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Theoretical Calculation of Thermodynamic Properties of Polybrominated Diphenyl Ethers

Xia Zeng,[†] Peter K. Freeman,[†] Yury V. Vasil'ev,[†] Valery G. Voinov,[†] Staci L. Simonich,[*,†,‡] and Douglas F. Barofsky[†]

Department of Chemistry and Department of Environmental and Molecular Toxicology,
Oregon State University, Corvallis, Oregon 97331

The thermodynamic properties of 39 polybrominated diphenyl ethers (PBDEs) in the ideal gas phase have been calculated using Gaussian 03 on the B3LYP/6-31G(d)//B3LYP/6-31G(d) level. Their thermodynamic and other physicochemical properties show a strong dependence on the bromine substitution pattern. The PBDE congeners' enthalpies of formation increase with an increasing number of bromines. The thermodynamic properties of congeners with the same number of bromines also show dependence on the bromine substitution pattern, especially for ortho-substituted congeners. PBDE congeners with one phenyl ring fully brominated, such as 2,3,4,5,6-PeBDE, 2,3,4,4′,5,6-HxBDE, 2,2′,3,4,4′,5,6-HpBDE, and 2,3,3′,4,4′,5,6-HpBDE, were found to be the least stable among the analogues. The effects of bromine substitution pattern have been quantitatively studied by group additivity method (GAM) based on the output of the theoretical calculations. The results of the GAM were consistent with theoretical calculations, proving that theoretical calculations are reliable. Furthermore, the GAM model can be used to predict the thermodynamic properties for all of the 209 PBDE congeners.

Introduction

Polybrominated diphenyl ether (PBDE) flame retardants are widely used as additives in polymers for textiles, electronics, and home furnishings. They have been widely detected in biotic and abiotic matrices including sediments, air, water, fish, marine mammals, human plasma, and human milk.[1−5] As the use of PBDEs has increased in recent years,[6] their concentrations in the environment have also increased.[7] A meta-analysis of the published PBDE concentration data carried out in a recent review[8] indicates that PBDEs have migrated in large quantities from industrial products to the environment and to people and, furthermore, that their concentrations have increased exponentially.

Similar to the other polyhalogenated aromatic compounds, such as polychlorinated biphenyls (PCBs), polychlorodibenzo-*p*-dioxins (PCDDs), polychlorodibenzofurans (PCDFs), and polybromodibenzo-*p*-dioxins (PBDDs), the physical, chemical, and biological properties of PBDE congeners strongly depend on the halogen substitution pattern.[9,10] Although extensive studies have been conducted to measure the presence of PBDEs in the environment, their vapor pressures,[11] and their octanol−air partition coefficients,[12] none have been conducted to measure their thermodynamic properties. This is due to the limited availability of pure compounds and to experimental difficulties, such as photodegradation of highly brominated PBDE congeners, associated with some of the congeners. Therefore, theoretical calculations are of interest for estimating the thermodynamic properties of PBDEs. Since there are no experimental values of thermodynamic properties available for PBDEs to compare with the calculated quantities, the uncertainty of the thermodynamic quantities cannot be estimated.

Density functional theory (DFT) calculations were carried out in this work to estimate the enthalpy of formation (ΔH_f) and the Gibbs free energy of formation (ΔG_f) of PBDEs in the gas phase at 298.15 K and 101.325 kPa. Similar calculations have been performed on PBDDs,[13] PCDDs,[10] and PCDFs.[14] Unlike dibenzo-*p*-dioxin and dibenzofuran and their halogenated derivatives, diphenyl ether (DE), and thus the PBDEs, has an ether bond about which the two phenyl rings can rotate relatively freely. Finding the most energetically favorable geometries for PBDEs is a complicated, time-consuming process; therefore, it would be impractical to perform DFT calculations for all of the 209, theoretically possible, PBDE congeners. Consequently, commercial availability of standards and importance in environmental research[7,15] were used to select the 39 congeners listed in Table 1 to illustrate this theoretical approach for PBDEs.

Computational Methods

Using Gaussian 03,[16] geometry optimizations and energy calculations were performed at the B3LYP/6-31G(d) level. Frequency calculations were also performed for all of the possible geometries to ensure they were minimal on the potential energy surface. Thermal energy (E_{thermal}) was calculated as the sum of zero point energy and thermal energy corrections for molecular translation (E_{trans}), rotation (E_{rot}), and vibration (E_{vib}) at 298.15 K. Enthalpy (H), at 298.15 K and 1 atm, was obtained by adding RT to the electronic energy (E_e) and thermal energy. These data, as well as the Gibbs free energy (G), were obtained from the Gaussian output file in hartrees and converted to kJ/mol (1 hartree = 2625.50 kJ/mol).

Like PCDDs and PBDDs, PBDEs have a variable number of halogens attached to two phenyl rings that are

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[*] Corresponding author. Telephone: (541)737-9194. Fax: (541)737-2062. E-mail: staci.simonich@orst.edu.
[†] Department of Chemistry.
[‡] Department of Environmental and Molecular Toxicology.

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Table 1. Thermodynamic Data of PBDEs from DFT Calculations[a]

