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DFT calculation on PBPXs: Their gas phase thermodynamic function and implication of Br substituted position

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ABSTRACT

Using Gaussian 03 program, the thermodynamic properties of 135 polybrominated phenoxazines (PBPXs) have been calculated by density functional theory (DFT) at the B3LYP/6-31G* level. Based on the output data of Gaussian, the isodesmic reactions are designed to calculate standard enthalpy of formation (ΔH_f°) and standard Gibbs energy of formation (ΔG_f°) of PBPXs congeners. The relations of these thermodynamic parameters with the number and position of Br atom substitution (N_{PBS}) are discussed, and the order of relative stability of PBPX congeners is theoretically proposed according to the relative magnitude of their ΔG_f°. In addition, the values of molar heat capacities at constant pressure ($C_{p,m}$) from 200 to 1000 K for PBPX congeners are calculated, and the temperature dependence relations of this parameter is obtained using the least-squares method.

1. Introduction

Phenoxazine (PX) derivatives are a group of important organic synthetic intermediates and widely used in the synthesis of medicine, in biology and dyestuffs. The preparation and characterisation of *N*-alkyl phenoxazine dyes [1], and the multi-site inhibition of human plasma cholinesterase by cationic phenoxazine dyes have been reported [2]. The modulation of the polymer electronic and optical properties by introduction of phenoxazine was investigated with quantum-chemical techniques [3], and the relationship between the cytotoxicity of 15 phenoxazine derivatives and 11 physical parameters (descriptors) was delineated by semi-empirical molecular-orbital methods [4].

In the past, B3LYP density functional theory calculations have been carried out on a number of polychlorodibenzofurans (PCDFs) using 6-31G* and 6-311G basis sets to estimate their heats of formation based on the known experimental values for dibenzofuran, benzene and chlorobenzene [5]. Moreover, Zeng et al. [6] calculated the thermodynamic properties of 39 polybrominated diphenyl ethers (PBDEs) in the ideal gas state at the B3LYP/6-31G* level in Gaussian 03 program. Kroon et al. [7] predicted thermal decomposition mechanisms, temperatures and the activation energies of the thermal breakdown reactions of ionic liquids using ab initio quantum chemical calculations (DFT-B3LYP). Larowe et al. [8] calculated the thermodynamic properties of biomolecules at high temperatures and pressures. In addition, the thermodynamic data of polychlorinated dibenzo-*p*-dioxins (PCDDs), PCDFs, polychlorinated biphenyls (PCBs) and polychlorinated phenoxathiins (PCPTs) have been calculated by DFT [9–12]. It was found that the isomers with lower free energy have higher formation ratio, i.e., the formation ratio of isomers are consistent with their relative stabilities. Also, thermodynamic data of polybrominated dibenzo-furans (PBDFs) and polybrominated naphthalenes (PBNs) were calculated by the same method [13,14], and the relative stability of their isomers was theoretically proposed.

Dioxin-like chemicals are a family of ubiquitous environmental contaminants known to produce a broad spectrum of toxic effects in animals, some of which include carcinogenicity, teratogenicity, immunotoxicity, and endocrine toxicity. Dioxin-like chemicals consist, in part, of PCDDs, PCDFs, and PCBs. Dioxin-like compounds (PCDD/PBDF) are formed as a class of pollutants during combustion processes and are by-products of a wide range of chemical processes such as the manufacture of PVC, pesticides, incineration, pulp and paper bleaching, and the smelting and recycling of metals. These hazardous compounds have no useful purpose and are widely dispersed in the environment. They tend to bind to organic matter in sediments and soils, accumulate in fatty tissues, and they can be transported over long distances from the source of emission. In the environment, they can be quickly transported to great distances through evaporation and condensation cycles. Polychloridized phenoxazines (PCPXs) or polybrominated phenoxazines (PBPXs) also are one of dioxin-like chemicals. However, there is little research

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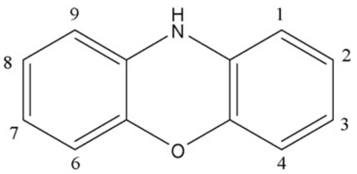

Fig. 1. Structure and the systematic numbering of PX.

concerning the thermodynamic data, and the source and the occurrence of PBPXs in environment. Therefore we attempt to study the thermodynamic properties and the order of relative stability of dioxin-like chemicals, to provide basic data for studying their formation, degradation and environmental risk of these dioxin-like chemicals.

