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Theoretical Calculation of Thermodynamic Properties of Polybrominated Dibenzo-*p*-dioxins

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Heat capacities and entropies for 76 polybrominated dibenzo-*p*-dioxins (PBDDs) in the gas state at 298.15 K and 101.325 kPa have been computed using the density functional theory (B3LYP/6-31G(d)) with Gaussian 98. Based on the output data of Gaussian, three methods were employed to calculate enthalpies and Gibbs energies of formation of the 76 PBDDs in the gaseous state at 298.15 K and 101.325 kPa. To assess the three methods, thermodynamic properties of 16 compounds were first calculated by B3LYP/6-31G(d) and compared with reference values. For predicting the enthalpies of formation of the reference compounds, method 2 has the smallest average absolute deviation from the experimental data. All values for the heat capacity, entropy, enthalpy, and energy of formation of the 76 PBDDs increase as the number of substituted bromines increases. For isomers of tetrabromodibenzo-*p*-dioxins, 1,3,6,8-TeBDD, 1,3,7,8-TeBDD, 1,3,7,9-TeBDD, and the most toxic compound 2,3,7,8-TeBDD are more stable than the others and easier to form during the formation process.

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1. Introduction

Polybrominated dibenzo-*p*-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) can be formed by chemical, photochemical, or thermal reactions from precursors and by so-called de novo synthesis. PBDDs and PBDFs have been found as contaminants in brominated organic chemicals and, in particular, in flame retardants: polybrominated diphenyl ethers (PBDEs), decabromobiphenyl (decaBB or DBB), 1,2-bis(tribromophenoxy)ethane, tetrabromobisphenol A (TBBPA), and others. They have been detected in distillation residues of some bromophenols and bromoanilines and in wastes from chemical laboratories. Brominated flame retardants and their precursors appear to be a main source of PBDDs and PBDFs.

As concluded by the World Health Organization (WHO), the potential of PBDDs and PBDFs for biological (e.g., enzyme induction) and toxic effects is similar to that of the polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs). PBDDs and PBDFs are contaminants that are more or less similar to PCDDs and PCDFs in their persistence and toxicity.[1]

There is much less information on PBDDs and PBDFs than on their chlorinated analogues, and there are very few experimental data on their physical and chemical properties. The analytical methods for separating and identifying the individual brominated congeners are much less advanced than those for their chlorinated analogues, and only few reference standards are available. Current analytical methods are able to quantify total brominated homologue groups and also to detect but not quantify the mixed brominated/chlorinated congeners. Because of the complexity of analytical procedures, it has been possible to characterize and determine only a small number of PBDD/Fs and PXDD/Fs, and only a few of the compounds have CAS registry numbers.

In this study, the thermodynamic properties (heat capacity, entropy, and Gibbs energy of formation) in the gaseous state at 298.15 K and 101.325 kPa were computed for all 76 PBDDs using density functional theory (DFT) with Gaussian 98 programs.[2] The purpose of the study was to obtain a consistent set of thermodynamic values for PBDDs. The discrepancy between the calculated results and available experimental values for 16 compounds (brominated arenes) is also discussed. The present thermodynamic data are, to our knowledge, the first set of calculated data reported on PBDDs.

2. Computational Methods

Becke's three-parameter hybrid functional combined with the gradient-correlation functional of Lee, Yang, and Parr (LYP), denoted B3LYP, was employed in the computations using DFT. The all-electron 6-31G(d) basis set was employed. Geometries were optimized using analytic gradient techniques, that is, the Berny algorithm with redundant internal coordinates. The stationary points on the potential energy surface were characterized by calculations of vibrational frequencies, which were done analytically at DFT levels. Following the geometry optimization, frequencies were calculated using the same method at a stationary point. The zero-point vibrational energies (ZPE) calculated at the DFT level were scaled by 0.9804.[3]

Throughout this paper, all calculations for PBDDs were carried out with B3LYP/6-31G(d) Opt Freq. This computational model level is different from those which have been applied to calculate the thermodynamic values of dioxin congeners serially.[4−6]

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

2.1. Entropy and Heat Capacity. The entropy and heat capacity can be directly obtained from the output of

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Table 1. Enthalpies of Formation for Gaseous Atoms and Entropy and ($H_{298K} - H_{0K}$) Values for Elements in Their Reference State from Experiments[a]

atoms	state	$\Delta_f H°$(0K)/kJ·mol^{-1}	$\Delta_f H°$(298K)/kJ·mol^{-1}	state	$S°$(298K)/J·mol^{-1}·K^{-1}	$H_{298K} - H_{0K}$/kJ·mol^{-1}
C	gas	711.19 ± 0.46	716.67 ± 0.46	reference state	5.74 ± 0.21	1.051
H	gas	216.035 ± 0.006	217.999 ± 0.006	reference state	65.340 ± 0.017	4.238
Br	gas	117.92 ± 0.06	111.86 ± 0.06	reference state	76.103	12.255
O	gas	246.79 ± 0.10	249.17 ± 0.10	reference state	102.574 ± 0.018	4.342
N	gas	470.82 ± 0.10	472.68 ± 0.10	reference state	95.805 ± 0.010	4.335

[a] Chase, 1998 (ref 15).

Gaussian programs. The equations used for computing thermochemical data in the programs are equivalent to those given in statistical mechanics texts.[7,8]

2.2. Enthalpy and Gibbs Energy of Formation. The following equations are employed to calculate the absolute internal energy (U), enthalpy (H), and Gibbs energy (G) of the molecule at zero Kelvin and the specified temperature (T):[7−9]

$$U_{0K} = E_{elec} + E_{zpe} \tag{1}$$

$$U_T = U_{0K} + (E_{trans} + E_{rot} + E_{vib})_T \tag{2}$$

$$H_T = U_T + RT \tag{3}$$

$$G_T = H_T - TS \tag{4}$$

where E_{elec} is the internal energy due to electronic motion and E_{zpe} the zero point energy of the molecule at 0 K (a correction to the electronic energy). E_{trans}, E_{rot}, and E_{vib} are the thermal energy corrections due to the effects of molecular translation, rotation, and vibration at the specified temperature, respectively.

In this study, E_{elec} is computed at the B3LYP level. E_{trans}, E_{rot}, and E_{vib} can be rapidly calculated using statistical thermodynamics. All the values of E_{elec}, E_{zpe}, U_T, H_T, and G_T are given in hartrees (atomic units, 1 hartree = 2625.51 kJ·mol^{-1}) by the output of the program.

On the basis of these absolute energy values, enthalpy and Gibbs energy of formation can be calculated by different methods.

2.2.1. Method 1. The enthalpies of formation at 0 K were calculated by subtracting the calculated atomization energies ($\sum D_0$) from the known enthalpies of formation of the isolated atoms. The enthalpies of formation at 298.15 K were calculated by correction to the enthalpies of formation at 0 K. This method is the common theoretical method for calculating the enthalpy of formation used by many studies.[6,9−11]

For the computation of enthalpies of formation, Curtiss et al.[11] tested seven density functional methods: B3LYP, BP86, B3P86, BPW91, B3PW91, and SVWN with 148 molecules. Of these seven DFT methods, the B3LYP method has the smallest average absolute deviation (13.0 kJ·mol^{-1}) from the experimental values.

The calculation procedure is as follows:

$$\Delta_f H°(M,0\text{K}) = \sum x\Delta_f H°(X,0\text{K}) - \sum D_0(M) = \sum x\Delta_f H°(X,0\text{K}) - [\sum xU(X,0\text{K}) - U(M,0\text{K})] \tag{5}$$

$$\Delta_f H°(M,298\text{K}) = \Delta_f H°(M,0\text{K}) + [H°(M,298\text{K}) - H°(M,0\text{K})] - \sum x(H_{298K} - H_{0K})_X \tag{6}$$

$$\Delta_f G°(M,298\text{K}) = \Delta_f H°(M,298\text{K}) - T\Delta S = \Delta_f H°(M,298\text{K}) - T[S°(M,298\text{K}) - \sum xS°(X,298\text{K})] \tag{7}$$

where $\Delta_f H°$ and $\Delta_f G°$ are the standard-state enthalpy and Gibbs energy of formation of the ideal gas, respectively. M stands for the molecule of the compound, X identifies each element which composes M, and x is the stoichiometric coefficient of the constituent. $(H_{298K} - H_{0K})_X$ is the formation enthalpy correction from 0 K to 298 K for elements in the reference state.

