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Thermodynamic properties and relative stability of polybrominated phenoxathiins by density functional theory

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The thermodynamic properties of 135 polybrominated phenoxathiins (PBPTs) in the ideal gas state at 298.15 K and 1.013×10^5 Pa have been calculated at the B3LYP/6-31G* level using Gaussian 03 program. The isodesmic reactions were designed to calculate standard enthalpy of formation ($\Delta_f H^\ominus$) and standard free energy of formation ($\Delta_f G^\ominus$) of PBPTs congeners. The relations of these thermodynamic parameters with the number and position of Br atom substitution (N_{PBS}) were discussed, and it was found that there exist good correlations between thermodynamic parameters (entropy ($S^\ominus$), $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$) and N_{PBS}. According to the relative magnitude of their $\Delta_f G^\ominus$, the order of relative stability of PBPT congeners was theoretically proposed. Moreover, using a statistical thermodynamics calculation program based on Gaussian output files, the values of molar heat capacity at constant pressure ($C_{p,m}$) from 200 to 1800 K for PBPT congeners were calculated, and the temperature dependence relation of them was obtained using the least-squares method.

Key words: Polybrominated phenoxathiins, the number and position of Br atom substitution (N_{PBS}), thermodynamic property, relative stability, molar heat capacity at constant pressure ($C_{p,m}$).

INTRODUCTION

Phenoxathiin (PT) derivatives can be used in the prophylaxis and treatment of mental disorders as inhibitors of monoamine oxidase. The thermodynamic properties of PT have been reported (Steele et al., 1993), the structures of six molecules (dibenzodioxine, 1,4,6,9-tetrazathianthrene, thianthrene, 1-azathianthrene, 1,4-diazathianthrene and PT) previously studied by X-ray and electron diffraction have been calculated using MM3 and ab initio (3-21G* basis set) methods (Mastryukov et al., 1997), and the structure of PT as well as the effect including electronegative nitrogen atoms in the arene rings of PT have been studied using the ab initio method at the B3LYP/(6-31+G)+d basis set level (Iman et al., 2005) . Moreover, several properties of the excited singlet state (natural lifetimes, fluorescence quantum yields, sol-solvatochromicity, etc.) of some 3-substituted phenoxa-

thin derivatives (methyl, formyl and acetyl) have been investigated by means of absorption and steady-state fluorescence spectroscopy (Ionescu et al., 1999). The aqueous solubilities of phenanthrene and several solid three-ring aromatic heterocycles (thianthrene, phenothiazine, PT, phenoxazine, et al.) at temperatures ranging from 313K to the solute melting point and at a pressure of 5 MPa were also reported (Karasek et al., 2007). But there is hardly any research concerning the thermodynamic data of polybrominated phenoxathiins (PBPTs). For studying their generation, degradation and environmental risk, it is important to know the thermodynamic properties of PBPTs.

In the previous reports, the thermodynamic data of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorodibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and polychlorinated phenoxathiins (PCPTs) have been calculated by DFT (Wang et al., 2005a; Wang et al., 2003; Wang et al., 2005b; Wei et al., 2008).It was found that the isomers with lower free energy have higher formation ratio, that is, the formation ratio of isomers

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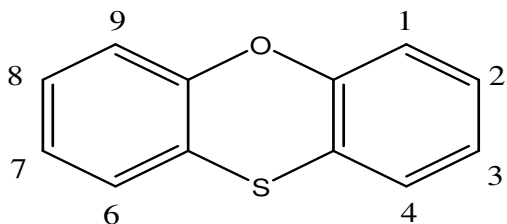
Figure 1. Molecular structures and atomic numbering of phenoxathiin (PT).

are consistent with their relative stabilities. Also, thermo-dynamic data of polybrominated dibenzo-furans (PBDFs) and polybrominated naphthalenes (PBNs) were calculated by the same method (Yu et al., 2006; Yuan et al., 2006), and the relative stability of their isomers was theoretically proposed.

The purpose of the study was to calculate the thermodynamic properties for 135 PBPTs. Then, the relationships between these parameters and the numbers and positions of Br substitution (N_{PBS}) were studied. By designing isodesmic reactions, the standard enthalpies of formation ($\Delta_f H^\ominus$) and the standard Gibbs energies of formation ($\Delta_f G^\ominus$) for all PBPTs were also obtained. On the basis of the relative magnitude of their $\Delta_f G^\ominus$, the relative stability order of PBPT congeners was theoretically proposed and then compared with that of polychlorinated dibenzo-p-dioxin (PCDD) isomers. Finally, the molar heat capacity $C_{p,m}$ values at 200 - 1800 K of PBPT congeners were calculated using statistical thermodynamics calculation program.