In this study, the thermodynamic properties for the 135 PBPXs were calculated with density functional theory (DFT). By designing isodesmic reactions, the standard enthalpies of formation (ΔH_f°) and the standard Gibbs energies of formation (ΔG_f°) for all PBPXs were also obtained. Then, the relationships between these parameters and the numbers and positions of Br substitution (N_{PBS}) were studied. According to the relative magnitude of their ΔG_f°, the relative stability order of PBPX congeners was theoretically proposed. Finally, the $C_{p,m}$ values at 200–1000 K for PBPX congeners were calculated using a statistical thermodynamics calculation program [15].

2. Theory and calculation

The structure and carbon atomic numbering of PX is illustrated in Fig. 1. Theoretical calculation of the thermodynamic properties for 135 PBPXs in the gaseous phase were performed by DFT methods with Gaussian 03 program [16]. All the quantum mechanical computation was performed using the procedure of B3LYP/6-31G*. The zero-point vibrational energies, calculated on optimized molecular structures, were scaled by 0.9804 so that known systematic errors in calculated frequencies might be eliminated. The standard state entropy (S°), the absolute enthalpy (H°) and Gibbs free energies (G°) were obtained directly from DFT calculations (Gaussion's output file).

In this paper, PBPX isomers with one to eight bromine atoms are represented by the notation MBPXs, DBPXs, Tri-BPXs, TBPXs, Penta-BPXs, Hexa-BPXs, Hepta-BPXs and OBPX, respectively. In addition, the positions of Br substitution (PBS) are consisted of the number of the substituting Br atoms on different positions of the parent compound and the number of relative positions of these Br atoms. The numbers of bromine atoms at positions 1 or 9 were defined as N_1; the numbers of bromine atoms at positions 2 or 8 were defined as N_2; the numbers of bromine atoms at positions 3 or 7 were defined as N_3; the numbers of bromine atoms at positions 4 or 6 were defined as N_4; the pair numbers of ortho, meta and para positions of bromine atoms on one benzene ring were symbolized as N_o, N_m and N_p, respectively. Moreover, the parameters mentioned above are defined as a general designation N_{PBS}, where N is the number of Br atom substitutions and that subscript PBS indicates the positions.

Because no experimental data of ΔH_f° and ΔG_f° for PBPXs is available, in this study, reaction 1 was designed for calculating ΔH_f° and ΔG_f°. Lee et al. [17] used the isodesmic reaction to calculate the ΔH_f° and ΔG_f° of PCDDs and obtained results consistent to experimental results. It seems reasonable to expect that estimates of the thermodynamic properties of PBPXs, from DFT calculations based on isodesmic reactions, will be similarly accurate.

$$\mathrm{PX} + n\,\mathrm{bromobenzene} = \mathrm{PBPX} + n\,\mathrm{benzene} \qquad (1)$$

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

$$\Delta H_r^\circ = [H^\circ_{\mathrm{PBPX}} + n\,H^\circ_{\mathrm{benzene}}] - [H^\circ_{\mathrm{PX}} + n\,H^\circ_{\mathrm{bromobenzene}}] \qquad (2)$$

Similarly, following Eq. (3) also yields ΔH_r°:

$$\Delta H_r^\circ = [\Delta H^\circ_{\mathrm{f\,PBPX}} + n\,\Delta H^\circ_{\mathrm{f\,benzene}}] - [\Delta H^\circ_{\mathrm{f\,PX}} + n\,\Delta H^\circ_{\mathrm{f\,bromobenzene}}] \qquad (3)$$

So Eq. (4) could be obtained from Eq. (3) and Eq. (2):

$$\Delta H^\circ_{\mathrm{f\,PBPX}} = H^\circ_{\mathrm{PBPX}} + n\,H^\circ_{\mathrm{benzene}} - n\,H^\circ_{\mathrm{bromobenzene}} - H^\circ_{\mathrm{PX}} - n\,\Delta H^\circ_{\mathrm{f\,benzene}} + n\,\Delta H^\circ_{\mathrm{f\,bromobenzene}} + \Delta H^\circ_{\mathrm{f\,PX}} \qquad (4)$$

