Thermodynamic Property and Relative Stability of 76 Polybrominated Naphthalenes by Density Functional Theory

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The fully optimized calculation of naphthalene and 75 polybrominated naphthalenes (PBNs) in the ideal gas phase were carried out at the B3LYP/6-31G* level. The corresponding thermodynamic parameters, including standard enthalpy, standard Gibbs energy, standard entropy, standard heat capacity at constant volume, and standard thermal energy (i.e., the sum of zero-point energy and thermal energy corrections for molecular translation, rotation, and vibration), were calculated according to temperature correction. In addition, the dependences of some thermodynamic parameters on the number and the position of bromine substituent are discussed. With each additional bromine atom being introduced to the PBNs, the increments of standard entropy and standard heat capacity at constant volume are about 41 $J\cdot mol^{-1}\cdot K^{-1}$ and 17 $J\cdot mol^{-1}\cdot K^{-1}$, respectively, and the decrease of standard thermal energy is about 48 $kJ\cdot mol^{-1}$. By designing isodesmic reactions, the standard enthalpy of formation and the standard Gibbs energy of formation were obtained. On the basis of the magnitude of the relative standard Gibbs energy of formation, the relative stability of PBN isomers was theoretically proposed in this work. Furthermore, comparison of the standard formation enthalpies values, obtained from the B3LYP/6-31G* method as well as four semiempirical methods (AM1, MNDO-d, MNDO, and PM3), was made for PBNs.

Introduction

Polychlorinated naphthalenes (PCNs) play an important role as environmental contaminants, and PCN isomers have been detected and quantified in several matrices including sediments, water, air, and biota.[1−4] In the same way, polybrominated naphthalenes (PBNs) are also very important because people have found that persistent organic pollutants (POPs) with substituted bromine as well as those with substituted chlorine are harmful. Like PCNs, PBNs also appear to be resistant to chemical transformations and have low biological degradation rate. These substances have widespread and diverse uses. Therefore, knowledge of the thermodynamic property of PBNs is of importance. Ribeiro et al.[5] studied enthalpies of combustion of each of the two bromonaphthalenes, while Frenkel et al.[6] reported ideal-gas properties of 1- and 2-bromonaphthalenes and 1,4- and 2,3-dibromonaphthalenes. However, due to limits of PBN samples and analytical complexity, it is somewhat difficult to obtain overall physiochemical properties of the toxic materials in the environment. Because of the relatively low precision of the semiempirical methods, such as AM1 and PM3, it is necessary to use a high-precision method to calculate the thermodynamic data of PBN isomers for predicting their environmental fate and behavior.

We have calculated thermodynamic data of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlordibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and PCNs.[7−10] The data evaluated via the first principles are greatly different from those of AM1 and PM3.

The objective of the present study is to calculate the thermodynamic property and relative stability of 76 PBNs by fully optimized calculation at the B3LYP/6-31G* level[11] in the gas state at 0 K and 101.325 kPa. According to temperature correction, standard enthalpies (H^{θ}), standard Gibbs energies (G^{θ}), standard entropy (S^{θ}), standard heat capacities at constant volume (C^{θ}_{v}), and standard thermal energy ($E^{\theta}_{\mathrm{thermal}}$) (i.e., the sum of zero-point energy and thermal energy corrections for molecular translation (E_{trans}), rotation (E_{rot}), and vibration (E_{vib})) for 76 PBNs, were obtained. By designing isodesmic reactions, the standard enthalpies of formation ($\Delta_f H^{\theta}$) and the standard Gibbs energies of formation ($\Delta_f G^{\theta}$) for all PBNs were obtained. Also, the stability order of the isomers was discussed in accordance with the magnitude of the relative standard Gibbs energy of formation.

Computational Method

Using Gaussian 98,[12] geometry optimizations and energy calculations were performed at the B3LYP/6-31G* level. In this study, all molecules refer to their ideal gas state at 0 K, and frequency calculations were also performed for all of the possible geometries to ensure they were minimal on the potential energy surface. At 298.15 K and 101.325 kPa, the values of H^{θ} and G^{θ} were obtained from the Gaussian output in E_h and converted to $kJ\cdot mol^{-1}$ (1 hartree or $E_h = 2625.50\ kJ\cdot mol^{-1}$). As for the values of G^{θ} and H^{θ}, the reference states are isolated electrons and nuclei at 298.15 K.

Like PCDDs and PBDDs, PBNs have a variable number of halogens attached to two phenyl rings. In this study, PBN isomers with one to seven bromine atoms are represented by the notation mono-BNs (monobromonaphthalenes), di-BNs (dibromonaphthalenes), tri-BNs (tribromonaphthalenes), TBNs

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(tetrabromonaphthalenes), penta-BNs (pentabromonaphthalenes), hexa-BNs (hexabromonaphthalenes), and hepta-BNs (heptabromonaphthalenes), respectively. The PBN with eight bromine atoms on the phenyl ring is represented by Octa-BN (octabromonaphthalene).