COMPUTATIONAL METHODS

The structure and atomic numbering of PT are illustrated in Figure 1. With Gaussian 03 program(Frisch et al., 2003), geometry optimizations, frequency and energy calculations were performed at the B3LYP/6-31G* level at the state of 298.15 K and 1.013×10⁵ Pa. Standard enthalpies ($H^\ominus$), standard Gibbs energies ($G^\ominus$) and standard entropy ($S^\ominus$) for 135 PBPTs were obtained. As for the notation in this paper, PBPT isomers with one to eight bromine atoms are represented by MBPTs, DBPTs, tri-BPTs, TBPTs, penta-BPTs, hexa-BPTs, hepta-BPTs and OBPT, respectively. In addition, the positions of Br substitution (PBS) include the number of substituting Br atoms on the different positions of parent compound and the number of relative positions for these Br atoms. The number of bromine atoms at positions 1 and/or 9 is defined as N_1. Similarly, the number of bromine atoms at positions 2 and/or 8, 3 and/or 7, 4 and/or 6 is defined as N_2, N_3, N_4, respectively. The pair numbers of ortho, meta and para positions of bromine atoms on one benzene ring are symbolized as N_o, N_m and N_p, respectively. Moreover, the parameters mentioned above are defined as a general designation N_{PBS}.

In this study, reaction 1 was designed for calculating $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$:

PT + nbromobenzene = PBPT+nbenzene   (1)

From the reaction above, $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$ of PBPTs can been obtained, as follows:

$$\Delta_f H^\ominus_{PBPT} = H^\ominus_{PBPT} + nH^\ominus_{benzene} - nH^\ominus_{bromobenzene} - H^\ominus_{PT} - n\Delta_f H^\ominus_{benzene} + n\Delta_f H^\ominus_{bromobenzene} + \Delta_f H^\ominus_{PT} \qquad (2)$$

$$\Delta_f G^\ominus_{PBPT} = G^\ominus_{PBPT} + nG^\ominus_{benzene} - nG^\ominus_{bromobenzene} - G^\ominus_{PT} - n\Delta_f G^\ominus_{benzene} + n\Delta_f G^\ominus_{bromobenzene} + \Delta_f G^\ominus_{PT} \qquad (3)$$

The experimental values of $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$ for benzene, bromobenzene and PT are listed in Table 1, including the values of $H^\ominus$ and $G^\ominus$ calculated at the B3LYP/6-31G* level for these compounds.

In order to validate the precision of the method, some thermodynamic data of halogen aroma compounds with experimental data were calculated using the same method (Wang et al., 2004), which indicates the method used in this study is of high precision. Furthermore, it was found that the relative stabilities from calculated results were in good agreement to the ratio of these isomers mensurated in the environment when we studied PCDDs, which proves veracity of the method.

RESULTS AND DISCUSSIONS

The calculation results of thermodynamic properties for all the 135 PBPTs in the gaseous state at 298.15 K and 1.013×10⁵ Pa are listed in Table 2.

Relation of the numbers and positions of bromine substitute (N_{PBS}) to $S^\ominus$

Up to date, there hasn't been experimental thermodynamic data of PBPTs reported systematically. In this work, $S^\ominus$ was predicted by ab initio calculations using the B3LYP/6-31G* method. The results are presented in Table 2. Using multiple linear regression method of the SPSS 12.0 for Windows program, the relation between N_{PBS} and $S^\ominus$ can be obtained, as Eq. (4). From Eq. (4), the conclusions can be obtained: $S^\ominus$ increase with the substitute number of bromine atoms increasing, but the effect of N_o, N_m and N_p on $S^\ominus$ aren't prominent. Because, only N_o was contained in the correlation equation of $S^\ominus$, and the coefficient (-2.36) of N_o is less than that of other variables. So it is suggested that the main influence factor of $S^\ominus$ for PBPTs is the substitute numbers of bromine atoms, rather than their relative position.

$S^\ominus$= 416.67 + 38.35N_1+ 41.22N_2+ 41.597N_3+ 42.24N_4 - 2.36N_o

R^2=0.999 SE= 1.44

The squared regression coefficient R^2 is 0.999 and the standard error SE is 1.44, which shows that there exist good correlations between the values obtained from Gaussian 03 program and those from correlative equations. So $S^\ominus$ can be predicted easily by obtained N_{PBS} of PBPTs, that is, the $S^\ominus$ values of PBPTs obviously vary with the substitute number and position of bromine atoms.

Calculated results of $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$ values and relative stability of isomer groups.

With the design of isodesmic reactions, $\Delta_f H^\ominus$ and $\Delta_f G^\ominus$ of

Table 1. Thermodynamic data of benzene, bromobenzene and PT.

Number	Name	$\Delta_f H^{\ominus}/(kJ \cdot mol^{-1})$	$\Delta_f G^{\ominus}/(kJ \cdot mol^{-1})$	$H^{\ominus}/(hartree^c)$	$G^{\ominus}/(hartree)$
1	benzene	82.9[a]	129.7[a]	-232.14258	-232.17302
2	bromobenzene	105.0[a]	138.5[a]	-2803.25621	-2803.29306
3	PT	61.55[b]	177.69[b]	-935.32437	-935.37158

[a]data from reference (Yao et al., 1985), [b] data from reference (Steele et al., 1993) , and other data from B3LYP/6-31G* calculations, [c] 1 Hartree = 2625.50 kJ·mol^{-1}.

