Delta_f H^\circ$ (298.15 K) for 1,4-dioxane,³⁰ ethane,⁵⁴ and ethylene.⁵⁴ There is no experimental or literature data on $\Delta_f H^\circ$ (298.15 K) for 1,4-dioxin as we know.

The enthalpy of formation of 2,3-benzodioxin, $\Delta_f H^\circ$ (298.15 K) = -71.2 kJ·mol⁻¹, is obtained from reaction (R2) based on $\Delta_f H^\circ$ (298.15 K) of 1,4-dioxin. We have not found any literature values for the $\Delta_f H^\circ$ (298.15 K) of 2,3-benzodioxin.

TABLE 4. Enthalpies of formation for reference species (and literature citations)

Species	$\Delta_f H^\circ(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$
C ₂ H ₄	52.4 ± 0.5 ⁵⁴
C ₂ H ₆	-84.0 ± 0.4 ⁵⁴
C ₃ H ₈	-104.7 ± 0.5 ³⁰
1,4-Dioxane	-315.8 ± 0.8 ³⁰
Cyclopentane	-74.6 ± 0.8 ³⁰
Cyclohexane	-123.4 ± 0.8 ³⁰
1,3-Cyclohexadiene	106.2 ± 0.9 ³⁰
Furan	-34.9 ± 0.7 ³⁰
Cyclopentadiene	134.3 ± 1.5 ³⁰
Benzene	82.6 ± 0.7 ³⁰
Chlorobenzene	52.0 ± 1.3 ³⁰
Dimethyl ether	-184.1 ± 0.5 ³⁰
Phenol	-96.4 ± 0.9 ³⁰
2-Chlorophenol	-131.8 ± 9.3 (See Table 5)
3-Chlorophenol	-127.7 ± 9.3 (See Table 5)
Dibenzo- <i>p</i> -dioxin	-50.1 ± 2.2 ³⁶
Dibenzofuran	55.3 ± 0.4 ³²

The enthalpy of formation of dibenzo-*p*-dioxin, $\Delta_f H^\circ(298.15 \text{ K}) = -51.8 \text{ kJ}\cdot\text{mol}^{-1}$, is obtained from the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level in reaction (R3) based on the $\Delta_f H^\circ(298.15 \text{ K})$ of 2,3-benzodioxin. This result is in good agreement with the experimental value, $\Delta_f H^\circ(298.15 \text{ K}) = -50.1 \pm 2.2 \text{ kJ}\cdot\text{mol}^{-1}$, determined by Pimenova *et al.*³⁶ in 2002. We adopt the value of Pimenova *et al.*,³⁶ in reactions (R4)–(R9) for the enthalpy of formation calculations of other mono- and di-chlorinated dibenzo-*p*-dioxins.

The enthalpy of formation of furan, $\Delta_f H^\circ(298.15 \text{ K}) = -36.4 \text{ kJ}\cdot\text{mol}^{-1}$, is calculated from reaction (R10) and the literature values of $\Delta_f H^\circ(298.15 \text{ K})$ for cyclopentadiene, *n*-propane, and dimethyl ether. The result is 1.5–4.2 $\text{kJ}\cdot\text{mol}^{-1}$ lower than the data compiled by Pedley *et al.*³⁰ and the two calculation results of Feller and Franz⁵⁵ ($-32.2 \pm 2.1 \text{ kJ}\cdot\text{mol}^{-1}$) and Notario *et al.*³⁴ ($-33.5 \text{ kJ}\cdot\text{mol}^{-1}$), respectively.

The enthalpy of formation of 2,3-benzofuran, $\Delta_f H^\circ(298.15 \text{ K}) = 17.0 \text{ kJ}\cdot\text{mol}^{-1}$, is obtained from reaction (R11) based on the $\Delta_f H^\circ(298.15 \text{ K})$ value of furan computed above. This result is in good agreement with the available literature data of Steele and Chirico⁵⁶ ($13.6 \pm 0.7 \text{ kJ}\cdot\text{mol}^{-1}$) and Notario *et al.*³⁴ ($16.7 \text{ kJ}\cdot\text{mol}^{-1}$).

The enthalpy of formation of dibenzofuran, $\Delta_f H^\circ(298.15 \text{ K}) = 58.2 \text{ kJ}\cdot\text{mol}^{-1}$, is obtained in reaction (R12) based on the $\Delta_f H^\circ(298.15 \text{ K})$ value of 2,3-benzofuran we obtained above. This result is 2.9 $\text{kJ}\cdot\text{mol}^{-1}$ higher than the experimental values of Chirico *et al.*³² The value of Chirico *et al.*,³² $55.3 \pm 0.3 \text{ kJ}\cdot\text{mol}^{-1}$, is adopted in the calculations of mono- and di-chloro furans in reactions (R13)–(R18).

The calculated $\Delta_f H^\circ(298.15 \text{ K})$ values for 12 mono- and di-chloro DD/Fs are shown in Table 6. The average of two values calculated at B3LYP/6-311+G(3df,2p) by two isodesmic reactions is our recommended $\Delta_f H^\circ(298.15 \text{ K})$ value for each species of mono- and di-chloro DD/Fs (Table 7).

The error for DFT- $\Delta_f H^\circ(298.15 \text{ K})$ listed in Table 7 comprises the standard deviation of two calculated $\Delta_f H^\circ(298.15 \text{ K})$ values (at B3LYP/6-311+G(3df,2p) level and two isodesmic reactions), the cumulative uncertainties in $\Delta_f H^\circ(298.15 \text{ K})$ for the reference species in Table 5, as well as the uncertainty from ZPVE calculations, $1.8 \text{ kJ}\cdot\text{mol}^{-1}$.^{45,57}

Our calculated and recommended thermochemical properties for dibenzo-*p*-dioxin, dibenzofuran and 12 mono- and di-chlorinated DD/Fs are compared with available literature data and MOPAC6/PM3 results in Table 7. It is seen that for 1- and 2-chloro dibenzo-*p*-dioxins our DFT results are 3–18 $\text{kJ}\cdot\text{mol}^{-1}$ lower than the experimental data of Kolesov *et al.*³⁵ The GA estimations by Shaub²² are significantly lower than our DFT calculation results, the differences range from 22.2 $\text{kJ}\cdot\text{mol}^{-1}$ for 1-chlorodibenzo-*p*-dioxin to 109 $\text{kJ}\cdot\text{mol}^{-1}$ for 2,8-dichlorodibenzo-*p*-dioxin. The PM3- $\Delta_f H^\circ(298.15 \text{ K})$ results are generally ~ 8 and ~ 55

TABLE 5. Comparison of calculated $\Delta_f H^\circ(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$ for selected chlorobenzenes and chlorophenols with literature data

Species	Pedley <i>et al.</i> ³⁰	Cox and Pilcher ²⁹	NIST-TRC ⁵⁸	Yan <i>et al.</i> ⁶³	Platnov and Simulin ⁵³	León <i>et al.</i> ⁵⁰	DFT ^a
1,2-Dichlorobenzene	30.2 ± 2.1	29.7 ± 1.6	29.7		33.0	34.0 ± 2.0	34.1 ± 3.9
1,3-Dichlorobenzene	25.7 ± 2.1	25.5 ± 2.1	25.5		28.1	24.6 ± 2.0	24.7 ± 3.9
1,4-Dichlorobenzene	22.5 ± 1.5	22.2 ± 1.3	22.2		24.6	24.8 ± 2.0	24.7 ± 3.9
1,2,3-Trichlorobenzene			9.0	8.2 ± 1.8	3.8	19.2 ± 2.5	19.5 ± 6.4
1,2,4-Trichlorobenzene			-0.2	4.9 ± 1.6	-8.0	9.1 ± 2.5	9.4 ± 6.4
1,3,5-Trichlorobenzene			-6.9	-2.6 ± 1.4	-13.3	0.6 ± 2.5	0.6 ± 6.4
1,2,3,4-Tetrachlorobenzene			-9.6		-25.4	6.2 ± 2.9	6.5 ± 8.9
1,2,3,5-Tetrachlorobenzene			-20.1		-34.9	-3.4 ± 2.9	-3.1 ± 8.9
1,2,4,5-Tetrachlorobenzene			-23.4		-32.6	-4.8 ± 2.9	-4.3 ± 8.9
Pentachlorobenzene			-29.0		-40.0	-5.9 ± 3.2	-4.4 ± 11.4
Hexachlorobenzene	-35.5 ± 9.4	-36.0 ± 9.6	-33.9		-44.7	-4.5 ± 3.2	-2.6 ± 13.9
2-Chlorophenol							-131.9 ± 6.5
3-Chlorophenol	-153.3 ± 8.7	-153.6 ± 8.8					-127.8 ± 6.5
4-Chlorophenol	-145.8 ± 8.7	-146.0 ± 8.8					-125.6 ± 6.5

^aDensity functional theory, calculated at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) from unpublished work in this group.

TABLE 6. Calculated $\Delta_f H^\circ(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$ using isodesmic reactions

Species	From R_{xns}	B3LYP/6-31G(d,p)	B3LYP/6-311+G(3df,2p)	$X_{\text{avg}} \pm \sigma^{\text{a}}$
		//B3LYP/6-31G(d,p)		
1,4-Dioxin (1)	(R1a)	-102.3	-93.6	-86.0 ± 7.0
	(R1b)	-86.7	-84.7	
	(R1c)	-83.3	-79.8	
2,3-Benzodioxin (2)	(R2)	-75.2	-71.2	
Dibenzo- <i>p</i> -dioxin (3)	(R3)	-56.0	-51.8	
1CDD (4)	(R4a)	-70.3	-70.8	-70.1 ± 1.1
	(R4b)	-69.8	-69.3	
2CDD (5)	(R5a)	-77.8	-77.9	-77.2 ± 1.0
	(R5b)	-77.7	-76.5	
16DCDD (6)	(R6a)	-89.8	-90.8	-89.3 ± 2.1
	(R6b)	-88.7	-87.8	
18DCDD (7)	(R7a)	-96.9	-97.9	-96.4 ± 2.1
	(R7b)	-96.2	-95.0	
19DCDD (8)	(R8a)	-88.0	-89.6	-88.1 ± 2.1
	(R8b)	-86.0	-86.9	
28DCDD (9)	(R9a)	-104.4	-105.3	-103.9 ± 2.0
	(R9b)	-104.3	-102.5	
Furan (10)	(R10)	-45.0	-36.4	
2,3-Benzofuran (11)	(R11)	15.0	17.0	
Dibenzofuran (12)	(R12)	55.9	58.2	
3CDF (13)	(R13a)	26.2	25.9	26.6 ± 1.0
	(R13b)	26.3	27.3	
4CDF (14)	(R14a)	33.1	32.5	33.3 ± 1.1
	(R14b)	33.6	34.1	
16DCDF (15)	(R15a)	4.7	3.7	5.2 ± 2.1
	(R15b)	5.3	6.6	
36DCDF (16)	(R16a)	5.2	4.0	5.5 ± 2.1
	(R16b)	5.9	7.0	
37DCDF (17)	(R17a)	-1.8	-2.9	-1.5 ± 2.0
	(R17)	-1.6	0.0	
46DCDF (18)	(R18)	13.0	11.2	12.7 ± 2.1
	(R18)	14.1	14.2	

^aAverage of data from B3LYP/6-311+G(3df,2p) level only.