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.[14] Among these methods, the second was found to yield the most accurate results. Lee et al.[15] also used the isodesmic reaction to calculate the $\Delta_f H^\theta$ and $\Delta_f G^\theta$ of PCDDs and obtained results consistent to experimental results. Isodesmic reactions were also applied to calculate $\Delta_f H^\theta$ of dibenzo-*p*-dioxin, dibenzofuran, PCDDs, and PCDFs using DFT calculations.[16] Given the accuracy of these theoretical calculations for PBDDs and PCDDs, it seems reasonable to expect that the evaluated thermodynamic properties of PBNs, 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,[15] PBDDs,[13] and PBDEs,[17] served as the basis for calculating $\Delta_f H^\theta$ and $\Delta_f G^\theta$ for the PBNs. 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 to a certain extent.[18] Bromobenzene is structurally similar to PBN, and the experimental values of $\Delta_f H^\theta$ for bromobenzene and benzene are reliable.[19,20] Compared to the direct reaction of naphthalene with Br_2 or CH_4Br, as described by Li et al.,[13] reaction 1 should lead to more accurate results, given by

$$\text{naphthalene} + n\ \text{bromobenzene} = \text{PBN} + n\ \text{benzene} \tag{1}$$

The standard enthalpy change of the reaction ($\Delta_r H^\theta$) is equal to the sum of the standard enthalpies of the products as obtained from DFT calculations minus the sum of the standard enthalpies of reactants:

$$\Delta_r H^\theta = [H^\theta{}_{\text{PBN}} + nH^\theta{}_{\text{benzene}}] - [H^\theta{}_{\text{naphthalene}} + nH^\theta{}_{\text{bromobenzene}}] \tag{2}$$

The sum of the standard enthalpies of formation of the products minus that of the reactants also yields $\Delta_r H^\theta$:

$$\Delta_r H^\theta = [\Delta_f H^\theta{}_{\text{PBN}} + n\Delta_f H^\theta{}_{\text{benzene}}] - [\Delta_f H^\theta{}_{\text{naphthalene}} + n\Delta_f H^\theta{}_{\text{bromobenzene}}] \tag{3}$$

By substituting eq 3 into eq 2, $\Delta_f H^\theta{}_{\text{,PBN}}$ could be obtained by

$$\Delta_f H^\theta{}_{\text{PBN}} = H^\theta{}_{\text{PBN}} + nH^\theta{}_{\text{benzene}} - nH^\theta{}_{\text{bromobenzene}} - H^\theta{}_{\text{naphthalene}} - n\Delta_f H^\theta{}_{\text{benzene}} + n\Delta_f H^\theta{}_{\text{bromobenzene}} + \Delta_f H^\theta{}_{\text{naphthalene}} \tag{4}$$

Similarly, $\Delta_f G^\theta{}_{\text{PBN}}$ could be obtained

$$\Delta_f G^\theta{}_{\text{PBN}} = G^\theta{}_{\text{PBN}} + nG^\theta{}_{\text{benzene}} - nG^\theta{}_{\text{bromobenzene}} - G^\theta{}_{\text{naphthalene}} - n\Delta_f G^\theta{}_{\text{benzene}} + n\Delta_f G^\theta{}_{\text{bromobenzene}} + \Delta_f G^\theta{}_{\text{naphthalene}} \tag{5}$$

The experimental values of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ for bromobenzene, benzene, and naphthalene taken from refs 19 and 20 are listed in Table 1, which also lists the values of H^θ and G^θ calculated at the B3LYP/6-31G* level for the three compounds. The results of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ from eqs 4 and 5 for PBNs are listed in Table 2. At the B3LYP/6-31G* level, the mean absolute deviation of calculated thermochemical quantities from experiment for a variety of compounds is 33.05 kJ·mol^{-1}, and the standard deviation is 39.75 kJ·mol^{-1}.[21] Since all the values are from theoretical calculations, variables can be exactly repeatable.

Table 1. Experimental and Computational Thermodynamic Parameters of the Substances in the Ideal Gas State at 298.15 K[a]

compound	$\Delta_f H^\theta$ kJ·mol^{-1}	$\Delta_f G^\theta$ kJ·mol^{-1}	H^θ E_h	G^θ E_h
benzene	82.9[b]	129.66[b]	−232.14258[d]	−232.17302[d]
bromobenzene	105.0[b]	138.53[b]	−2803.25621[d]	−2803.29306[d]
naphthalene	150.96[c]	221.45[c]	−385.73715[d]	−385.77609[d]

[a] $\Delta_f H^\theta$ is the standard enthalpy of formation of the compound. $\Delta_f G^\theta$ is the standard Gibbs energy of formation of the compound. H^θ is the standard enthalpy. G^θ is the standard Gibbs energy. [b] From ref 19. [c] From ref 20. [d] Data obtained from B3LYP/6-31G* calculations.

