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DFT Study of Structural and Thermodynamic Properties for Polybrominated 5,10-Dihydrophenazines

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Abstract The structural and thermodynamic properties of 75 polybrominated 5,10-dihydrophenazines (PBDPs) 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 the Gaussian 03 program. The isodesmic reactions are developed to calculate the standard enthalpy of formation ($\Delta_f H^\theta$) and standard free energy of formation ($\Delta_f G^\theta$) of PBDP congeners. The relationships of these thermodynamic parameters with the number and position of the Br atom substitution (N_{PBS}) are discussed, and it is found that there exists a high correlation between thermodynamic parameters and N_{PBS}. In addition, the correlations between structural parameters and N_{PBS} are discussed. High correlations were found between the energy of the highest occupied molecular orbital (E_{HOMO}), the most negative atomic partial charge in the molecule (q^-) and N_{PBS}, and all R^2 values are larger than 0.90.

Keywords Density functional theory (DFT) · Method of position of Br substitution · Polybrominated 5,10-dihydrophenazines · Structural parameters · Thermodynamic parameters

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1 Introduction

5,10-dihydrophenazine (DHP) is an organic molecule known to be a good electron donor [1], which is observed from the reaction of phenazine with $Na_2S_2O_4/H_2O$. (The structure and atomic numbering are schematically depicted in Fig. 1.) Dihydrophenazine and derivatives reveal properties with a wide range of significant applications. In terms of the numbers and different positions of the bromine atoms, there are 75 possible structural patterns of polybrominated 5,10-dihydrophenazines (PBDPs). It is important to recognize the structural and thermodynamic properties of PBDPs for studying their generation, degradation, and potential environmental risk. Many research studies have been reported on DHP in recent years. For example, Zubiri et al. [2] studied the reaction of 5,10-dihydrophenazine with two equivalents of Ph_2PCl. On a similar note, Taniguchi et al. [1] studied DHP geometries of the donor-radical models optimized with the doublet states by B3LYP/6-31G*. Inzelt and Puskás [3] have studied the electrochemical transformations of phenazine at a gold electrode in aqueous acidic solutions. It was found that phenazine exhibits two successive one-electron reduction steps in acidic media, the second electron transfer in dilute phenazine solutions results in the formation of DHP in $HClO_4$, which desorbs from the electrode surface. Uehara et al. [4] employed eight dihydrophenazine derivatives for the study of electron transfer in the interface of an organic two-layer diode. However, there is hardly any research concerning the thermodynamic data of PBDPs.

In previous investigations, the thermodynamic data of polychlorinated dibenzofurans, polychlorinated dibenzo-*p*-dioxins, polychlorinated biphenyls, polychlorinated naphthalenes, and polybrominated naphthalenes [5–9] have been calculated. It was found that the isomers with reduced free energy have a high ratio of formation, i.e., the ratios of formation for isomers are consistent with their relative stabilities.

In the present study, 75 PBDPs were fully optimized at the B3LYP/6-31G* DFT level of theory. The correlations of structural and thermodynamic properties with the number and position of Br substitution (N_{PBS}) are discussed. By design of a series of isodesmic reactions, the standard enthalpies of formation ($\Delta_f H^\theta$) and the standard Gibbs energies of formation ($\Delta_f G^\theta$) of 75 PBDPs were obtained.

2 Computational Method

All calculations were carried out with the GAUSSIAN03 suite of codes [10]. The geometries of all PBDPs were optimized at the B3LYP/6-31G* level of theory, and frequency calculations were performed to ensure that the species are minimum structures along the potential energy surface. We have calculated other systems using B3LYP

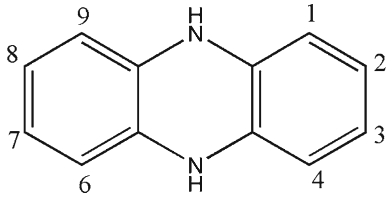


Fig. 1 Molecular structure and atomic numbering of 5,10-dihydrophenazine (DHP)

[9,11,12], and the results indicate that B3LYP is acceptable, so the B3LYP model was used in this study.

The polarizability of a molecule (α) is a measure of its ability to respond to an electric field and to acquire an electric dipole moment. Strictly speaking, it is a tensor quantity that relates changes in the three-dimensional electron density distribution of the molecule to the strength of applied electric fields. In a coordinate system which is placed at the origin of the molecule, only the three components α_{xx}, α_{yy}, and α_{zz}, which reflect perturbations in the x-, y-, and z-coordinates, are unique. They increase with the size of the species either by an increase in the number of electrons or by an expansion of the molecular radius.

Other structural descriptors, the dipole moment (μ), energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), most negative atomic partial charge in the molecule (q^-), most positive atomic partial charge in the molecule (q^+), and the most positive partial charge on a hydrogen atom ($q\mathrm{H}^+$), are obtained directly from the Gaussian output files in this work. All of the charges were derived from the Mulliken partition.

Thermodynamic parameters, standard enthalpies (H^θ), standard Gibbs energies (G^θ), standard entropies (S^θ), standard heat capacities at constant volume (C_v^θ), and thermal corrections to energy (E_{th}^θ) are also obtained from the Gaussian output files. These thermodynamic parameters were calculated in the gaseous state at 298.15 K and 1.013×10^5 Pa.

In the present study, PBDP isomers with one to eight bromine atoms are represented by the notation MBDP, DBDP, Tri-BDP, TBDP, penta-BDP, hexa-BDP, hepta-BDP, and OBDP, respectively. The numbers of the positions of the Br substitution (N_{PBS}) are defined as follows: the number of Br atoms at positions α (1, 4, 6, and 9 being α positions) and β (2, 3, 7, and 8 being β positions) are defined as N_α and N_β; the pair of numbers of ortho, meta, and para positions in which two bromine atoms are located on one benzene ring are symbolized as N_{o}, N_{m}, and N_{p}, the number of bromine atoms at positions 1 and 9 (or 4 and 6) synchronously is $N_{1,9}$, respectively. Isodesmic reaction 1 (Eq. 1) was designed to calculate $\Delta_{\mathrm{f}}H^\theta$ and $\Delta_{\mathrm{f}}G^\theta$ of PBDPs in this study.