$\text{kJ}\cdot\text{mol}^{-1}$ higher than the DFT calculated $\Delta_f H^\circ(298.15 \text{ K})$ for these dibenzo-*p*-dioxins and dibenzofurans.

3.3. $S^\circ(298.15 \text{ K})$ and $C_p^\circ(T)$ ($5 \leq T/\text{K} \leq 6000$)

$S^\circ(298.15 \text{ K})$ and $C_p^\circ(T)$ values, obtained from the frequencies along with moments of inertia based on the optimized B3LYP/6-31G(d,p) structure and using the SMCPS⁴⁹ computer program, are listed in Tables 8 and 9. Heat capacities for the temperature range of 5–6000 K are listed in the Appendix (Supplemental Materials 3).

Our calculated $S^\circ(298.15 \text{ K})$ and $C_p^\circ(T)$ values for dibenzo-*p*-dioxin and dibenzofuran are in good agreement with the NIST-TRC⁵⁸ values. The PM3 determined $S^\circ(298.15 \text{ K})$ and $C_p^\circ(T)$ values are generally in good agreement with the DFT calculated results for mono- and dichloro DD/Fs.

3.4. Group Values

Group values are derived to allow estimation of larger molecules based on these dibenzo-*p*-dioxin and dibenzofuran structures, as well as estimation of larger PCDD/Fs. Group additivity also permits estimation of biradical species and

inclusion of other substituents.^{59,60} The GA strategy and nomenclature developed by Dorofeeva *et al.*³³ is adopted because we feel it is more straightforward to use than the method of Wu *et al.*²³ The method for GA is summarized here with examples provided:

- (1) The skeletons of dioxin and furan rings (C_4O_2 and C_4O , no hydrogens) in dibenzo-*p*-dioxin and dibenzofuran are the two basic groups, named as DD and DF. These two groups alone can **not** be used to calculate values of 1,4-dioxin and furan;



- (2) The C_B/H , C_B/Cl groups on dibenzo-*p*-dioxins and dibenzofurans are the same as those groups in benzene and chlorobenzene;
- (3) No interaction between the two benzo rings on dibenzo-*p*-dioxins and dibenzofurans is considered;
- (4) The *ortho* (*meta*) interactions between Cl and the dioxin (furan) ring are named as ORT/Cl/DD (ORT/Cl/DF) and

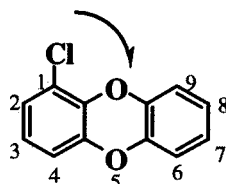
TABLE 7. Ideal gas phase enthalpies of formation: $\Delta_f H^\circ(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$ ^{a,b}

Species	Expt.	Review	MOPAC6/PM3	Group additivity	DFT ^c
1,4-Dioxin (1)			-138.6		-86.0
2,3-Benzodioxin (2)			-91.0		-71.2
Dibenzo- <i>p</i> -dioxin (3)	-50.1±2.2 ³⁶ -59.2±4.4 ^{35,64}	-62.6 ⁵⁸	-39.5	-62.8 ²² -55.0 ²⁴ -59.2±3.8 ³³	-51.8 -61.3±1.4 ⁵⁰
1CDD (4)	-88.2±4.8 ³⁵		-60.2	-95.0 ²² -89.8±10.0 ³³	-70.1±15.3 -79.8±4.9 ⁵⁰
2CDD (5)	-74.1±3.3 ³⁵		-66.3	-137.7 ²² -89.8±10.0 ³³	-77.2±15.3 -87.0±4.9 ⁵⁰
16DCDD (6)			-80.9	-127.2 ²²	-89.3±26.6
18DCDD (7)			-86.9	-170.0 ²²	-96.4±26.6
19DCDD (8)			-80.7	-127.2 ²²	-88.1±26.6
28DCDD (9)			-92.6	-212.7 ²²	-103.9±26.5
Furan (10)		-34.7 ⁵⁸ -34.9±0.7 ³⁰	-16.9		-36.4 -33.5 ³⁴ -32.2±2.1 ⁵⁵
2,3-Benzofuran (11)	13.6±0.7 ⁵⁶		50.2		17.0 16.7 ³⁴
Dibenzofuran (12)	55.3±0.3 ³⁵ 47.3±4.6 ³¹	83.4±4.7 ³⁰ 83.3±5.0 ²⁹	106.7	55.3 ²⁴ 55.3±0.3 ³³	58.2 51.9±6.7 ³⁴ 84.1 ⁶⁵
3CDF (13)			79.1		26.6±13.4
4CDF (14)			85.8		33.3±13.5
16DCDF (15)			61.5		5.2±24.7
36DCDF (16)			58.3		5.5±24.7
37DCDF (17)			52.0		-1.5±24.6
46DCDF (18)			65.0		12.7±14.6

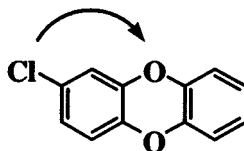
^aData without superscript are work in this study.^bData in bold are recommended.^cDensity functional theory, calculated at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) in this study if no superscript.

MET/CI/DD (MET/CI/DF). No para interaction between Cl and the dioxin (furan) ring is considered. (These are adjustments for *ortho* and *meta* positions relative to the *para*)

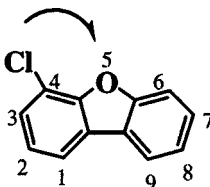
ORT/CI/DD



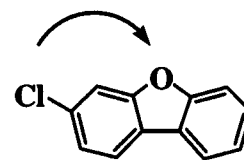
MET/CI/DD



ORT/CI/DF



MET/CI/DF



According to the above GA rules we have the following equations for the dibenzo-*p*-dioxin, dibenzofuran, and the 12 mono-, and di-chlorinated dibenzo-*p*-dioxins and dibenzofurans:

$$\text{dibenzo-}p\text{-dioxin} = \text{DD} + 8 C_B/\text{H}, \quad (1)$$

$$\text{dibenzofuran} = \text{DF} + 8 C_B/\text{H}, \quad (2)$$

$$1\text{CDD} = \text{DD} + 7 C_B/\text{H} + C_B/\text{Cl} + \text{ORT/CI/DD}, \quad (3)$$

$$2\text{CDD} = \text{DD} + 7 C_B/\text{H} + C_B/\text{Cl} + \text{MET/CI/DD}, \quad (4)$$

$$16\text{DCDD} = \text{DD} + 6 C_B/\text{H} + 2 C_B/\text{Cl} + \text{ORT/CI/DD}, \quad (5)$$

$$18\text{DCDD} = \text{DD} + 6 C_B/\text{H} + 2 C_B/\text{Cl} + \text{ORT/CI/DD} + \text{MET/CI/DD}, \quad (6)$$

TABLE 8. Ideal gas phase entropies: $S^\circ(298.15\text{ K})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ a,b

Species	Expt.	Review	MOPAC6/PM3	Statistical thermodynamics	DFT ^c
1,4-Dioxin (1)			281.4		284.3
2,3-Benzodioxin (2)			347.3		347.1
Dibenzo- <i>p</i> -dioxin (3)		387.7 ⁵⁸	392.3	387.8 ²¹ 396.5 ³³	389.4
1CDD (4)			440.1	420.9 ²¹ 437.4 ³³	436.5
2CDD (5)			440.6		436.6
16DCDD (6)			464.4		460.9
18DCDD (7)			470.4		466.3
19DCDD (8)			464.9		460.8
28DCDD (9)			459.4		460.5
Furan (10)		267.2 ⁵⁸	268.1		266.5
2,3-Benzo furan (11)			329.2		325.9
Dibenzofuran (12)	374.4±0.6³²		378.4	375.9 ³³	373.9
3CDF (13)			413.6		409.7
4CDF (14)			412.3		409.7
16DCDF (15)			443.3		438.9
36DCDF (16)			443.3		439.9
37DCDF (17)			437.9		434.0
46DCDF (18)			437.8		434.1

^aData without superscript are work in this study.

^bData in bold are recommended.

^cDensity functional theory, calculated at B3LYP/6-31G(d,p) in this study.

$$19\text{DCDD} = \text{DD} + 6 C_B/\text{H} + 2 C_B/\text{Cl} + \text{ORT}/\text{Cl}/\text{DD}, \quad (7)$$

$$28\text{DCDD} = \text{DD} + 6 C_B/\text{H} + 2 C_B/\text{Cl} + 2\text{MET}/\text{Cl}/\text{DD}, \quad (8)$$

$$3\text{CDF} = \text{DF} + 7 C_B/\text{H} + C_B/\text{Cl} + \text{MET}/\text{Cl}/\text{DF}, \quad (9)$$

$$4\text{CDF} = \text{DF} + 7 C_B/\text{H} + C_B/\text{Cl} + \text{ORT}/\text{Cl}/\text{CF}, \quad (10)$$

$$16\text{DCDF} = \text{DF} + 6 C_B/\text{H} + 2 C_B/\text{Cl} + \text{ORT}/\text{Cl}/\text{DF} \\ + \text{MET}/\text{Cl}/\text{DF}, \quad (11)$$

$$36\text{DCDF} = \text{DF} + 6 C_B/\text{H} + 2 C_B/\text{Cl} + \text{ORT}/\text{Cl}/\text{DF} \\ + \text{MET}/\text{Cl}/\text{DF}, \quad (12)$$

$$37\text{DCDF} = \text{DF} + 6 C_B/\text{H} + 2 C_B/\text{Cl} + 2\text{MET}/\text{Cl}/\text{DF}, \quad (13)$$

$$46\text{DCDF} = \text{DF} + 6 C_B/\text{H} + 2 C_B/\text{Cl} + 2\text{ORT}/\text{Cl}/\text{DF}. \quad (14)$$

The above relationships are for enthalpies and heat capacities. Entropy values are intrinsic (include no symmetry component). The method for derivation of these groups is described by Sun and Bozzelli.⁶¹

All groups used in this study are listed in Table 10. C_B/H group is calculated from one sixth of benzene, and C_B/Cl group is from chlorobenzene minus five times the value of C_B/H group.

3.4.1. DD and DF

These two groups are derived from the thermochemical properties of dibenzo-*p*-dioxin and dibenzofuran and Eqs. (1) and (2).

$$\text{DD} = \text{dibenzo-}p\text{-dioxin} - 8 C_B/\text{H}; \\ \text{DF} = \text{dibenzofuran} - 8 C_B/\text{H}.$$

3.4.2. ORT/Cl/DD, ORT/Cl/DF, MET/Cl/DD, MET/Cl/DF

ORT/Cl/DD is the average value from Eqs. (3) and (5); MET/Cl/DD is the average value from Eqs. (4) and (8); ORT/Cl/DF is the average value from Eqs. (9) and (13); MET/Cl/DF is the average value from Eqs. (10) and (14).