congener no.	congener name[a]	E_e	H	G	ΔH_f	ΔG_f	S	rel abund	H average
		hartree	hartree	hartree	kJ/mol	kJ/mol	J/mol·K		hartree
BDE-1	2-MoBDE	−3109.61470	−3109.42678	−3109.47944	82.72	189.05	463.28	0.7201	−3109.42678
	2-MoBDE #2	−3109.61480	−3109.42678	−3109.47975	82.71	188.24	465.98	1	
BDE-2	3-MoBDE	−3109.61737	−3109.42944	−3109.48235	75.73	181.40	465.51	1	−3109.42939
	3-MoBDE #2	−3109.61724	−3109.42933	−3109.48206	76.02	182.15	463.95	0.7371	
BDE-3	4-MoBDE	−3109.61707	−3109.42909	−3109.48222	76.64	181.76	467.37	1	−3109.42909
BDE-7	2,4-DiBDE	−5680.71757	−5680.53828	−5680.59532	110.89	204.50	501.78	0.4331	−5680.53845
	2,4-DiBDE #2	−5680.71792	−5680.53853	−5680.59611	110.22	202.43	506.50	1	
BDE-8	2,4′-DiBDE	−5680.71905	−5680.53971	−5680.59705	107.13	199.94	504.47	1	−5680.53954
	2,4′-DiBDE #2	−5680.71878	−5680.53936	−5680.59698	108.06	200.13	506.94	0.9246	
BDE-10	2,6-DiBDE	−5680.71609	−5680.53675	−5680.59415	114.90	207.55	505.02	1	−5680.53675
BDE-12	3,4-DiBDE	−5680.71811	−5680.53880	−5680.59610	109.52	202.44	504.07	0.9072	−5680.53873
	3,4-DiBDE #2	−5680.71795	−5680.53867	−5680.59619	109.85	202.20	506.01	1	
BDE-13	3,4′-DiBDE	−5680.72109	−5680.54179	−5680.59936	101.65	193.87	506.45	1	−5680.54183
	3,4′-DiBDE #2	−5680.72117	−5680.54187	−5680.59932	101.46	193.99	505.40	0.9545	
BDE-15	4,4′-DiBDE	−5680.72094	−5680.54160	−5680.60034	102.16	191.30	516.77	1	−5680.54160
BDE-17	2,2′,4-TrBDE	−8251.81967	−8251.64892	−8251.71022	141.31	222.50	539.31	1	−8251.64879
	2,2′,4-TrBDE #2	−8251.81931	−8251.64859	−8251.70984	142.17	223.50	538.82	0.6665	
BDE-25	2,3′,4-TrBDE	−8251.82173	−8251.65113	−8251.71329	135.51	214.44	546.87	0.9197	−8251.65120
	2,3′,4-TrBDE #2	−8251.82187	−8251.65127	−8251.71337	135.14	214.23	546.31	1	
BDE-28	2,4,4′-TrBDE	−8251.82164	−8251.65093	−8251.71267	136.03	216.07	543.13	0.5370	−8251.65084
	2,4,4′-TrBDE #2	−8251.82154	−8251.65080	−8251.71326	136.39	214.53	549.49	1	
BDE-30	2,4,6-TrBDE	−8251.81790	−8251.64725	−8251.70946	145.69	224.51	547.23	1	−8251.64725
BDE-32	2,4′,6-TrBDE	−8251.82020	−8251.64944	−8251.71165	139.96	218.75	547.31	1	−8251.64944
BDE-33	2′,3,4-TrBDE	−8251.81988	−8251.64924	−8251.71090	140.49	220.73	542.46	0.7232	−8251.64935
	2′,3,4-TrBDE #2	−8251.82012	−8251.64943	−8251.71120	139.97	219.92	543.42	1	
BDE-35	3,3′,4-TrBDE	−8251.82174	−8251.65114	−8251.71319	135.47	214.71	545.83	1	−8251.65110
	3,3′,4-TrBDE #2	−8251.82162	−8251.65106	−8251.71314	135.70	214.84	546.17	0.9504	
	3,3′,4-TrBDE #3	−8251.82170	−8251.65111	−8251.71301	135.55	215.17	544.57	0.8317	
	3,3′,4-TrBDE #4	−8251.82171	−8251.65109	−8251.71305	135.61	215.07	545.06	0.8631	
BDE-37	3,4,4′-TrBDE	−8251.82159	−8251.65095	−8251.71292	135.98	215.41	545.20	0.9091	−8251.65097
	3,4,4′-TrBDE #2	−8251.82163	−8251.65098	−8251.71301	135.90	215.17	545.73	1	
BDE-47	2,2′,4,4′-TeBDE	−10822.92214	−10822.76001	−10822.82656	170.57	236.73	585.54	1	−10822.76005
	2,2′,4,4′-TeBDE #2	−10822.92241	−10822.76015	−10822.82570	170.20	239.01	576.64	0.3988	
BDE-49	2,2′,4,5′-TeBDE	−10822.92236	−10822.76032	−10822.82622	169.75	237.62	579.78	0.8290	−10822.76043
	2,2′,4,5′-TeBDE #2	−10822.92258	−10822.76052	−10822.82640	169.23	237.16	579.58	1	
BDE-51	2,2′,4,6′-TeBDE	−10822.92134	−10822.75917	−10822.82428	172.76	242.74	572.73	1	−10822.75917
	2,2′,4,6′-TeBDE #2	−10822.91732	−10822.75538	−10822.82043	182.72	252.83	572.30	0.0171	
BDE-66	2,3′,4,4′-TeBDE	−10822.92233	−10822.76035	−10822.82672	169.67	236.33	583.83	0.8604	−10822.76040
	2,3′,4,4′-TeBDE #2	−10822.92243	−10822.76045	−10822.82686	169.42	235.96	584.25	1	
BDE-71	2,3′,4′,6-TeBDE	−10822.92113	−10822.75905	−10822.82573	173.08	238.93	586.58	1	−10822.75897
	2,3′,4′,6-TeBDE #2	−10822.92093	−10822.75889	−10822.82566	173.51	239.11	587.40	0.9285	
BDE-75	2,4,4′,6-TeBDE	−10822.92191	−10822.75987	−10822.82692	170.92	235.80	589.81	1	−10822.75987
BDE-77	3,3′,4,4′-TeBDE	−10822.92197	−10822.76005	−10822.82656	170.46	236.73	585.14	1	−10822.76005
	3,3′,4,4′-TeBDE #2	−10822.92201	−10822.76006	−10822.82618	170.44	237.74	581.69	0.6658	
BDE-85	2,2′,3,4,4′-PeBDE	−13394.01961	−13393.86611	−13393.93563	212.90	270.05	611.60	1	−13393.86611
BDE-99	2,2′,4,4′,5-PeBDE	−13394.02239	−13393.86883	−13393.93878	205.78	261.80	615.37	0.5186	−13393.86888
	2,2′,4,4′,5-PeBDE #2	−13394.02199	−13393.86864	−13393.93879	206.27	261.76	617.17	0.5274	
	2,2′,4,4′,5-PeBDE #3	−13394.02247	−13393.86904	−13393.93940	205.23	260.17	618.99	1	
BDE-100	2,2′,4,4′,6-PeBDE	−13394.02209	−13393.86954	−13393.93709	203.91	266.22	594.29	1	−13393.86891
	2,2′,4,4′,6-PeBDE #2	−13394.01915	−13393.86590	−13393.93561	213.45	270.11	613.22	0.2077	
BDE-116	2,3,4,5,6-PeBDE	−13394.00976	−13393.85689	−13393.92705	237.13	292.60	617.20	1	−13393.85689
BDE-119	2,3′,4,4′,6-PeBDE	−13394.02246	−13393.86911	−13393.94020	205.03	258.07	625.36	0.5567	−13393.86919
	2,3′,4,4′,6-PeBDE #2	−13394.02259	−13393.86923	−13393.94075	204.72	256.62	629.19	1	
BDE-128	2,2′,3,3′,4,4′-HxBDE	−15965.11633	−15964.97190	−15965.04592	256.09	300.18	651.20	1	−15964.97194
	2,2′,3,3′,4,4′-HxBDE #2	−15965.11668	−15964.97201	−15965.04556	255.78	301.13	647.00	0.6823	
BDE-138	2,2′,3,4,4′,5′-HxBDE	−15965.11940	−15964.97459	−15965.04831	249.02	293.91	648.52	0.4841	−15964.97470
	2,2′,3,4,4′,5′-HxBDE #2	−15965.11938	−15964.97476	−15965.04899	248.57	292.11	653.05	1	
BDE-140	2,2′,3,4,4′,6′-HxBDE	−15965.11999	−15964.97539	−15965.04926	246.91	291.40	649.89	1	−15964.97535
	2,2′,3,4,4′,6′-HxBDE #2	−15965.11568	−15964.97126	−15965.04497	257.76	302.67	648.47	0.0106	
BDE-153	2,2′,4,4′,5,5′-HxBDE	−15965.12222	−15964.97731	−15965.05152	241.89	285.47	652.93	0.1495	−15964.97670
	2,2′,4,4′,5,5′-HxBDE #2	−15965.12136	−15964.97661	−15965.05332	243.72	280.76	674.83	1	
BDE-154	2,2′,4,4′,5,6′-HxBDE	−15965.12294	−15964.97819	−15965.05235	239.56	283.29	652.45	1	−15964.97812
	2,2′,4,4′,5,6′-HxBDE #2	−15965.11912	−15964.97455	−15965.04863	249.11	293.06	651.70	0.0194	
BDE-166	2,3,4,4′,5,6-HxBDE	−15965.11356	−15964.96928	−15965.04402	262.95	305.16	657.51	1	−15964.96928
BDE-181	2,2′,3,4,4′,5,6-HpBDE	−18536.21440	−18536.07879	−18536.15675	296.36	328.88	685.88	1	−18536.07872
	2,2′,3,4,4′,5,6-HpBDE #2	−18536.21061	−18536.07514	−18536.15293	305.95	338.91	684.37	0.0174	
BDE-183	2,2′,3,4,4′,5′,6-HpBDE	−18536.21938	−18536.08345	−18536.16163	284.11	316.06	687.76	0.8613	−18536.08353
	2,2′,3,4,4′,5′,6-HpBDE #2	−18536.21961	−18536.08367	−18536.16177	283.55	315.69	687.12	1	
	2,2′,3,4,4′,5′,6-HpBDE #3	−18536.21576	−18536.08002	−18536.15819	293.12	325.10	687.69	0.0225	
BDE-190	2,3,3′,4,4′,5,6-HpBDE	−18536.21395	−18536.07840	−18536.15751	297.39	326.90	695.96	0.5131	−18536.07848
	2,3,3′,4,4′,5,6-HpBDE #2	−18536.21407	−18536.07853	−18536.15814	297.05	325.24	700.36	1	
BDE-209	DecaBDE	−26249.50214	−26249.39314	−26249.48288	433.79	431.67	789.54	1	−26249.39314