$$\text{5,10-dihydrophenazine (DHP)} + n\text{-bromobenzene} = \text{PBDP} + n\text{-benzene} \quad (1)$$

The standard enthalpy change of the reaction ($\Delta_{\mathrm{r}}H^\theta$) is equal to the sum of the standard enthalpies of the products obtained from DFT calculations minus the sum of the standard enthalpies of the reactants:

$$\Delta_{\mathrm{r}}H^\theta = \left[H_{\mathrm{PBDP}}^\theta + nH_{\mathrm{benzene}}^\theta\right] - \left[H_{\mathrm{DHP}}^\theta + nH_{\mathrm{bromobenzene}}^\theta\right] \quad (2)$$

Similarly, Eq. 3 also yields $\Delta_{\mathrm{r}}H^\theta$:

$$\Delta_{\mathrm{r}}H^\theta = \left[\Delta_{\mathrm{f}}H_{\mathrm{PBDP}}^\theta + n\Delta_{\mathrm{f}}H_{\mathrm{benzene}}^\theta\right] - \left[\Delta_{\mathrm{f}}H_{\mathrm{DHP}}^\theta + n\Delta_{\mathrm{f}}H_{\mathrm{bromobenzene}}^\theta\right] \quad (3)$$

Thus, the following equation can be obtained from Eqs. 2 and 3:

$$\Delta_\mathrm{f} H^\theta_\mathrm{PBDP} = H^\theta_\mathrm{PBDP} + nH^\theta_\mathrm{benzene} - nH^\theta_\mathrm{bromobenzene} - H^\theta_\mathrm{DHP} - n\Delta_\mathrm{f} H^\theta_\mathrm{benzene} + n\Delta_\mathrm{f} H^\theta_\mathrm{bromobenzene} + \Delta_\mathrm{f} H^\theta_\mathrm{DHP} \tag{4}$$

Similarly, $\Delta_\mathrm{f} G^\theta_\mathrm{PBDP}$ could be obtained from

$$\Delta_\mathrm{f} G^\theta_\mathrm{PBDP} = G^\theta_\mathrm{PBDP} + nG^\theta_\mathrm{benzene} - nG^\theta_\mathrm{bromobenzene} - G^\theta_\mathrm{DHP} - n\Delta_\mathrm{f} G^\theta_\mathrm{benzene} + n\Delta_\mathrm{f} G^\theta_\mathrm{bromobenzene} + \Delta_\mathrm{f} G^\theta_\mathrm{DHP} \tag{5}$$

To obtain $\Delta_\mathrm{f} H^\theta_\mathrm{DHP}$, the following equation was used:

$$12\mathrm{C} + 10\mathrm{H} + 2\mathrm{N} = \mathrm{DHP} \tag{6}$$

The following equations are employed to calculate the absolute internal energy (U), enthalpies (H), and Gibbs energies (G) of the molecule at 0 K and the specified temperature (T) [13]:

$$U_{0\mathrm{K}} = E_\mathrm{elec} + E_\mathrm{ZPE} \tag{7}$$

$$\begin{aligned} U_T &= U_{0\mathrm{K}} + (E_\mathrm{trans} + E_\mathrm{rot} + E_\mathrm{vib})_T \\ &= (E_\mathrm{elec} + E_\mathrm{ZPE}) + \left\{ \frac{3}{2}RT + RT + R\sum_{i=1}^{3N-6} (h\nu/k)\left[\frac{1}{2} + \frac{1}{\exp(h\nu/kT) - 1}\right]\right\} \end{aligned} \tag{8}$$

$$H_T = U_T + RT \tag{9}$$

$$\begin{aligned} \Delta_\mathrm{f} H^\mathrm{O}(M, 0\,\mathrm{K}) &= \sum x\Delta_\mathrm{f} H^\mathrm{O}(X, 0\,\mathrm{K}) - \sum D_0(M) \\ &= \sum x\Delta_\mathrm{f} H^\mathrm{O}(X, 0\,\mathrm{K}) - \left[\sum xU(X, 0\,\mathrm{K}) - U(M, 0\,\mathrm{K})\right] \end{aligned} \tag{10}$$

$$\Delta_\mathrm{f} H^\mathrm{O}(M, 298\,\mathrm{K}) = \Delta_\mathrm{f} H^\mathrm{O}(M, 0\,\mathrm{K}) + \left[H^\mathrm{O}(M, 298\,\mathrm{K}) - H^\mathrm{O}(M, 0\,\mathrm{K})\right] - \sum x(H_{298\,\mathrm{K}} - H_{0\,\mathrm{K}})_X \tag{11}$$

Similarly, Eq. 12 was designed to obtain $\Delta_\mathrm{f} G^\theta_\mathrm{DHP}$:

$$\mathrm{N}_2 + 12\mathrm{C}_{(\mathrm{graphite})} + 5\mathrm{H}_2 = \text{5,10-dihydrophenazine (DHP)} \tag{12}$$

So

$$\Delta_\mathrm{r} S^\theta = S^\theta_\mathrm{DHP} - S^\theta_{\mathrm{N}_2} - 12S^\theta_\mathrm{C} - 5S^\theta_{\mathrm{H}_2} \tag{13}$$

$$\Delta_\mathrm{f} G^\theta_\mathrm{DHP} = \Delta_\mathrm{r} H^\theta_\mathrm{DHP} - T\Delta_\mathrm{r} S^\theta_\mathrm{DHP} \tag{14}$$

From Eqs. 6–14, $\Delta_\mathrm{f} H^\theta_\mathrm{DHP}$ is $-212.03\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta_\mathrm{f} G^\theta_\mathrm{DHP}$ is $400.50\ \mathrm{kJ \cdot mol^{-1}}$. The experimental values of $\Delta_\mathrm{f} H^\theta$ and $\Delta_\mathrm{f} G^\theta$ for bromobenzene and benzene are listed

Table 1 Thermodynamic data used for calculating $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of PBDPs

Number	Formula or name	$\Delta_f H^\theta$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$\Delta_f G^\theta$ ($\text{kJ} \cdot \text{mol}^{-1}$)	H^θ (Hartree)	G^θ (Hartree)	S^θ ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
1	Benzene	82.9[a]	129.7[a]	–232.142	–232.173	–
2	Bromobenzene	105.0[a]	138.5[a]	–2803.256	–2803.293	–
3	DHP	−212.03[b]	400.50[c]	–572.605	–572.651	414.40
4	Graphite (C)	0[a]	–	–	–	5.74[a]
5	N_2	0[a]	–	–	–	191.51[a]
6	Hydrogen (H_2)	0[a]	–	–	–	130.57[b]

[a] Data from Ref. [15]
[b] Data from Eq. 11 calculation
[c] Data from Eq. 14 calculation and other data from B3LYP/6-31G* calculations

in Table 1, including the values of H^θ and G^θ calculated at the B3LYP/6-31G* level for these compounds. At the B3LYP/6-31G* level, the mean absolute deviation of calculated thermochemical quantities from experiment for a variety of compounds is $33.05\ \text{kJ} \cdot \text{mol}^{-1}$ and the standard deviation is $39.75\ \text{kJ} \cdot \text{mol}^{-1}$ [14].