Dixon et al.[12,13] have used high-level ab initio electronic structure theory to calculate the heats of formation of CBr, CHBr, CBr_2, and other small halogenated compounds. It was found that the spin−orbit corrections must be applied to the atomization energies of these compounds, especially brominated compounds, as the atomic energies are calculated incorrectly without spin−orbit corrections. An atomic spin−orbit correction of −3.51 kcal·mol^{-1} (−14.69 kJ·mol^{-1}) for Br on the basis of the excitation energy tables of Moore[14] was proposed. The spin−orbit correction ΔE_{SO} of −14.69 kJ·mol^{-1} per Br atom was applied to the calculations of atomization energy ($\sum D_0$) in this study.

$\Delta_f H°(X)$, $S°(X,298\text{ K})$, and $(H_{298K} - H_{0K})_X$ are tabulated in Table 1, cited from the NIST-JANAF Thermochemical Tables.[15] The absolute standard-state entropy $S°(X,298\text{ K})$ used for elemental carbon, hydrogen, bromine, and oxygen (reference state) should be (5.740, 130.680/2, 152.206/2, and 205.147/2) J·mol^{-1}·K^{-1}, respectively, not the values cited in Ochterski's paper[9] (not in the reference state).

The calculated thermochemistry values using B3LYP/6-31G(d) for C, H, Br, O, H_2, Br_2, CH_4, CH_3Br, C_6H_6, C_6H_5-Br, dibenzo-*p*-dioxin (DD), and 2,3,7,8-tetrabromodibenzo-*p*-dioxin (TBDD) are listed in Table 2; all values are in hartrees.

Method 1 is illustrated with the example calculations for bromomethane and TBDD as follows:

For bromomethane (CH_3Br),

$$\sum D_0(CH_3Br) = \{[1 \times U(\text{C},0\text{K}) + 3 \times U(\text{H},0\text{K}) + 1 \times U(\text{Br},0\text{K})] - U(CH_3Br,0\text{K})\} + 1 \times \Delta E_{SO} = \{[1 \times (-37.846280) + 3 \times (-0.500273) + 1 \times (-2571.656918)] - (-2611.579925)\} \times 2625.51 + 1 \times (-14.69) = 1497.4\ \text{kJ·mol}^{-1}$$

$$\Delta_f H°(CH_3Br,0\text{K}) = [1 \times \Delta_f H°(\text{C},0\text{K}) + 3 \times \Delta_f H°(\text{H},0\text{K}) + 1 \times \Delta_f H°(\text{Br},0\text{K})] - \sum D_0(CH_3Br) = (1 \times 711.19 + 3 \times 216.035 + 1 \times 117.92) - 1497.4 = -20.2\ \text{kJ·mol}^{-1}$$

$$\Delta_f H°(CH_3Br,298\text{K}) = \Delta_f H°(CH_3Br,0\text{K}) + [H°(CH_3Br,298\text{K}) - H°(CH_3Br,0\text{K})] - [1 \times (H_{298K} - H_{0K})_C + 3 \times (H_{298K} - H_{0K})_H + 1 \times (H_{298K} - H_{0K})_{Br}] = (-20.2) + [(-2611.575866) - (-2611.579925)] \times 2625.51 - (1 \times 1.051 + 3 \times 4.238 + 1 \times 12.255) = -35.6\ \text{kJ·mol}^{-1}$$

$$\Delta_f G°(CH_3Br,298\text{K}) = \Delta_f H°(CH_3Br,298\text{K}) - 298.15 \times [S°(CH_3Br,298\text{K}) - 1 \times S°(\text{C},298\text{K}) - 3 \times S°(\text{H},298\text{K}) - 1 \times S°(\text{Br},298\text{K})] = (-35.6) - 298.15 \times (255.191 - 1 \times 5.740 - 3 \times 65.340 - 1 \times 76.103)/1000 = -28.8\ \text{kJ·mol}^{-1}$$

Table 2. Calculated Thermochemistry Values in the Gas Phase at 101.325 kPa by B3LYP/6-31G(d) (hartrees)

substance	U_{0K} (=H_{0K})[a]	U_{298K}[b]	H_{298K}[b]	G_{298K}[b]
C	−37.846 280	−37.844 864	−37.843 920	−37.860 825
H	−0.500 273	−0.498 857	−0.497 913	−0.510 927
Br	−2 571.656 918	−2 571.655 502	−2 571.654 558	−2 571.673 748
O	−75.060 623	−75.059 207	−75.058 263	−75.075 575
H_2	−1.165 536	−1.163 175	−1.162 231	−1.177 023
Br_2	−5 143.398 381	−5 143.395 626	−5 143.394 682	−5 143.422 540
CH_4	−40.474 045	−40.471 177	−40.470 233	−40.493 715
CH_3Br	−2 611.579 925	−2 611.576 811	−2 611.575 866	−2 611.604 846
C_6H_6	−232.149 871	−232.145 411	−232.144 467	−232.175 017
C_6H_5Br	−2 803.264 629	−2 803.258 848	−2 803.257 904	−2 803.294 903
DD	−612.362 477	−612.352 659	−612.351 714	−612.398 258
TBDD	−10 896.808 498	−10 896.792 547	−10 896.791 602	−10 896.856 484

[a] U_{0K} and H_{0K} are the absolute internal energy and enthalpy of the molecule at 0 K. [b] U_{298K}, H_{298K}, and G_{298K} are the absolute internal energy, enthalpy, and Gibbs energy of the molecule at 298.15 K, respectively (1 hartree = 2625.51 kJ·mol^{-1}).

For TBDD ($C_{12}H_4Br_4O_2$),

$$\Delta_f H°(\mathrm{TBDD,0K}) = [12 \times \Delta_f H°(\mathrm{C,0K}) + 4 \times \Delta_f H°(\mathrm{H,0K}) + 4 \times \Delta_f H°(\mathrm{Br,0K}) + 2 \times \Delta_f H°(\mathrm{O,0K})] - \{12 \times U(\mathrm{C,0K}) + 4 \times U(\mathrm{H,0K}) + 4 \times U(\mathrm{Br,0K}) + 2 \times U(\mathrm{O,0K}) - U(\mathrm{TBDD,0K}) + 4 \times \Delta E_{\mathrm{SO}}\} = (12 \times 711.185 + 4 \times 216.035 + 4 \times 117.917 + 2 \times 246.790) - \{[12 \times (-37.846280) + 4 \times (-0.500273) + 4 \times (-2571.656918) + 2 \times (-75.060623) - (-10896.808498)] \times 2625.51 + 4 \times (-14.69)\} = 174.7\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_f H°(\mathrm{TBDD,298K}) = \Delta_f H°(\mathrm{TBDD,0K}) + [H(\mathrm{TBDD,298K}) - H(\mathrm{TBDD,0K})] - [12 \times (H_{298K} - H_{0K})_{\mathrm{C}} + 4 \times (H_{298K} - H_{0K})_{\mathrm{H}} + 4 \times (H_{298K} - H_{0K})_{\mathrm{Br}} + 2 \times (H_{298K} - H_{0K})_{\mathrm{O}}] = 174.7 + [(-10896.791602) - (-10896.808498)] \times 2625.51 - (12 \times 1.051 + 4 \times 4.238 + 4 \times 12.255 + 2 \times 4.342) = 131.8\ \mathrm{kJ{\cdot}mol^{-1}}$$

2.2.2. Method 2. Using B3LYP/6-31G(d), it was found that the enthalpy of formation results for benzene and DD calculated by method 1 differ greatly from the experimental data. Therefore, a simple method, method 2, was proposed here.