[a] For the congeners with more than one conformation isomer, “#2” was added to the congener name representing the second conformation, “#3” for the third conformation, and so on. The relative abundance is 1 for the most stable conformation of a congener. rel abund = relative abundance.

Table 2. Thermodynamic Data Used to Calculate ΔH_f and ΔG_f of PBDEs

	DE	bromobenzene	benzene	graphite	H_2	O_2
H/hartree	−538.31625[a]	−2803.25621[a]	−232.14255[a]			
ΔH_f/kJ/mol	52.0[c]	105.4[c]	82.9[d]			
G/hartree	−538.36453[a]	−2803.29372[a]	−232.17535[a]			
ΔG_f/kJ/mol	171.04384[b]	138.6[e]	129.7[d]			
S/J/mol·K	425.22501[a]			5.7[d]	130.7[d]	205.2[d]

[a] Data from DFT calculation. [b] Calculated from eq 4. [c] Data from ref 19. [d] Data from ref 20. [e] Data from ref 13.

connected to each other by an ether bond. In this study, PBDE congeners with one to seven bromine atoms are represented by the notation MoBDE, DiBDE, TrBDE, TeBDE, PeBDE, HxBDE, and HpBDE, respectively. The PBDE with 10 bromine atoms on the phenyl ring is represented by DecaBDE.

In a previous study,[13] three methods were applied to estimate the thermodynamic properties of PBDDs: calculation from isolated atoms; calculation from isodesmic reactions; and Benson's method.[17] Among these methods, the second was found to yield the most accurate results. Lee et al.[10] also used the isodesmic reaction to calculate the ΔH_f and ΔG_f of PCDDs and obtained results consistent to experimental results. Isodesmic reactions were also applied to calculate ΔH_f of dibenzo-*p*-dioxin, dibenzofuran, PCDDs, and PCDFs using DFT calculations.[14] Given the accuracy of these theoretical calculations for PBDDs and PCDDs, it seems reasonable to expect that estimates of the thermodynamic properties of PBDEs, from DFT calculations based on isodesmic reactions, will be similarly accurate.

In this study, reaction 1, which is similar to the isodesmic reaction used to calculate thermodynamic data for the PCDDs[10] and PBDDs,[13] served as the basis for calculating ΔH_f and ΔG_f for the PBDEs. In an isodesmic reaction, the number of each type of chemical bond does not change. Therefore, systematic errors associated with, for instance, low basis sets and incomplete correction for electron correlation, can be canceled out in these reactions.[18] Bromobenzene is structurally similar to a PBDE, and the experimental values of ΔH_f for bromobenzene and benzene are reliable.[19,20] Compared to the direct reaction of DE with Br_2 or CH_4Br, as described by Li et al.,[13] reaction 1 should lead to more accurate results, given by:

$$\mathrm{DE} + n\mathrm{bromobenzene} = \mathrm{PBDE} + n\mathrm{benzene} \qquad (1)$$

The enthalpy change of the reaction (ΔH_r) is equal to the sum of the absolute enthalpies of the products as obtained from DFT calculations minus the sum of the absolute enthalpies of reactants:

$$\Delta H_r = [H_{\mathrm{PBDE}} + nH_{\mathrm{benzene}}] - [H_{\mathrm{DE}} + nH_{\mathrm{bromobenzene}}] \qquad (2)$$

The sum of the enthalpies of formation of the products minus that of the reactants also yields ΔH_r:

$$\Delta H_r = [\Delta H_{f_{\mathrm{PBDE}}} + n\Delta H_{f_{\mathrm{benzene}}}] - [\Delta H_{f_{\mathrm{DE}}} + n\Delta H_{f_{\mathrm{bromobenzene}}}] \qquad (3)$$

The ΔH_f for any given PBDE was calculated by substituting the calculated enthalpies of the respective compounds listed in Table 2 for the PBDE, benzene, DE, and bromobenzene into eq 2, and substituting the literature values of ΔH_f listed in Table 2 for benzene, DE, and bromobenzene into eq 3, eliminating ΔH_r between the two equations, and solving for ΔH_f of PBDEs.