3 Results and Discussion

All of the structural and thermodynamic properties, with N_{PBS} of the PBDPs, calculated at the B3LYP/6-31G* level, are listed in Table 2.

3.1 Geometry of the Molecule

The geometries of all PBDPs were optimized at the B3LYP/6-31G* level of theory, and the molecules are almost planar (the geometry of the molecules is shown as follows where D is the dihedral angle for four marker atoms) (Fig. 2).

3.2 Comparison of the Calculated Results at Different Levels

S^θ, E^θ_{th}, C^θ_V, H^θ, and G^θ of the DBDPs were also calculated at the HF/6-31G* level, and are listed in Table 3. As seen from Table 3, the differences of H^θ and G^θ between the calculated results at the two different levels were small, but those of S^θ, E^θ_{th}, and C^θ_V were large. Based on this comparative analysis, the B3LYP/6-31G* level is acceptable because the precision of the B3LYP/6-31G* method is higher than that of the HF/6-31G* one.

In addition, in order to further validate the precision of the method, we have calculated some thermodynamic data of halogen aromatic compounds with experimental data, using the same method. The calculated thermodynamic parameters and experimental values are listed in Table 4. As seen from Table 4, the following conclusions can be obtained: 2,2′-DCB, thiophenol, and 1,2-DCB possess the largest discrepancies of $\Delta_f H^\theta$, S^θ, and $\Delta_f G^\theta$ with values of $17.0\ \text{kJ} \cdot \text{mol}^{-1}$, $-3.1\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and

Table 2 Structural and thermodynamic parameters of PBDPs from DFT calculations and N_{PBS}

Molecule	E_{HOMO} (eV)	q^- (e)	a_{xx} (10^{-30} esu)	a_{yy} (10^{-30} esu)	a_{zz} (10^{-30} esu)	E_{th} (kJ · mol^{-1})	C_V^θ (J · mol^{-1} · K^{-1})	S^θ (J · mol^{-1} · K^{-1})	H^θ (Hartree)	G^θ (Hartree)	$\Delta_{\mathrm{f}} H^\theta$ (kJ · mol^{-1})	$\Delta_{\mathrm{f}} G^\theta$ (kJ · mol^{-1})	$\Delta_{\mathrm{f}} G_R^\theta$ (kJ · mol^{-1})	N_α	N_β	N_{o}	N_{m}	N_{p}	$N_{1,9}$
DHP	−0.1590	−0.7858	232.4	141.5	46.2	534.393	180.347	411.404	−572.605	−572.651	−212.03	400.50		0	0	0	0	0	0
MBDP																			
1	−0.1661	−0.8057	240.7	181.9	55.5	512.310	197.322	451.253	−3143.720	−3143.772	−195.87	408.40	0.00	1	0	0	0	0	0
2	−0.1671	−0.7936	279.2	154.2	56.5	512.013	198.016	453.366	−3143.718	−3143.770	−189.67	413.97	5.57	0	1	0	0	0	0
DBDP																			
1,2	−0.1706	−0.8161	297.1	184.5	64.6	489.725	214.589	491.499	−5714.830	−5714.886	−163.85	432.05	15.41	1	1	1	0	0	0
1,3	−0.1731	−0.8132	291.9	193.4	65.4	489.846	214.999	493.344	−5714.833	−5714.889	−170.17	425.18	8.54	1	1	0	1	0	0
1,4	−0.1713	−0.8256	215.4	261.5	64.2	490.185	214.397	492.938	−5714.835	−5714.891	−177.30	418.17	1.53	2	0	0	0	1	0
1,6	−0.1725	−0.8180	259.4	214.6	64.6	490.223	214.313	492.013	−5714.836	−5714.892	−179.10	416.64	0.00	2	0	0	0	0	0
1,7	−0.1737	−0.8130	296.7	188.2	65.5	489.892	214.970	493.540	−5714.834	−5714.890	−172.61	422.68	6.04	1	1	0	0	0	0
1,8	−0.1733	−0.8167	292.0	191.8	65.3	489.871	215.012	493.821	−5714.834	−5714.890	−172.35	422.85	6.21	1	1	0	0	0	0
1,9	−0.1714	−0.8428	262.3	209.3	64.0	490.080	214.480	492.842	−5714.836	−5714.891	−177.48	418.01	1.37	2	0	0	0	0	1
2,3	−0.1722	−0.8058	316.5	175.6	65.1	489.595	215.317	493.930	−5714.828	−5714.884	−158.25	436.92	20.28	0	2	1	0	0	0
2,7	−0.1743	−0.8035	333.9	164.1	65.9	489.432	215.961	496.469	−5714.831	−5714.888	−166.36	428.05	11.41	0	2	0	0	0	0
2,8	−0.1742	−0.8040	326.3	170.3	66.5	489.553	215.832	496.080	−5714.831	−5714.888	−166.18	428.35	11.71	0	2	0	0	0	0
Tri-BDP																			
1,2,3	−0.1754	−0.8284	332.2	209.4	73.3	467.118	231.978	532.063	−8285.939	−8286.000	−129.28	458.13	30.09	1	2	2	1	0	0
1,2,4	−0.1759	−0.8287	306.7	229.5	73.4	467.641	231.371	531.820	−8285.944	−8286.005	−142.89	444.60	16.55	2	1	1	1	1	0
1,2,6	−0.1770	−0.8260	316.4	217.7	73.8	467.621	231.409	531.573	−8285.946	−8286.006	−146.52	441.04	12.99	2	1	1	0	0	0
1,2,7	−0.1779	−0.8222	353.1	193.4	74.5	467.344	232.120	533.627	−8285.943	−8286.004	−139.85	447.11	19.06	1	2	1	0	0	0
1,2,8	−0.1778	−0.8227	342.4	201.7	74.4	467.340	232.066	533.159	−8285.943	−8286.004	−139.58	447.51	19.46	1	2	1	0	0	0