Because the absolute enthalpy (*H*) and Gibbs energy (*G*) values of the molecule can be obtained through theoretical calculation, it is easy to obtain the reaction enthalpy and Gibbs energy for any reaction using these energy values by eqs 8 and 10. In another way, the reaction enthalpy and Gibbs energy can be calculated by eqs 9 and 11, respectively.

$$\Delta_r H°(298\mathrm{K}) = \sum(H_{298K})_{\mathrm{products}} - \sum(H_{298K})_{\mathrm{reactants}} \tag{8}$$

$$\Delta_r H°(298\mathrm{K}) = \sum(\Delta_f H°_{298K})_{\mathrm{products}} - \sum(\Delta_f H°_{298K})_{\mathrm{reactants}} \tag{9}$$

$$\Delta_r G°(298\mathrm{K}) = \sum(G_{298K})_{\mathrm{products}} - \sum(G_{298K})_{\mathrm{reactants}} \tag{10}$$

$$\Delta_r G°(298\mathrm{K}) = \sum(\Delta_f G°_{298K})_{\mathrm{products}} - \sum(\Delta_f G°_{298K})_{\mathrm{reactants}} \tag{11}$$

Combining these equations and using the experimental data of enthalpy and Gibbs energy of formation for H_2, Br_2, CH_4, CH_3Br, C_6H_6, C_6H_5Br, and DD,[15−19] the unknown enthalpy and Gibbs energy of formation of TBDD can be calculated from the three reactions shown in Chart 1 (all reactants and products are in the gas state).

The average values of enthalpy and Gibbs energy of formation of TBDD calculated from reactions I, II, and III are 64.3 kJ·mol^{-1} and 144.4 kJ·mol^{-1}, respectively.

2.2.3. Method 3 (Benson's Method). The third method for estimating the enthalpies of formation is consistent with the group additivity technique developed by Benson.[20] It is a traditional empirical method. Benson group values have been substantially refined during the years; for example, the CHETAH program[21] by ASTM International predicts thermochemical properties using a modern Benson application. The available values of group contributions to the enthalpy of formation given by CHETAH 7.3 are listed in Table 3. For TBDD,

$$\Delta_f H°_{\mathrm{TBDD}} = 4(\mathrm{C_bH}) + 4(\mathrm{C_bBr}) + 4[\mathrm{C_b{-}(O)}] + 2[\mathrm{O{-}(C_b)_2}] + \Delta_{\mathrm{ring}} + 2\Delta_{\mathrm{ortho}} = 4 \times 13.807 + 4 \times 44.769 + 4 \times (-3.766) + 2 \times (-78.659) + 8.368 + 2 \times 3.138 = 76.6\ \mathrm{kJ{\cdot}mol^{-1}}$$

3. Results and Discussion

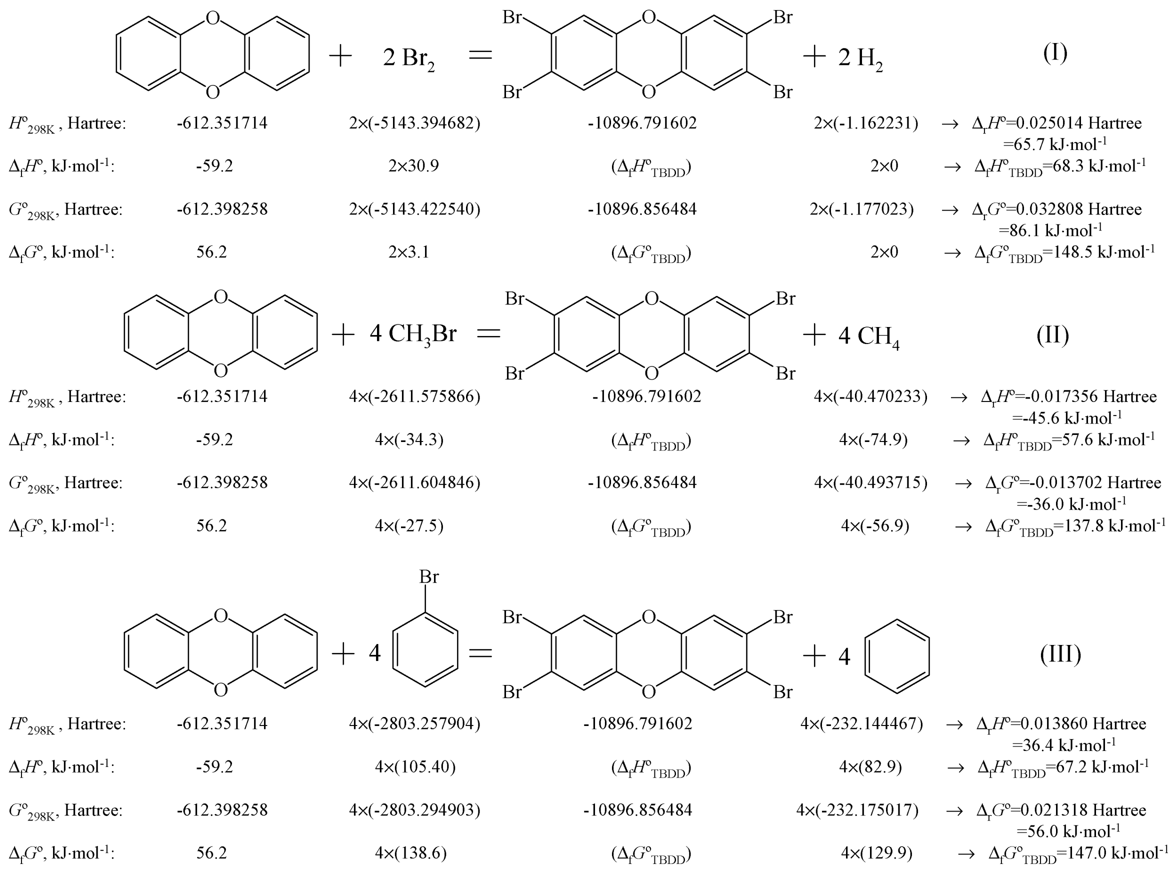
To assess the accuracy of the three methods used to predict the enthalpy and Gibbs energy of formation, the thermodynamic properties of 16 compounds (brominated arenes) were first calculated and compared with available experimental data.

3.1. Discrepancy Analysis for the Computation of Thermodynamics. For brominated arenes, in fact, only minimal experimental thermodynamic data are available. Table 4 shows the calculation results of *U*, *G*, *H*, *S*, C_p, $\Delta_f H$, and $\Delta_f G$ for benzene, bromobenzenes, benzoic acid, bromobenzoic acids, naphthalene, and bromonaphthalenes in the standard-state ideal gas at 298.15 K and 101.325 kPa.

As shown, the calculated results of heat capacity and absolute entropy are in good agreement with experimental data, although few such data are available. On the properties of heat capacity and absolute entropy, the calculation results obtained by B3LYP/6-31G(d) seem to be accurate, since Gaussian employs the mature theoretical methods of statistical thermodynamics to compute these two thermodynamic properties, and this computational level is moderate.