The same method was used to calculate ΔG_f for the PBDEs from the calculated values of G and the literature values of ΔG_f listed in Table 2. An experimental value for ΔG_f of DE was not available; hence, eq 4 was used to calculate this quantity:

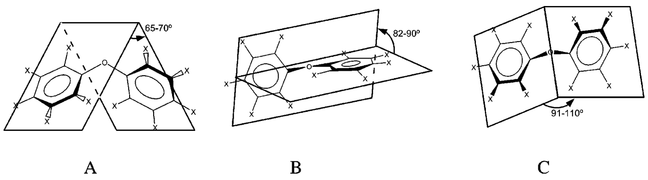


Figure 1. Stable conformations of PBDE congeners (X = H or Br): (A) the planes of the phenyl rings form an acute angle (65−70°); (B) the planes form a dihedral close to a right angle, with one phenyl ring in the same plane as the C−O−C bond and the other ring perpendicular to the ether plane (82−90°); (C) the planes form an obtuse dihedral angle (91−110°).

$$\Delta G_{f_{\mathrm{DE}}} = \Delta H_{f_{\mathrm{DE}}} - T\left(S_{\mathrm{DE}} - \left[12S_{\mathrm{graphite}} + 5S_{\mathrm{H_2}} + \frac{1}{2}S_{\mathrm{O_2}}\right]\right) \qquad (4)$$

where T is the specified temperature (298.15 K) and S is the entropy.

According to Zhu and Bozzelli,[14] DFT calculations produce entropy data for dibenzodioxin (DD) and dibenzofuran (DF) that agree very well with experimental and statistical thermodynamic values. Since DE is structurally similar to DD and DF, it is reasonable to assume that the results obtained in the present study for DE are reliable

Results and Discussion

All of the energies and other thermodynamic quantities calculated for the 39 PBDEs investigated in this study are listed in Table 1.

Conformational Isomers of PBDE Congeners. Because of the low energy barrier for the phenyl rings' rotation about the ether bond and the rotation of phenyl rings lead to multiple local minima on potential energy surface, each congener can have several stable conformations. After performing DFT calculations on all of the 39 PBDE congeners, it was found that these stable conformations fell into three groups (Figure 1). Generally, for a given congener, the conformation with the largest dihedral angle (Figure 1C) had the lowest energy.

The conformational isomers for each congener differ in certain patterns. For the congeners with bromine in the ortho positions on both phenyl rings (i.e., with 2,2′ bromines), the distance between the bromines determines the relative energy of the isomers. For most of the congeners studied with 2,2′ bromines, the conformational isomer of any given congener with the greatest distance between the 2,2′ bromines was the most stable.

Most of the congeners were found to have two or more conformational isomers; however, the following were found to have only one: 4-MoBDE; 2,6-DiBDE; 4,4′-DiBDE; 2,4,6-TrBDE; 2,4′,6-TrBDE; 2,4,4′,6-TeBDE; 2,2′,3,4,4′-PeBDE; 2,3,4,5,6-PeBDE; 2,3,4,4′,5,6-HxBDE; and DecaBDE. Most of these latter congeners have symmetric structures: either