PBPTs were obtained and listed in Table 2. Furthermore, the values of $\Delta_f H^{\ominus}$ as well as those of $\Delta_f G^{\ominus}$ are both different for isomers with the same substitute numbers of bromine atoms because their substitute positions of bromine are different. For example, among the 38 isomers of TBPTs, 2,4,6,8-TBPT possesses the lowest value of $\Delta_f G^{\ominus}$, and 1,2,3,4-TBPT possesses the highest corresponding value, where the discrepancy of them is 34.83 kJ·mol^{-1}. In the same way, the $\Delta_f G^{\ominus}$ of 1,2,4,6,8-Penta- BPT is lower than those of the other 28 isomers, and 1,2,3,4,9-Penta-BPT is higher than those of the others, where the discrepancy of them is 23.41 kJ·mol^{-1}.

On the basis of the lowest $\Delta_f G^{\ominus}$ of isomers with the same substitute numbers of bromine atoms, the relative standard Gibbs energies of formation ($\Delta_f G^{\ominus}_R$) were obtained by the $\Delta_f G^{\ominus}$ of other isomers minus the lowest $\Delta_f G^{\ominus}$ of isomers having the same numbers of substituent, and also listed in Table 2. Then according to the magnitude of $\Delta_f G^{\ominus}_R$, the theoretic relative stability orders of the isomers were proposed.

For the PBPT compounds in each isomer group, the isomers with the lower $\Delta_f G^{\ominus}_R$ values are relatively more stabe, whereas those with the higher $\Delta_f G^{\ominus}_R$ values are more unstable. Thus, the relative stability of each isomer group can be determined, and the most stable and unstable isomers are listed in Table 3. The gas phase thermodynamic functions of polychlorinated dibenzo-p-dioxins (PCDDs) have been calculated by DFT method and designed isodesmic reactions (Wang et al. 2004). The relative contents of isomers were found to correlate with the values of free energies, that is, the isomer with lower free energy has higher relative content. So it can be expected that the formation ratio of isomer with lower $\Delta_f G^{\ominus}_R$ is higher, while the formation ratio of isomer with higher $\Delta_f G^{\ominus}_R$ is lower, which is similar to that of PCDDs. Using multiple linear regression method, the correlation expressions of $\Delta_f H^{\ominus}$ and $\Delta_f G^{\ominus}$ to N_{PBS} were summarized and presented as Eq.(5) and Eq.(6), respectively.

$$\Delta_f H^{\ominus} = 41.68 + 38.06N_1 + 33.84N_2 + 33.79N_3 + 33.84N_4 + 5.39N_o \quad (5)$$

$$R^2 = 0.980 \; SE = 8.20$$

$$\Delta_f G^{\ominus} = 172.62 + 26.49N_1 + 19.44N_2 + 19.75N_3 + 21.11N_4 + 9.09N_o \quad (6)$$

$$R^2 = 0.998 \; SE = 1.79$$

Equations (5 and 6) clearly demonstrate that the substitute number and position of bromine atoms influence the values of $\Delta_f H^{\ominus}$ and $\Delta_f G^{\ominus}$. From Equations 5 and 6, the conclusions can be obtained: (i) the values of $\Delta_f H^{\ominus}$ and $\Delta_f G^{\ominus}$ increase with the substitute number of bromine atoms increasing, and the effect of N_1 is important. When N_1 is changed from 0 to 1, the value of $\Delta_f H^{\ominus}$ and $\Delta_f G^{\ominus}$ increases 38.06 and 26.49 kJ·mol^{-1}, respectively. But the effect of N_m and N_p on $\Delta_f H^{\ominus}$ is not prominent. So it can be concluded that N_1, N_2, N_3, N_4 and N_o are the primary influence factors of the values of $\Delta_f H^{\ominus}$ and $\Delta_f G^{\ominus}$, and the effect of N_o is smaller than that of N_1, N_2, N_3 and N_4. (ii) the squared correlation coefficients R^2 of Eqs. (5 and 6) are 0.980 and 0.998, respectively. So the values of $\Delta_f H^{\ominus}$ and $\Delta_f G^{\ominus}$ can be predicted by N_{PBS} of PBPTs obtained.