Table 2 continued

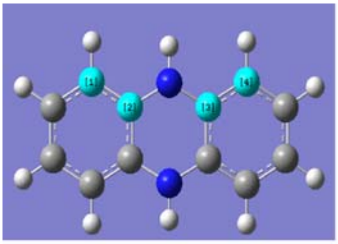
Molecule	E_{HOMO} (eV)	q^- (e)	a_{xx} (10^{-30} esu)	a_{yy} (10^{-30} esu)	a_{zz} (10^{-30} esu)	E_{th} (kJ · mol^{-1})	C_V^θ (J · mol^{-1} · K^{-1})	S^θ (J · mol^{-1} · K^{-1})	H^θ (Hartree)	G^θ (Hartree)	$\Delta_{\mathrm{f}}H^\theta$ (kJ · mol^{-1})	$\Delta_{\mathrm{f}}G^\theta$ (kJ · mol^{-1})	$\Delta_{\mathrm{f}}G_R^\theta$ (kJ · mol^{-1})	$N\alpha$	$N\beta$	N_{o}	N_{m}	N_{p}	$N_{1,9}$
1,2,9	−0.1760	−0.8490	310.9	219.4	73.2	467.533	231.513	532.577	−8285.945	−8286.006	−144.82	442.44	14.40	2	1	1	0	0	1
1,3,6	−0.1791	−0.8266	300.7	236.1	74.3	467.654	231.890	533.657	−8285.948	−8286.009	−152.53	434.41	6.37	2	1	0	1	0	0
1,3,7	−0.1800	−0.8219	340.8	209.3	75.1	467.361	232.643	535.594	−8285.946	−8286.006	−145.88	440.48	12.44	1	2	0	1	0	0
1,3,8	−0.1801	−0.8220	345.9	203.1	75.1	467.324	232.647	535.284	−8285.945	−8286.006	−145.77	440.69	12.64	1	2	0	1	0	0
1,3,9	−0.1785	−0.8459	311.1	224.6	73.9	467.558	232.032	534.565	−8285.948	−8286.008	−151.17	435.50	7.46	2	1	0	1	0	1
1,4,6	−0.1771	−0.8572	273.4	252.9	73.1	467.922	231.312	534.719	−8285.950	−8286.011	−158.58	428.05	0.00	3	0	0	0	1	1
1,4,7	−0.1785	−0.8337	313.1	226.8	74.0	467.738	231.881	534.134	−8285.948	−8286.009	−153.15	433.64	5.60	2	1	0	0	1	0
2,3,6	−0.1785	−0.8262	330.8	212.3	74.2	467.332	232.229	533.493	−8285.943	−8286.004	−140.41	446.59	18.54	1	2	1	0	0	0
2,3,7	−0.1797	−0.8090	367.4	188.6	75.2	467.118	232.752	534.665	−8285.941	−8286.002	−133.75	452.89	24.85	0	3	1	0	0	0
TBDP																			
1,2,3,4	−0.1778	−0.8461	348.4	245.6	81.2	444.546	248.647	571.924	−10857.050	−10857.114	−98.47	480.68	40.79	2	2	3	2	1	0
1,2,3,6	−0.1817	−0.8370	345.5	247.9	82.5	444.977	248.638	571.488	−10857.054	−10857.119	−111.17	468.11	28.22	2	2	2	1	0	0
1,2,3,7	−0.1826	−0.8310	385.1	222.2	83.3	444.554	249.496	573.108	−10857.052	−10857.117	−104.49	474.31	34.42	1	3	2	1	0	0
1,2,3,8	−0.1825	−0.8331	383.9	222.3	83.2	444.583	249.475	573.158	−10857.052	−10857.117	−104.28	474.50	34.61	1	3	2	1	0	0
1,2,3,9	−0.1810	−0.8570	347.0	243.9	82.0	444.826	248.756	571.752	−10857.054	−10857.119	−109.88	469.32	29.43	2	2	2	1	0	1
1,2,4,6	−0.1811	−0.8639	330.2	257.8	82.0	445.404	248.132	572.911	−10857.059	−10857.124	−123.68	455.08	15.19	3	1	1	1	1	1
1,2,4,7	−0.1823	−0.8423	367.9	235.1	82.9	445.111	249.023	574.974	−10857.057	−10857.122	−118.02	460.22	20.33	2	2	1	1	1	0
1,2,4,8	−0.1823	−0.8404	359.0	243.0	82.9	445.073	249.044	575.254	−10857.057	−10857.122	−117.88	460.28	20.38	2	2	1	1	1	0
1,2,4,9	−0.1811	−0.8636	319.5	267.0	82.0	445.445	248.111	572.911	−10857.059	−10857.124	−123.72	455.14	15.25	3	1	1	1	1	1
1,2,6,7	−0.1814	−0.8316	373.9	222.6	82.8	445.069	248.454	571.346	−10857.055	−10857.120	−113.60	465.73	25.83	2	2	2	0	0	0
1,2,6,8	−0.1830	−0.8361	358.2	241.4	83.2	444.994	249.069	573.831	−10857.057	−10857.123	−119.31	459.28	19.38	2	2	1	1	0	0