Similarly, $\Delta G_f^\circ{}_{\mathrm{PBPX}}$ could be obtained by Eq. (5):

$$\Delta G^\circ_{\mathrm{f\,PBPX}} = G^\circ_{\mathrm{PBPX}} + n\,G^\circ_{\mathrm{benzene}} - n\,G^\circ_{\mathrm{bromobenzene}} - G^\circ_{\mathrm{PX}} - n\,\Delta G^\circ_{\mathrm{f\,benzene}} + n\,\Delta G^\circ_{\mathrm{f\,bromobenzene}} + \Delta G^\circ_{\mathrm{f\,PX}} \qquad (5)$$

To obtain $\Delta G^\circ_{\mathrm{f\,PX}}$, Eq. (6) was designed:

$$12\,\mathrm{C_{(Graphite)}} + 9/2\,\mathrm{H_2} + 1/2\,\mathrm{O_2} + 1/2\,\mathrm{N_2} = \mathrm{C_{12}H_9ON} \qquad (6)$$

So:

$$\Delta S_r^\circ = S^\circ(\mathrm{PX}) - 12S^\circ(\mathrm{C}) - 9/2\,S^\circ(\mathrm{H_2}) - 1/2\,S^\circ(\mathrm{O_2}) - 1/2\,S^\circ(\mathrm{N_2}) \qquad (7)$$

$$\Delta H_r^\circ = \Delta H_f^\circ(\mathrm{PX}) - 12\,H^\circ(\mathrm{C}) - 9/2\,H^\circ(\mathrm{H_2}) - 1/2\,H^\circ(\mathrm{O_2}) - 1/2\,H^\circ(\mathrm{N_2}) = \Delta H_f^\circ(\mathrm{PX}) \qquad (8)$$

$$\Delta G_r^\circ = \Delta G_f^\circ(\mathrm{PX}) - 12\,G^\circ(\mathrm{C}) - 9/2\,G^\circ(\mathrm{H_2}) - 1/2\,G^\circ(\mathrm{O_2}) - 1/2\,G^\circ(\mathrm{N_2}) = \Delta G_f^\circ(\mathrm{PX}) \qquad (9)$$

$$\Delta G_r^\circ(\mathrm{PX}) = \Delta G_f^\circ(\mathrm{PX}) = \Delta H_r^\circ(\mathrm{PX}) - T\ \Delta S_r^\circ(\mathrm{PX}) = \Delta H_f^\circ(\mathrm{PX}) - T\ \Delta S_r^\circ(\mathrm{PX}) \qquad (10)$$

The experimental values of ΔH_f° and ΔG_f° for benzene, bromobenzene and PX are listed in Table 1, including the calculated values of H° and G° at the B3LYP/6-31G* level. The experimental values of compounds mentioned above are taken from reference [18].

Using a statistical thermodynamics calculation program [15], ideal-gas thermodynamic functions such as molar entropy, heat capacity, and enthalpy content, can be computed easily from the molecular partition function. All the necessary information is usually included in the output file from a vibrational frequency calculation executed using the quantum chemistry software from Gaussian, Inc. The statistical thermodynamics calculation program will automatically extract the essential data from a Gaussian output file and compute thermodynamic functions at several temperatures. So the $C_{p,m}$ values at 200–1000 K for PBPX congeners were calculated with it.

Table 1
Thermodynamic data used for calculating ΔH_f° and ΔG_f° of PBPXs.

No.	Name	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	H° (kJ mol^{-1})	G° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})
1	Benzene	82.9[a]	129.66[a]	−609490.3	−609570.2	
2	Bromobenzene	105.02[a]	138.53[a]	−7359949.1	−7360045.9	
3	Phenoxazine (PX)	94.0 [a]	231.55[b]	−1555547.4	−1555669.5	409.77
4	Graphite (C)	0[a]				5.74[a]
5	Nitrogen (N_2)	0[a]				205.03[a]
6	Hydrogen (H_2)	0[a]				130.57[a]
7	Oxygen (O_2)	0[a]				191.50[a]

[a] Data from [18].

[b] Predicted from Eqs. (6)–(10), and others data from B3LYP/6-31G* calculations.