When the enthalpy of formation is calculated for those compounds, the results by method 1 differ from the experimental values. The absolute deviations are from 23.5 to 59.6 kJ·mol^{-1}, and the average deviation is 41.3 kJ·mol^{-1}. The reason is that the model chemistry (B3LYP/6-31G(d))

Chart 1



(I)

H°_{298K}, Hartree:	-612.351714	2×(-5143.394682)	-10896.791602	2×(-1.162231)	→ Δ_rH°=0.025014 Hartree =65.7 kJ·mol^{-1}
Δ_fH°, kJ·mol^{-1}:	-59.2	2×30.9	($\Delta_fH^{\circ}_{TBDD}$)	2×0	→ $\Delta_fH^{\circ}_{TBDD}$=68.3 kJ·mol^{-1}
G°_{298K}, Hartree:	-612.398258	2×(-5143.422540)	-10896.856484	2×(-1.177023)	→ Δ_rG°=0.032808 Hartree =86.1 kJ·mol^{-1}
Δ_fG°, kJ·mol^{-1}:	56.2	2×3.1	($\Delta_fG^{\circ}_{TBDD}$)	2×0	→ $\Delta_fG^{\circ}_{TBDD}$=148.5 kJ·mol^{-1}

(II)

H°_{298K}, Hartree:	-612.351714	4×(-2611.575866)	-10896.791602	4×(-40.470233)	→ Δ_rH°=-0.017356 Hartree =-45.6 kJ·mol^{-1}
Δ_fH°, kJ·mol^{-1}:	-59.2	4×(-34.3)	($\Delta_fH^{\circ}_{TBDD}$)	4×(-74.9)	→ $\Delta_fH^{\circ}_{TBDD}$=57.6 kJ·mol^{-1}
G°_{298K}, Hartree:	-612.398258	4×(-2611.604846)	-10896.856484	4×(-40.493715)	→ Δ_rG°=-0.013702 Hartree =-36.0 kJ·mol^{-1}
Δ_fG°, kJ·mol^{-1}:	56.2	4×(-27.5)	($\Delta_fG^{\circ}_{TBDD}$)	4×(-56.9)	→ $\Delta_fG^{\circ}_{TBDD}$=137.8 kJ·mol^{-1}

(III)

H°_{298K}, Hartree:	-612.351714	4×(-2803.257904)	-10896.791602	4×(-232.144467)	→ Δ_rH°=0.013860 Hartree =36.4 kJ·mol^{-1}
Δ_fH°, kJ·mol^{-1}:	-59.2	4×(105.40)	($\Delta_fH^{\circ}_{TBDD}$)	4×(82.9)	→ $\Delta_fH^{\circ}_{TBDD}$=67.2 kJ·mol^{-1}
G°_{298K}, Hartree:	-612.398258	4×(-2803.294903)	-10896.856484	4×(-232.175017)	→ Δ_rG°=0.021318 Hartree =56.0 kJ·mol^{-1}
Δ_fG°, kJ·mol^{-1}:	56.2	4×(138.6)	($\Delta_fG^{\circ}_{TBDD}$)	4×(129.9)	→ $\Delta_fG^{\circ}_{TBDD}$=147.0 kJ·mol^{-1}

Table 3. Values[a] of Group Additivity Contributions to the Enthalpy of Formation of PBDDs

	group				correction			
	C_bH	C_bBr	$C_b-(O)$	$O-(C_b)_2$	Δ_{ring}	Δ_{ortho}	Δ_{gauche}	Δ_{cis}
ΔH°_f/kJ·mol^{-1}	13.807	44.769	−3.766	−78.659	8.368	3.138	8.368	−1.255

[a] CHETAH 7.3, 2002 (ref 21).

employed due to the tradeoff of accuracy and cost is not accurate enough for the absolute internal energy calculation.

The enthalpy of formation values calculated using method 2 are in good agreement with the experimental data of reference compounds. The average absolute deviation from experimental values by method 2 is 4.8 kJ·mol^{-1}, and the largest absolute deviation is 20.3 kJ·mol^{-1}.

The predicted values using method 3 are also in reasonable agreement with the experimental data. The average absolute deviation from experimental values for method 3 is 9.8 kJ·mol^{-1}, and the largest absolute deviation is 27.0 kJ·mol^{-1}.

Table 4 shows that the deviations in predicting the enthalpies of formation of 2,4,6-tribromoaniline and 2,4,6-tribromophenol by method 2 are larger than those of the other compounds by the same method. Allot and Finch[25] reported the experimental enthalpies of formation: (159.0 ± 2.6) kJ·mol^{-1} for 2,4,6-$C_6H_2Br_3NH_2$ and (−0.9 ± 2.5) kJ·mol^{-1} for 2,4,6-$C_6H_2Br_3OH$; at the same time, they gave the estimated Δ_fH°: (155.5 ± 12.5) kJ·mol^{-1} for 2,4,6-$C_6H_2Br_3NH_2$ and (−28.0 ± 12.5) kJ·mol^{-1} for 2,4,6-$C_6H_2Br_3OH$ using the Cox scheme.[31] The estimated value for 2,4,6-$C_6H_2Br_3OH$ by Allot and Finch is close to the value by this study but differs from the experimental value. Unfortunately, only one experimental value is available.

For predictions of the enthalpies of formation of 2,4,6-$C_6H_2Br_3NH_2$ and 2,4,6-$C_6H_2Br_3OH$, the absolute deviations by method 3 are 27.0 kJ·mol^{-1} and 3.7 kJ·mol^{-1}, respectively. Method 3 assumes that each substitution of Br for H on the benzene ring produces an increment of 7.4 kcal·mol^{-1} (31.0 kJ·mol^{-1}) in Δ_fH°. However, the experimental data show that the energy increment per Br substitution is 31.8 kJ·mol^{-1} for 2,4,6-$C_6H_2Br_3OH$ and 24.0 kJ·mol^{-1} for 2,4,6-$C_6H_2Br_3NH_2$, although the only difference between the two compounds is an NH_2 versus an OH group.

The results show that the traditional Benson's method of group additivity (method 3) is still one of the most accurate methods for estimating formation enthalpy, and the calculation process is very simple and fast.

However, Benson's method can only give a very rough correction for cis−trans isomerization empirically. In estimating the enthalpies of isomers, method 2 is superior to Benson's method, although methods 1 and 2 are far more computationally expensive.

Compared with the selected experimental data, method 2 has the smallest absolute deviation among the three

Table 4. Comparison between Calculated Thermodynamic Parameters and Reference Data in the Gas Phase at 298.15 K and 101.325 kPa

compound	formula	U/hartree	H/hartree	G/hartree	C_p/J·mol^{-1}·K^{-1}		$S°$/J·mol^{-1}·K^{-1}	
					calcd	ref	calcd	ref
benzene	C_6H_6	−232.145 411	−232.144 467	−232.175 017	81.8	82.53[a]	269.0	269.31[a]
bromobenzene	C_6H_5Br	−2803.258 8485	−2803.257 9045	−2803.294 9035	99.3		325.8	
1,2-dibromobenzene	1,2-$C_6H_4Br_2$	−5374.368 5004	−5374.367 5564	−5374.408 9934	116.2		364.9	
1,3-dibromobenzene	1,3-$C_6H_4Br_2$	−5374.370 8092	−5374.369 8652	−5374.411 5972	116.8		367.9	
1,4-dibromobenzene	1,4-$C_6H_4Br_2$	−5374.370 8251	−5374.369 8801	−5374.410 9691	116.6		361.8	
benzoic acid	C_6H_5COOH	−420.701 2583	−420.700 3143	−420.740 5733	124.4		354.5	
2-bromobenzoic acid	2-$C_6H_4BrCOOH$	−2991.805 0285	−2991.804 0665	−2991.850 8085	141.7		411.6	
3-bromobenzoic acid	3-$C_6H_4BrCOOH$	−2991.813 1838	−2991.812 2398	−2991.857 2338	141.8		396.2	
4-bromobenzoic acid	4-$C_6H_4BrCOOH$	−2991.814 0273	−2991.813 0833	−2991.858 0373	141.9		395.9	
aniline	$C_6H_5NH_2$	−287.480 1316	−287.479 1866	−287.514 2136	102.6		308.4	
2,4,6-tribromoaniline	2,4,6-$C_6H_2Br_3NH_2$	−8000.822 1527	−8000.821 2087	−8000.869 8097	152.7		428.0	
phenol	C_6H_5OH	−307.356 5143	−307.355 5703	−307.391 1383	101.5	103.60[a]	313.2	315.71[a]
2,4,6-tribromophenol	2,4,6-$C_6H_2Br_3OH$	−8020.693 0940	−8020.692 1500	−8020.741 4250	151.8		433.9	
naphthalene	$C_{10}H_8$	−385.740 8631	−385.739 9181	−385.777 7621	131.7	133.02[b]	333.3	
1-bromonaphthalene	1-$C_{10}H_7Br$	−2956.853 7649	−2956.852 8209	−2956.896 5459	148.8		385.0	
2-bromonaphthalene	2-$C_{10}H_7Br$	−2956.854 1686	−2956.853 2246	−2956.897 1446	149.2		386.8	