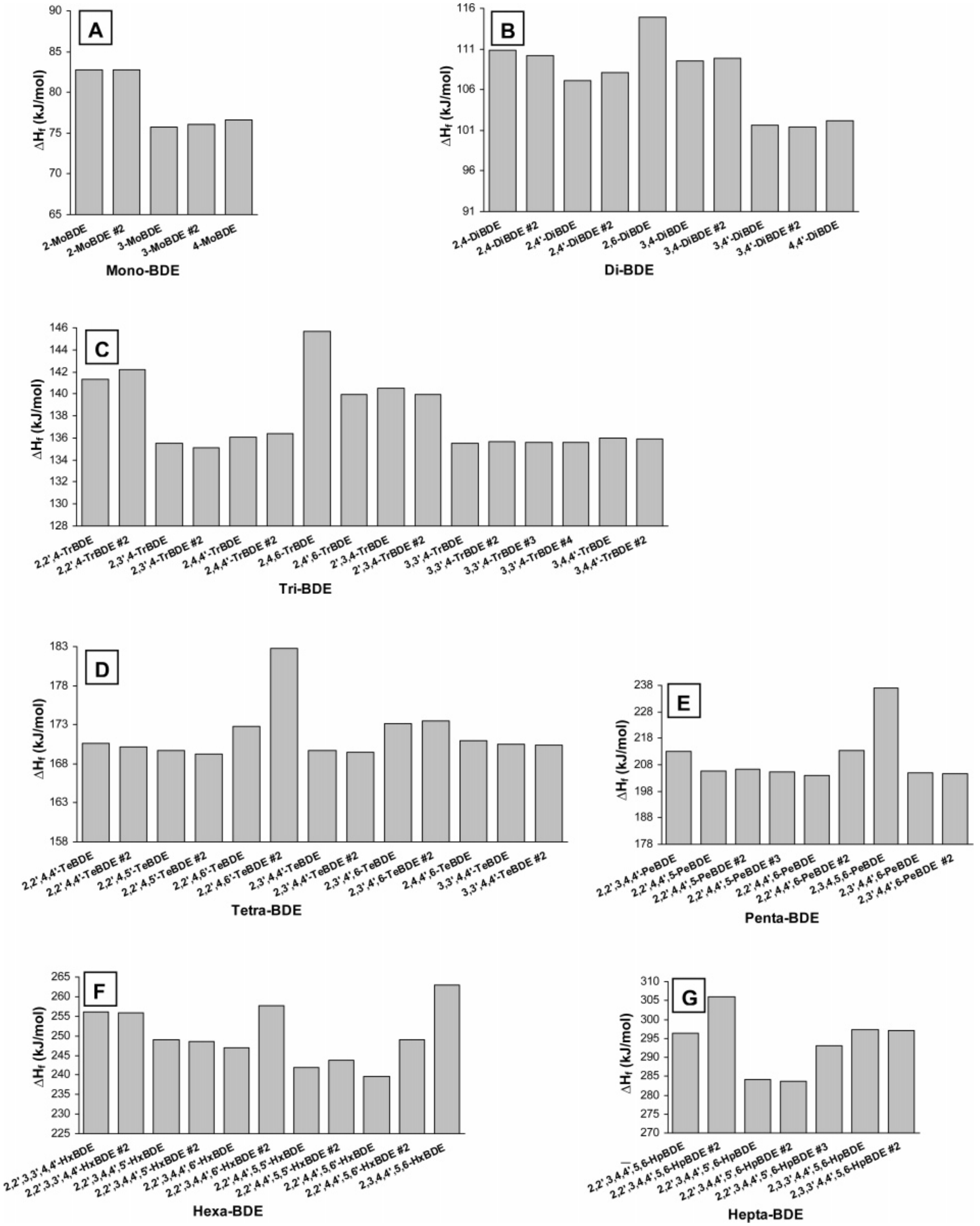


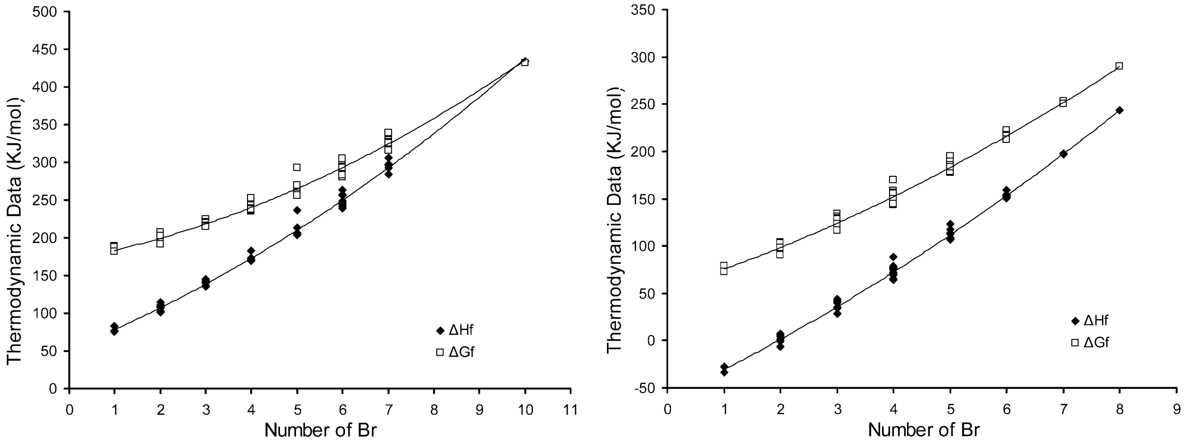
Figure 2. ΔH_f for the studied conformations of PBDEs from DFT calculation, with congeners in homologue groups displayed in panels A through G. For the congeners with more than one conformation isomer, "#2" was added to the congener name representing the second conformation, "#3" for the third conformation, and so on.

C_S symmetry (2,6-DiBDE, 2,4,6-TrBDE, 2,4′,6-TrBDE, 2,4,4′,6-TeBDE, 2,3,4,5,6-PeBDE, and 2,3,4,4′,5,6-HxBDE) or C_2 symmetry (4,4′-DiBDE and DecaBDE).

Energy Difference between PBDE Congeners. The energy differences between the different conformations of a PBDE congener were found, in general, to be much smaller than the energy differences between congeners within homologues (Figure 2). The ΔG_f of the PBDE congeners also exhibit similar differences.

It was determined in an earlier study[13] that the energy differences between PBDD congeners are strongly affected by the intramolecular halogenic repulsion, position, and number. An analysis of these factors in the present study indicates that the inter-congener energy differences for PBDEs are similarly affected.

Mono-BDE. Mono-BDE with the ortho position bromine, 2-MoBDE, is distinguished by a higher energy than the other Mono-BDE congeners, 3-MoBDE and 4-MoBDE



A. PBDE 39 congeners

B. PBDD 76 congeners

Figure 3. ΔH_f and ΔG_f for PBDE and PBDD[13] congeners from DFT calculations. The trend lines are results of polynomial fitting.

(Figure 2A). The difference between the latter two is very small, indicating that bromination in the meta and para positions does not yield an increase of energy as much as the ortho isomer. Comparison of the stability of these three congeners leads to a quantitative estimation of the effect of bromine-position.

Di-BDE. 2,6-DiBDE is the least stable dibrominated PBDE studied (Figure 2B) because it has two ortho bromines in its structure. The congeners with no ortho bromines are more stable than those with only one ortho bromine. If the two bromines are on separate phenyl rings, the energy is considerably lower than when both bromines are on the same ring, for example, 2,4-DiBDE versus 2,4′-DiBDE and 3,4-DiBDE versus 3,4′-DiBDE. This suggests that the effect of intramolecular Br−Br repulsion on one phenyl ring is much larger than the repulsion between the two rings.

Tri-BDE. The least stable of the tri-brominated PBDE studied is 2,4,6-TrBDE (Figure 2C), which has all of the bromines on the same phenyl ring and two of them in ortho positions. The congeners with one ortho bromine are less stable than those with no ortho bromine: the energies of 2,3′,4-TrBDE and 2,4,4′-TrBDE are very close, as are those of 3,3′,4-TrBDE and 3,4,4′-TrBDE. This indicates that the positions of meta and para substitution contribute similarly to the energy. The calculated energies of 2,4,4′-TrBDE and 3,4,4′-TrBDE are nearly equal (Table 1) even though 2,4,4′-TrBDE has one ortho bromine. This result suggests that the energy-contribution from the 3,4 Br−Br repulsion in 3,4,4′-TrBDE is similar to that of the ortho bromine in 2,4,4′-TrBDE.

Tetra-BDE. The least stable tetra brominated PBDE studied is 2,2′,4′,6-TetraBDE, which has three ortho bromines (Figure 2D); the next least stable compound is 2,3′,4,6′-TetraBDE because it has two ortho bromines and two adjacent bromines on one ring. The electronic energy of one of the conformational isomers of 2,2′,4,6′-TetraBDE was found to be 9.96 kJ/mol higher than that of the other isomer shown in Figure 2D. The former conformation is not stable and most likely converts to the more stable conformation.

Penta-BDE, Hexa-BDE, and Hepta-BDE. The least stable of the Penta-BDE congeners studied is 2,3,4,5,6-PeBDE, which has five adjacent bromines on the same phenyl ring (Figure 2E). Similarly, the least stable of the Hexa- and Hepta-BDEs studied are 2,3,4,4′,5,6-HexaBDE (Figure 2F) and 2,2′,3,4,4′,5,6-HpBDE (Figure 2G), respectively.