3.4.3. Comparison of Results from Group Additivity with Recommended Calculated Data

A comparison of the calculated thermochemical properties of the 12 mono-, di-CDD/Fs with GA results is listed in Table 11. The GA results are in good agreement with the recommended values. The differences are all within ± 1.6 $\text{kJ}\cdot\text{mol}^{-1}$ for $\Delta_f H^\circ(298.15\text{ K})$. The differences for $S^\circ(298.15\text{ K})$ are all within ± 8.8 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. There are almost no differences between calculated and GA heat capacities at 300–1500 K.

The interaction of a chlorine in an *ortho* position with the oxo link (ORT/Cl/DD) is 10.9 $\text{kJ}\cdot\text{mol}^{-1}$, which is higher than the interaction of *meta* position (MET/Cl/DD), 3.6 $\text{kJ}\cdot\text{mol}^{-1}$. In contrast, the interaction of *ortho* position (ORT/Cl/DF) is 2.1 $\text{kJ}\cdot\text{mol}^{-1}$, lower than the interaction of *meta* position (MET/Cl/DF), 9.0 $\text{kJ}\cdot\text{mol}^{-1}$. Each interaction of ORT/Cl/DD or MET/Cl/DD lowers the $S^\circ(298.15\text{ K})$ of PCDD by 7 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; but smaller change (3 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) occurs for PCDF. The four types of interactions do not have a significant effect on the heat capacities.

TABLE 9. Ideal gas phase heat capacities: $C_p^\circ(T)/J\cdot K^{-1}\cdot mol^{-1}$ ^{a,b}

Species		300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
1,4-Dioxin (1)	DFT	81.8	105.8	125.6	141.2	163.8	179.3	202.0
	PM3	82.0	106.2	126.1	141.9	164.8	180.4	203.2
2,3-Benzodioxin (2)	DFT	129.9	171.0	205.0	231.9	270.5	296.5	333.7
	PM3	128.2	168.4	202.2	229.3	268.9	295.8	329.9
Dibenzo- <i>p</i> -dioxin (3)	DFT	178.4	236.5	284.5	322.6	377.2	413.7	465.4
	PM3	175.0	231.1	278.6	317.0	394.1	411.4	465.1
	Review ⁵⁸	177.0	236.2	284.8	323.9	379.6	416.6	
	Statistical thermodynamics ³³	180.2						
1CDD (4)	DFT	194.4	251.5	298.2	335.1	387.6	422.2	470.7
	PM3	190.8	245.9	292.0	329.3	383.4	419.6	470.1
	Statistical thermodynamics ³³	195.9						
2CDD (5)	DFT	194.8	251.8	298.5	335.4	387.8	422.4	470.7
	PM3	190.8	245.9	292.1	329.3	383.4	419.6	470.1
16DCDD (6)	DFT	210.5	266.4	311.9	347.6	397.9	430.8	476.0
	PM3	206.4	263.1	305.5	341.5	393.4	427.9	475.1
18DCDD (7)	DFT	210.8	266.9	312.3	347.9	398.1	430.9	476.0
	PM3	206.5	260.7	305.5	341.5	393.4	427.9	475.1
19DCDD (8)	DFT	210.4	266.4	311.9	347.6	397.9	430.8	476.0
	PM3	206.5	260.7	305.5	341.5	393.5	427.9	475.1
28DCDD (9)	DFT	211.1	267.2	312.6	348.2	398.4	431.1	476.1
	PM3	205.6	260.0	304.9	341.0	393.1	427.6	475.0
Furan (10)	DFT	64.5	87.1	105.9	120.9	142.3	156.9	178.3
	PM3	65.2	87.1	105.6	120.5	142.2	157.0	178.8
	Review ⁵⁸	65.6	87.5	107.7	124.1	143.8	157.6	180.1
2,3-Benzo furan (11)	DFT	112.8	152.2	184.9	211.0	248.4	273.6	309.8
	PM3	112.7	150.9	183.1	209.1	247.1	273.0	310.1
Dibenzofuran (12)	DFT	161.7	217.5	264.1	301.2	354.6	390.5	441.3
	PM3	160.5	214.6	260.4	297.5	351.9	388.9	441.3
	Statistical thermodynamics ³³	163.5						
3CDF (13)	DFT	178.0	232.9	278.2	314.1	365.2	399.1	446.6
	PM3	176.0	229.1	273.6	309.5	361.8	397.0	446.2
4CDF (14)	DFT	177.6	232.4	277.7	313.6	364.9	398.9	446.6
	PM3	175.6	228.8	273.3	309.3	361.7	396.9	446.2
16CDF (15)	DFT	193.5	247.4	291.5	326.2	375.3	407.5	451.8
	PM3	191.5	243.6	286.8	321.5	371.7	405.1	451.2
36CDF (16)	DFT	193.9	247.8	291.9	326.6	375.6	407.6	451.9
	PM3	191.6	243.7	286.9	321.6	371.8	405.2	451.2
37CDF (17)	DFT	194.3	248.3	292.3	326.9	376.3	407.8	452.0
	PM3	191.9	244.0	287.2	321.9	372.0	405.3	451.3
46CDF (18)	DFT	193.5	247.2	291.3	326.1	375.3	407.4	451.9
	PM3	191.6	243.6	286.9	321.5	371.8	405.2	451.3

^aData without superscript are work in this study at B3LYP/6-31G(d,p) level.

^bDFT and PM3 are from calculations in this study.

It is seen from the groups in Table 10 that chlorination (a H atom replaced by a Cl atom in the benzene ring) results in a -30.6 $\text{kJ}\cdot\text{mol}^{-1}$ ($C_B/\text{Cl}-C_B/\text{H}$) change. As more Cl atoms are added this chlorination value decreases; this is accounted for by the Cl/Cl interaction groups.

We also list the $\Delta_f H^\circ(298.15\text{ K})$ of gaseous 23DCDD and 2378TCDD by Papina *et al.*⁶² in Table 12. They measured for 23DCDD, $\Delta_f H^\circ(298.15\text{ K}) = -111.9 \pm 6.9$ $\text{kJ}\cdot\text{mol}^{-1}$, by rotating-bomb calorimetry and estimated for 2378TCDD, $\Delta_f H^\circ(298.15\text{ K}) = -164.6$ $\text{kJ}\cdot\text{mol}^{-1}$. We estimate $\Delta_f H^\circ(298.15\text{ K})$ of 23DCDD and 2378TCDD as -96.4 and -142.7 $\text{kJ}\cdot\text{mol}^{-1}$ using GA shown in Eqs. (15a) and (16a), which are 16 and 22 $\text{kJ}\cdot\text{mol}^{-1}$, respectively, higher than the values by Papina *et al.*, but close to the calculation results of León *et al.*⁵⁰

$$23\text{DCDD} = \text{DD} + 6 C_B/\text{H} + 2 C_B/\text{Cl} + 2 \text{MET}/\text{Cl}/\text{DD} + \text{ORT}/\text{Cl}/\text{Cl}; \quad (15a)$$

$$2378\text{TCDD} = \text{DD} + 4 C_B/\text{H} + 4 C_B/\text{Cl} + 4 \text{MET}/\text{Cl}/\text{DD} + 2 \text{ORT}/\text{Cl}/\text{Cl}. \quad (16a)$$

If we do not considered the interaction between the two Cl atoms on this same benzo ring, i.e.,

$$23\text{DCDD} = \text{DD} + 6 C_B/\text{H} + 2 C_B/\text{Cl} + 2 \text{MET}/\text{Cl}/\text{DD}; \quad (15b)$$

$$2378\text{TCDD} = \text{DD} + 4 C_B/\text{H} + 4 C_B/\text{Cl} + 4 \text{MET}/\text{Cl}/\text{DD}. \quad (16b)$$

THERMOCHEMICAL PROPERTIES OF CHLORINATED DIBENZODIOXINS AND DIBENZOFURANS 1725

TABLE 10. Group values for PCDD/F^a

Groups	$\Delta_f H^\circ$ (298.15 K)	S° (298.15 K)	$C_p^\circ(T)$							
			300 K	400 K	500 K	600 K	800 K	1000 K	1500 K	
Central groups										
C _B /H	Benson ⁶⁶	13.8	48.1	13.5	18.4	22.7	26.1	31.2	34.7	40.0
C _B /Cl ^b		-16.8	78.3	29.6	33.8	36.9	39.0	41.8	43.4	45.2
DD	This work	-160.3	10.2	70.8	89.1	103.1	113.6	127.6	135.9	145.7
	Dorofeeva <i>et al.</i> ³³	-169.3	20.8	11.8						19.3
DF	This work	-54.9	-11.0	54.1	70.2	82.7	92.2	105.0	112.6	121.6
	Dorofeeva <i>et al.</i> ³³	-54.8	-5.0	4.6						-4.6
Interaction groups										
ORT/Cl/Cl ^c		12.8	-1.5	-0.5	-0.5	-0.4	-0.3	-0.1	0.0	0.0
ORT/Cl/DD	This work	10.9	7.0	-0.2	-0.4	-0.5	-0.4	-0.2	-0.1	0.0
MET/Cl/DD	This work	3.6	6.9	0.2	0.0	-0.1	-0.1	0.0	0.0	0.0
ORT/Cl/DF	This work	2.1	2.7	0.2	0.0	0.0	0.0	0.1	0.0	0.1
MET/Cl/DF	This work	9.0	2.8	-0.3	-0.5	-0.6	-0.5	-0.3	-0.2	0.0

^a $\Delta_f H^\circ(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$; $S^\circ(298.15\text{ K})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; $C_p^\circ(T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^bFrom C_B/H and NIST-TRC (Ref. 58) thermochemical properties of chlorobenzene.