From discussion above, the reason for those compounds with bromines being attached at N_1 are most unstable may be that: (i) the distance between the bromine replaced at N_1 and the oxygen atom is shorter than that between the bromine replaced at N_4 and the sulfur atom, so the repulsive force between the bromine and oxygen atom is obviously stronger than the latter. (ii) the bromine and the oxygen atom possesses negative charge, while the sulfur atom has positive charge, so there will be the repulsive force between the bromine replaced at N_1 and the oxygen atom. Taking 1-MBPT as an example, the distance (between the bromine and the oxygen atom) and charge (the bromine and the oxygen atom) is 0.3028 nm, -0.1027e and -0.5464e, respectively, while 0.3266 nm, -0.1024e and 0.2325e for 4-MBPT, respectively.

The temperature dependence of molar heat capacity of PBPTs at constant pressure

The values of molar heat capacity at constant pressure ($C_{p,m}$) for PBPTs congeners have not been previously reported. So the values of $C_{p,m}$ (from 200 to 1800 K) were calculated using statistical thermodynamics calculation program (Raff, 2001) based on Gaussian output files.

Based on the calculated values of $C_{p,m}$ of PBPTs at different temperature (T), the relations between $C_{p,m}$ and temperature were obtained using the least square method, as Equation (7).

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

Table 2. The thermodynamic parameters of PBPTs from DFT calculations at B3LYP/6-31G* level and N_{PBS}.

Molecule	$S^{\ominus}$	$\Delta_f H^{\ominus}$	$\Delta_f G^{\ominus}$	$\Delta_f G^{\ominus}_R$	Coefficients of Eq.7 for $C_{p,m}$					N_1	N_2	N_3	N_4	N_o	N_m	N_p
	$J \cdot mol^{-1} \cdot K^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	a	b	c	d	SE							
PT	415.79	61.55	177.69		566.70	4.83	-1.65	1.54	1.50	0	0	0	0	0	0	0
MBPT																
1	456.32	39.37	200.95	6.50	573.25	1.44	-1.59	1.47	1.34	1	0	0	0	0	0	0
2	457.81	33.32	194.45	0.00	572.85	1.52	-1.58	1.46	1.33	0	1	0	0	0	0	0
3	457.40	33.84	195.09	0.64	572.88	1.53	-1.58	1.46	1.33	0	0	1	0	0	0	0
4	457.60	34.72	195.91	1.47	572.89	1.51	-1.58	1.46	1.33	0	0	0	1	0	0	0
DBPT																
1,2	495.30	127.45	227.09	14.73	580.08	-2.06	-1.53	1.39	1.17	1	1	0	0	1	0	0
1,3	497.38	122.10	221.12	8.76	579.75	-1.96	-1.53	1.39	1.18	1	0	1	0	0	1	0
1,4	497.03	122.47	221.60	9.23	579.73	-1.96	-1.52	1.39	1.17	1	0	0	1	0	0	1
1,6	497.19	120.74	219.81	7.45	579.56	-1.91	-1.52	1.39	1.18	1	0	0	1	0	0	0
1,7	497.41	120.10	219.10	6.74	579.50	-1.89	-1.52	1.39	1.18	1	0	1	0	0	0	0
1,8	497.41	119.89	218.89	6.53	579.54	-1.92	-1.52	1.39	1.17	1	1	0	0	0	0	0