compound	$\Delta_f H°$/kJ·mol^{-1}			ref value	reference	deviation/kJ·mol^{-1}			$\Delta_f G°$/kJ·mol^{-1}		
	method 1	method 2	method 3			method 1	method 2	method 3	method 1	method 2	method 3
benzene	109.5	82.9[d]	82.9[c]	82.93 ± 0.50	18	26.6			156.5	129.9	129.9
bromobenzene	131.5	104.4	105.0[c]	105.4 ± 4.1	19	26.1	−1.0		164.7	137.6	138.2
1,2-dibromobenzene	163.5	136.4	139.1	133.9 ± 8.4	22	29.6	2.5	5.2	188.2	161.2	163.9
1,3-dibromobenzene	157.4	130.4	125.5[c]	133.9 ± 8.4	22	23.5	−3.5	−8.4	181.3	154.2	149.4
1,4-dibromobenzene	157.4	130.3	134.7	126.4 ± 8.4	22	31.0	3.9	8.3	183.1	156.0	160.4
benzoic acid	−240.1	−294.1[e]	−290.2[c]	−294.1 ± 2.2	19	54.0			−155.8	−211.5	−205.9
2-bromobenzoic acid	−192.7	−248.6	−256.7	−246.9 ± 2.1	23	54.2	−1.7	−9.8	−122.1	−178.1	−186.2
3-bromobenzoic acid	−214.1	−270.1	−259.2	−268.3 ± 1.5	23	54.2	−1.8	9.1	−139.0	−194.9	−184.1
4-bromobenzoic acid	−216.3	−272.3	−262.6	−275.9 ± 1.4	23	59.6	3.6	13.3	−141.1	−197.1	−187.4
aniline	131.5	87.0[f]	86.9[c]	87.03 ± 0.88	24	44.5			214.8	152.8	152.6
2,4,6-tribromoaniline	193.0	147.9	186.0	159.0 ± 2.6	25	34.0	−11.1	27.0	250.3	199.3	225.8
phenol	−43.1	−96.4[g]	−96.4[c]	−96.36 ± 0.59	26	53.3			53.5	−32.0	−32.0
2,4,6-tribromophenol	32.7	−21.2	2.8	−0.9 ± 2.5	25	33.6	−20.3	3.7	70.7	16.8	40.8
naphthalene	197.4	150.6[h]	150.8[c]	150.6 ± 1.1	27	46.8			271.0	224.2	223.8
1-bromonaphthalene	220.8	173.8	181.5	174.3 ± 5.6	28	46.5	−0.5	7.2	282.1	235.2	242.9
2-bromonaphthalene	219.7	172.7	181.5	175.6 ± 2.3	28	44.1	−2.9	5.9	280.6	233.6	242.4

[a] Barin, 1989 (ref 29). [b] Thermodynamics Research Center, 1997 (ref 30). [c] Experimental values, CHETAH 7.3, 2002 (ref 21). [d] Reference 18. [e] Reference 19. [f] Reference 24. [g] Reference 26. [h] Reference 27.

methods under the condition of B3LYP/6-31G(d). As indicated by Foresman and Frisch,[3] model chemistries that are known to be quite reliable for optimizing geometries can be quite poor at predicting absolute thermochemical properties, but such methods could be quite accurate at predicting other molecular properties, vibrational frequencies, and a variety of relative energy values: energy differences to similar molecules, reaction energies, and so on. The main reason method 2 can offer more accurate results is that the systematic errors in the method often cancel out across the systems being compared. Another reason is due to its use of experimental values as benchmarks.

3.2. Calculation Results of the Thermodynamic Properties of PBDDs. The calculation results of U, G, H, S, C_p, $\Delta_f H$, and $\Delta_f G$ for all the 76 PBDDs in the gas phase at 298.15 K and 101.325 kPa are listed in Table 5.

As the substitute number of bromine increases, both the heat capacity and the absolute entropy of gaseous PBDDs increase.

For predicting enthalpies of formation of PBDDs, the values obtained by method 2 and method 3 are in good agreement, except heptabromodibenzo-*p*-dioxins and octabromodibenzo-*p*-dioxin. As the substitution number of bromine increases, the enthalpies of formation by the three methods increase. The values of Gibbs energy of formation thus have the same tendency.

The enthalpy of formation results of PBDDs predicted by method 1 are always much higher than those by method 2. The differences between the two methods are from 60 to 67 kJ·mol^{-1}.

Because of the lack of experimental data, the corrections for cis−trans isomerization used in method 3 are very rough, and the level sequence of energies of isomers is different from that predicted by method 1 and method 2. Using free energy of formation values calculated by method 2, Figures 1−5 show clearly the differences among isomers.

Among 22 isomers of tetrabromodibenzo-*p*-dioxins, the Gibbs energies of 1,3,6,8-tetrabromodibenzo-*p*-dioxin (1,3,6,8-TeBDD), 1,3,7,8-tetrabromodibenzo-*p*-dioxin (1,3,7,8-TeBDD), 1,3,7,9-tetrabromodibenzo-*p*-dioxin (1,3,7,9-TeBDD), and 2,3,7,8-tetrabromodibenzo-*p*-dioxin (TBDD, the most toxic compound in PBDDs) are lower than those of the other 18 isomers (see Figure 3). This means that these 4 isomers are more stable and easier to form during the formation process.

In the same way, 2,7-DiBDD and 2,8-DiBDD are easier to form than the other 8 isomers of dibromodibenzo-*p*-dioxins. 1,3,7-TrBDD, 1,3,8-TrBDD, and 2,3,7-TrBDD are easier to form than the other 11 isomers of tribromodibenzo-*p*-dioxins. For the isomers of pentabromodibenzo-*p*-dioxins, 1,2,4,6,8-PeDBB, 1,2,4,7,8-PeDBB, and 1,2,4,7,9-PeDBB are easier to form than the others. For the isomers