Results and Discussion

The structure and atomic numbering of naphthalene is illustrated in Figure 1. If the numbers of bromine atoms at positions 1, 4, 5, or 8 are defined as N_α, the numbers of bromine atoms at positions 2, 3, 6, or 7 are defined as N_β; the numbers of bromine at ortho, meta, and para positions are symbolized as N_o, N_m, and N_p; and the numbers of dibromine at positions 1 and 8 (or 4 and 5) are $N_{1,8}$, respectively. All of the energies and other thermodynamic quantities calculated for 76 PBNs of the ideal gas state at 298.15 K are listed in Table 2.

Relation of S^θ, $E^\theta{}_{\text{thermal}}$, $C^\theta{}_v$ and the Substitution of Bromine. The dependence of PBN thermodynamic properties on the number of bromines was investigated. Based on the thermodynamic values calculated in this study, PBN isomers become less stable as the number of bromines increases. The correlation of S^θ, $E^\theta{}_{\text{thermal}}$, and $C^\theta{}_v$ with the number N for PBNs can be described as follows in eqs (6 to 8) using the least-squares method:

$$S^\theta/\text{J·mol}^{-1}\text{·K}^{-1} = 344.01 + 41.39N_\alpha + 40.84N_\beta + 5.07N_{1,8} - 2.85N_o - 0.98N_m - 4.20N_p \tag{6}$$

$$r^2 = 0.9953 \qquad \text{SE} = 4.260$$

$$E^\theta{}_{\text{thermal}}/\text{kJ·mol}^{-1} = 794.31 - 47.68N_\alpha - 48.88N_\beta - 4.29N_{1,8} - 1.03N_o - 0.56N_m - 0.84N_p \tag{7}$$

$$r^2 = 0.9999 \qquad \text{SE} = 0.901$$

$$C^\theta{}_v/\text{J·mol}^{-1}\text{·K}^{-1} = 120.78 + 16.65N_\alpha + 17.19N_\beta + 1.42N_{1,8} - 0.01N_o + 0.19N_m + 0.40N_p \tag{8}$$

$$r^2 = 0.9998 \qquad \text{SE} = 0.434$$

where r^2 is the squared correlation coefficient and SE is the standard error. From eqs (6 to 8), r^2 is close to 1.0 and SE is small, which shows that the correlations of S^θ, E^θ, and $C^\theta{}_v$ with the position of bromine atoms are good.

Calculation Result of $\Delta_f H^\theta$ and $\Delta_f G^\theta$. Using the same method mentioned above, the correlation expressions of $\Delta_f H^\theta$ and $\Delta_f G^\theta$ to the number and position of bromine substituent can be summarized. The correlations of both eqs (9 and 10) are very well due to the corresponding large r^2, which all clearly demonstrate the influence of the number and the position of

Table 2. Thermodynamic Parameters of PBNs from DFT Calculations[a]