In previous reports, Grabda et al. have predicted the gas phase thermodynamic properties of PBDEs, PBBs, PBPs, HBCD and TBBPA using DFT method [19]. They assessed the quality of the DFT predictions obtained by comparison of the calculated data with certain experimentally-measured properties of brominated arenes available in the literature. And results showed that the average standard deviations calculated for these comparisons amount to 2.6 and 12.7 J mol^{-1} K^{-1} for $C_{p,m}$ and S°, respectively, and 7.5 k J mol^{-1} for ΔH_f°. It follows that the parameters obtained by DFT calculations at only a moderate level of the theoretical depth are accurate; and the absolute enthalpy (H°) and Gibbs energy (G°) functions applied for estimating the ΔH_f° and ΔG_f° through their equations of thermodynamic relationships derived from the law of energy conservation (similar to Eqs. (2)–(5) in this paper) afford high quality results. Moreover, the method selected here was also successfully used in estimation of the ΔH_f° and ΔG_f° values for polybrominated dibenzo-*p*-dioxins and dibenzofurans [20], and 39 selected congeners of PBDEs [6]. The results show that the method used in this study is of high precision.

3. Results and discussion

In addition, the values of total energy (E) for DBPXs were calculated at levels of B3LYP and MP2. By defining the smallest value of E at each level as zero, ΔE_R was obtained as the values for the other isomers minus the smallest value, and these values are also listed in Table 2. The variation of ΔE_R for DBPXs is shown in Fig. 2. Comparing ΔE_R as shown in Table 2 and Fig. 2, it was found that ΔE_R of 3,4-DBPX calculated using three methods are all maximum and that of 1,9-DBPX are all minimum. In addition, the discrepancy of ΔE_R between the two compounds, by MP2/6-31G*, B3LYP/6-311G and B3LYP/6-31G*, is 27.13, 26.52 and 27.81 kJ mol^{-1}, respectively. The values of E calculated using three methods are different, but the order of the relative magnitude and the change tendency of ΔE_R are in agreement, which indicated calculation using this method to be a valid procedure. Moreover, the calculated values of thermodynamic properties for all the 135 PBPXs in the gaseous state are available as Supplementary Material.

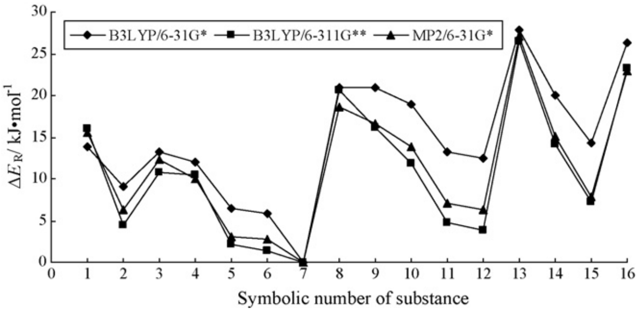

Fig. 2. The change tendency of ΔE_R for DBPXs at different levels.

3.1. *Relation of the numbers and positions of bromine substitute (N_{PBS}) to S°*

We have used the multiple linear regression method of the SPSS 12.0 for Windows program, to obtain the relations between N_{PBS} and S°, as following Eq. (11), which has the largest squared regression coefficient R^2 (0.998) and the smallest standard error SE (2.24). So Eq. (11) is thus recommended and taken as model (I) in this study, and it can be used to predict the S° with reasonable accuracy. From model (I), it can been shown that S° increase with the increasing number of bromine atoms substituted for hydrogen. The main factor of influencing S° values of PBPXs is the numbers of bromine atoms, and the order of the effect is $N_3 > N_2 > N_1 > N_4$.

$$S^\Theta = 409.45 + 41.90N_1 + 42.11N_2 + 42.17N_3 + 39.54N_4 - 2.56N_o + 0.47N_m - 1.14N_p \\ R^2 = 0.998 \qquad SE = 2.24 \tag{11}$$

3.2. *Calculated results of $\Delta_f H^\circ$ and $\Delta_f G^\circ$ value and relative stability of isomer groups*

With the design of isodesmic reactions, ΔH_f° and ΔG_f° of PBPXs were obtained and are available as Supplementary Material. To investigate relative Gibbs energies of formation we take the lowest ΔG_f° of isomers with the same numbers of substituent bromine

Table 2
Comparison of ΔE_R calculated at different levels.