Table 5. Thermodynamic Data of Gaseous PBDDs at 298.15 K and 101.325 kPa

						$\Delta_f H°$/kJ·mol^{-1}			$\Delta_f G°$/kJ·mol^{-1}		
compound	U/hartree	H/hartree	G/hartree	$S°$/J·mol^{-1}·K^{-1}	C_p/J·mol^{-1}·K^{-1}	method 1	method 2	method 3	method 1	method 2	method 3
DD	−612.352 659	−612.351 714	−612.398 258	409.9	180.6	7.4	−59.2[a]	−53.6	122.7	56.2	61.8
1-MoBDD	−3 183.462 327	−3 183.461 383	−3 183.512 553	450.6	197.5	39.3	−27.5	−22.6	145.7	78.9	83.8
2-MoBDD	−3 183.464 505	−3 183.463 561	−3 183.514 941	452.5	198.2	33.6	−33.3	−22.6	139.4	72.6	83.3
1,2-DiBDD	−5 754.571 009	−5 754.570 065	−5 754.625 846	491.2	214.6	73.8	6.7	11.5	171.3	104.2	109.0
1,3-DiBDD	−5 754.573 184	−5 754.572 240	−5 754.628 080	491.7	215.0	68.1	1.0	18.8	165.4	98.4	116.2
1,4-DiBDD	−5 754.571 270	−5 754.570 326	−5 754.626 124	491.4	214.3	73.1	6.0	7.1	170.5	103.5	104.6
1,6-DiBDD	−5 754.571 807	−5 754.570 863	−5 754.626 728	491.9	214.4	71.7	4.6	8.4	169.0	101.9	105.7
1,7-DiBDD	−5 754.573 852	−5 754.572 908	−5 754.628 857	492.7	215.0	66.3	−0.7	8.4	163.4	96.3	105.4
1,8-DiBDD	−5 754.573 817	−5 754.572 873	−5 754.628 758	492.1	215.0	66.4	−0.6	8.4	163.6	96.6	105.6
1,9-DiBDD	−5 754.571 278	−5 754.570 334	−5 754.626 199	492.0	214.4	73.1	6.0	8.4	170.4	103.3	105.7
2,3-DiBDD	−5 754.573 156	−5 754.572 212	−5 754.628 000	491.3	215.1	68.1	1.1	11.5	165.6	98.6	109.0
2,7-DiBDD	−5 754.575 993	−5 754.575 049	−5 754.631 045	493.1	215.6	60.7	−6.4	8.4	157.6	90.6	105.3
2,8-DiBDD	−5 754.576 007	−5 754.575 062	−5 754.630 986	492.5	215.5	60.6	−6.4	8.4	157.8	90.8	105.5
1,2,3-TrBDD	−8 325.678 510	−8 325.677 566	−8 325.737 613	528.8	231.8	111.3	44.1	45.6	200.9	133.6	135.1
1,2,4-TrBDD	−8 325.679 145	−8 325.678 201	−8 325.738 678	532.6	231.5	109.7	42.4	52.9	198.1	130.8	141.3
1,2,6-TrBDD	−8 325.680 208	−8 325.679 264	−8 325.739 630	531.6	231.5	106.9	39.6	42.5	195.6	128.3	131.2
1,2,7-TrBDD	−8 325.682 340	−8 325.681 396	−8 325.741 703	531.1	232.0	101.3	34.0	42.5	190.1	122.9	131.3
1,2,8-TrBDD	−8 325.682 210	−8 325.681 266	−8 325.741 808	533.1	232.1	101.6	34.4	42.5	189.9	122.6	130.7
1,2,9-TrBDD	−8 325.679 815	−8 325.678 871	−8 325.739 302	532.2	231.5	107.9	40.7	42.5	196.4	129.2	131.0
1,3,6-TrBDD	−8 325.682 193	−8 325.681 249	−8 325.741 928	534.3	231.9	101.7	34.4	49.8	189.5	122.3	137.7
1,3,7-TrBDD	−8 325.684 379	−8 325.683 435	−8 325.743 967	533.0	232.4	95.9	28.7	49.8	184.2	116.9	138.0
1,3,8-TrBDD	−8 325.684 292	−8 325.683 347	−8 325.744 018	534.3	232.6	96.2	28.9	49.8	184.1	116.8	137.7
1,3,9-TrBDD	−8 325.681 787	−8 325.680 843	−8 325.741 525	534.4	232.0	102.7	35.5	49.8	190.6	123.3	137.6
1,4,6-TrBDD	−8 325.679 909	−8 325.678 965	−8 325.739 622	534.1	231.3	107.7	40.4	38.1	195.6	128.3	126.0
1,4,7-TrBDD	−8 325.682 440	−8 325.681 495	−8 325.742 126	533.9	231.8	101.0	33.8	38.1	189.0	121.8	126.1
2,3,6-TrBDD	−8 325.682 216	−8 325.681 272	−8 325.741 631	531.5	231.9	101.6	34.4	42.5	190.3	123.1	131.2
2,3,7-TrBDD	−8 325.684 377	−8 325.683 433	−8 325.743 941	532.8	232.5	95.9	28.7	42.5	184.3	117.0	130.8
1,2,3,4-TeBDD	−10 896.783 290	−10 896.782 346	−10 896.846 897	568.4	248.4	156.1	88.6	79.7	237.0	169.5	160.6
1,2,3,6-TeBDD	−10 896.787 482	−10 896.786 538	−10 896.851 269	570.0	248.7	145.1	77.6	76.6	225.5	158.0	157.0
1,2,3,7-TeBDD	−10 896.789 561	−10 896.788 617	−10 896.853 409	570.6	249.2	139.6	72.1	76.6	219.9	152.4	156.8
1,2,3,8-TeBDD	−10 896.789 484	−10 896.788 540	−10 896.853 407	571.2	249.3	139.8	72.3	76.6	219.9	152.4	156.6
1,2,3,9-TeBDD	−10 896.787 117	−10 896.786 173	−10 896.851 076	571.5	248.6	146.0	78.5	76.6	226.0	158.5	156.6
1,2,4,6-TeBDD	−10 896.787 739	−10 896.786 795	−10 896.851 929	573.6	248.3	144.4	76.9	83.9	223.8	156.3	163.3
1,2,4,7-TeBDD	−10 896.790 122	−10 896.789 178	−10 896.854 328	573.7	248.8	138.1	70.7	83.9	217.5	150.0	163.2
1,2,4,8-TeBDD	−10 896.790 195	−10 896.789 251	−10 896.854 302	572.8	248.8	137.9	70.5	83.9	217.5	150.1	163.5
1,2,4,9-TeBDD	−10 896.787 698	−10 896.786 754	−10 896.851 970	574.3	248.4	144.5	77.0	83.9	223.7	156.2	163.0
1,2,6,7-TeBDD	−10 896.788 614	−10 896.787 669	−10 896.852 316	569.3	248.4	142.1	74.6	76.6	222.8	155.3	157.2
1,2,6,8-TeBDD	−10 896.790 488	−10 896.789 543	−10 896.854 561	572.5	249.0	137.2	69.7	83.9	216.9	149.4	163.6
1,2,6,9-TeBDD	−10 896.788 354	−10 896.787 410	−10 896.852 383	572.2	248.2	142.8	75.3	72.2	222.6	155.1	152.0
1,2,7,8-TeBDD	−10 896.790 525	−10 896.789 580	−10 896.854 333	570.2	248.9	137.1	69.6	76.6	217.5	150.0	156.9
1,2,7,9-TeBDD	−10 896.790 161	−10 896.789 217	−10 896.854 232	572.5	249.0	138.0	70.6	83.9	217.7	150.2	163.6
1,2,8,9-TeBDD	−10 896.788 188	−10 896.787 243	−10 896.852 072	570.9	248.5	143.2	75.7	76.6	223.4	155.9	156.7
1,3,6,8-TeBDD	−10 896.792 422	−10 896.791 478	−10 896.856 776	575.0	249.4	132.1	64.6	91.2	211.0	143.6	170.2
1,3,6,9-TeBDD	−10 896.790 219	−10 896.789 275	−10 896.854 573	575.0	248.7	137.9	70.4	79.5	216.8	149.3	158.4
1,3,7,8-TeBDD	−10 896.792 414	−10 896.791 470	−10 896.856 564	573.2	249.5	132.1	64.6	83.9	211.6	144.1	163.4
1,3,7,9-TeBDD	−10 896.792 098	−10 896.791 154	−10 896.856 403	574.6	249.4	133.0	65.5	91.2	212.0	144.5	170.3
1,4,6,9-TeBDD	−10 896.788 006	−10 896.787 062	−10 896.852 397	575.3	247.9	143.7	76.2	67.8	222.5	155.1	146.6
1,4,7,8-TeBDD	−10 896.790 554	−10 896.789 610	−10 896.854 642	572.7	248.8	137.0	69.5	72.2	216.6	149.2	151.8
2,3,7,8-TeBDD	−10 896.792 547	−10 896.791 602	−10 896.856 484	571.3	249.5	131.8	64.3	76.6	211.8	144.3	156.6
1,2,3,4,6-PeBDD	−13 467.891 841	−13 467.890 897	−13 467.960 070	609.1	265.3	190.9	123.2	110.7	262.9	195.2	182.6
1,2,3,4,7-PeBDD	−13 467.894 139	−13 467.893 195	−13 467.962 397	609.4	265.9	184.9	117.2	110.7	256.8	189.1	182.6
1,2,3,6,7-PeBDD	−13 467.895 714	−13 467.894 770	−13 467.963 863	608.4	265.7	180.7	113.0	110.7	252.9	185.2	182.9
1,2,3,6,8-PeBDD	−13 467.897 545	−13 467.896 601	−13 467.965 828	609.6	266.1	175.9	108.2	118.0	247.8	180.1	189.8
1,2,3,6,9-PeBDD	−13 467.895 365	−13 467.894 421	−13 467.963 901	611.8	265.5	181.7	113.9	106.3	252.8	185.1	177.4
1,2,3,7,8-PeBDD	−13 467.897 638	−13 467.896 694	−13 467.965 776	608.3	266.0	175.7	108.0	110.7	247.9	180.2	182.9
1,2,3,7,9-PeBDD	−13 467.897 185	−13 467.896 241	−13 467.965 861	613.1	266.3	176.9	109.2	118.0	247.7	180.0	188.8
1,2,3,8,9-PeBDD	−13 467.895 335	−13 467.894 391	−13 467.963 795	611.2	265.7	181.7	114.0	110.7	253.1	185.4	182.0
1,2,4,6,7-PeBDD	−13 467.896 010	−13 467.895 066	−13 467.964 797	614.1	265.3	180.0	112.3	118.0	250.5	182.8	188.5
1,2,4,6,8-PeBDD	−13 467.897 791	−13 467.896 847	−13 467.966 827	616.2	265.8	175.3	107.6	125.3	245.1	177.4	195.2
1,2,4,6,9- PeBDD	−13 467.895 718	−13 467.894 774	−13 467.964 421	613.3	265.0	180.7	113.0	113.6	251.5	183.8	184.3
1,2,4,7,8-PeBDD	−13 467.898 160	−13 467.897 216	−13 467.966 533	610.4	265.7	174.3	106.6	118.0	245.9	178.2	189.6
1,2,4,7,9-PeBDD	−13 467.897 823	−13 467.896 879	−13 467.966 567	613.7	265.6	175.2	107.5	125.3	245.8	178.1	195.9
1,2,4,8,9-PeBDD	−13 467.895 964	−13 467.895 020	−13 467.964 495	611.8	265.3	180.1	112.4	118.0	251.3	183.6	189.2
1,2,3,4,6,7-HxBDD	−16 038.999 967	−16 038.999 023	−16 039.072 715	648.9	282.4	226.8	158.9	144.8	290.2	222.2	208.1
1,2,3,4,6,8-HxBDD	−16 039.001 793	−16 039.000 849	−16 039.074 876	651.9	282.8	222.1	154.1	152.1	284.5	216.6	214.5
1,2,3,4,6,9-HxBDD	−16 038.999 784	−16 038.998 840	−16 039.072 614	649.6	282.1	227.3	159.4	140.4	290.4	222.5	203.5
1,2,3,4,7,8-HxBDD	−16 039.002 067	−16 039.001 123	−16 039.074 504	646.2	282.7	221.3	153.4	144.8	285.5	217.5	208.9
1,2,3,6,7,8-HxBDD	−16 039.002 587	−16 039.001 643	−16 039.075 172	647.5	282.8	220.0	152.0	144.8	283.7	215.8	208.5
1,2,3,6,7,9-HxBDD	−16 039.002 920	−16 039.001 976	−16 039.075 954	651.4	282.5	219.1	151.2	152.1	281.7	213.7	214.7
1,2,3,6,8,9-HxBDD	−16 039.002 903	−16 039.001 958	−16 039.075 878	650.9	282.5	219.1	151.2	152.1	281.9	213.9	214.8
1,2,3,7,8,9-HxBDD	−16 039.002 468	−16 039.001 524	−16 039.074 950	646.6	282.7	220.3	152.4	144.8	284.3	216.4	208.8
1,2,4,6,7,9-HxBDD	−16 039.003 335	−16 039.002 391	−16 039.076 437	652.0	281.9	218.0	150.1	159.4	280.4	212.5	221.8
1,2,4,6,8,9-HxBDD	−16 039.003 342	−16 039.002 398	−16 039.076 585	653.3	282.1	218.0	150.1	159.4	280.0	212.1	221.4
1,2,3,4,6,7,8-HpBDD	−18 610.106 890	−18 610.105 946	−18 610.183 989	687.2	299.5	265.9	197.8	178.9	321.1	252.9	234.0
1,2,3,4,6,7,9-HpBDD	−18 610.107 186	−18 610.106 242	−18 610.185 109	694.5	299.2	265.2	197.0	186.2	318.1	250.0	239.1
1,2,3,4,6,7,8,9-OBDD	−21 181.211 102	−21 181.210 158	−21 181.292 768	727.5	316.2	312.2	243.8	213.0	358.5	290.1	259.3