molecule	H^{θ} / E_h	$E^{\theta}_{\text{thermal}}$ / kJ·mol^{-1}	C^{θ}_{v} / $\text{J·mol}^{-1}\text{·K}^{-1}$	S^{θ} / $\text{J·mol}^{-1}\text{·K}^{-1}$	$\Delta_f H^{\theta\, b}$ / kJ·mol^{-1}	$\Delta_f G^{\theta\, c}$ / kJ·mol^{-1}	relative $\Delta_f G^{\theta}$ / kJ·mol^{-1}
naphthalene	−385.73715	794.13	120.46	342.85	150.96	221.45	
Mononapthalenes							
1	−2956.85026	746.15	137.56	382.63	174.44	236.67	1.58
2	−2956.85069	745.20	137.98	384.15	173.31	235.09	0.00
Dinaphthalenes							
1,2	−5527.95984	696.75	154.69	421.81	207.16	261.31	11.03
1,3	−5527.96255	696.80	155.10	423.91	200.05	253.57	3.29
1,4	−5527.96217	698.10	154.49	422.15	201.04	255.08	4.80
1,5	−5527.96239	697.68	154.77	422.92	200.49	254.31	4.03
1,6	−5527.96325	696.87	155.08	424.07	198.22	251.70	1.42
1,7	−5527.96310	696.90	154.96	423.83	198.61	252.15	1.87
1,8	−5527.94801	696.22	154.85	428.16	238.23	290.48	40.20
2,3	−5527.96018	696.31	154.84	422.82	206.27	260.12	9.84
2,6	−5527.96358	695.92	155.54	425.87	197.34	250.28	0.00
2,7	−5527.96360	695.88	155.55	425.68	197.31	250.30	0.02
Trinaphthalenes							
1,3,6	−8099.07503	647.28	172.56	464.92	225.17	270.06	0.00
1,3,5	−8099.07405	648.27	172.08	463.22	227.75	273.14	3.08
1,3,7	−8099.07490	647.40	172.47	465.11	225.52	270.36	0.30
1,4,6	−8099.07462	648.43	171.91	463.38	226.25	271.60	1.54
1,2,4	−8099.07080	648.11	171.73	461.67	236.28	282.14	12.08
1,2,5	−8099.07156	648.31	171.74	461.42	234.29	280.22	10.16
1,2,6	−8099.07245	647.32	172.16	463.06	231.93	277.38	7.32
1,2,7	−8099.07237	647.39	172.05	462.66	232.15	277.72	7.66
1,6,7	−8099.07227	647.56	171.89	462.78	232.43	277.96	7.90
2,3,6	−8099.07262	646.45	172.50	464.62	231.50	276.48	6.42
1,2,3	−8099.06789	647.20	171.72	460.07	243.91	290.25	20.19
1,3,8	−8099.05993	646.74	172.30	469.02	264.81	308.48	38.42
1,4,5	−8099.05806	647.29	172.05	477.96	269.74	310.82	40.76
1,2,8	−8099.05493	643.38	172.15	496.21	275.47	328.16	58.10
Tetranaphthalenes							
1,3,5,7	−10670.18539	598.74	189.36	503.86	255.87	292.75	0.00
1,2,4,6	−10670.18295	598.88	188.91	501.92	262.26	299.73	6.98
1,2,4,7	−10670.18298	598.69	189.00	502.18	262.18	299.57	6.82
1,2,5,7	−10670.18300	598.45	189.20	502.57	262.12	299.39	6.64
1,3,6,7	−10670.18376	598.06	189.32	503.63	260.13	297.08	4.33
1,4,6,7	−10670.18344	599.51	188.54	501.34	260.97	298.60	5.85
1,2,5,6	−10670.18056	598.95	188.69	499.75	268.54	306.65	13.90
1,3,6,8	−10670.17144	596.88	189.85	510.85	292.48	327.28	34.53
1,2,3,5	−10670.17917	598.50	188.74	499.67	272.20	310.33	17.58
1,3,5,8	−10670.16956	597.60	189.45	513.22	294.94	331.52	38.77
1,2,3,6	−10670.18016	597.61	189.17	500.87	269.59	307.36	14.61
1,2,3,7	−10670.18002	597.34	189.22	501.35	269.94	307.58	14.83
1,2,3,4	−10670.17437	597.91	188.59	497.41	284.79	323.58	30.83
1,2,6,7	−10670.18136	598.23	188.85	501.00	266.44	304.17	11.42
1,2,4,5	−10670.16639	597.77	189.07	514.17	305.75	339.60	46.85
2,3,6,7	−10670.18151	597.57	189.18	502.33	266.05	303.39	10.64
1,2,4,8	−10670.16430	596.46	189.63	506.13	311.22	347.43	54.68
1,2,5,8	−10670.16493	596.40	189.67	506.27	309.57	345.73	52.98
1,2,6,8	−10670.16658	596.31	189.60	517.31	305.25	338.14	45.39
1,4,5,8	−10670.15092	593.25	191.13	507.76	346.36	382.08	89.33
1,2,3,8	−10670.16230	595.64	189.44	506.05	316.49	352.67	59.92
1,2,7,8	−10670.16183	594.39	190.22	503.93	315.23	354.57	61.82
Pentanaphthalenes							
1,2,3,5,7	−13241.29040	548.66	206.14	540.51	300.58	330.14	3.24
1,2,4,6,7	−13241.29165	549.37	205.71	540.34	297.30	326.90	0.00
1,2,4,5,7	−13241.27767	547.97	206.37	550.34	334.02	360.71	33.81
1,2,4,6,8	−13241.27553	546.43	207.11	547.57	339.63	367.08	40.18
1,2,3,4,6	−13241.28638	548.22	205.95	538.58	311.15	341.28	14.38
1,2,3,5,6	−13241.28804	548.68	205.85	538.91	306.78	336.81	9.91
1,2,3,6,7	−13241.28878	548.08	206.02	539.93	304.84	334.57	7.67
1,2,4,5,6	−13241.27315	546.75	206.67	545.09	345.88	374.07	47.17
1,2,4,7,8	−13241.27121	544.94	207.55	541.60	350.98	380.21	53.31
1,2,3,5,8	−13241.27204	546.04	206.84	542.53	348.79	377.75	50.85
1,2,3,6,8	−13241.27365	545.58	207.04	548.33	344.56	371.79	44.89
1,2,4,5,8	−13241.25796	542.52	208.63	544.51	385.76	414.11	87.21
1,2,3,4,5	−13241.26696	544.74	207.08	540.46	362.13	391.70	64.80
1,2,3,7,8	−13241.26911	543.95	207.51	541.07	356.49	385.87	58.97
Hexanaphthalenes							
1,2,3,4,6,7	−15812.39507	498.89	222.66	576.42	346.22	368.67	0.92
1,2,3,5,6,7	−15812.39533	498.58	222.88	577.17	345.52	367.75	0.00
1,2,3,4,5,7	−15812.37811	494.78	224.48	582.10	390.75	411.50	43.75
1,2,3,5,6,8	−15812.38022	496.10	223.95	582.40	385.20	405.86	38.11
1,2,3,5,7,8	−15812.37823	494.57	224.68	579.22	390.42	412.03	44.28
1,2,4,5,6,8	−15812.36497	491.82	226.10	581.73	425.25	446.12	78.37
1,2,4,5,7,8	−15812.36493	491.69	226.16	581.87	425.35	446.17	78.42