Table 2 continued

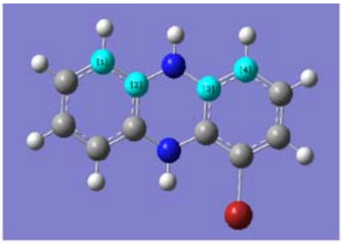
Molecule	E_{HOMO} (eV)	q^- (e)	a_{xx} (10^{-30} esu)	a_{yy} (10^{-30} esu)	a_{zz} (10^{-30} esu)	E_{th} (kJ · mol^{-1})	C_V^θ (J · mol^{-1} · K^{-1})	S^θ (J · mol^{-1} · K^{-1})	H^θ (Hartree)	G^θ (Hartree)	$\Delta_\text{f} H^\theta$ (kJ · mol^{-1})	$\Delta_\text{f} G^\theta$ (kJ · mol^{-1})	$\Delta_\text{f} G_R^\theta$ (kJ · mol^{-1})	N_α	N_β	N_o	N_m	N_p	$N_{1,9}$
1,2,6,9	−0.1816	−0.8618	332.5	253.8	82.2	445.387	248.203	573.999	−10857.060	−10857.125	−125.38	453.16	13.26	3	1	1	0	1	1
1,2,7,8	−0.1828	−0.8314	386.5	218.9	83.4	444.726	249.266	573.241	−10857.053	−10857.118	−106.93	471.83	31.94	1	3	2	0	0	0
1,2,7,9	−0.1822	−0.8586	368.5	229.9	82.6	444.935	249.186	575.028	−10857.057	−10857.122	−117.92	460.30	20.41	2	2	1	1	0	1
1,2,8,9	−0.1802	−0.8573	361.2	230.2	82.1	444.893	248.634	572.643	−10857.055	−10857.120	−111.60	467.34	27.45	2	2	2	0	0	1
1,3,6,8	−0.1847	−0.8417	358.9	245.4	83.5	445.010	249.776	577.815	−10857.060	−10857.125	−125.14	452.25	12.36	2	2	0	2	0	0
1,3,6,9	−0.1833	−0.8669	326.2	265.5	82.6	445.387	248.814	577.831	−10857.062	−10857.128	−131.40	446.00	6.10	3	1	0	1	1	1
1,3,7,8	−0.1839	−0.8427	384.9	227.9	83.3	444.788	250.128	577.919	−10857.055	−10857.121	−113.10	464.27	24.38	1	3	1	1	0	0
1,3,7,9	−0.1836	−0.8651	360.2	245.0	82.9	444.956	249.973	580.015	−10857.059	−10857.125	−124.08	452.67	12.77	2	2	0	2	0	1
1,4,6,9	−0.1819	−0.8809	286.4	292.9	81.7	445.876	247.672	577.246	−10857.064	−10857.130	−137.67	439.89	0.00	4	0	0	0	2	2
1,4,7,8	−0.1829	−0.8502	351.2	249.4	82.6	445.232	249.124	576.702	−10857.058	−10857.123	−120.34	457.39	17.49	2	2	1	0	1	0
2,3,7,8	−0.1835	−0.8303	411.2	209.7	83.3	444.575	250.371	577.333	−10857.051	−10857.116	−101.22	476.32	36.43	0	4	2	0	0	0
Penta-BDP																			
1,2,3,4,6	−0.1834	−0.8751	361.7	282.5	90.0	422.308	265.236	614.697	−13428.164	−13428.234	−78.80	491.22	24.66	3	2	3	2	1	1
1,2,3,4,7	−0.1852	−0.8435	400.9	258.0	91.3	422.028	265.897	611.308	−13428.162	−13428.231	−73.13	497.90	31.35	2	3	3	2	1	0
1,2,3,6,7	−0.1854	−0.8477	405.7	253.1	91.3	422.262	265.860	612.358	−13428.164	−13428.233	−77.76	492.96	26.40	2	3	3	1	0	0
1,2,3,6,8	−0.1875	−0.8467	398.0	263.5	91.8	422.316	266.295	614.563	−13428.166	−13428.236	−83.27	486.78	20.23	2	3	2	2	0	0
1,2,3,6,9	−0.1861	−0.8584	365.6	281.7	90.9	422.663	265.370	615.086	−13428.168	−13428.238	−89.60	480.31	13.75	3	2	2	1	1	1
1,2,3,7,8	−0.1868	−0.8463	426.8	243.4	91.8	422.078	266.630	614.010	−13428.161	−13428.231	−71.23	498.99	32.44	1	4	3	1	0	0
1,2,3,7,9	−0.1868	−0.8673	401.9	258.9	91.5	422.262	266.387	615.328	−13428.165	−13428.235	−82.24	487.59	21.03	2	3	2	2	0	1
1,2,3,8,9	−0.1852	−0.8622	403.6	250.0	91.1	422.187	265.776	611.814	−13428.163	−13428.233	−76.09	494.79	28.24	2	3	3	1	0	1
1,2,4,6,7	−0.1853	−0.8700	389.3	261.5	91.0	422.806	265.186	614.249	−13428.168	−13428.238	−90.26	479.89	13.34	3	2	2	1	1	1