1,9	494.29	124.62	224.56	12.20	579.93	-1.98	-1.53	1.39	1.19	2	0	0	0	0	0	0
2,3	496.18	121.82	221.20	8.83	579.66	-1.94	-1.52	1.39	1.17	0	1	1	0	1	0	0
2,4	498.84	117.09	215.67	3.31	579.31	-1.88	-1.52	1.38	1.16	0	1	0	1	0	1	0
2,6	499.23	114.89	213.36	1.00	579.09	-1.81	-1.52	1.38	1.16	0	1	0	1	0	0	0
2,7	498.76	114.28	212.89	0.53	579.06	-1.79	-1.52	1.38	1.17	0	1	1	0	0	0	0
2,8	499.26	113.90	212.36	0.00	579.10	-1.82	-1.52	1.38	1.16	0	2	0	0	0	0	0
3,4	496.47	123.46	222.75	10.38	579.66	-1.97	-1.52	1.39	1.17	0	0	1	1	1	0	0
3,6	499.31	115.56	214.00	1.64	579.07	-1.79	-1.52	1.38	1.17	0	0	1	1	0	0	0
3,7	498.72	114.88	213.50	1.14	579.06	-1.78	-1.52	1.38	1.17	0	0	2	0	0	0	0
4,6	501.14	116.10	214.00	1.63	579.04	-1.79	-1.52	1.38	1.16	0	0	0	2	0	0	0
Tri-BPT																
1,2,3	534.14	164.93	256.59	22.62	587.05	-6.00	-1.47	1.32	1.02	1	1	1	0	2	1	0
1,2,4	536.40	158.93	249.92	15.95	586.77	-5.53	-1.47	1.32	1.02	1	1	0	1	1	1	1
1,2,6	536.57	155.41	246.35	12.38	586.35	-5.41	-1.46	1.31	1.02	1	1	0	1	1	0	0
1,2,7	536.09	154.96	246.05	12.07	586.33	-5.39	-1.46	1.31	1.02	1	1	1	0	1	0	0
1,2,8	536.38	154.68	245.67	11.70	586.38	-5.43	-1.46	1.31	1.02	1	2	0	0	1	0	0
1,2,9	533.58	159.53	251.36	17.39	586.72	-5.48	-1.47	1.32	1.03	2	1	0	0	1	0	0
1,3,4	536.61	159.28	250.20	16.23	586.72	-5.51	-1.47	1.32	1.02	1	0	1	1	1	1	1
1,3,6	538.49	150.16	240.52	6.55	585.96	-5.28	-1.46	1.31	1.02	1	0	1	1	0	1	0
1,3,7	538.81	149.76	240.03	6.06	585.97	-5.28	-1.46	1.31	1.03	1	0	2	0	0	1	0
1,3,8	538.67	149.36	239.67	5.70	585.95	-5.28	-1.46	1.31	1.02	1	1	1	0	0	1	0
1,3,9	535.78	154.02	245.19	11.22	586.38	-5.37	-1.47	1.32	1.03	2	0	1	0	0	1	0
1,4,6	539.64	150.52	240.54	6.57	585.92	-5.28	-1.46	1.31	1.02	1	0	0	2	0	0	1
1,4,7	539.09	150.24	240.42	6.45	585.95	-5.28	-1.46	1.31	1.03	1	0	1	1	0	0	1
1,4,8	538.95	149.81	240.04	6.06	585.96	-5.29	-1.46	1.31	1.02	1	1	0	1	0	0	1
1,4,9	535.50	154.49	245.75	11.78	586.38	-5.37	-1.47	1.32	1.03	2	0	0	1	0	0	1
1,6,7	536.41	156.18	247.16	13.19	586.35	-5.39	-1.46	1.31	1.02	1	0	1	1	1	0	0
1,6,8	538.93	150.05	240.29	6.32	585.96	-5.29	-1.46	1.31	1.02	1	1	0	1	0	1	0
1,7,8	536.28	154.97	245.99	12.02	586.31	-5.37	-1.47	1.31	1.03	1	1	1	0	1	0	0
2,3,4	535.08	160.68	252.06	18.09	586.62	-5.51	-1.46	1.31	1.01	0	1	1	1	2	1	0
2,3,6	537.61	150.11	240.73	6.76	585.90	-5.27	-1.46	1.31	1.02	0	1	1	1	1	0	0
2,3,7	537.81	149.51	240.08	6.11	585.89	-5.26	-1.46	1.31	1.02	0	1	2	0	1	0	0
2,3,8	537.79	149.03	239.60	5.63	585.90	-5.28	-1.46	1.31	1.02	0	2	1	0	1	0	0
2,4,6	543.03	144.96	233.97	0.00	585.50	-5.19	-1.45	1.30	1.01	0	1	0	2	0	1	0
2,4,7	540.72	144.78	234.48	0.51	585.54	-5.19	-1.46	1.30	1.01	0	1	1	1	0	1	0