Molecule	ΔE_R (kJ mol^{-1})			Molecule	ΔE_R (kJ mol^{-1})		
	B3LYP/6-31G*	B3LYP/6-311G**	MP2/6-31G*		B3LYP/6-31G*	B3LYP/6-311G**	MP2/6-31G*
1,2	13.91	16.05	15.58	2,4	20.93	16.13	16.63
1,3	9.03	4.43	6.27	2,6	18.92	11.77	13.83
1,4	13.28	10.77	12.26	2,7	13.30	4.83	7.06
1,6	12.04	10.51	10.03	2,8	12.47	3.78	6.36
1,7	6.45	2.12	3.14	3,4	27.81	26.52	27.13
1,8	5.85	1.40	2.77	3,6	20.05	14.13	15.01
1,9	0.00	0.00	0.00	3,7	14.25	7.20	7.88
2,3	20.99	20.57	18.68	4,6	26.30	23.22	23.00

Table 3
The most stable and the least stable isomer in different isomer groups.

Substance	The most stable isomer	The least stable isomer
MBPXs	1-MBPX	4-MBPX
DBPXs	1,9-DBPX	3,4-DBPX
Tri-BPXs	1,3,9-Tri-BPX	2,3,4-Tri-BPX
TBPXs	1,3,7,9-TBPX	2,3,4,6-TBPX
Penta-BPXs	1,2,4,7,9-Penta-BPX	2,3,4,6,7-Penta-BPX
Hexa-BPXs	1,2,3,6,8,9-Hexa-BPX	2,3,4,6,7,8-Hexa-BPX
Hepta-BPXs	1,2,3,4,7,8,9-Hepta-BPX	1,2,3,4,6,7,8-Hepta-BPX

atoms to be zero, i.e. a standard state. The relative standard Gibbs energies of formation ($\Delta_R G_f^\circ$) were obtained by ΔG_f° of other isomers minus the lowest ΔG_f° of isomers with the same substituent numbers (These values are also listed in the Supplementarty Data.) From these values, it is found that the values of ΔH_f° and ΔG_f° increase with increasing number of bromine atoms, i.e. with increasing bromination stability decreases. Furthermore, the values of ΔH_f° and ΔG_f° vary between isomers with the same number of bromine atoms. For example, among the 38 isomers of TBPXs, 1,3,7,9-TBPX possesses the lowest value of ΔG_f°, and 2,3,4,6-TBPX possesses the highest corresponding value, where the discrepancy of them ($\Delta_R G_f^\circ$) is 43.35 kJ mol^{-1}. In the same way, the $\Delta_R G_f^\circ$ of 1,2,4,7,9-penta-BPX is lower than those of the other 28 isomers, and 2,3,4,6,7-Penta-BPT is higher than those of the others, where the discrepancy of them ($\Delta_R G_f^\circ$) is 34.74 kJ mol^{-1}.

Using multiple linear regression method, the correlation expressions of ΔH_f° and ΔG_f° to N_{PBS} are summarized and presented in Eqs. (12) and (13), respectively, which are called model (II) and model (III), respectively. Eqs (12) and (13) clearly demonstrate that the substitute number and position of bromine atoms influence the values of ΔH_f° and ΔG_f°.

$$\begin{aligned} &\Delta H_f^\circ = 91.32 + 19.46N_1 + 25.37N_2 + 26.28N_3 + 32.35N_4 + 8.44N_o + 2.79N_m + 1.55N_p \\ &R^2 = 1.000 \qquad \mathrm{SE} = 0.68 \end{aligned} \tag{12}$$

$$\begin{aligned} &\Delta G_f^\circ = 228.96 + 10.57N_1 + 16.42N_2 + 17.31N_3 + 24.16N_4 + 9.21N_o + 2.65N_m + 1.89N_p \\ &R^2 = 0.999 \qquad \mathrm{SE} = 0.92 \end{aligned} \tag{13}$$

From Eqs. (12) and (13), the following conclusions can be obtained:

i. The values of ΔH_f° increase with the substitute number of bromine atoms, and the effect of N_4 is important. When N_4 increases 1, the value of ΔH_f° increases 32.35 kJ mol^{-1}.
ii. The values of ΔG_f° also increase with the number of bromine atoms, and N_4 is the primary influence on the values of ΔG_f°. When N_4 increases 1, the value of ΔG_f° increases 24.16 kJ mol^{-1}, which suggests that those compounds with bromines being attached at position 4 or 6 are most unstable than others.
iii. N_o, N_m and N_p have great effects on the values of ΔH_f°, as well as ΔG_f°, with the following order: $N_o > N_m > N_p$, which indicate that bromine atom located at *ortho* position significantly decreases the stability of the congeners. The lower stability of the *ortho* substituted PBPXs certainly results from repulsive force between the bromine atoms.
iv. The squared correlation coefficients R^2 of Eqs. ((12) and (13)) are 1.000 and 0.999, respectively. Thus the values of ΔH_f° and ΔG_f° can be predicted from the N_{PBS} of PBPXs which have been obtained.