Table 2 continued

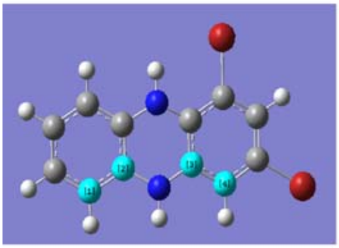
Molecule	E_{HOMO} (eV)	q^{-} (e)	a_{xx} (10^{-30} esu)	a_{yy} (10^{-30} esu)	a_{zz} (10^{-30} esu)	E_{th} (kJ · mol^{-1})	C_V^{θ} (J · mol^{-1} · K^{-1})	S^{θ} (J · mol^{-1} · K^{-1})	H^{θ} (Hartree)	G^{θ} (Hartree)	$\Delta_{\mathrm{f}}H^{\theta}$ (kJ · mol^{-1})	$\Delta_{\mathrm{f}}G^{\theta}$ (kJ · mol^{-1})	$\Delta_{\mathrm{f}}G_R^{\theta}$ (kJ · mol^{-1})	N_{α}	N_{β}	N_{o}	N_{m}	N_{p}	$N_{1,9}$
1,2,4,6,8	−0.1871	−0.8710	374.6	280.2	91.5	422.793	265.755	617.370	−13428.171	−13428.241	−95.93	473.29	6.74	3	2	1	2	1	1
1,2,4,6,9	−0.1860	−0.8831	345.7	294.8	90.7	423.228	264.575	618.680	−13428.173	−13428.243	−102.28	466.56	0.00	4	1	1	1	2	2
1,2,4,7,8	−0.1875	−0.8455	401.4	260.8	92.1	422.622	265.843	613.605	−13428.166	−13428.236	−84.65	485.69	19.14	2	3	2	1	1	0
1,2,4,7,9	−0.1875	−0.8669	379.2	274.1	91.7	422.743	265.713	615.973	−13428.171	−13428.240	−95.81	473.83	7.27	3	2	1	2	1	1
1,2,4,8,9	−0.1851	−0.8705	376.6	272.5	90.9	422.806	265.161	614.157	−13428.168	−13428.238	−89.95	480.23	13.68	3	2	2	1	1	1
Hexa-BDP																			
1,2,3,4,6,7	−0.1872	−0.8834	423.4	286.2	98.9	399.756	282.102	656.265	−15999.273	−15999.348	−45.08	516.16	20.53	3	3	4	2	1	1
1,2,3,4,6,8	−0.1891	−0.8839	417.6	296.4	99.4	399.735	282.692	654.399	−15999.275	−15999.350	−50.86	510.94	15.31	3	3	3	3	1	1
1,2,3,4,6,9	−0.1888	−0.8845	380.5	316.1	99.0	400.241	281.215	647.997	−15999.278	−15999.351	−57.30	506.41	10.78	4	2	3	2	2	2
1,2,3,4,7,8	−0.1885	−0.8712	446.7	279.3	99.4	399.513	283.265	659.394	−15999.271	−15999.346	−39.75	520.57	24.93	2	4	4	2	1	0
1,2,3,6,7,8	−0.1904	−0.8483	441.1	278.4	100.4	399.547	282.843	650.507	−15999.272	−15999.346	−41.32	521.64	26.01	2	4	4	2	0	0
1,2,3,6,7,9	−0.1893	−0.8837	421.9	292.3	99.6	400.003	282.487	663.059	−15999.277	−15999.352	−54.03	505.19	9.56	3	3	3	2	1	1
1,2,3,6,8,9	−0.1893	−0.8835	419.6	419.6	99.5	400.070	282.416	657.495	−15999.277	−15999.351	−53.93	506.94	11.31	3	3	3	2	1	1
1,2,3,7,8,9	−0.1885	−0.8841	447.1	274.7	274.7	399.539	283.274	660.135	−15999.271	−15999.346	−40.34	519.75	24.12	2	4	4	2	0	1
1,2,4,6,7,9	−0.1899	−0.8841	401.8	302.2	302.2	400.697	281.265	652.989	−15999.281	−15999.356	−66.59	495.64	0.00	4	2	2	2	2	2
1,2,4,6,8,9	−0.1898	−0.8850	391.5	312.0	99.6	400.614	281.387	652.244	−15999.281	−15999.355	−66.53	495.91	0.28	4	2	2	2	2	2
Hepta-BDP																			
1,2,3,4,6,7,8	−0.1919	−0.8864	461.2	311.5	107.8	376.945	299.256	695.184	−18570.381	−18570.460	−8.66	544.60	11.29	3	4	5	3	1	1
1,2,3,4,6,7,9	−0.1925	−0.8869	434.9	326.7	107.9	377.476	298.302	690.389	−18570.386	−18570.465	−21.38	533.31	0.00	4	3	4	3	2	2
OBDP																			
1,2,3,4,6,7,8,9	−0.1950	−0.8885	475.4	345.4	116.1	354.477	314.854	720.941	−21141.491	−21141.573	24.01	573.21		4	4	6	4	2	2