Table 2. (Continued)

molecule	H^θ E_h	$E^\theta_{thermal}$ $kJ·mol^{-1}$	C^θ_v $J·mol^{-1}·K^{-1}$	S^θ $J·mol^{-1}·K^{-1}$	$\Delta_f H^{\theta\,b}$ $kJ·mol^{-1}$	$\Delta_f G^{\theta\,c}$ $kJ·mol^{-1}$	relative $\Delta_f G^\theta$ $kJ·mol^{-1}$
			Hexanaphthalenes				
1,2,3,4,5,6	−15812.37402	493.43	224.90	577.94	401.49	423.49	55.74
1,2,3,4,5,8	−15812.35944	490.34	226.24	578.57	439.77	461.58	93.83
1,2,3,6,7,8	−15812.37619	493.57	224.79	579.97	395.77	417.16	49.41
			Heptanaphthalenes				
1,2,3,4,5,6,7	−18383.48113	443.13	242.00	615.57	440.71	455.08	0.00
1,2,3,4,5,6,8	−18383.46660	439.75	243.68	616.39	478.85	492.99	37.90
			Octanaphthalenes				
1,2,3,4,5,6,7,8	−20954.56865	387.55	261.42	652.96	531.35	538.18	

[a] H^θ is standard enthalpy. S^θ is standard entropy. C^θ_v is standard heat capacity at constant volume. $E^\theta_{thermal}$ is standard thermal energy (i.e., the sum of zero-point energy and thermal energy corrections for molecular translation (E_{trans}), rotation (E_{rot}), and vibration (E_{vib})). $\Delta_f H^\theta$ is the standard enthalpy of formation of the compound. $\Delta_f G^\theta$ is the standard Gibbs energy of formation of the compound. [b] Calculated by eq 4. [c] Calculated by eq 5.

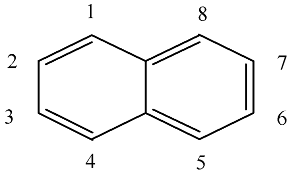

Figure 1. Structure and atomic numbering of naphthalene.

bromine on the value of $\Delta_f H^\theta$ and $\Delta_f G^\theta$:

$$\Delta_f H^\theta/\mathrm{kJ{\cdot}mol^{-1}} = 147.62 + 24.53N_\alpha + 23.77N_\beta + 46.63N_{1,8} + 12.14N_o + 3.40N_m + 3.78N_p \quad (9)$$

$$r^2 = 0.9988 \qquad \mathrm{SE} = 2.7383$$

$$\Delta_f G^\theta/\mathrm{kJ{\cdot}mol^{-1}} = 218.26 + 16.01N_\alpha + 14.97N_\beta + 46.05N_{1,8} + 13.25N_o + 3.17N_m + 3.98N_p \quad (10)$$

$$r^2 = 0.9978 \qquad \mathrm{SE} = 3.1770$$

The relationship between $\Delta_f G^\theta$ and the number as well as the position of chlorine substituent for gas-phase PCNs, which we have already established,[7] is as shown in eq 11:

$$\Delta_f G^\theta/\mathrm{kJ{\cdot}mol^{-1}} = 295.21 - 8.11N_\alpha - 12.82N_\beta + 38.83N_{1,8} + 12.56N_o + 0.02N_m + 1.64N_p \quad (11)$$

By comparing eq 10 with eq 11, it can be found that the influences of the number and the position at $N_{1,8}$, N_o, N_m, and N_p of the substituent groups on $\Delta_f G^\theta$ are quite similar to both chlorine substitute of PCNs and bromine substitute of PBNs, respectively. However, the substituent positions at α and β causes reversed difference of the $\Delta_f G^\theta$ value of PBNs and those of PCNs. The influence of the relative position (N_α and N_β) of bromines on the relative standard Gibbs energy of formation is positive for PBNs but that is negative for PCNs. That is, standard Gibbs energy of formation of PBNs increases with N_{Br} (the numbers of substituent bromine atoms) increasing, while that of PCNs decreases with N_{Cl} (the numbers of substituent chlorine atoms) increasing.