[a] Kolesov et al., 1998 (ref 16).

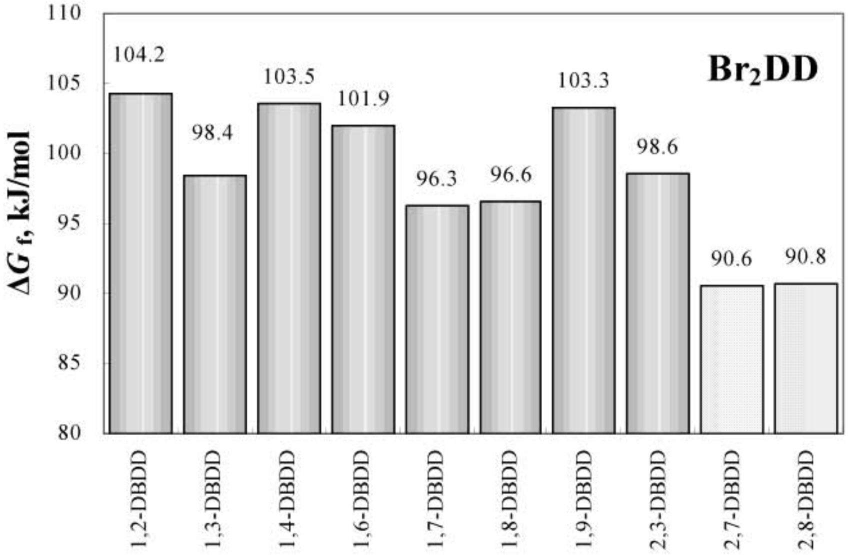


Figure 1. Comparison of Gibbs energies of formation of dibromodibenzo-*p*-dioxin isomers.

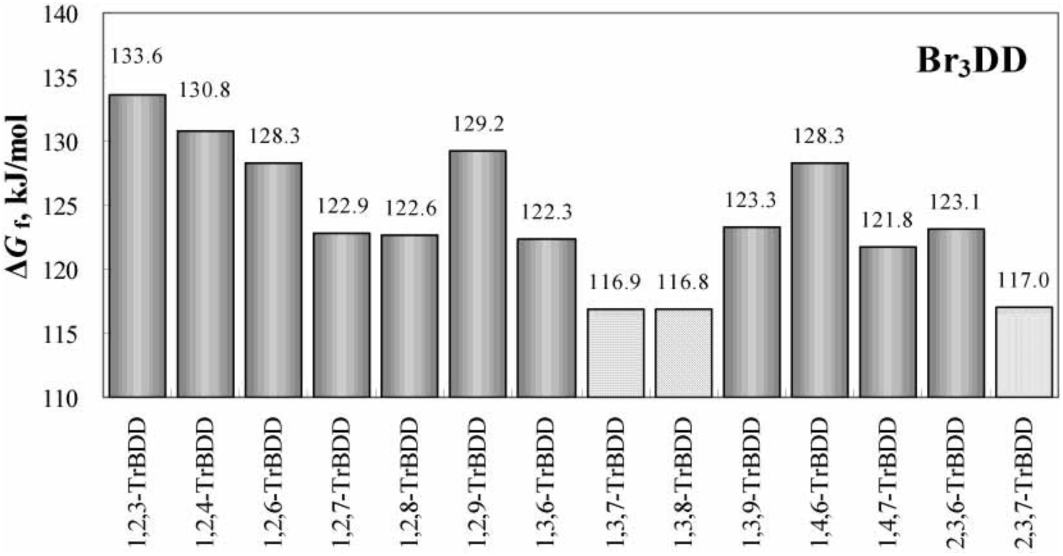


Figure 2. Comparison of Gibbs energies of formation of tribromodibenzo-*p*-dioxin isomers.