Table 2. Contd

2,4,8	540.03	144.15	234.05	0.08	585.54	-5.21	-1.46	1.30	1.01	0	2	0	1	0	1	0
2,6,7	537.92	150.30	240.84	6.87	585.89	-5.29	-1.46	1.31	1.01	0	1	1	1	1	0	0
3,4,6	540.46	151.19	240.97	7.00	585.54	-5.19	-1.46	1.30	1.02	0	0	1	2	1	0	0
3,4,7	538.40	151.02	241.41	7.44	585.84	-5.26	-1.46	1.31	1.02	0	0	2	1	1	0	0
TBPT																
1,2,3,4	572.45	205.89	289.73	34.83	594.26	-9.27	-1.41	1.25	0.86	1	1	1	1	3	2	1
1,2,3,6	574.95	193.32	276.41	21.52	593.36	-8.97	-1.41	1.24	0.87	1	1	1	1	2	1	0
1,2,3,7	575.25	193.10	276.10	21.21	593.34	-8.96	-1.41	1.24	0.88	1	1	2	0	2	1	0
1,2,3,8	575.08	192.86	275.92	21.03	593.38	-8.98	-1.41	1.24	0.87	1	2	1	0	2	1	0
1,2,3,9	572.14	197.40	281.34	26.44	593.75	-9.05	-1.41	1.25	0.88	2	1	1	0	2	1	0
1,2,4,6	578.78	187.27	269.22	14.32	592.99	-8.85	-1.40	1.24	0.88	1	1	0	2	1	1	1
1,2,4,7	577.20	186.92	269.35	14.45	592.99	-8.84	-1.40	1.24	0.88	1	1	1	1	1	1	1
1,2,4,8	577.90	186.65	268.86	13.97	593.01	-8.87	-1.40	1.24	0.88	1	2	0	1	1	1	1
1,2,4,9	574.69	190.93	274.10	19.21	593.37	-8.93	-1.41	1.25	0.89	2	1	0	1	1	1	1
1,2,6,7	575.35	191.14	274.12	19.22	593.15	-8.89	-1.40	1.24	0.88	1	1	1	1	2	0	0
1,2,6,8	577.50	185.25	267.59	12.69	592.88	-8.83	-1.40	1.24	0.87	1	2	0	1	1	1	0
1,2,6,9	574.66	189.48	272.67	17.77	593.22	-8.89	-1.41	1.24	0.89	2	1	0	1	1	0	1
1,2,7,8	575.09	190.16	273.21	18.32	593.15	-8.88	-1.41	1.24	0.88	1	2	1	0	2	0	0
1,2,7,9	575.04	189.07	272.14	17.25	593.19	-8.88	-1.41	1.24	0.88	2	1	1	0	1	1	0
1,2,8,9	571.98	194.34	278.32	23.42	593.60	-9.01	-1.41	1.24	0.88	2	2	0	0	2	0	0
1,3,4,6	579.85	187.87	269.51	14.61	592.95	-8.83	-1.40	1.24	0.88	1	0	1	2	1	1	1
1,3,4,7	577.74	187.28	269.54	14.65	592.95	-8.82	-1.40	1.24	0.88	1	0	2	1	1	1	1
1,3,4,8	577.63	186.89	269.19	14.30	592.99	-8.85	-1.40	1.24	0.88	1	1	1	1	1	1	1
1,3,4,9	574.15	191.24	274.58	19.68	593.39	-8.92	-1.41	1.25	0.89	2	0	1	1	1	1	1
1,3,6,7	577.87	186.12	268.34	13.45	592.76	-8.77	-1.40	1.24	0.88	1	0	2	1	1	1	0
1,3,6,8	580.31	180.18	261.68	6.79	592.48	-8.71	-1.40	1.24	0.88	1	1	1	1	0	2	0
1,3,6,9	577.21	184.47	266.90	12.00	592.83	-8.76	-1.40	1.24	0.89	2	0	1	1	0	1	1
1,3,7,8	577.95	185.15	267.35	12.46	592.79	-8.76	-1.40	1.24	0.89	1	1	2	0	1	1	0
1,3,7,9	577.32	184.00	266.39	11.49	592.87	-8.78	-1.41	1.24	0.89	2	0	2	0	0	2	0
1,4,6,7	579.07	186.11	267.98	13.09	592.67	-8.74	-1.40	1.24	0.88	1	0	1	2	1	0	1
1,4,6,8	581.13	180.45	261.71	6.81	592.45	-8.69	-1.40	1.23	0.88	1	1	0	2	0	1	1
1,4,6,9	577.43	184.51	266.87	11.97	592.81	-8.76	-1.40	1.24	0.89	2	0	0	2	0	0	2
1,4,7,8	578.06	185.37	267.54	12.64	592.76	-8.75	-1.40	1.24	0.89	1	1	1	1	1	0	1
2,3,4,9	579.79	188.77	270.42	15.52	592.79	-9.00	-1.40	1.23	0.87	1	1	1	1	2	1	0
2,3,4,6	577.77	188.72	270.98	16.09	592.83	-8.82	-1.40	1.23	0.87	0	1	1	2	2	1	0
2,3,4,7	576.41	188.04	270.71	15.81	592.83	-8.83	-1.40	1.23	0.86	0	1	2	1	2	1	0
2,3,4,8	575.51	193.98	276.91	22.01	593.30	-8.94	-1.40	1.24	0.87	0	2	1	1	2	1	0
2,3,6,7	576.73	185.86	268.43	13.53	592.71	-8.76	-1.40	1.23	0.88	0	1	2	1	2	0	0
2,3,6,8	579.83	179.80	261.44	6.54	592.36	-8.67	-1.40	1.23	0.87	0	2	1	1	1	1	0
2,3,7,8	577.32	184.83	267.22	12.33	592.72	-8.75	-1.40	1.23	0.88	0	2	2	0	2	0	0
2,4,6,7	581.04	180.58	261.86	6.97	592.30	-8.67	-1.40	1.23	0.87	0	1	1	2	1	1	0
2,4,6,8	584.36	174.60	254.89	0.00	591.97	-8.58	-1.39	1.23	0.87	0	2	0	2	0	2	0
3,4,6,7	580.60	186.66	268.07	13.18	592.55	-8.72	-1.40	1.23	0.88	0	0	2	2	2	0	0
Penta-BPT																
1,2,3,4,6	614.76	234.28	309.11	18.31	600.49	-12.59	-1.35	1.17	0.74	1	1	1	2	3	2	1
1,2,3,4,7	614.34	234.34	309.30	18.50	600.53	-12.60	-1.35	1.17	0.74	1	1	2	1	3	2	1
1,2,3,4,8	613.51	233.79	309.00	18.19	600.53	-12.62	-1.35	1.17	0.73	1	2	1	1	3	2	1
1,2,3,4,9	610.87	238.22	314.21	23.41	600.92	-12.70	-1.35	1.17	0.74	2	1	1	1	3	2	1
1,2,3,6,7	614.00	229.38	304.43	13.63	600.16	-12.45	-1.35	1.17	0.75	1	1	2	1	3	1	0
1,2,3,6,8	616.63	223.65	297.93	7.13	599.86	-12.38	-1.34	1.17	0.75	1	2	1	1	2	2	0
1,2,3,6,9	613.48	227.87	303.08	12.28	600.25	-12.45	-1.35	1.17	0.76	2	1	1	1	2	1	1