Energy Difference between PBN Isomers. The energy differences between the different conformations of a PBN isomer were found, in general, to be much smaller than the energy differences between isomers within homologues. The $\Delta_f G^\theta$ of the PBN isomers also exhibit similar differences.

It was determined in an earlier study[13] that the energy differences between PBDD isomers are strongly affected by the intramolecular halogenic repulsion, position, and number. An analysis of these factors in the present study indicates that the inter-isomer energy differences for PBNs are similarly affected. Table 3 lists $\Delta_f H^\theta$, $\Delta_f G^\theta$, and Br−Br nonbonding distance of some isomers.

Table 3. Standard Enthalpy of Formation ($\Delta_f H^\theta$), Standard Gibbs Energy of Formation ($\Delta_f G^\theta$), and Br−Br Nonbonding Distance of 1,2-DiBN, 1,8-DiBN, and 2,3-DiBN[a]

isomer	$\Delta_f H^\theta$ $kJ·mol^{-1}$	$\Delta_f G^\theta$ $kJ·mol^{-1}$	Br−Br nonbonding distance Å
1,2-DiBN	207.16	261.31	3.357
1,8-DiBN	238.23	290.48	3.274
2,3-DiBN	206.27	260.48	3.391

[a] $\Delta_f H^\theta$ was calculated by eq 4; $\Delta_f G^\theta$ was calculated by eq 5.

1,8-DiBN is distinguished by a higher energy than the other isomers, 1,2-DiBN and 2,3-DiBN. The difference between the latter two is very small, indicating that the repulsing force of the two bromine atoms at positions 1 and 8 is obvious in this case. Comparison of the stability of these three isomers leads to a quantitative estimation of the effect of bromine position. The same conclusion is found in other substituted isomers. Table 3 shows that Br−Br nonbonding distance of 1,8-DiBN is shorter than those of 1,2- and 2,3-DiBN, which indicates that 1,8-DiBN is the most unstable in the three isomers (i.e., repulsion between bromine atoms is the largest). The same conclusion was found for each isomer group.

Comparison with Literature Data. In this study, we calculated $S_{T,m}$, $C_{p,m}$, $\Delta_0^T H_m/T$, and $\Delta_0^T G_m/T$ for 1- and 2-bromonaphthalenes, 2,3-dibromonaphthalene, and octabromonaphthalene (scale factor for frequency = 0.95) and compared the calculated data with literature data.[6] $S_{T,m}$ is molar entropy at T/K, $C_{p,m}$ is molar heat capacity at constant pressure, $\Delta_0^T H_m/T$ is specific thermal correction to molar enthalpy, and $\Delta_0^T G_m/T$ is specific thermal correction to molar Gibbs energy. The data are listed in Table 4, which indicate that the calculation data in this work match well with those reported in the literature. The maximum discrepancies of $S_{T,m}$, $C_{p,m}$, $\Delta_0^T H_m/T$, and $\Delta_0^T G_m/T$ are −1.25, 0.65, 0.92, and −0.31 for 1-bromonaphthalenes; −1.55, −3.23, −0.76, and −2.47 for 2-bromonaphthalenes; and −0.88, −8.67, −1.41, and −7.58 for 2,3-dibromonaphthalene respectively. While in our other study,[7] we found that the calculated data of S^θ are in agreement with experiment for 1,2-, 1,3-, and 1,4-dichlorobenzene at 298.15 K, which indicated that our calculation method is feasible. Ribeiro et al.[5] derived the standard molar enthalpy at 298.15 K, 174.3 ± 5.6 $kJ·mol^{-1}$ for 1-mono-PBN and 175.6 ± 2.3 $kJ·mol^{-1}$ for 2-PBN. In this study, the corresponding calculation data are (174.44 and 173.31) $kJ·mol^{-1}$ respectively, which is close to that from literature.