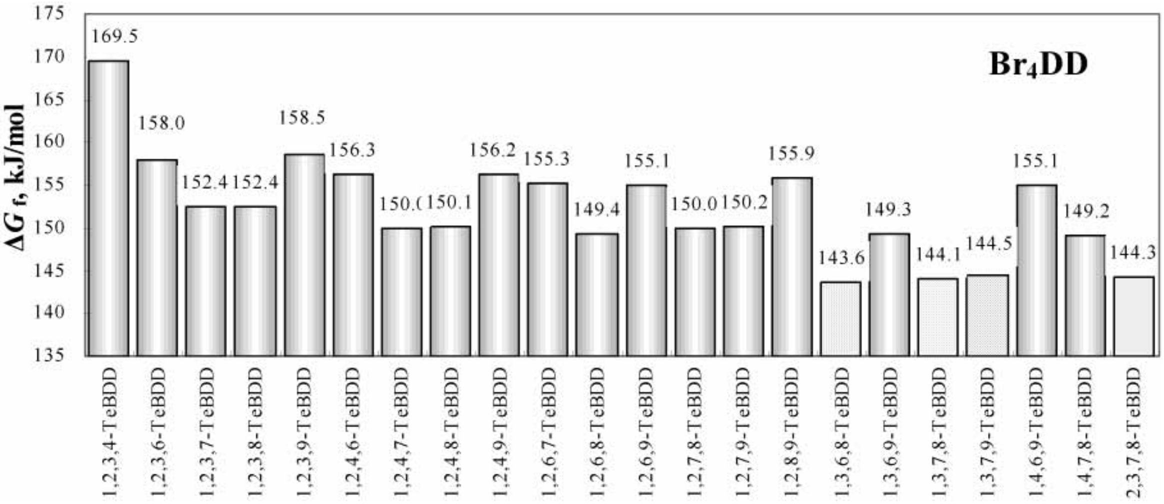


Figure 3. Comparison of Gibbs energies of formation of tetrabromodibenzo-*p*-dioxin isomers.

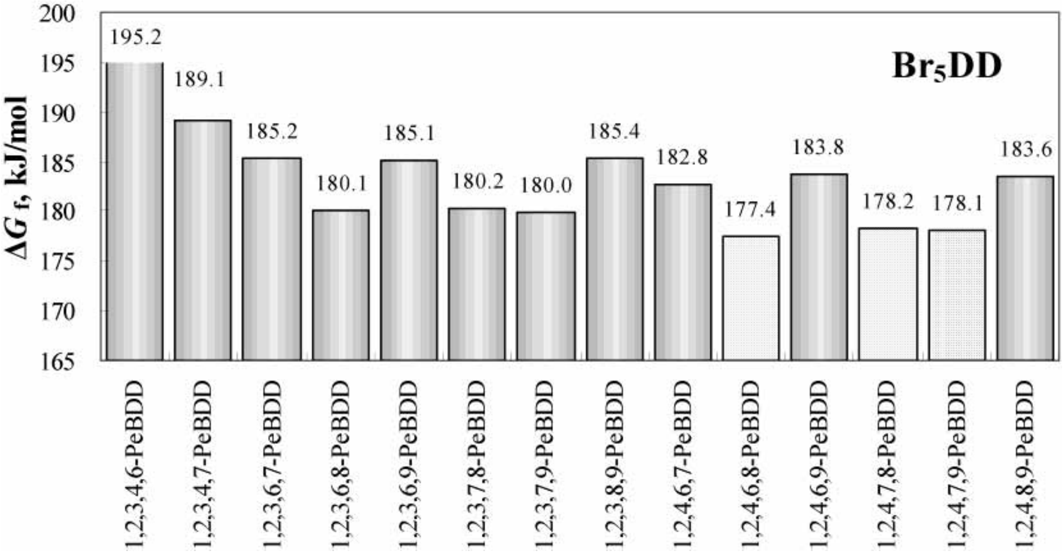


Figure 4. Comparison of Gibbs energies of formation of pentabromodibenzo-*p*-dioxin isomers.

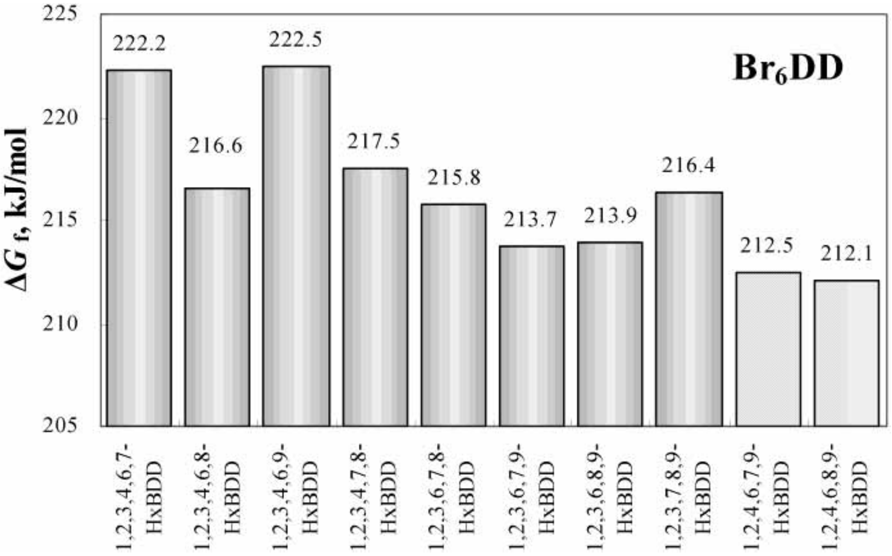


Figure 5. Comparison of Gibbs energies of formation of hexabromodibenzo-*p*-dioxin isomers.

of hexabromodibenzo-*p*-dioxins, 1,2,4,6,7,9-HxBDD and 1,2,4,6,8,9-HxBDD are easier to form than the others.

4. Conclusion

(1) Under the computing level of B3LYP/6-31G(d), method 2 has the smallest average absolute deviation and maximum absolute deviation, (4.8 and 20.3) kJ·mol^{-1}, from the experimental values of formation enthalpy of the reference compounds, and method 2 is simpler than method 1.

(2) Benson's method is still an accurate method for estimating thermodynamic properties, and calculation procedures are very simple and much faster than methods 1 and 2. But this method can only give much rougher corrections for cis−trans isomerization empirically. Method 2 is superior to Benson's method in predicting the formation enthalpies of isomers.

(3) All the heat capacity, entropy, enthalpy, and Gibbs energy of formation values for the 76 PBDDs increase as the substitute number of bromine increases. The values of enthalpy and Gibbs energy of formation of PBDDs calculated by method 2 are recommended.

(4) For isomers of tetrabromodibenzo-*p*-dioxins, 1,3,6,8-TeBDD, 1,3,7,8-TeBDD, 1,3,7,9-TeBDD, and the most toxic compound 2,3,7,8-TeBDD are more stable than the others and easier to form during the formation process.

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