^cFrom thermochemical properties of 1,2-dichlorobenzene.⁵²

Then $\Delta_f H^\circ(298.15\text{ K})$ of 23DCDD and 2378TCDD are estimated as -109.2 and -168.2 kJ·mol⁻¹ using GA in Eqs. (15b) and (16b), respectively. These values show smaller discrepancies, 2.7 and -3.6 kJ·mol⁻¹, respectively, from the values by Papina *et al.*

We have calculated parameters for the 12 mono- or dichlorinated dibenzo-*p*-dioxins and dibenzofurans which do not have the ORT/Cl/Cl interactions. The six new groups, DD, DF, ORT/Cl/DD, MET/Cl/DD, ORT/Cl/DF, and MET/

Cl/DF are derived independently from the ORT/Cl/Cl group. When group additivity is used for 23DCDD or 2378TCDD, in which there is an interaction between the two adjacent Cl atoms on the same benzo ring, we adopt the ORT/Cl/Cl group value, 12.8 kJ·mol⁻¹ for enthalpy, from 1,2-dichlorobenzene. The results in Table 12 show that omission of this ORT/Cl/Cl correction results in better agreement for the enthalpy estimate of 23DCDD and 2378TCDD with values in the literature. Additional experimental or computa-

TABLE 11. Comparison of thermochemical properties from group additivity with the recommended values^a

		$\Delta_f H^\circ$ (298.15 K)	S° (298.15 K)	$C_p^\circ(T)$						
				300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
1CDD (4)	Calc ^a	-70.1	436.5	194.4	251.5	298.2	335.1	387.6	422.2	470.7
	GA	-69.9	432.3	194.4	251.5	298.2	335.1	387.6	422.2	470.7
2CDD (5)	Calc ^a	-77.2	436.6	194.8	251.8	298.5	335.4	387.8	422.4	470.7
	GA	-77.1	432.2	194.8	251.8	298.5	335.4	387.8	422.4	470.7
16DCDD (6)	Calc ^a	-89.3	461.0	210.5	266.4	311.9	347.6	397.9	430.8	476.0
	GA	-89.6	469.4	210.4	266.4	311.9	347.6	397.9	430.8	476.0
18DCDD (7)	Calc ^a	-96.4	466.3	210.8	266.9	312.3	347.9	398.1	430.9	476.0
	GA	-96.9	469.4	210.8	266.8	312.3	347.9	398.1	430.9	476.0
19DCDD (8)	Calc ^a	-88.0	460.8	210.4	266.4	311.9	347.6	397.9	430.8	476.0
	GA	-89.6	469.4	210.4	266.4	311.9	347.6	397.9	430.8	476.0
28DCDD (9)	Calc ^a	-103.9	460.5	211.1	267.2	312.6	348.2	398.4	431.1	476.1
	GA	-104.1	469.3	211.1	267.2	312.6	348.2	398.3	431.1	476.1
3CDF (13)	Calc ^a	26.6	409.7	178.0	232.9	278.2	314.1	365.2	399.1	446.6
	GA	26.7	406.8	178.0	232.9	278.2	314.1	365.3	399.1	446.7
4CDF (14)	Calc [*]	33.3	409.7	177.6	232.4	277.7	313.6	364.9	398.9	446.6
	GA	33.6	406.9	177.6	232.4	277.7	313.6	364.9	398.9	446.6
16DCDF (15)	Calc ^a	5.2	438.9	193.5	247.4	291.5	326.2	375.3	407.5	451.8
	GA	5.1	439.8	193.9	247.8	291.8	326.5	375.6	407.6	451.9
36DCDF (16)	Calc ^a	5.5	439.9	193.9	247.8	291.9	326.6	375.6	407.6	451.9
	GA	5.1	439.8	193.9	247.8	291.8	326.5	375.6	407.6	451.9
37DCDF (17)	Calc ^a	-1.5	434.0	194.3	248.3	292.3	326.9	376.3	407.8	452.0
	GA	-1.8	439.8	194.4	248.3	292.3	327.0	376.0	407.8	452.0
46DCDF (18)	Calc ^a	12.7	434.1	193.5	247.2	291.3	326.1	375.3	407.4	451.9
	GA	12.0	439.8	193.5	247.3	291.3	326.1	375.2	407.4	451.9

^aSee Tables 7, 8, and 9; $\Delta_f H^\circ(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$; $S^\circ(298.15\text{ K})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; $C_p^\circ(T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

TABLE 12. Comparison of thermochemical properties of 23DCDD and 2378TCDD from group additivity with literature values^a

		$\Delta_f H^\circ$ (298.15 K)	S° (298.15 K)	$C_p^\circ(T)$						
				300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
2,3-Dichloro dibenzo- <i>p</i> -dioxin (23DCDD) Symmetry=2	Papina <i>et al.</i> ⁶²	-111.9								
	León <i>et al.</i> ⁵⁰	-102.0								
	Kolesov <i>et al.</i> ³⁵	-111.9								
	Shaub ²²	-204.0								
	Thompson ²⁴	-106.5								
	Dorofeeva <i>et al.</i> ³³	-112								
	GA ^b	-96.4	449.3	211.8	266.8	312.4	348.1	398.3	431.0	476.1
GA ^c	-109.2	456.5	212.3	267.3	312.8	348.4	398.4	431.0	476.1	
2,3,7,8-Tetrachloro dibenzo- <i>p</i> -dioxin (2378TCDD) Symmetry=4	Papina <i>et al.</i> ⁶²	-164.6								
	León <i>et al.</i> ⁵⁰	-141.7								
	Ritter/Bozzelli ⁶⁷	-440.6								
	Shaub ²²	-345								
	Dorofeeva <i>et al.</i> ³³	-164								
	GA ^b	-142.7	503.5	245.1	297.1	340.4	373.6	419.4	448.3	486.8
	GA ^c	-168.2	517.9	246.1	298.1	341.2	374.1	419.6	448.4	486.7

^a $\Delta_f H^\circ(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$; $S^\circ(298.15\text{ K})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; $C_p^\circ(T)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

^bThis work, using Eqs. (15a) or (16a), consider ORT/Cl/Cl.

^cThis work, using Eqs. (15b) or (16b), not consider ORT/Cl/Cl.

tional studies by the research community are needed to improve our knowledge on the enthalpies of these higher chlorinated dibenzo-*p*-dioxins and dibenzofurans.

4. Summary

The structures of dibenzo-*p*-dioxin, dibenzofuran, and 12 mono-, di-chlorodibenzo-*p*-dioxins and dibenzofurans are studied by B3LYP/6-31G(d,p) DFT calculations. The recommended enthalpy of formation values, $\Delta_f H^\circ(298.15\text{ K})$, of each chlorinated dibenzo-*p*-dioxin and dibenzofuran species is the average of values from two isodesmic reactions calculated the B3LYP/6-311+G(3df,2p) level based on the B3LYP/6-31G(d,p) optimized geometry. $S^\circ(298.15\text{ K})$ and $C_p^\circ(T)$ ($5 \leq T/\text{K} \leq 6000$) are determined by B3LYP/6-31G(d,p) optimized geometries and frequencies. The thermodynamic properties are determined for two groups (DD and DF) and four interaction groups (ortho/Cl/DD, meta/Cl/DD, ortho/Cl/DF, and meta/Cl/DF) which are useful for group additivity estimation of thermochemical data, namely, $\Delta_f H^\circ(298.15\text{ K})$, $S^\circ(298.15\text{ K})$, and $C_p^\circ(T)$, on higher chlorinated PCDD/Fs.

5. Acknowledgments

The authors gratefully acknowledge funding from the USEPA Northeast Research Center and the USEPA-CalTech-MIT-NJIT Research Center on Airborne Organics. They also acknowledge and thank Professor Lev Krasnoperov for discussions on low frequency vibrations.

6. References

- D. M. Wagrowski and R. A. Hites, *Environ. Sci. Technol.* **34**, 2952 (2000).
- P. Tan, I. Hurtado, D. Nuschütz, and G. Eriksson, *Environ. Sci. Technol.* **35**, 1867 (2001).
- J. A. Mulholland, U. Akki, Y. Yang, and J. Ryu, *Chemosphere* **42**, 719 (2000).
- A. Yazawa, S. Nakazawa, and N. Menad, *Chemosphere* **39**, 2419 (1999).
- R. Weber and H. Hagenmaier, *Chemosphere* **38**, 529 (1999).
- Y. Yang, J. A. Mulholland, and U. Akki, Formation of furans by gas-phase reactions of chlorophenols., 27th International Symposium on Combustion, Boulder, CO, 1998.
- H. Grotheer and R. Louw, The reaction of phenoxy radicals with monochlorobenzene and its meaning for gas-phase dioxin formation in incineration, 26th International Symposium on Combustion, University of Naples, Italy, 1996.
- A. Fadli, C. Brioso, C. Baillet, and J.-P. Sawerysyn, *Chemosphere* **38**, 2835 (1998).
- K. S. Lin, H. P. Wang, and M. C. Li, *Chemosphere* **36**, 2075 (1998).
- I. Wiater and R. Louw, *Eur. J. Org. Chem.* 261 (1999).
- I. Wiater and R. Louw, *Organohalogen Compounds* **41**, 77 (1999).
- R. Louw, H. Grotheer, M. J. Kanters, and I. Wiater, *Organohalogen Compounds* **27**, 26 (1996).
- H. Grotheer and R. Louw, *Combust. Sci. Technol.* **134**, 45 (1998).
- S. B. Ghorishi and E. R. Altwicker, *Chemosphere* **32**, 133 (1996).
- J. Kanters and R. Louw, *Chemosphere* **32**, 89 (1996).
- J. M. Kanters and R. Louw, *Chemosphere* **33**, 1889 (1996).
- P. M. Sommeling, P. Mulder, and R. Louw, *Chemosphere* **29**, 2015 (1994).
- J. Kanters and R. Louw, *Chemosphere* **29**, 1919 (1994).
- S. S. Sidhu and P. Edwards (Personal communications, University of Dayton Research Institute, Dayton, OH, 2001).
- Y. Okamoto and M. Tomonari, *J. Phys. Chem. A* **103**, 7686 (1999).
- W. M. Shaub, *Thermochim. Acta* **58**, 11 (1982).
- W. M. Shaub, *Thermochim. Acta* **55**, 59 (1982).
- Y. G. Wu, S. N. Patel, E. R. Ritter, and J. W. Bozzelli, *Thermochim. Acta* **222**, 153 (1993).
- D. Thompson, *Thermochim. Acta* **261**, 7 (1995).
- O. V. Dorofeeva and L. V. Gurvich, *Zh. Fiz. Khim.* **70**, 7 (1996).
- A. V. Fokin, N. P. Vorobieva, N. I. Raevskii, Y. A. Borisov, and A. F. Kolomiets, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2544 (1989).
- C. J. Koester and R. A. Hites, *Chemosphere* **17**, 2355 (1988).
- N. Saito and A. Fuwa, *Chemosphere* **40**, 131 (2000).