Calculated Enthalpy and Gibbs Free Energy of Formation of the PBDEs. Most of the conformations of a given congener differ in energy by no more than 1.0 kJ/mol (Figure 2). Because the different conformations could exist in nature with comparable abundances, the less stable conformations cannot simply be disregarded in favor of the most stable conformations when characterizing a congener. The energies of the various conformations should be weighted in accordance with their relative abundances when computing the average energy of the congener. The weighted averages of thermodynamic data, for a congener, should be more realistic and, thus, more reliable than simple averages or averages that disregard the less stable conformations. The equilibrium constant (k) for conversion from one conformation to another can be calculated from the difference in ΔG_f between the conformations, as in

$$\Delta(\Delta G_f) = -RT\ln(k) \qquad (5)$$

Effect of Bromine Substitution Pattern on PBDE Thermodynamic Properties. It has been shown experimentally in a previous study[21] that PBDE congeners with one fully brominated phenyl ring, such as 2,3,4,5,6-PeBDE, 2,3,4,4′,5,6-HxBDE, 2,2′,3,4,4′,5,6-HpBDE, and 2,3,3′,4,4′,5,6-HpBDE, are the most susceptible to photochemical decomposition among the highly brominated PBDEs. The results calculated in our study, shown in Figure 2E through G, indicate that these congeners are the least stable among the respective homologues, which is consistent with experimental observation.[21]

The dependence of PBDE thermodynamic properties on the number of bromines was investigated. Based on the thermodynamic values calculated in this study, PBDE congeners become less stable as the number of bromines increases (Figure 3A). Deca-BDE, which has a fully brominated structure, has the highest ΔG_f. The fitted lines for ΔH_f and ΔG_f seem to converge at Deca-BDE, but the thermodynamic data indicate that ΔG_f is smaller than ΔH_f for Deca-BDE; thus, this perbrominated structure is entropically unfavorable. Indeed, Deca-BDE has been observed in previous studies[22−24] to be photolytically unstable. The other 38 PBDE congeners studied here have an entropy increase during formation. The order of stability calculated in this study (Figure 3A) is in agreement with the increasing rate of PBDE decomposition with increasing numbers of bromine reported in an early study.[22]

The PBDDs, which have structures and physicochemical properties that are similar to those of the PBDEs, have

Table 3. Group Additivity Components for PBDEs

name	definition	calculated by	example
ΔH_1	difference in enthalpy as compared to meta position on phenyl ring	comparing enthalpy of 2-MoBDE, 3-MoBDE, and 4-MoBDE	0 kJ/mol for meta 6.86 kJ/mol for ortho 0.79 kJ/mol for para
ΔH_2	intramolecular Br−Br repulsion in one phenyl ring	isodesmic reactions of 2,3-DiBDE, 2,4-DiBDE, 2,5-DiBDE, 2,6-DiBDE, 3,4-DiBDE, and 3,5-DiBDE	eqs 6 and 7
ΔH_3	intramolecular Br−Br repulsion between two phenyl rings	isodesmic reactions of 2,2′-DiBDE, 2,3′-DiBDE, 2,4′-DiBDE, 3,3′-DiBDE, 3,4′-DiBDE, and 4,4′-DiBDE	eqs 8 and 9

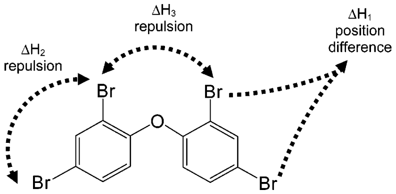


Figure 4. Group additivity components for 2,2′,4,4′-TeBDE.

been extensively studied. For example, the value of ΔH_f and ΔG_f for the PBDDs, as calculated by Li et al.[13] (Figure 3B), increase with successive bromination in a manner analogous to that of PBDEs, and the congeners with one fully brominated phenyl ring are the least stable among the PBDDs' homologues. We can conclude from Li et al. and from this study that bromination of DD and DE is thermodynamically unfavorable and that chlorination of DD is thermodynamically favored, as stated in a previous study.[10]

In the latter study, Lee et al.,[10] based on Benson's group additivity method (GAM),[17] analyzed the effect of chlorination position and Cl−Cl intramolecular repulsion on the energy of formation for PCDDs. This method has been adapted in this study to quantitatively analyze the effect of Br substitution patterns on the energy of formation for PBDEs. All of the components of this method are listed in Table 3 and illustrated schematically in Figure 4 for a PBDE congener. The enthalpies discussed in the remainder of this report will be a weighted average of all of the conformations studied for the PBDE congener in question.

ΔH_1 is the difference in enthalpy between a specific Br position in study and the most stable position on the phenyl ring. 3-MoDE was found to be the most stable of the Mono-BDEs; therefore, ΔH_1 is 0 kJ/mol for the meta position. ΔH_2 and ΔH_3 are the Br−Br repulsions in one phenyl ring and between two phenyl rings, respectively.

ΔH_2 for bromines at position 2 and 3 is calculated using the following equations:

$$\text{2,3'-DiBDE} + \text{DE} = \text{2'-MoBDE} + \text{3'-MoBDE} \tag{6}$$

$$\Delta H_2(2,3) = H_{2,3-\text{DiBDE}} + H_{\text{DE}} - H_{2-\text{MoBDE}} - H_{3-\text{MoBDE}} \tag{7}$$

The calculation of ΔH_3 for bromines at the position 2 and 2′ is demonstrated by the following equations:

$$\text{2,2'-DiBDE} + \text{DE} = \text{2'-MoBDE} + \text{2'-MoBDE} \tag{8}$$

$$\Delta H_3(2,2') = H_{2,2'-\text{DiBDE}} + H_{\text{DE}} - 2H_{2-\text{MoBDE}} \tag{9}$$

Additional DFT calculations were performed for the enthalpies of 2,3-DiBDE, 2,5-DiBDE, 3,5-DiBDE, 2,2′-DiBDE, 2,3′-DiBDE, and 3,3′-DiBDE (Table 4) because they were not among the 39 congeners initially studied.