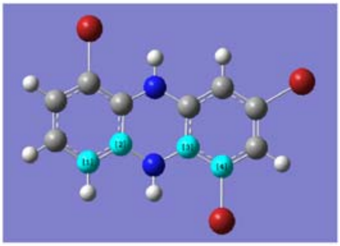
DHP D=0.000



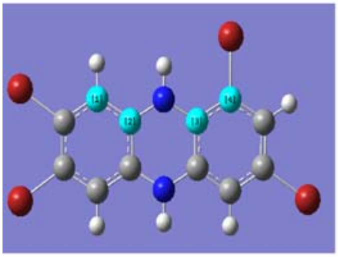
1-MBDP D=-0.198



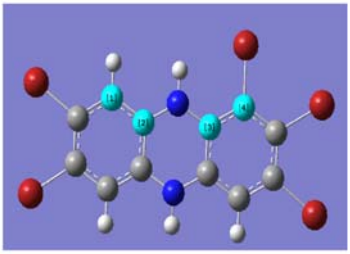
1,3-DBDP D=-0.107



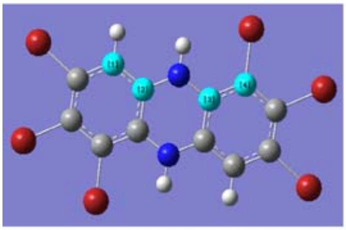
1,3,6-Tri-BDP D=-0.824



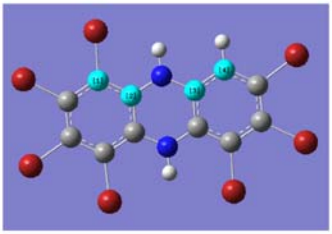
1,3,7,8-TBDP D= -0.582



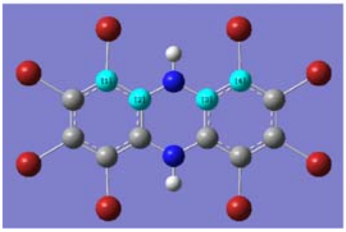
1,2,3,7,8- Penta-BDP D=-0.569



1,2,3,6,7,8- Hexa-BDP D= -0.540



1,2,3,4,6,7,8- Hepta-BDP D= 0.000



1,2,3,4,6,7,8,9- OBDP D=0.000

Fig. 2 Geometry of the molecules

Table 3 Comparison of data calculated at HF/6-31G* and B3LYP/6-31G* levels

Molecule	S^{θ} (J · mol^{-1} · K^{-1})			E_{th}(kJ · mol^{-1})			C_V^{θ} (J · mol^{-1} · K^{-1})			H^{θ} (Hartree)			G^{θ} (Hartree)		
	HF	B3LYP	Diff	HF	B3LYP	Diff	HF	B3LYP	Diff	HF	B3LYP	Diff	HF	B3LYP	Diff
Di-															
12	473.834	491.499	−17.665	521.067	489.725	31.342	198.271	214.589	−16.318	−5707.554	−5714.830	7.276	−5707.608	−5714.886	7.278
13	476.252	493.344	−17.092	521.126	489.846	31.280	198.819	214.999	−16.180	−5707.558	−5714.833	7.274	−5707.613	−5714.889	7.276
14	474.411	492.938	−18.527	521.720	490.185	31.535	198.112	214.397	−16.284	−5707.560	−5714.835	7.275	−5707.614	−5714.891	7.278
16	474.282	492.013	−17.732	521.791	490.223	31.568	198.054	214.313	−16.259	−5707.561	−5714.836	7.275	−5707.615	−5714.892	7.277
17	476.173	493.540	−17.368	521.255	489.892	31.363	198.686	214.970	−16.284	−5707.560	−5714.834	7.274	−5707.614	−5714.890	7.276
18	476.156	493.821	−17.665	521.243	489.871	31.372	198.673	215.012	−16.339	−5707.560	−5714.834	7.274	−5707.614	−5714.890	7.276
19	474.394	492.842	−18.447	521.649	490.080	31.568	198.083	214.480	−16.397	−5707.560	−5714.836	7.275	−5707.614	−5714.891	7.277
23	475.838	493.930	−18.092	520.682	489.595	31.087	198.882	215.317	−16.435	−5707.554	−5714.828	7.274	−5707.608	−5714.884	7.276
27	478.139	496.469	−18.330	520.745	489.432	31.313	199.305	215.961	−16.657	−5707.558	−5714.831	7.273	−5707.613	−5714.888	7.275
28	478.122	496.080	−17.958	520.745	489.553	31.192	199.305	215.832	−16.527	−5707.558	−5714.831	7.273	−5707.613	−5714.888	7.275

Table 4 Difference between the calculated thermodynamic parameters and experimental values

Number	Name	$\Delta_f H^\theta$ (kJ · mol^{-1})			S^θ (J · mol^{-1} · K^{-1})			$\Delta_f G^\theta$ (kJ · mol^{-1})		
		Exp.[a]	Cal.	Diff.	Exp.[a]	Cal.	Diff.	Exp.[a]	Cal.	Diff.
1	Benzene	82.9			269.3	268.2	−1.1	129.7	129.9	0.2
2	Chlorobenzene	54.4			313.5	313.3	−0.2	99.2	99.2	0.0
4	1,2-Dichlorobenzene	30.0	40.6	10.6	341.5	342.1	0.6	82.7	93.4	10.7
3	1,3-Dichlorobenzene	28.1	30.0	1.9	343.5	343.5	0.0	78.6	82.2	3.6
5	1,4-Dichlorobenzene	24.6	29.8	5.2	336.7	337.7	1.0	77.2	83.9	6.7
6	1,1′-Biphenyl	182.1			392.7	391.7	−1.0	280.1	280.3	0.2
7	2,2′-Dichloro-1,1′-biphenyl	126.8	143.8	17.0	–	461.8	–	–	270.8	–
8	4,4′-Dichloro-1,1′-biphenyl	120.1	125.6	5.5	–	452.5	–	–	255.5	–
9	Benzenethiol	111.5			336.7	333.6	−3.1	147.6		

[a] Taken from Ref. [15]

10.7 kJ · mol^{-1}, respectively, which demonstrated the reliability of the method, so the B3LYP/6-31G* calculation for all 75 PBDPs was chosen in the present study.

3.3 Relations of Thermodynamic Properties and N_{PBS}

Using multiple linear regression with the SPSS 12.0 code, the correlations of E^θ_{th}, H^θ, and G^θ with N_{PBS} for PBDPs can be obtained, and the results are presented in Table 5.

Table 5 shows that there are good correlations between E^θ_{th}, H^θ, G^θ, and N_{PBS}. From Eqs. 15–17, it can be seen that E_{th}, H^θ, and G^θ changed with N_{PBS}. As the substitute numbers of bromine atoms increases, values of E_{th}, H^θ, and G^θ decrease. But the number of relative positions for these Br atoms (N_{m}, N_{p}, and $N_{1,9}$) has a small effect on the values of E_{th}, H^θ, and G^θ. For example, when N_{o} is increased by one, E_{th}, H^θ, and G^θ increase by −0.205 kJ · mol^{-1}, 0.004 Hartree, and 0.004 Hartree, respectively. In addition, N_{m}, N_{p}, and $N_{1,9}$ do not enter the correlative equation, so they have the smallest effect on E_{th}, H^θ, and G^θ. Thus, it can be concluded that the substitute number of bromine atoms is the primary influence on the values of E_{th}, H^θ, and G^θ.

3.4 Calculated Results of $\Delta_f H^\theta$ and $\Delta_f G^\theta$

With the design of new isodesmic reactions, the $\Delta_f H^\theta$ and $\Delta_f G^\theta$ values of PBDPs were obtained. Defining the lowest $\Delta_f G^\theta$ of isomers with the same number of substituents to be zero, the relative standard Gibbs energies of formation were obtained by the $\Delta_f G^\theta$ of other isomers minus the lowest $\Delta_f G^\theta$ of isomers with the same number of substituents, which are also listed in Table 2. It is found that the values of $\Delta_f G^\theta$ increase with an increase in the number of substituted bromine atoms. But the

Table 5 Correlations of thermodynamic and structural descriptors with N_{PBS} for PBDPs

Eqs.	Descriptor	Constant	N_α	N_β	N_{o}	N_{m}	N_{p}	$N_{1,9}$	R^2	SE
15	H^θ	−572.607	−2571.114	−2571.113	0.004				1.000	0.00086
16	G^θ	−572.653	−2571.119	−2571.117	0.004				1.000	0.00091
17	E^θ_{th}	534.557	−22.200	−22.450	−0.205				1.000	0.14039
18	$\Delta_{\mathrm{f}} H^\theta$	−215.540	19.193	23.666	9.193	2.666			0.999	1.77368
19	$\Delta_{\mathrm{f}} G^\theta$	412.579	10.972	15.062	9.685	2.467			0.997	1.74310
20	E_{HOMO}	−0.161	−0.005	−0.007	0.002	0.001			0.991	0.00066
21	E_{LUMO}	−0.023			−0.004	−0.007			0.519	0.01105
22	$q-$	−0.790	−0.017	−0.009			0.005	−0.012	0.916	0.00777
23	a_{xx}	228.701	17.012	46.459					0.961	10.88747
24	a_{yy}	168.275	24.229			24.080			0.644	32.70788
25	a_{zz}	50.671		11.673		2.317		21.139	0.330	29.87450
26	$q\mathrm{H}^+$	0.326	0.008	0.002			−0.008	0.009	0.835	0.00488
27	μ	2.121				−0.362			0.100	1.02477