- ²⁹ J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic, New York, 1970).
- ³⁰ J. B. Pedley, R. O. Naylor, and S. P. Kirby, *Thermodynamic Data of Organic Compounds*, 2nd ed. (Chapman and Hall, London, 1986).
- ³¹ R. Sabbah, *Bull. Soc. Chim. Fr.* **128**, 350 (1991).
- ³² R. D. Chirico, B. E. Gammon, S. E. Knipmeyer, A. Nguyen, M. M. Strube, C. Tsonopoulos, and W. V. Steele, *J. Chem. Thermodyn.* **22**, 1075 (1990).
- ³³ O. V. Dorofeeva, V. S. Iorish, and N. F. Moiseeva, *J. Chem. Eng. Data* **44**, 516 (1999).
- ³⁴ R. Notario, M. V. Roux, and O. Castaño, *Phys. Chem. Chem. Phys.* **3**, 3717 (2001).
- ³⁵ V. P. Kolesov, O. V. Dorofeeva, V. S. Iorish, T. S. Papina, V. A. Lukyanova, and S. V. Melkhanova, *Mendeleev Commun.* 143 (1999).
- ³⁶ S. M. Pimenova, S. V. Melkhanova, V. P. Kolesov, P. I. Demyanov, and A. N. Fedotov, *J. Chem. Thermodyn.* **34**, 385 (2002).
- ³⁷ G. Liu, X. Song, J. Yu, and X. Qian, *Chin. J. Chem. Phys. (Huaxue Wuli Xubao)* **14**, 414 (2001).
- ³⁸ C. A. Davies, E. Freedman, D. J. Frurip, G. R. Hertel, W. H. Seaton, and D. N. Treweek, *CHETAH, the ASTM Chemical Thermodynamic and Energy Release Evaluation Program*, 2nd ed. (1990).
- ³⁹ M. J. Frisch *et al.*, GAUSSIAN 94 (Gaussian, Inc., Pittsburgh, PA, 1995).
- ⁴⁰ L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **106**, 1063 (1997).
- ⁴¹ J. L. Durant, *Chem. Phys. Lett.* **256**, 595 (1996).
- ⁴² J. L. Durant and C. M. Rohlffing, *J. Chem. Phys.* **98**, 8031 (1993).
- ⁴³ G. A. Petersson, D. K. Malick, W. G. Wilson, J. W. Ochterski, J. A. Montgomery, Jr. and M. J. Frisch, *J. Chem. Phys.* **109**, 10570 (1998).
- ⁴⁴ M. W. Wong and L. Radom, *J. Phys. Chem. A* **102**, 2237 (1998).
- ⁴⁵ A. P. Scott and L. Radom, *J. Phys. Chem.* **100**, 16502 (1996).
- ⁴⁶ W. Hehre, L. Radom, P. R. Schleyer, and J. A. Pople, *Ab-initio Molecular Orbital Theory* (Wiley & Sons, New York, 1986).
- ⁴⁷ P. C. Redfern, P. Zapol, L. A. Curtiss, and K. Raghavachari, *J. Phys. Chem. A* **104**, 5850 (2000).
- ⁴⁸ C. Chen and J. W. Bozzelli, *J. Phys. Chem. A* (submitted).
- ⁴⁹ C. Sheng, Ph.D. dissertation, New Jersey Institute of Technology, Newark, NJ, 2002.
- ⁵⁰ L. A. León, R. Notario, J. Quijano, and C. Sánchez, *J. Phys. Chem. A* **106**, 6618 (2002).
- ⁵¹ A. Nicolaides, A. Rauk, M. N. Glukhovtsev, and L. Radom, *J. Phys. Chem.* **100**, 17460 (1996).
- ⁵² L. Zhu, C. Chen, and J. W. Bozzelli (unpublished).
- ⁵³ V. A. Platonov and Y. N. Simulin, *Russ. J. Phys. Chem. (Engl. Transl.)* **59**, 179 (1985).
- ⁵⁴ J. A. Manion, *J. Phys. Chem. Ref. Data* **31**, 123 (2002).
- ⁵⁵ D. Feller and J. A. Franz, *J. Phys. Chem. A* **104**, 9017 (2000).
- ⁵⁶ W. V. Steele and R. D. Chirico, Cooperative Agreement No. FC22-83FE60149 (NIPEP-457), IIT Research Institute, NIPEP, Bartlesville, OK, 1990.
- ⁵⁷ L. Zhu, C. Chen, and J. W. Bozzelli, *J. Phys. Chem. A* **104**, 9197 (2000).
- ⁵⁸ K. N. Marsh, R. C. Wilhoit, M. Frenkel, and D. Yin, *Thermodynamic Properties of the Substances in Ideal Gas State: Linear and Non-Linear Function Coefficients Data Files and Computer Codes to Regenerate the Values of Thermodynamic Properties*, Version 1.0 m. (Thermodynamics Research Center, The Texas Engineering Experiment Station, Texas A&M University System, College Station, TX, 1994); Currently at U.S. National Institute of Standards and Technology, Boulder, CO.
- ⁵⁹ E. R. Ritter, *J. Chem. Info. Comp. Sci.* **31**, 400 (1991).
- ⁶⁰ E. R. Ritter and J. W. Bozzelli, *Int. J. Chem. Kinet.* **23**, 767 (1991).
- ⁶¹ H. Sun and J. W. Bozzelli, *J. Phys. Chem. A* **105**, 4504 (2001).
- ⁶² T. S. Papina, V. P. Kolesov, V. A. Lukyanova, V. F. Golovkov, C. A. Chernov, and V. P. Vorobieva, *J. Chem. Thermodyn.* **30**, 431 (1998).
- ⁶³ H. Yan, J. Gu, X. An, and R. Hu, *Huaxue Xuebao* **45**, 1184 (1987).
- ⁶⁴ V. A. Lukyanova, V. P. Kolesov, N. V. Avramenko, V. P. Vorobieva, and V. F. Golovkov, *Zh. Fiz. Khim.* **71**, 406 (1997).
- ⁶⁵ N. L. Allinger and L. Yan, *J. Am. Chem. Soc.* 11918 (1993).
- ⁶⁶ S. W. Benson, *Thermochemical Kinetics* (Wiley, New York, 1976).
- ⁶⁷ E. R. Ritter and J. W. Bozzelli, *Combust. Sci. Technol.* **101**, 153 (1994).

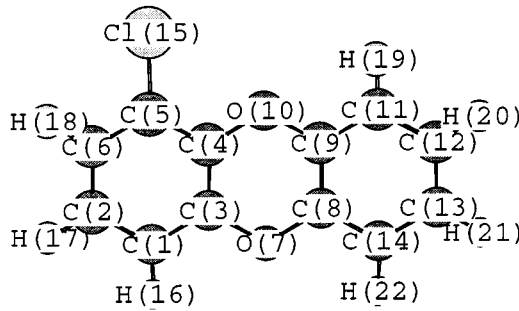
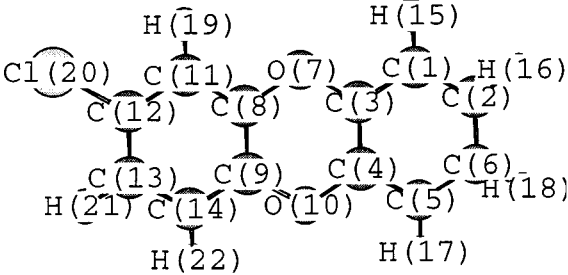
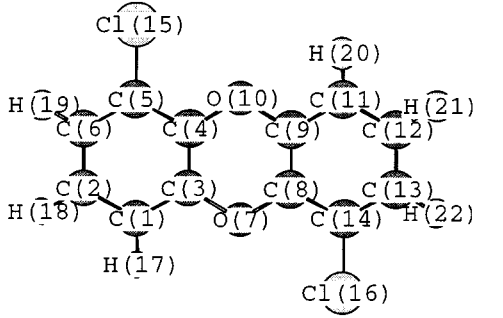
7. Appendix: List of Supplemental Materials

SUPPLEMENTAL MATERIALS 1: Geometries at B3LYP/6-31G(d,p) level (in Å and degree)

Species (ID #)	Structure	Bond length	Bond angle	Dihedral angle			
1,4-Dioxin (1)		r21	1.330				
		r32	1.389	d321	123.98		
		r43	1.389	d432	112.07	d4321	0.00
		r54	1.330	d543	123.95	d5432	0.00
		r65	1.389	d654	123.98	d6543	0.00
		r71	1.081	d712	123.29	d7123	180.00
		r82	1.081	d821	123.23	d8213	180.00
		r94	1.081	d943	112.79	d9432	180.00
		r105	1.081	d1054	123.23	d10543	180.00
		2,3-Benzodioxin (2)		r21	1.399		
r32	1.393			d321	120.02		
r43	1.399			d432	120.00	d4321	0.00
r54	1.389			d543	119.98	d5432	0.02
r61	1.389			d612	119.98	d6123	-0.03
r76	1.385			d761	118.13	d7612	-179.96
r87	1.383			d876	114.42	d8761	-179.58
r98	1.330			d987	123.71	d9876	-0.43
r109	1.383			d1098	123.72	d10987	0.00
r111	1.085			d1112	121.66	d11123	179.99
r122	1.085			d1221	119.56	d12213	-180.00
r133	1.085			d1332	120.43	d13321	-180.00
r144	1.085			d1443	121.65	d14432	-179.99
r158	1.080	d1587	112.72	d15876	179.55		
r169	1.081	d1698	123.57	d16987	179.98		
Dibenzo- <i>p</i> -dioxin (3)		r21	1.397				
		r31	1.390	d312	119.87		
		r43	1.400	d431	120.08	d4312	0.00
		r54	1.390	d543	120.09	d5431	0.00
		r62	1.394	d621	120.05	d6213	0.00
		r73	1.381	d731	118.12	d7312	-179.99
		r87	1.381	d873	116.41	d8731	-179.98
		r98	1.400	d987	121.79	d9873	-0.03
		r109	1.381	d1098	121.80	d10987	0.00
		r118	1.390	d1187	118.13	d11873	179.97
		r1211	1.397	d12118	119.87	d121187	-180.00
		r1312	1.394	d131211	120.04	d1312118	.00
		r149	1.390	d1498	120.08	d14987	180.00
		r151	1.085	d1512	121.71	d15123	180.00
		r162	1.085	d1621	119.55	d16213	-180.00
		r175	1.085	d1754	118.42	d17543	180.00
		r186	1.085	d1862	120.41	d18621	180.00
r1911	1.085	d19118	118.42	d191187	0.00		
r2012	1.085	d201211	119.55	d201218	180.00		
r2113	1.085	d211312	120.40	d21131211	-180.00		
r2214	1.085	d22149	118.42	d221498	-180.00		
Dibenzo furan	r21	1.399					
1-Chloro	r21	1.396					
Dibenzo- <i>p</i> -dioxin (1CDD) (4)		r31	1.389	d312	119.63		
		r43	1.402	d431	120.80	d4312	0.00
		r54	1.396	d543	118.83	d5431	0.00
		r62	1.392	d621	120.44	d6213	0.00
		r73	1.379	d731	117.87	d7312	-180.00
		r87	1.382	d873	116.75	d8731	-180.00
		r98	1.398	d987	121.62	d9873	0.00

THERMOCHEMICAL PROPERTIES OF CHLORINATED DIBENZODIOXINS AND DIBENZOFURANS 1729

SUPPLEMENTAL MATERIALS 1: Geometries at B3LYP/6-31G(d,p) level (in Å and degree)—Continued