Table 2. Contd

1,2,3,7,8	614.24	228.72	303.71	12.90	600.20	-12.45	-1.35	1.17	0.75	1	2	2	0	3	1	0
1,2,3,7,9	613.32	227.56	302.82	12.02	600.26	-12.46	-1.35	1.17	0.76	2	1	2	0	2	2	0
1,2,3,8,9	611.03	232.82	308.76	17.96	600.56	-12.56	-1.35	1.17	0.76	2	2	1	0	3	1	0
1,2,4,6,7	617.91	223.13	297.02	6.21	599.83	-12.35	-1.34	1.17	0.76	1	1	1	2	2	1	1
1,2,4,6,8	620.11	217.57	290.80	0.00	599.54	-12.27	-1.34	1.16	0.75	1	2	0	2	1	2	1
1,2,4,6,9	615.93	221.91	296.39	5.59	599.92	-12.34	-1.35	1.17	0.76	2	1	0	2	1	1	2
1,2,4,7,8	616.21	222.61	297.01	6.21	599.90	-12.35	-1.35	1.17	0.76	1	2	1	1	2	1	1
1,2,4,7,9	615.84	221.66	296.17	5.37	599.95	-12.36	-1.35	1.17	0.76	2	1	1	1	1	2	1
1,2,4,8,9	612.83	226.38	301.78	10.98	600.30	-12.47	-1.35	1.17	0.76	2	2	0	1	2	1	1
1,2,6,7,8	614.22	229.33	304.32	13.52	600.19	-12.47	-1.35	1.17	0.75	1	2	1	1	3	1	0
1,2,6,7,9	613.09	226.92	302.25	11.45	600.29	-12.45	-1.35	1.17	0.76	2	1	1	1	2	1	1
1,3,4,6,7	619.15	223.69	297.21	6.41	599.72	-12.30	-1.34	1.17	0.76	1	0	2	2	2	1	1
1,3,4,6,8	620.06	217.88	291.13	0.33	599.48	-12.25	-1.34	1.16	0.75	1	1	1	2	1	2	1
1,3,4,6,9	616.14	221.85	296.27	5.47	599.83	-12.31	-1.35	1.17	0.76	2	0	1	2	1	1	2
1,3,4,7,8	616.27	222.91	297.29	6.49	599.86	-12.33	-1.35	1.17	0.76	1	1	2	1	2	1	1
1,3,4,7,9	615.68	222.10	296.66	5.85	599.93	-12.34	-1.35	1.17	0.76	2	0	2	1	1	2	1
1,3,6,7,8	616.85	224.34	298.55	7.75	599.76	-12.33	-1.34	1.16	0.75	1	1	2	1	2	2	0
1,4,6,7,8	617.95	224.29	298.17	7.37	599.73	-12.32	-1.34	1.16	0.75	1	1	1	2	2	1	1
2,3,4,6,7	631.84	224.72	294.46	3.66	599.49	-12.25	-1.34	1.16	0.75	0	1	2	2	3	1	0
2,3,4,6,8	622.26	218.64	291.23	0.43	599.27	-12.21	-1.34	1.16	0.74	0	2	1	2	2	2	0
2,3,4,7,8	616.20	223.95	298.35	7.55	599.68	-12.32	-1.34	1.16	0.75	0	2	2	1	3	1	0
Hexa-BPT																
1,2,3,4,6,7	654.55	270.47	337.04	11.80	607.27	-16.07	-1.29	1.09	0.64	1	1	2	2	4	2	1
1,2,3,4,6,8	656.56	264.72	330.69	5.45	606.99	-16.01	-1.28	1.09	0.64	1	2	1	2	3	3	1
1,2,3,4,6,9	652.72	268.87	335.99	10.75	607.38	-16.08	-1.29	1.10	0.65	2	1	1	2	3	2	2
1,2,3,4,7,8	653.54	270.00	336.87	11.63	607.35	-16.09	-1.29	1.09	0.64	1	2	2	1	4	2	1
1,2,3,4,7,9	652.26	268.63	335.88	10.64	607.40	-16.09	-1.29	1.10	0.65	2	1	2	1	3	3	1
1,2,3,4,8,9	649.71	273.53	341.54	16.30	607.77	-16.21	-1.29	1.10	0.65	2	2	1	1	4	2	1
1,2,3,6,7,8	652.61	267.92	335.07	9.83	607.20	-16.03	-1.29	1.09	0.65	1	2	2	1	4	2	0
1,2,3,6,7,9	652.42	265.32	332.53	7.29	607.26	-16.00	-1.29	1.10	0.66	2	1	2	1	3	2	1
1,2,3,6,8,9	651.82	264.88	332.27	7.03	607.29	-16.03	-1.29	1.10	0.66	2	2	1	1	3	2	1
1,2,3,7,8,9	649.78	271.20	339.19	13.95	607.63	-16.15	-1.29	1.10	0.65	2	2	2	0	4	2	0
1,2,4,6,7,8	656.45	261.64	327.65	2.41	606.81	-15.90	-1.29	1.09	0.65	1	2	1	2	3	2	1
1,2,4,6,7,9	654.93	258.79	325.25	0.01	606.91	-15.89	-1.29	1.10	0.67	2	1	1	2	2	2	2
1,2,4,6,8,9	654.44	258.64	325.24	0.00	606.98	-15.92	-1.29	1.10	0.66	2	2	0	2	2	2	2
1,3,4,6,7,8	658.16	261.89	327.39	2.15	606.72	-15.85	-1.28	1.09	0.66	1	1	2	2	3	2	1
1,3,4,6,7,9	655.27	259.16	325.52	0.28	606.87	-15.86	-1.29	1.10	0.67	2	0	2	2	2	2	2
2,3,4,6,7,8	658.60	262.64	328.00	2.76	606.61	-15.85	-1.28	1.09	0.65	0	2	2	2	4	2	0
Hepta-BPT																
1,2,3,4,6,7,8	694.08	308.95	367.33	1.61	614.30	-19.64	-1.23	1.02	0.59	1	2	2	2	5	3	1
1,2,3,4,6,7,9	691.74	306.73	365.81	0.09	614.46	-19.65	-1.23	1.03	0.60	2	1	2	2	4	3	2
1,2,3,4,6,8,9	691.15	306.46	365.72	0.00	614.51	-19.68	-1.23	1.03	0.60	2	2	1	2	4	3	2
1,2,3,4,7,8,9	688.15	312.58	372.73	7.02	614.81	-19.78	-1.23	1.03	0.59	2	2	2	1	5	3	1
OBPT																
1,2,3,4,6,7,8,9	727.93	353.35	405.25		621.95	-23.41	-1.17	0.95	0.60	2	2	2	2	6	4	2