The results of the group additivity approach for the 39 congeners are shown in Table 5. In this table, relative ΔH_f DFT is the difference in ΔH_f (from DFT calculation) between the congener in question and the first congener in its homologue group (Figure 5A through G). Relative ΔH_f GAM is the difference of the sum of ΔH_1, ΔH_2, and ΔH_3 for the same congener compared to the first congener of the homologue group. Plotting the values of relative ΔH_f DFT and relative ΔH_f GAM together on the same bar graph (Figure 5) shows that GAM predicts essentially the same effect of a given bromine substitution pattern on thermodynamic properties as does the corresponding DFT calculation. However, some congeners, especially for those with two ortho bromines on a same phenyl ring, the differences between relative ΔH_f DFT and relative ΔH_f GAM are fairly great, which may due to the fact that GAM model cannot describe the thermodynamic properties as accurate as DFT method, especially for ortho bromines.

Table 4. Enthalpies of Additional PBDE Congeners

congeners	H/hartree	congeners	H/hartree
2,3-DiBDE	−5680.53625	2,2′-DiBDE	−5680.53684
2,5-DiBDE	−5680.53891	2,3′-DiBDE	−5680.53954
3,5-DiBDE	−5680.54124	3,3′-DiBDE	−5680.54194

Intramolecular repulsion causes the ΔH_f to increase nonlinearly with increasing number of bromines. This is reflected in the positive nonlinear curvature of a plot of DFT calculated ΔH_f versus bromine number (Figure 6). Furthermore, the congeners with the same number of bromines also differ due to various substitution positions and different repulsion effects. This is also demonstrated in Figure 6 by the scattered points for the DFT calculated values.

It is of interest to look at the trend of ΔH_f without considering the Br substitution position and intramolecular Br−Br repulsion. GAM corrected ΔH_f is the result of ΔH_f from DFT calculation subtracted by the sum of ΔH_1, ΔH_2, and ΔH_3. In contrast to the curve of ΔH_f from DFT calculation, the values of GAM corrected ΔH_f fall very well on a straight line when plotted against the number of bromines (Figure 6). The collapse of ΔH_f values on to a straight line indicates that the correction from GAM eliminates the difference between congeners with the same degree of bromination. The slope of the line resulting from linear regression implies that the ΔH_f increases 21.98 kJ/mol for each addition of a single bromine when the substitution position and intramolecular repulsion are not considered.

By using the reaction

$$\text{DE} + \text{bromobenzene} = \text{3'-MoBDE} + \text{benzene} \tag{10}$$

the change in enthalpy due to bromination of DE at the 3-position can be calculated. The product of this reaction, 3-MoBDE, has the substitution position of lowest energy and cannot exhibit any effect due to intramolecular Br−Br repulsion. The increase of ΔH_f in going from DE to 3-MoBDE is 23.85 kJ/mol, which is only 1.87 kJ/mol more than predicted by the slope obtained from ΔH_f GAM

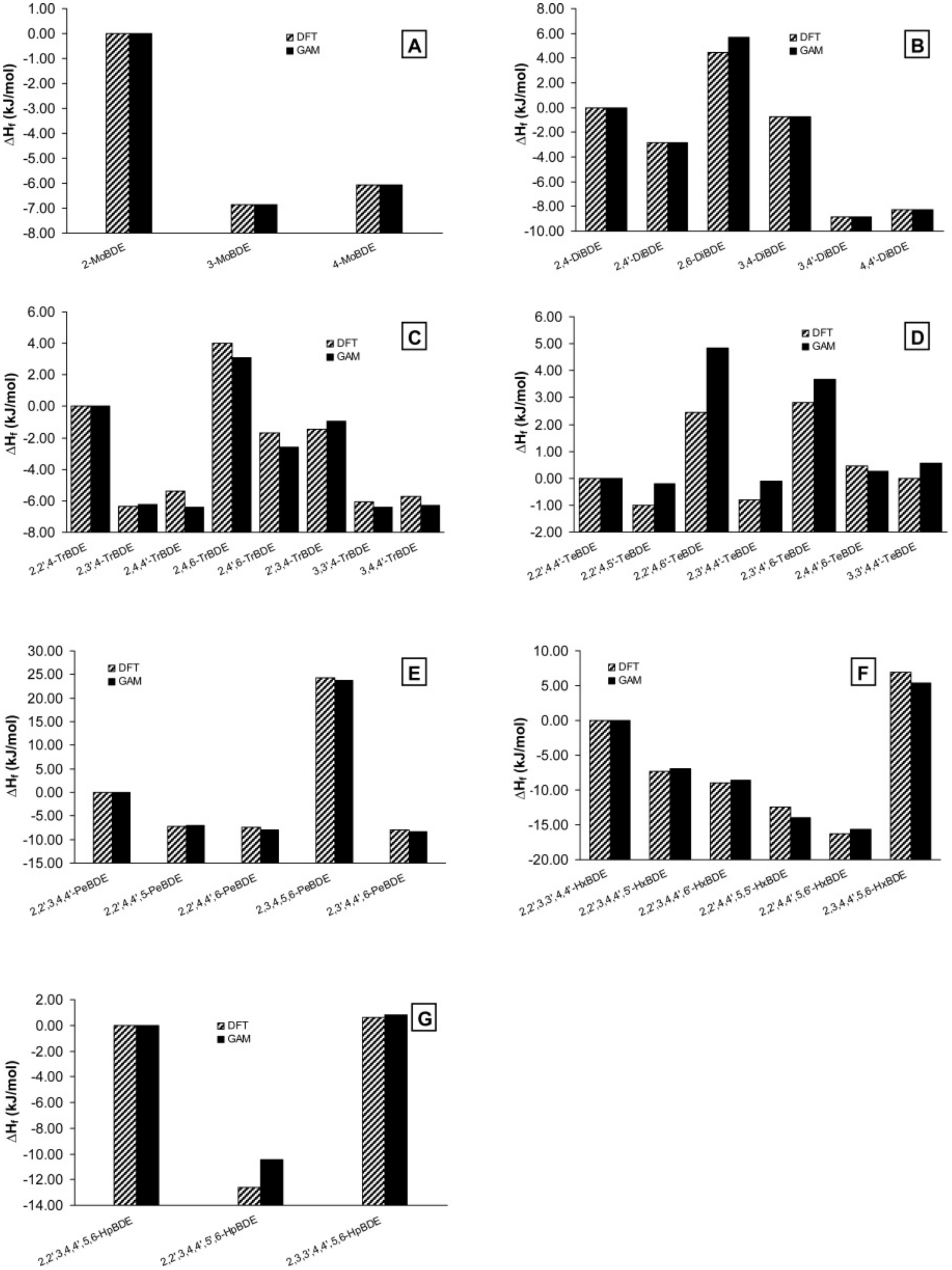


Figure 5. Comparison of relative ΔH_f from DFT calculation to GAM model, with congeners in homologue groups plotted in panels A through G. Relative ΔH_f DFT is the difference in ΔH_f (from DFT calculation) between the congener in question and the first congener in the homologue group. Relative ΔH_f GAM is the difference of the sum of ΔH_1, ΔH_2, and ΔH_3 for the same congener as compared to the first congener of the group.

corrected versus Br number (Figure 6). The consistency between the results from GAM model and those obtained from DFT calculation give credence to the latter's use for calculating the thermodynamic properties of PBDEs. The linear correlation between the GAM corrected ΔH_f and bromine number makes it possible to predict ΔH_f for any PBDE congeners.