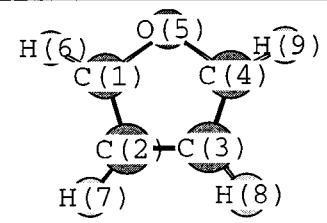
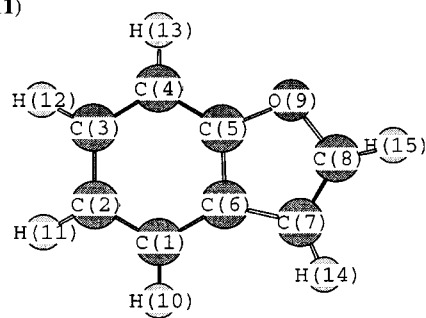
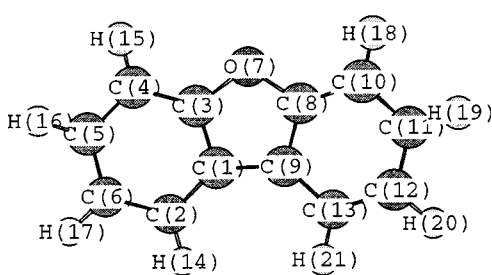
	r104	1.372	d1043	122.12	d10431	179.99	
	r119	1.389	d1198	120.29	d11987	-179.99	
	r1211	1.397	d12119	119.67	d121198	0.00	
	r1312	1.395	d131211	120.09	d1312119	0.00	
	r148	1.390	d1487	118.26	d14873	-180.00	
	r155	1.750	d1554	119.18	d15543	-180.00	
	r161	1.084	d1612	121.86	d16123	-180.00	
	r172	1.085	d1721	119.76	d17213	180.00	
	r186	1.083	d1862	121.32	d18621	-180.00	
	r1911	1.085	d19119	118.50	d191198	180.00	
	r2012	1.085	d201211	119.53	d2012119	-180.00	
	r2113	1.085	d211312	120.37	d21131211	180.00	
	r2214	1.085	d22148	118.54	d221487	0.00	
	<hr/>						
	2-Chloro	r21	1.397				
Dibenzo- <i>p</i> -dioxin	r31	1.390	d312	119.78			
(2CDD)	r43	1.399	d431	120.17	d4312	0.00	
(5)	r54	1.390	d543	120.10	d5431	0.00	
	r62	1.395	d621	120.06	d6213	0.00	
	r73	1.383	d731	118.06	d7312	-180.00	
	r87	1.377	d873	116.37	d8731	-179.97	
	r98	1.400	d987	121.88	d9873	-0.03	
	r109	1.378	d1098	121.84	d10987	0.00	
	r118	1.390	d1187	117.74	d11873	179.97	
	r1211	1.395	d12118	119.01	d121187	179.99	
	r1312	1.392	d131211	121.33	d1312118	0.00	
	r149	1.389	d1498	119.85	d14987	-180.00	
	r151	1.085	d1512	121.76	d15123	-180.00	
	r162	1.085	d1621	119.54	d16213	180.00	
	r175	1.085	d1754	118.45	d17543	180.00	
	r186	1.085	d1862	120.38	d18621	-180.00	
	r1911	1.083	d19118	119.31	d191187	0.00	
	r2012	1.758	d201211	118.97	d2012118	-180.00	
	r2113	1.083	d211312	120.43	d21131211	180.00	
	r2214	1.085	d22149	118.55	d221498	-180.00	
<hr/>							
1,6-Dichloro	r21	1.396					
Dibenzo- <i>p</i> -dioxin	r31	1.389	d312	119.42			
(16DCDD)	r43	1.400	d431	120.95	d4312	0.00	
(6)	r54	1.396	d543	118.96	d5431	0.00	
	r62	1.392	d621	120.50	d6213	0.00	
	r73	1.380	d731	117.85	d7312	179.96	
	r87	1.374	d873	116.91	d8731	179.67	
	r98	1.400	d987	121.89	d9873	0.35	
	r104	1.374	d1043	121.89	d10431	179.98	
	r119	1.389	d1198	120.96	d11987	179.97	
	r1211	1.396	d12119	119.42	d121198	0.00	
	r1312	1.392	d131211	120.51	d1312119	0.00	
	r148	1.396	d1487	119.15	d14873	-179.67	
	r155	1.749	d1554	119.25	d15543	180.00	
	r1614	1.749	d16148	119.25	d161487	0.03	
	r171	1.084	d1712	122.04	d17123	179.99	
	r182	1.085	d1821	119.77	d18213	-179.99	
	r196	1.083	d1962	121.26	d19621	179.99	
	r2011	1.084	d20119	118.55	d201198	180.00	
	r2112	1.085	d211211	119.76	d2112119	-179.99	
	r2213	1.083	d221312	121.26	d22131211	180.00	

SUPPLEMENTAL MATERIALS 1: Geometries at B3LYP/6-31G(d,p) level (in Å and degree)—Continued

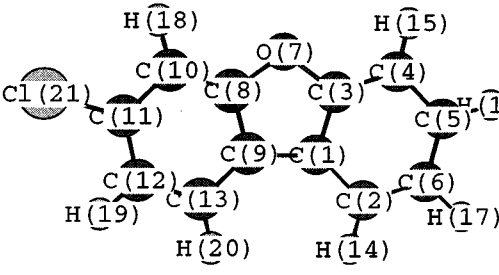
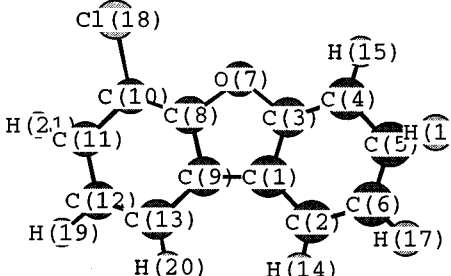
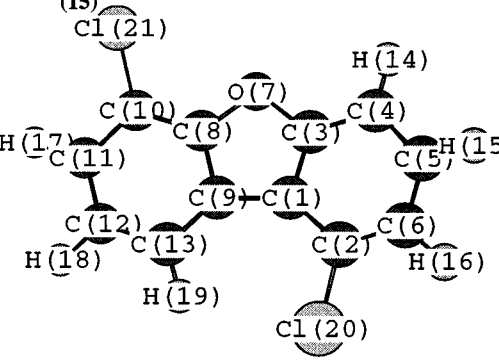
1,8-Dichloro	r21	1.396				
Dibenzo- <i>p</i> -dioxin	r31	1.389	d312	120.29		
(18DCDD)	r43	1.398	d431	119.88	d4312	0.00
(7)	r54	1.389	d543	120.56	d5431	0.00
	r62	1.393	d621	119.10	d6213	0.00
	r73	1.379	d731	118.47	d7312	179.99
	r87	1.380	d873	116.75	d8731	179.92
	r98	1.401	d987	121.30	d9873	0.08
	r109	1.375	d1098	122.05	d10987	0.00
	r119	1.396	d1198	118.97	d11987	179.99
	r1211	1.397	d12119	120.66	d121198	0.00
	r1312	1.392	d131211	119.54	d1312119	0.00
	r148	1.389	d1487	117.89	d14873	-179.92
	r1514	1.084	d15148	118.52	d151487	0.00
	r161	1.085	d1612	121.08	d16123	180.00
	r172	1.083	d1721	120.53	d17213	-180.00
	r1811	1.749	d18119	119.25	d181198	180.00
	r1912	1.084	d191211	119.18	d1912119	-180.00
	r2013	1.085	d201312	119.75	d20131211	180.00
	r215	1.083	d2154	119.31	d21543	-180.00
	r226	1.756	d2262	119.70	d22621	180.00
<hr/>						
1,9-Dichloro	r21	1.396				
Dibenzo- <i>p</i> -dioxin	r31	1.389	d312	119.47		
(19DCDD)	r43	1.400	d431	120.88	d4312	0.00
(8)	r54	1.396	d543	119.02	d5431	0.00
	r62	1.392	d621	120.49	d6213	0.00
	r73	1.379	d731	117.94	d7312	179.96
	r87	1.379	d873	117.08	d8731	179.67
	r98	1.400	d987	121.17	d9873	0.36
	r109	1.375	d1098	121.99	d10987	0.00
	r119	1.396	d1198	119.01	d11987	179.97
	r1211	1.397	d12119	120.57	d121198	0.00
	r1312	1.392	d131211	119.59	d1312119	0.00
	r148	1.389	d1487	117.95	d14873	-179.67
	r155	1.747	d1554	119.35	d15543	-180.00
	r1614	1.084	d16148	118.61	d161487	0.03
	r171	1.084	d1712	121.92	d17123	179.99
	r182	1.085	d1821	119.75	d18213	-179.99
	r196	1.083	d1962	121.27	d19621	180.00
	r2011	1.747	d20119	119.33	d201198	180.00
	r2112	1.084	d211211	119.14	d2112119	-179.99
	r2213	1.085	d221312	119.76	d22131211	180.00
<hr/>						
2,8-Dichloro	r21	1.395				
Dibenzo- <i>p</i> -dioxin	r31	1.390	d312	118.95		
(28DCDD)	r43	1.399	d431	120.47	d4312	0.00
(9)	r54	1.389	d543	119.86	d5431	0.00
	r62	1.393	d621	121.30	d6213	0.00
	r73	1.379	d731	117.67	d7312	180.00
	r87	1.379	d873	116.32	d8731	179.97
	r98	1.399	d987	121.85	d9873	0.03
	r109	1.379	d1098	121.83	d10987	0.00
	r118	1.390	d1187	117.67	d11873	-179.97
	r1211	1.395	d12118	118.94	d121187	-180.00
	r1312	1.393	d131211	121.30	d1312118	0.00
	r149	1.389	d1498	119.86	d14987	180.00
	r151	1.083	d1512	121.70	d15123	180.00
	r162	1.756	d1621	118.98	d16213	-180.00

THERMOCHEMICAL PROPERTIES OF CHLORINATED DIBENZODIOXINS AND DIBENZOFURANS 1731

SUPPLEMENTAL MATERIALS 1: Geometries at B3LYP/6-31G(d,p) level (in Å and degree)—Continued

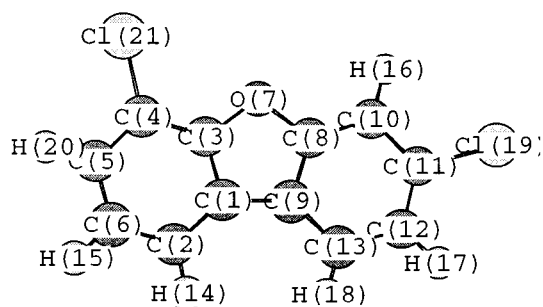
	r175	1.085	d1754	118.61	d17543	-180.00
	r186	1.083	d1862	120.40	d18621	180.00
	r1911	1.083	d19118	119.37	d191187	0.00
	r2012	1.757	d201211	118.98	d2012118	180.00
	r2113	1.083	d211312	120.40	d21131211	180.00
	r2214	1.085	d22149	118.60	d221498	180.00
Furan (10)	r21	1.360				
	r32	1.435	d321	106.10		
	r43	1.361	d432	106.10	d4321	0.00
	r54	1.364	d543	110.51	d5432	0.00
	r61	1.079	d612	133.70	d6123	-180.00
	r72	1.080	d721	126.51	d7213	180.00
	r83	1.080	d832	127.39	d8321	180.00
	r94	1.079	d943	133.70	d9432	-180.00
2,3-Benzofuran (11)	r21	1.392				
	r32	1.408	d321	121.37		
	r43	1.394	d432	121.28	d4321	0.00
	r54	1.390	d543	116.41	d5432	0.00
	r61	1.403	d612	118.44	d6123	0.00
	r76	1.444	d761	135.93	d7612	179.98
	r87	1.355	d876	106.03	d8761	179.97
	r95	1.370	d954	125.96	d9543	179.99
	r101	1.086	d1012	120.75	d10123	179.99
	r112	1.086	d1121	119.49	d11213	-180.00
	r123	1.086	d1232	119.40	d12321	-180.00
	r134	1.084	d1343	122.24	d13432	180.00
	r147	1.080	d1476	127.68	d14761	0.00
	r158	1.079	d1587	132.55	d15876	-179.99
Dibenzo furan (12)	r21	1.399				
	r31	1.408	d312	118.99		
	r43	1.388	d431	123.34	d4312	0.00
	r54	1.396	d543	116.66	d5431	0.00
	r62	1.394	d621	118.62	d6213	0.00
	r73	1.377	d731	111.63	d7312	-179.99
	r87	1.377	d873	105.99	d8731	0.00
	r98	1.408	d987	111.63	d9873	0.00
	r108	1.388	d1087	125.03	d10873	-180.00
	r1110	1.396	d11108	116.66	d111087	-179.99
	r1211	1.405	d121110	121.33	d1211108	0.00
	r1312	1.394	d131211	121.06	d13121110	0.00
	r142	1.086	d1421	120.77	d14213	180.00
	r154	1.084	d1543	121.22	d15431	-180.00
	r165	1.086	d1654	119.18	d16543	-180.00
	r176	1.086	d1762	119.58	d17621	-180.00
	r1810	1.084	d18108	121.22	d181087	0.00
	r1912	1.086	d191210	119.19	d1912108	179.99
	r2013	1.086	d201311	119.36	d20131110	-180.00
	r2111	1.086	d211112	120.60	d21111211	180.00
3-Chloro Dibenzo furan (3CDF) (13)	r21	1.399				
	r31	1.408	d312	119.00		
	r43	1.387	d431	123.40	d4312	0.00
	r54	1.396	d543	116.59	d5431	0.00
	r62	1.394	d621	118.56	d6213	0.00
	r73	1.379	d731	111.60	d7312	180.00
	r87	1.374	d873	105.95	d8731	0.00
	r98	1.408	d987	111.73	d9873	0.00