R^2 is the squared correlation coefficient, *SE* the standard error stability of the isomer becomes weaker as the values of $\Delta_f G^\theta$ increase. Furthermore, the values of $\Delta_f G^\theta$ are different for isomers with the same substitute numbers of bromine atoms because their substituent positions differ. For example, among the 14 isomers of penta-BDPs, 1,2,4,6,9-penta-BDP possesses the lowest value of $\Delta_f G^\theta$, and 1,2,3,7,8-penta-BDP possesses the highest corresponding value, where the discrepancy between them is 32.44 $\text{kJ} \cdot \text{mol}^{-1}$. In the same way, $\Delta_f G^\theta$ of 1,2,4,6,7,9-hexa-BDP is lower, and 1,2,3,6,7,8-hexa-BDP is higher than those of the other isomers, where the discrepancy between them is calculated to be around 26.01 $\text{kJ} \cdot \text{mol}^{-1}$.

Using the SPSS 12.0 for the Windows program, correlations of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ with N_{PBS} for PBDPs can be obtained, as shown in Eqs. 18 and 19. Equations 18 and 19 clearly demonstrate that the substitute number and position of bromine atoms influence the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$. From Eqs. 18 and 19, the conclusion can be obtained that the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ increase with an increase in the number of substituted bromine atoms, and the effect of N_β is important. When N_β increases by 1, the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ increase by 23.666 $\text{kJ} \cdot \text{mol}^{-1}$ and 15.062 $\text{kJ} \cdot \text{mol}^{-1}$, respectively. But the effects of N_p and $N_{1,9}$ on $\Delta_f H^\theta$ and $\Delta_f G^\theta$ are not prominent. So it can be concluded that N_α, N_β, N_o, and N_m are the primary influence factors on the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$, and the effect of N_m is smaller than that of the others. N_o and N_m also have a great effect on the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$, and the order of the effect is $N_\text{o} > N_\text{m}$. The relationships between the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ calculated at the B3LYP/6-31G* level and predicted by Eqs. 18 and 19 are shown in

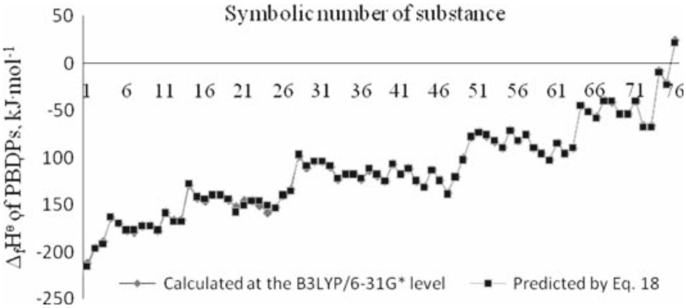


Fig. 3 $\Delta_f H^\theta$ of PBDPs calculated at the B3LYP/6-31G* level and predicted by Eq. 18

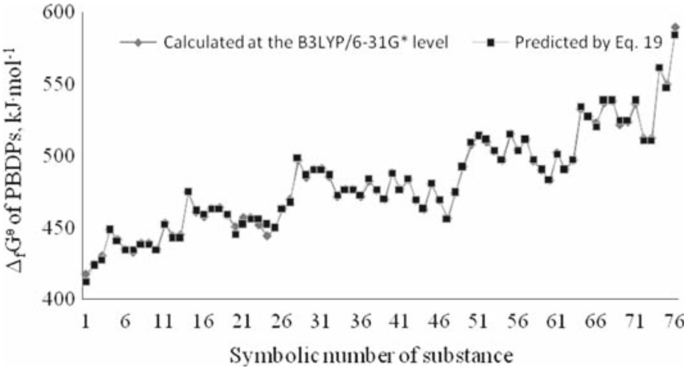


Fig. 4 $\Delta_f G^\theta$ of PBDPs calculated at the B3LYP/6-31G* level and predicted by Eq. 19

Figs. 3 and 4. From the figures, it can be found that the difference between them is very small. The squared correlation coefficients R^2 of Eqs. 18 and 19 are 0.999 and 0.997, respectively. So the values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ can be predicted by the N_{PBS} of PBDP.

3.5 Relations of Structural Parameters and N_{PBS}

The dependence of the PBDP structural parameters on the number of bromines was also investigated. Using the SPSS 12.0 program, the correlations of the structural parameters with N_{PBS} for PBDPs are shown in Table 5 (Eqs. 20–27).

Good correlations are found between some structural parameters (q^- and E_{HOMO}) and N_{PBS}. The R^2 values of q^- and E_{HOMO} are all larger than 0.90. So, q^- and E_{HOMO} can be accurately calculated by N_{PBS} obtained from the molecular structure. At the same time, Table 5 also shows that the correlations between E_{LUMO}, μ, and N_{PBS} are very low (all R^2 values are smaller than 0.519). R^2 values of $q\mathrm{H}^+$ with N_{PBS} are 0.835. It indicates that the values of $q\mathrm{H}^+$ increase with the number of substituted bromine atoms. As for a, the correlations between N_{PBS} and α_{xx}, α_{yy}, and α_{zz} are 0.961, 0.644, and 0.330, respectively, which may be related to the structure (the molecules are almost in the same plane).

4 Conclusion

Fully optimized calculations of 75 PBDPs were carried out at the B3LYP/6-31G* level within the GAUSSIAN03 program, and their structural and thermodynamic parameters were obtained. By designing isodesmic reactions, the standard enthalpies of formation ($\Delta_f H^\theta$) and the standard Gibbs energies of formation ($\Delta_f G^\theta$) were also calculated. The correlations between structural and thermodynamic parameters and N_{PBS} were discussed. It was found that there exist high correlations between some structural and thermodynamic parameters and N_{PBS}. These parameters include E_{th}, H^θ, G^θ, $\Delta_f H^\theta$, $\Delta_f G^\theta$, E_{HOMO}, and q^-.

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