Table 4. Calculation Data of $S_{T,\mathrm{m}}$, $C_{p,\mathrm{m}}$, $\Delta_0^{\mathrm{T}}H_\mathrm{m}/T$ and $\Delta_0^{\mathrm{T}}G_\mathrm{m}/T$ for Some Compounds[a]

	T	$C_{p,\mathrm{m}}$			$S_{T,\mathrm{m}}$			$\Delta_0^{\mathrm{T}}H_\mathrm{m}/T$			$\Delta_0^{\mathrm{T}}G_\mathrm{m}/T$		
		J·mol·$^{-1}$·K^{-1}											
molecule	K	calcd[b]	calcd[c]	diff	calcd[b]	calcd[c]	diff	calcd[b]	calcd[c]	diff	calcd[b]	calcd[c]	diff
1-bromonaphthalene	298.15	153.85	153.33	0.52	389.14	388.50	0.64	84.99	84.07	0.92	304.15	304.46	−0.31
	300.00	154.72	154.24	0.48	390.10	389.45	0.65	85.35	84.47	0.88	304.75	304.99	−0.24
	400.00	200.00	200.57	−0.57	440.98	440.35	0.63	108.49	107.85	0.64	332.49	332.49	0.00
	500.00	237.40	238.50	−1.10	489.76	489.34	0.42	130.67	130.34	0.33	359.09	359.00	0.09
	600.00	267.19	268.44	−1.25	535.79	535.57	0.22	151.04	150.97	0.07	384.75	384.61	0.14
	700.00	290.91	292.16	−1.25	578.84	578.80	0.04	169.41	169.50	−0.09	409.43	409.30	0.13
	800.00	310.16	311.30	−1.14	618.97	619.11	−0.14	185.81	186.08	−0.27	433.16	433.04	0.12
	900.00	325.98	326.99	−1.01	656.45	656.71	−0.26	200.54	200.89	−0.35	455.91	455.82	0.09
	1000.00	339.11	340.04	−0.93	691.52	691.85	−0.33	213.76	214.17	−0.41	477.76	477.69	0.07
2-bromonaphthalene	298.15	154.26	153.75	0.51	388.05	390.07	−2.02	84.60	84.43	0.17	303.45	305.65	−2.20
	300.00	155.14	154.67	0.47	389.01	391.03	−2.02	85.02	84.87	0.15	303.99	306.18	−2.19
	400.00	200.37	200.92	−0.55	440.02	442.03	−2.01	108.37	108.25	0.12	331.65	333.79	−2.14
	500.00	237.65	238.78	−1.13	488.88	491.09	−2.21	130.62	130.70	−0.08	358.26	360.38	−2.12
	600.00	267.23	268.66	−1.43	534.91	537.37	−2.46	151.04	151.32	−0.28	383.87	386.06	−2.19
	700.00	290.83	292.35	−1.52	577.96	580.63	−2.67	169.37	169.83	−0.46	408.59	410.80	−2.21
	800.00	309.91	311.46	−1.55	618.09	620.96	−2.87	185.77	186.38	−0.61	432.32	434.58	−2.26
	900.00	325.60	327.13	−1.53	655.53	658.58	−3.05	200.46	201.18	−0.72	455.07	457.40	−2.33
	1000.00	338.65	340.17	−1.52	690.51	693.74	−3.23	213.68	214.44	−0.76	476.83	479.30	−2.47
2,3-dibromonaphthalene	298.15	170.58	170.47	0.11	421.65	429.61	−7.96	96.11	97.52	−1.41	325.54	332.11	−6.57
	300.00	171.46	171.37	0.09	422.74	430.66	−7.92	96.57	97.93	−1.36	326.17	332.72	−6.55
	400.00	215.86	216.27	−0.41	478.30	486.30	−8.00	121.00	122.08	−1.08	357.30	364.22	−6.92
	500.00	251.96	252.68	−0.72	530.52	538.62	−8.10	143.72	144.70	−0.98	386.80	393.92	−7.12
	600.00	280.37	281.23	−0.86	579.05	587.32	−8.27	164.22	165.17	−0.95	414.83	422.15	−7.32
	700.00	302.84	303.72	−0.88	624.03	632.43	−8.40	182.46	183.41	−0.95	441.57	449.01	−7.44
	800.00	320.87	321.72	−0.85	665.70	674.20	−8.50	198.70	199.63	−0.93	467.00	474.58	−7.58
	900.00	335.60	336.39	−0.79	704.36	712.97	−8.61	213.13	214.03	−0.90	491.23	498.94	−7.71
	1000.00	347.77	348.51	−0.74	740.39	749.06	−8.67	225.98	226.89	−0.91	514.41	522.16	−7.75
octabromonaphthalene	298.15		276.22			665.20			182.12			483.12	
	300.00		277.01			666.91			182.67			484.25	
	400.00		313.87			751.90			211.08			540.83	
	500.00		341.21			825.03			234.50			590.52	
	600.00		361.20			889.10			254.05			635.06	
	700.00		375.84			945.94			270.46			675.48	
	800.00		386.68			996.87			284.34			712.53	
	900.00		394.84			1042.90			296.18			746.72	
	1000.00		401.08			1084.84			306.37			778.47	

[a] $S_{T,\mathrm{m}}$ is molar entropy at T. $C_{p,\mathrm{m}}$ is molar heat capacity at constant pressure. $\Delta_0^{\mathrm{T}}H_\mathrm{m}/T$ is an average thermal correction to molar enthalpy between 0 and T. $\Delta_0^{\mathrm{T}}G_\mathrm{m}/T$ is an average thermal correction to molar Gibbs energy between 0 and T. [b] From ref 6. [c] From this work.