SUPPLEMENTAL MATERIALS 1: Geometries at B3LYP/6-31G(d,p) level (in Å and degree)—Continued

	r108	1.388	d1087	124.57	d10873	180.00
	r1110	1.394	d11108	115.84	d111087	-180.00
	r1211	1.403	d121110	122.52	d1211108	0.00
	r1312	1.393	d131211	120.07	d13121110	0.00
	r142	1.086	d1421	120.80	d14213	180.00
	r154	1.084	d1543	121.23	d15431	180.00
	r165	1.086	d1654	119.20	d16543	-180.00
	r176	1.085	d1762	119.57	d17621	180.00
	r1810	1.083	d18108	122.02	d181087	0.00
	r1912	1.084	d191211	119.35	d19121110	180.00
	r2013	1.085	d201312	119.92	d20131211	-180.00
	r2111	1.758	d211110	118.67	d2111108	-180.00
4-Chloro	r21	1.400				
Dibenzo furan	r31	1.407	d312	119.03		
(4CDF)	r43	1.387	d431	123.45	d4312	0.00
(14)	r54	1.396	d543	116.53	d5431	0.00
	r62	1.393	d621	118.51	d6213	0.00
	r73	1.379	d731	111.60	d7312	179.99
	r87	1.369	d873	105.82	d8731	0.00
	r98	1.409	d987	112.14	d9873	0.00
	r108	1.390	d1087	125.81	d10873	180.00
	r1110	1.394	d11108	117.92	d111087	-180.00
	r1211	1.403	d121110	120.57	d1211108	0.00
	r1312	1.393	d131211	121.39	d13121110	0.00
	r142	1.086	d1421	120.82	d14213	-180.00
	r154	1.084	d1543	121.23	d15431	180.00
	r165	1.086	d1654	119.19	d16543	-180.00
	r176	1.085	d1762	119.57	d17621	180.00
	r1810	1.748	d18108	120.76	d181087	0.00
	r1912	1.085	d191211	118.80	d19121110	180.00
	r2013	1.085	d201312	120.68	d20131211	180.00
	r2111	1.084	d211110	118.98	d2111108	180.00
	r21	1.399				
1,6-Dichloro	r31	1.410	d312	117.52		
Dibenzo furan	r43	1.387	d431	124.07	d4312	0.00
(16DCDF)	r54	1.395	d543	116.48	d5431	0.00
(15)	r62	1.392	d621	120.10	d6213	0.00
	r73	1.375	d731	111.31	d7312	-180.00
	r87	1.369	d873	106.06	d8731	0.00
	r98	1.409	d987	112.21	d9873	0.00
	r108	1.390	d1087	125.54	d10873	-180.00
	r1110	1.394	d11108	117.82	d111087	180.00
	r1211	1.403	d121110	120.51	d1211108	0.00
	r1312	1.393	d131211	121.61	d13121110	0.00
	r144	1.084	d1443	121.18	d14431	180.00
	r155	1.085	d1554	119.48	d15543	180.00
	r166	1.084	d1662	119.41	d16621	180.00
	r1711	1.084	d171110	118.99	d1711108	-180.00
	r1812	1.085	d181211	118.77	d18121110	180.00
	r1913	1.083	d191312	120.95	d19131211	-180.00
	r202	1.756	d2021	120.38	d20213	-180.00
	r2110	1.748	d21108	120.73	d211087	0.00
	r21	1.399				
3,6-Dichloro	r31	1.409	d312	119.60		
Dibenzo furan	r43	1.390	d431	122.16	d4312	0.00
(36DCDF)	r54	1.395	d543	117.79	d5431	0.00
(16)						

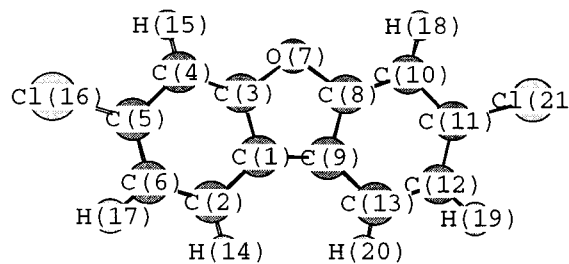
THERMOCHEMICAL PROPERTIES OF CHLORINATED DIBENZODIOXINS AND DIBENZOFURANS 1733

SUPPLEMENTAL MATERIALS 1: Geometries at B3LYP/6-31G(d,p) level (in Å and degree)—Continued



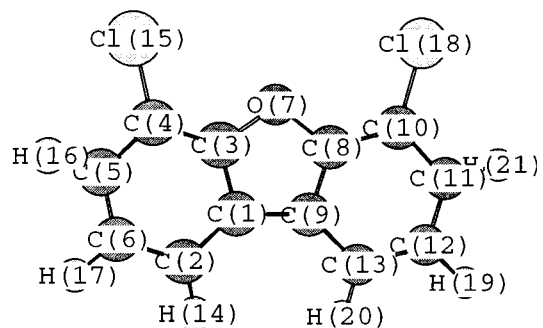
r62	1.393	d621	118.40	d6213	0.00
r73	1.371	d731	112.11	d7312	-180.00
r87	1.375	d873	105.78	d8731	0.00
r98	1.407	d987	111.71	d9873	0.00
r108	1.387	d1087	124.50	d10873	-180.00
r1110	1.394	d11108	115.72	d111087	-180.00
r1211	1.404	d121110	122.55	d1211108	0.00
r1312	1.392	d131211	120.12	d13121110	0.00
r142	1.085	d1421	120.90	d14213	-180.00
r156	1.085	d1562	119.78	d15621	-180.00
r1610	1.083	d16108	122.08	d161087	0.00
r1712	1.084	d171211	119.33	d17121110	180.00
r1813	1.085	d181312	119.96	d18131211	180.00
r1911	1.757	d191110	118.68	d1911108	180.00
r205	1.084	d2054	118.96	d20543	180.00
r214	1.747	d2143	120.80	d21431	-180.00

3,7-Dichloro
Dibenzo furan
(37DCDF)
(17)



r21	1.399				
r31	1.408	d312	118.75		
r43	1.387	d431	123.75	d4312	0.00
r54	1.394	d543	115.78	d5431	0.00
r62	1.393	d621	119.08	d6213	0.00
r73	1.375	d731	111.72	d7312	-180.00
r87	1.375	d873	105.89	d8731	0.00
r98	1.408	d987	111.72	d9873	0.00
r108	1.387	d1087	124.53	d10873	-180.00
r1110	1.394	d11108	115.78	d111087	-180.00
r1211	1.403	d121110	122.53	d1211108	0.00
r1312	1.393	d131211	120.12	d13121110	0.00
r142	1.085	d1421	120.99	d14213	-180.00
r154	1.083	d1543	122.08	d15431	180.00
r165	1.757	d1654	118.67	d16543	180.00
r176	1.084	d1762	120.54	d17621	-180.00
r1810	1.083	d18108	122.08	d181087	0.00
r1912	1.084	d191211	119.34	d19121110	180.00
r2013	1.085	d201312	119.93	d20131211	-180.00
r2111	1.757	d211110	118.67	d2111108	180.00

4,6-Dichloro
Dibenzo furan
(46DCDF)
(18)



r21	1.399				
r31	1.408	d312	119.66		
r43	1.390	d431	122.19	d4312	0.00
r54	1.394	d543	117.71	d5431	0.00
r62	1.393	d621	118.35	d6213	0.00
r73	1.371	d731	112.08	d7312	-179.99
r87	1.371	d873	105.69	d8731	0.00
r98	1.408	d987	112.08	d9873	0.00
r108	1.390	d1087	125.73	d10873	180.00
r1110	1.394	d11108	117.71	d111087	-180.00
r1211	1.403	d121110	120.66	d1211108	0.00
r1312	1.393	d131211	121.42	d13121110	0.00
r142	1.085	d1421	120.90	d14213	-180.00
r154	1.746	d1543	120.86	d15431	180.00
r165	1.084	d1654	118.93	d16543	-180.00
r176	1.085	d1762	119.80	d17621	180.00
r1810	1.746	d18108	120.86	d181087	0.00
r1912	1.085	d191211	118.78	d19121110	180.00
r2013	1.085	d201312	120.74	d20131211	-180.00
r2111	1.084	d211110	118.92	d2111108	-180.00

SUPPLEMENTAL MATERIALS 2: B3LYP/6-31G(d,p)-determined harmonic vibrational frequencies and moments of inertia of mono- and di-chloro dibenzo-*p*-dioxins and dibenzofurans