As discussion above, the values of ΔG_f° increase with the substitute number of bromine atoms, which indicate that the stability of the congeners decreases significantly. Thus in each group of isomers, the most stable and unstable isomers as indicated by the Gibbs energy of formation can be obtained, as listed in Table 3. These results can be used to examine whether the most stable isomers are the most abundant in the environment.

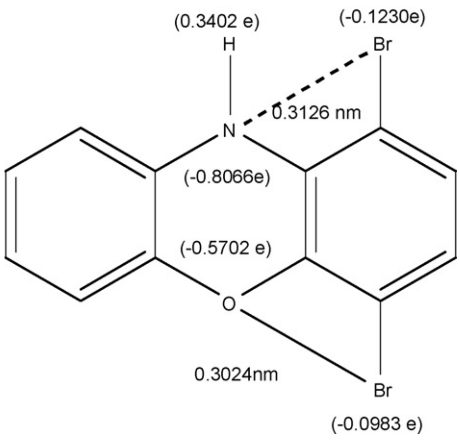

Fig. 3. The structure of 1, 4-DBPX.

As can be observed from Table 3, the most unstable isomers in MBPXs, DBPXs, Tr-BPXs, TBPXs, Penta-BPXs, Hexa-BPXs and Hepta-BPXs are all those with bromines being attached at the same aromatic ring and close to each other. On the contrary, the most stable isomers are all those with bromines replaced at two aromatic rings as possible, so that the bromines can be apart from each other.

From the discussion above, the reasons those compounds with bromines being attached at position 4 or 6 are most unstable may be that: (i) the distance between Br atom replaced at positions 4 or 6 and O atom is nearer than that between Br atom replaced at positions 1 or 9 and N atom, so the repulsive force between the bromine and oxygen atom is obviously stronger than the latter. (ii) Br and O atoms possess negative charge, while H atom linked with N has positive charge. So the higher stability of PBPXs, with bromines being attached at position 1 or 9, may results from intramolecular hydrogen bonding occuring between the hydrogen of the NH group and negative regions of the bromines. Taking 1, 4-DBPX as an example, data for these dimensions and charges can be obtained from the Gaussian output files, as shown in Fig. 3: the distance (between Br at positions 4 and O atom) and charge are 0.3024 nm, −0.0983 e (Br) and −0.5702 e (O), respectively, while 0.3126 nm, −0.1230 e (Br), −0.8066 (N) and 0.3402 e (H) for Br at positions 1 and N, respectively.

3.3. *The temperature dependence of molar heat capacity of PBPXs at constant pressure*

The values of molar heat capacity at constant pressure ($C_{p,m}$) for PBPXs congeners have not been reported. The values of $C_{p,m}$ (200–1000 K) have been accordingly calculated using a statistical thermodynamics calculation program based on Gaussian output files.

Using the calculated values of $C_{p,m}$ of PBPXs at different temperature (T), the relations between $C_{p,m}$ and temperature were obtained using the least square method, as Eq. (14).

$$C_{p,m} = a + b(10^{-3}T) + c(10^5 T^{-1}) + d(10^7 T^{-2}) \tag{14}$$

Constant *a*, and regression coefficients *b*, *c* and *d*, are listed in the Supplementary Material.

4. Conclusions

135 PBPXs were fully optimized at B3LYP/6-31G* level, and thus their H°, S° and G° were consequently obtained. In addition, ΔH_f° and ΔG_f° of formation for each PBPX molecule were calculated by isodesmic reactions. The result showed that all these thermodynamic parameters have close relationship with the numbers and positions of bromine substituents (N_{PBS}). Thus the enthalpies and Gibbs energies of formation for 135 PBPX congeners should be valuable in further thermodynamic modeling studies. According to the relative magnitude of their ΔG_f°, the order of relative stability of PBPX congeners was theoretically proposed. It is found that the most unstable isomers are all those with bromines being attached at the same aromic ring and close to each other, while the most stable isomers are all those with bromines substituted on the two aromic rings and in general as far apart from each other as possible. Moreover, it is determined that there is a very good relationship between $C_{p,m}$ and temperature for the PBPX congeners.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.12.030.

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