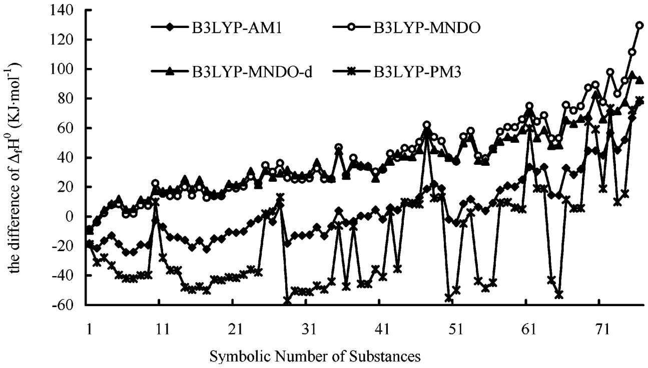

Figure 2. Comparison of Δ_fH^θ calculation data.

Comparison of the Calculated Δ_fH^θ of PBNs with Semiempirical Methods. In this study, the Δ_fH^θ of 76 PBNs were calculated by B3LYP/6-31G* level and compared with those obtained from four semiempirical methods: AM1, MNDO-d, MNDO, and PM3. Their differences are illustrated in Figure 2, in which the symbolic number in Table 2 was used as horizontal coordinate. From Figure 2, it can be seen that the differences between the values obtained by B3LYP and MNDO are close to those of B3LYP and MNDO-d, and both are larger than the differences between B3LYP and AM1, B3LYP and PM3.

Table 5. Most Stable and Unstable Isomer in Different Isomer Groups

substance	most stable isomer	tmost unstable isomer
mono-BN	2-	1-
di-BN	2,6-, 2,7-	1,8-
tri-BN	1,3,6-	1,2,8-
TBN	1,3,5,7-	1,4,5,8-
penta-BN	1,2,4,6,7-	1,2,4,5,8-
hexa-BN	1,2,3,5,6,7-	1,2,3,4,5,8-
hepta-BN	1,2,3,4,5,6,7-	1,2,3,4,5,6,8-

Relative Stability of Isomer Groups. The obtained relative standard Gibbs energy of formation, based on the lowest Δ_fG^θ of isomers with the same numbers of substituent, is also listed in Table 1. For the PBN compounds in each isomer group, the isomer with lower relative standard Gibbs energy of formation is relatively stable, while that with higher relative standard Gibbs energy of formation is unstable. Thus the relative stability of each isomer group can be determined, and the most stable isomer and most unstable one are listed in Table 5.

It can be seen from Table 5, the most unstable isomers in mono-BNs, di-BNs, tri-BNs, TBNs, penta-BNs, hexa-BNs, and hepta-BNs are all those with bromine being attached to 1,8 or 4,5 simultaneously. On the contrary, the bromines in the most stable isomers are reasonably distributed at two aromatic rings, and the substituent groups are relatively far away from each other. The conclusion is in agreement with eq 10. In addition, we compared the most stable and unstable isomer of PBNs with those of PCNs and found that those compounds are consistent in two groups.

Conclusion

The fully optimized calculation of naphthalene and 75 PBNs were carried out at the B3LYP/6-31G* level. S^{θ}, C^{θ}_{v}, $E^{\theta}_{\mathrm{thermal}}$, $\Delta_{\mathrm{f}}H^{\theta}$, and $\Delta_{\mathrm{f}}G^{\theta}$ of naphthalene and PBNs correlate with both the number and the position of bromine substituent. The values obviously increase when dibromine atoms being attached to 1,8 or 4,5 positions. With the numbers substituent increasing in PBNs, the values of S^{θ} and C^{θ}_{v} increase, but the value of $E^{\theta}_{\mathrm{thermal}}$ decreases. Also, the relative stability of PBN isomers was theoretically proposed in this work. By designing isodesmic reactions, the standard enthalpies of formation and the standard Gibbs energies of formation were obtained, from which the order of relative stability for PBNs was determined. In addition, we have also compared the standard enthalpies of formation obtained from the B3LYP/6-31G* method with those from four semiempirical methods.

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