Species (Symmetry No.)	Frequency (cm ⁻¹)	Ia	Ib	Ic
		(amu bohr ²)		
1,4-Dioxin (1) Sym=8	88 444 525 546 704 758 759 873 880 911 940 1040 1065 1078 1248 1319 1343 1437 1731 1787 3249 3253 3270 3273	288.38	335.82	624.20
2,3-Benzodioxin (2) Sym=2	78 175 295 387 464 490 498 544 559 585 693 751 755 765 826 857 867 915 931 966 1030 1063 1099 1123 1180 1186 1233 1306 1336 1357 1400 1502 1542 1652 1661 1763 3192 3204 3212 3219 3256 3276	590.01	1410.63	2000.63
Dibenzo- <i>p</i> -dioxin (3) Sym=8	35 126 232 241 273 304 399 442 456 465 542 551 556 574 623 680 682 696 742 763 765 854 856 857 861 903 931 932 966 966 1057 1058 1117 1137 1180 1180 1211 1219 1257 1298 1314 1335 1348 1373 1490 1512 1538 1548 1637 1642 1672 1685 3193 3193 3205 3205 3214 3214 3220 3220	845.26	3781.52	4626.78
1CDD (4) Sym=1	33 87 152 189 244 276 292 307 382 426 459 491 536 548 548 554 586 657 680 686 694 765 773 779 858 858 888 895 935 941 956 969 1057 1093 1126 1172 1180 1201 1217 1249 1271 1306 1337 1342 1371 1490 1509 1517 1544 1630 1634 1668 1680 3195 3204 3207 3216 3221 3222 3230	642.95	2122.30	2765.24
2CDD (5) Sym=1	30 103 165 167 240 288 288 342 350 454 457 463 478 552 562 580 584 648 669 692 726 748 765 817 858 858 866 872 932 934 935 969 1058 1098 1123 1145 1181 1210 1219 1256 1279 1307 1334 1344 1368 1452 1504 1533 1545 1633 1636 1668 1684 3196 3207 3214 3216 3222 3232 3234	978.34	6569.13	7547.47
16DCDD (6) Sym=2	31 57 136 155 174 214 248 280 307 356 367 415 432 517 533 537 546 550 558 617 666 681 693 705 774 775 830 857 891 892 924 959 959 964 1090 1096 1165 1175 1196 1215 1250 1252 1277 1336 1340 1366 1488 1506 1516 1519 1625 1630 1660 1673 3207 3208 3225 3225 3232 3232	2156.84	6261.18	8418.00
18DCDD (7) Sym=1	30 76 120 141 204 218 245 295 297 350 365 408 457 470 509 536 549 564 579 616 668 669 690 727 774 792 818 859 870 890 932 937 942 958 1093 1097 1139 1172 1201 1217 1248 1268 1285 1333 1341 1363 1453 1502 1514 1536 1628 1630 1661 1678 3207 3216 3223 3231 3233 3236	1985.21	7510.26	9495.47
19DCDD (8) Sym=2	32 56 117 157 200 211 251 278 308 328 389 400 447 519 533 538 546 551 556 608 681 683 693 700 774 775 802 888 889 889 934 949 958 959 1093 1095 1165 1176 1195 1215 1239 1261 1283 1336 1337 1366 1489 1510 1512 1519 1624 1631 1660 1673 3205 3205 3222 3222 3229 3230	2604.88	5171.64	7776.50
28DCDD (9) Sym=2	26 86 126 147 178 233 251 274 338 359 359 390 453 461 488 514 578 581 582 595 664 680 681 742 772 818 819 866 866 867 889 936 937 949 1097 1099 1134 1148 1210 1218 1257 1273 1289 1330 1345 1360 1442 1467 1530 1541 1628 1633 1662 1682 3215 3216 3233 3234 3235 3235	595.78	4649.85	5245.56
Furan (10) Sym=2	614 623 728 761 839 879 886 890 1022 1071 1098 1173 1220 1296 1430 1529 1614 3260 3271 3295 3301	190.78	195.04	385.81
2,3-Benzofuran (11) Sym=1	221 255 408 432 549 583 598 621 749 763 782 782 864 868 870 912 937 977 1037 1067 1129 1161 1180 1203 1287 1297 1372 1403 1493 1518 1592 1642 1670 3183 3195 3205 3219 3263 3291	460.68	1089.39	1550.07
Dibenzofuran (12) Sym=2	109 154 221 298 320 432 433 454 525 567 574 582 628 671 734 757 760 767 774 864 866 867 868 937 938 976 978 1022 1040 1047 1127 1139 1177 1184 1224 1231 1278 1312 1341 1375 1400 1484 1496 1514 1531 1636 1645 1653 1685 3186 3187 3196 3197 3208 3209 3222 3222	791.39	3015.08	3806.47
3CDF (13) Sym=1	69 146 165 200 279 318 344 359 440 453 509 540 575 577 607 657 711 728 756 767 768 823 864 866 870 913 939 948 979 1022 1043 1082 1131 1154 1182 1223 1231 1262 1295 1335 1370 1390 1463 1494 1499 1528 1627 1641 1650 1682 3188 3198 3201 3210 3223 3227 3239	814.78	5661.78	6476.56
4CDF (14) Sym=1	90 119 147 213 271 297 330 393 441 460 524 566 571 580 585 645 695 733 754 766 792 824 864 869 884 899 941 964 980 1038 1058 1086 1135 1171 1184 1212 1233 1265 1293 1339 1373 1396 1458 1492 1514 1528 1627 1642 1650 1682 3187 3194 3197 3208 3209 3221 3223	1372.63	4111.49	5484.12

THERMOCHEMICAL PROPERTIES OF CHLORINATED DIBENZODIOXINS AND DIBENZOFURANS 1735

SUPPLEMENTAL MATERIALS 2: B3LYP/6-31G(d,p)-determined harmonic vibrational frequencies and moments of inertia of mono- and di-chloro dibenzo-*p*-dioxins and dibenzofurans—Continued

Species (Symmetry No.)	Frequency (cm ⁻¹)	Ia	Ib	Ic
		(amu bohr ²)		
16DCDF (15) Sym=1	66 99 133 179 180 228 304 330 336 386 411 487 506 540 577 577 589 593 673 710 729 750 785 795 861 865 893 907 941 967 972 1050 1084 1093 1166 1172 1199 1226 1264 1282 1307 1370 1394 1454 1462 1511 1524 1620 1632 1645 1677 3200 3202 3220 3224 3230 3237	2012.77	5269.72	7282.49
36DCDF (16) Sym=1	67 97 118 190 219 225 280 321 352 385 404 442 516 532 572 577 605 609 661 730 737 746 789 824 835 864 871 901 919 950 966 1054 1082 1086 1152 1176 1211 1234 1261 1268 1326 1367 1386 1451 1475 1495 1524 1625 1633 1646 1678 3197 3202 3211 3223 3228 3241	1570.77	7137.61	8708.39
37DCDF (17) Sym=2	50 110 127 181 235 256 256 325 369 374 411 445 450 551 563 584 604 609 694 725 733 747 773 817 829 867 870 899 925 949 951 1022 1083 1083 1142 1162 1222 1231 1257 1275 1320 1367 1380 1460 1467 1493 1518 1624 1633 1646 1680 3200 3201 3226 3227 3239 3240	407.23	4292.25	4699.48
46DCDF (18) Sym=2	70 96 110 179 207 231 294 299 336 389 412 492 510 532 573 580 585 598 689 727 735 745 782 798 850 876 900 902 909 965 968 1078 1083 1090 1170 1181 1207 1230 1263 1263 1332 1370 1392 1450 1466 1515 1524 1625 1634 1645 1677 3195 3196 3209 3211 3222 3222	2274.83	4969.81	7244.64

SUPPLEMENTAL MATERIALS 3: Calculated heat capacities of 18 species at 5–6000 K (J·mol⁻¹·K⁻¹)^a

Temp (K)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
5	33.3	33.3	33.3	33.3	33.4	33.3	33.4	33.3	33.5	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3	33.3
50	38.2	40.4	45.1	50.0	49.4	55.1	54.6	55.4	54.1	33.3	34.1	39.9	44.5	44.9	50.0	49.9	49.5	50.5
100	41.5	50.8	62.8	73.0	72.7	83.3	82.9	83.2	82.7	33.5	42.1	56.2	65.8	66.5	76.4	76.1	75.5	76.8
200	56.8	85.9	115.9	131.3	131.5	146.7	146.9	146.6	147.0	43.1	72.2	103.1	118.5	118.4	133.6	133.9	133.9	133.8
298	80.7	129.0	177.2	193.2	193.6	209.2	209.6	209.2	209.9	64.1	112.0	160.5	176.9	176.4	192.4	192.8	193.2	192.3
300	81.2	129.9	178.4	194.4	194.8	210.5	210.8	210.4	211.2	64.5	112.8	161.7	178.0	177.6	193.5	193.9	194.3	193.5
400	105.0	171.0	236.5	251.5	251.8	266.4	266.9	266.4	267.2	87.1	152.2	217.5	232.9	232.4	247.4	247.8	248.3	247.2
500	124.8	204.9	284.5	298.2	298.5	311.9	312.3	311.9	312.6	105.9	184.9	264.1	278.2	277.7	291.5	291.9	292.3	291.3
600	140.5	231.9	322.6	335.1	335.4	347.6	347.9	347.6	348.2	120.9	211.0	301.2	314.1	313.6	326.2	326.6	327.0	326.1
700	153.0	253.3	352.9	364.3	364.5	375.7	375.9	375.6	376.2	132.7	231.7	330.8	342.5	342.1	353.6	353.8	354.2	353.4
800	163.2	270.5	377.2	387.6	387.8	398.0	398.1	397.9	398.4	142.3	248.4	354.6	365.2	364.9	375.3	375.6	375.8	375.3
900	171.6	284.7	397.2	406.6	406.7	416.0	416.2	416.0	416.3	150.2	262.2	374.2	383.8	383.5	393.0	393.2	393.4	392.9
1000	178.7	296.5	413.7	422.2	422.4	430.8	430.9	430.8	431.1	156.9	273.6	390.5	399.1	398.9	407.5	407.6	407.8	407.4
1500	201.5	333.7	465.4	470.7	470.7	476.0	476.0	476.0	476.1	178.3	309.8	441.3	446.6	446.6	451.8	451.9	452.0	451.9
2000	213.0	351.9	490.4	493.9	493.9	497.3	497.3	497.3	497.3	189.1	327.6	466.0	469.4	469.4	472.8	472.9	472.9	472.8
2500	219.4	361.8	504.0	506.3	506.3	508.6	508.7	508.7	508.7	195.1	337.2	479.4	481.7	481.7	484.0	484.0	484.1	484.0
3000	223.1	367.6	512.0	513.7	513.7	515.3	515.3	515.3	515.3	198.7	343.0	487.3	488.9	488.9	490.6	490.7	490.7	490.7
3500	225.6	371.3	517.0	518.3	518.3	519.6	519.6	519.6	519.6	201.0	346.6	492.2	493.5	493.5	494.8	494.8	494.8	494.8
4000	227.2	373.8	520.4	521.4	521.4	522.4	522.4	522.4	522.4	202.5	349.1	495.6	496.6	496.6	497.6	497.6	497.6	497.6
4500	228.3	375.6	522.8	523.6	523.6	524.4	524.4	524.4	524.4	203.6	350.8	497.9	498.7	498.7	499.5	499.5	499.6	499.6
5000	229.2	376.9	524.5	525.2	525.2	525.8	525.8	525.8	525.8	204.4	352.0	499.7	500.3	500.3	501.0	501.0	501.0	501.0
5500	229.7	377.8	525.8	526.3	526.3	526.9	526.9	526.9	526.9	205.0	353.0	501.0	501.5	501.5	502.0	502.0	502.0	502.0
6000	230.2	378.5	526.8	527.3	527.3	527.7	527.7	527.7	527.7	205.4	353.7	501.9	502.4	502.4	502.8	502.8	502.8	502.8

^aBased on B3LYP/6-31G(d,p) frequencies.