Conclusions

After optimization by DFT calculation, the geometries of the 39 PBDE congeners studied all fall into the three groups (Figure 1). It is likely that other undiscovered conformations may exist for some of these PBDE congeners; however, the thermodynamic properties calculated in this

Table 5. Enthalpy Data of Position and Repulsion Effects for PBDE Congeners

	kJ/mol					
congeners	ΔH_f	relative ΔH_f DFT	ΔH_1	ΔH_2	ΔH_3	relative ΔH_f GAM
2-MoBDE	82.72	0.00	6.86	0.00	0.00	0.00
3-MoBDE	75.85	−6.86	0.00	0.00	0.00	−6.86
4-MoBDE	76.64	−6.07	0.79	0.00	0.00	−6.07
2,4-DiBDE	110.42	0.00	7.65	3.06	0.00	0.00
2,4′-DiBDE	107.57	−2.85	7.65	0.00	0.22	−2.85
2,6-DiBDE	114.90	4.48	13.73	1.47	1.23	5.71
3,4-DiBDE	109.69	−0.73	0.79	9.20	0.00	−0.73
3,4′-DiBDE	101.56	−8.86	0.79	0.00	1.06	−8.86
4,4′-DiBDE	102.16	−8.26	1.58	0.00	0.88	−8.26
2,2′,4-TrBDE	141.66	0.00	14.52	3.06	1.44	0.00
2,3′,4-TrBDE	135.32	−6.34	7.65	3.06	2.07	−6.24
2,4,4′-TrBDE	136.26	−5.39	8.44	3.06	1.09	−6.42
2,4,6-TrBDE	145.69	4.03	14.52	7.60	0.00	3.09
2,4′,6-TrBDE	139.96	−1.70	14.52	1.47	0.44	−2.60
2′,3,4-TrBDE	140.19	−1.47	7.65	9.20	1.22	−0.95
3,3′,4-TrBDE	135.58	−6.07	0.79	9.20	2.63	−6.41
3,4,4′-TrBDE	135.94	−5.72	1.58	9.20	1.94	−6.31
2,2′,4,4′-TeBDE	170.47	0.00	15.31	6.13	2.54	0.00
2,2′,4,5′-TeBDE	169.46	−1.00	14.52	5.73	3.51	−0.21
2,2′,4,6′-TeBDE	172.93	2.46	21.38	4.54	2.89	4.83
2,3′,4,4′-TeBDE	169.67	−0.80	8.44	12.26	3.16	−0.11
2,3′,4′,6-TeBDE	173.29	2.82	14.52	10.67	2.45	3.66
2,4,4′,6-TeBDE	170.92	0.46	15.31	7.60	1.31	0.25
3,3′,4,4′-TeBDE	170.45	−0.01	1.58	18.39	4.57	0.57
2,2′,3,4,4′-PeBDE	212.90	0.00	15.31	24.96	4.61	0.00
2,2′,4,4′,5-PeBDE	205.64	−7.26	15.31	17.99	4.61	−6.97
2,2′,4,4′,6-PeBDE	205.55	−7.35	22.17	10.66	3.98	−8.06
2,3,4,5,6-PeBDE	237.13	24.22	14.52	54.02	0.00	23.66
2,3′,4,4′,6-PeBDE	204.84	−8.07	15.31	16.80	4.39	−8.38
2,2′,3,3′,4,4′-HxBDE	255.96	0.00	15.31	43.79	8.24	0.00
2,2′,3,4,4′,5′-HxBDE	248.72	−7.25	15.31	36.82	8.24	−6.97
2,2′,3,4,4′,6′-HxBDE	247.03	−8.94	22.17	29.50	7.06	−8.61
2,2′,4,4′,5,5′-HxBDE	243.48	−12.49	15.31	29.86	8.24	−13.94
2,2′,4,4′,5,6′-HxBDE	239.75	−16.22	22.17	22.53	7.06	−15.58
2,3,4,4′,5,6-HxBDE	262.95	6.98	15.31	54.02	3.44	5.42
2,2′,3,4,4′,5,6-HpBDE	296.53	0.00	22.17	57.08	8.12	0.00
2,2′,3,4,4′,5′,6-HpBDE	283.92	−12.61	22.17	44.03	10.69	−10.48
2,3,3′,4,4′,5,6-HpBDE	297.17	0.64	15.31	63.21	9.64	0.79
DecaBDE	433.79	0.00	29.03	108.03	25.20	0.00

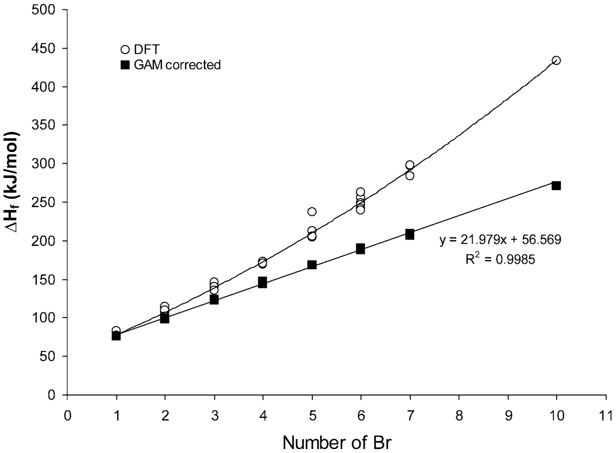


Figure 6. Comparison of enthalpy of formation between DFT calculation and GAM corrected results. The nonlinear trend line is the result of polynomial fitting, and the linear trend line is from linear regression.

study should not be affected by the missing conformations because the energy differences between different conformations of PBDE congeners are much smaller than the energy differences within homologues.

Use of the isodesmic reaction is a valid method for predicting the enthalpy and Gibbs free energy of formation of PBDEs from the results of DFT calculations and from known experimental values for other compounds. GAM yields results that are consistent with DFT calculation. The GAM model describes the effect of Br substitution pattern very well and can be potentially useful in predicting the thermodynamic properties of all of the 209 PBDE congeners.

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