Constant (a), and regression coefficients b, c and d, are listed in Table 2. From Table 2, the following conclusions can be drawn: (1) The $C_{p,m}$ values of PBPTs are in direct ratio to temperature T, T^1 and T^2. (2) All PBPT congeners have very good relationships between $C_{p,m}$ and temperature (T, T^1 and T^2), and the correlation coefficients (R^2) are all very close to 1.0. These indicated a good correlation between $C_{p,m}$ values and T.

Table 3. The most stable and unstable isomers in different isomer groups for PBPTs.

Compounds	The most stable isomer	The most unstable isomer
MBPT	2-	1-
DBPT	2,8-	1,2-
Tri-BPT	2,4,6-	1,2,3-
TBPT	2,4,6,8-	1,2,3,4-
Penta-BPT	1,2,4,6,8-	1,2,3,4,9-
Hexa-BPT	1,2,4,6,8,9-	1,2,3,4,8,9-
Hepta-BPT	1,2,3,4,7,8,9-	1,2,3,4,6,8,9-

Conclusions

135 PBPTs have been fully optimized at B3LYP/6-31G* level, and thus their $H^{\ominus}$, $S^{\ominus}$ and $G^{\ominus}$ values were consequently obtained. In addition, $\Delta_f H^{\ominus}$ and $\Delta_f G^{\ominus}$ of each PBPT molecule were calculated by isodesmic reactions. The results showed that all these thermodynamic parameters have close relationship with the numbers and positions of bromine substituents (N_{PBS}). So, the obtained $S^{\ominus}$, $\Delta_f H^{\ominus}$ and $\Delta_f G^{\ominus}$ for 135 PBPT congeners should be valuable in further thermodynamic modeling studies. According to the relative magnitude of their $\Delta_f G^{\ominus}$, the relative stability order of PBPT congeners was theoretically proposed. It is found that the most unstable isomers are all those with bromines being attached at the same aromatic ring and close to each other, while the most stable isomers are all those with bromines replaced at two aromatic rings , so that the bromines can be as apart from each other as possible. Moreover, there is a very good correlation relationship between $C_{p,m}$ and temperature for the PBPT congeners. In a word, this work about thermodynamic properties is useful and significant for studying the generation, degradation and potential environmental risk of PBPTs.

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