DFT Calculation on 76 Polybromophenazines: Their Thermodynamic Function and Stability†

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The thermodynamic functions, including enthalpy (H^{Θ}), entropy (S^{Θ}), and Gibbs free energy (G^{Θ}) for 76 polybromophenazines (PBPZs) in the gaseous state at 298.15 K and 101.325 kPa, have been calculated using the density functional theory (the B3LYP/6-31G*) with the Gaussian 03 program. On the basis of these data, the isodesmic reactions were designed to calculate the standard formation heat ($\Delta_f H^{\Theta}$) and standard Gibbs energy of formation ($\Delta_f G^{\Theta}$) of PBPZs. In addition, the dependences of these thermodynamic parameters on the number and positions of bromine substitutes (N_{PBS}) were discussed. It is suggested that $\Delta_f H^{\Theta}$ and $\Delta_f G^{\Theta}$ of PBPZs vary greatly with the substituent positions of bromine, with the influence order being position α > position β, while the S^{Θ} value is increased by 10 $J \cdot mol^{-1} \cdot K^{-1}$ by increasing each bromine atom to PBPZs. It was found that when two bromines substitute in the same aromatic ring the $\Delta_f H^{\Theta}$ and $\Delta_f G^{\Theta}$ increase effect is ortho > meta > para. The relative stability order of PBPZ congeners was theoretically proposed based on the relative magnitude of their $\Delta_f G^{\Theta}$. In addition, the values of molar heat capacity at constant pressure ($C_{p,m}$) for PBPZ congeners have been calculated.

Introduction

Phenazine (PZ) (the structure and atomic numbering of PZ are illustrated in Figure 1) shows properties with a wide range of significant applications.[1] Many phenazine compounds are found in nature and are produced by bacteria such as *Pseudomonas* spp., *Streptomyces* spp., and *Pantoea agglomerans*. These phenazine natural products have been implicated in the virulence and competitive outcome of producing organisms. For example, the phenazine pyocyanin produced by *Pseudomonas aeruginosa* contributes to its ability to colonize the lungs of cystic fibrosis patients. Similarly, phenazine-1-carboxylic acid, produced by a number of Pseudomonas, has been shown to be essential for the biological control activity of certain strains and the quantity increases in soil environments.[2,3] Natural and synthetic phenazines have attracted considerable attention because of their interesting biological activities,[4] i.e., antibiotic and anticancer agents.[5,6] Halosubstituted phenazines are useful as herbicides.[7] Because of the remarkable reluctance of phenazines to undergo electrophilic substitution reactions, the displacement of the halogen atoms of chlorophenazines by a variety of nucleophiles can play an important role in the production of a wide variety of phenazine derivatives.[8] As the use of chlorophenzines has increased in recent years, their concentrations in the environment have also increased. Using the in vitro bioassay for dioxin-like activity showed that tetrabromophenazine (T4BPZ) has a half-effective dose (ED50) of 10^{-7} M, which is about 10 000-fold less active than concomitantly tested 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxins.[9] The conclusion can be drawn that ploychlorophenzines (PCPZs) also have dioxin-like activity. While polybromophenazines (PBPZs) possess the analogous properties as PCPZs, so we take PBPZs into study.

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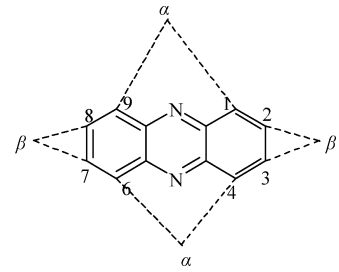

Figure 1. Numbering of the C-atoms of PZ.

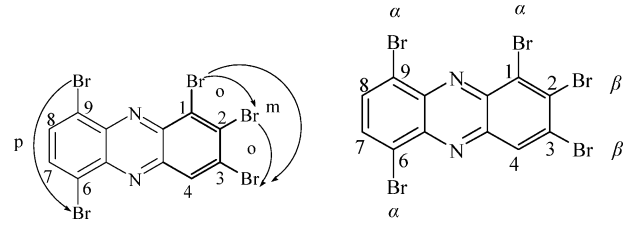

Figure 2. Positions for these Br atoms of 1,2,3,6,9-penta-BPZ.

It is important to know the thermodynamic properties of PBPZs for studying their generation, degradation, and environmental risk. So, the purpose of the study was to calculate the thermodynamic properties for 76 PBPZs with the Gaussian 03 program.[10] Then, the relations between these thermodynamic properties as mentioned above and positions of bromine substitutes (N_{PBS}) were studied. Finally, 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 PBPZs were also obtained. The molar heat capacity at constant pressure ($C_{p,m}$) values of PBPZs were calculated using the statistical thermodynamics calculation program at temperatures of (200 to 1000) K.

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Table 1. Thermodynamic Data Used for Calculating $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$ of PBPZs

number	formula or name	$\Delta_f H^\Theta$ (kJ·mol^{-1})	$\Delta_f G^\Theta$ (kJ·mol^{-1})	H^Θ (kJ·mol^{-1})	G^Θ (kJ·mol^{-1})	S^Θ (J·mol^{-1}·K^{-1})
1	benzene (PhH)	82.9[a]	129.66[a]	−609490.285	−609570.206	−
2	bromobenzene (BB)	105.0[a]	138.53[a]	−7359948.473	−7360045.223	−
3	phenazine (PZ)	237.0[a]	−	−1500278.386	−1500395.543	93.916
4	graphite (C)	0	−	−	−	5.74[a]
5	nitrogen (N_2)	0	−	−	−	45.77[a]
6	hydrogen (H_2)	0	−	−	−	130.57[a]

[a] Data from ref 11 and other data from B3LYP/6-31G* calculations.

Table 2. Thermodynamic Parameters and Experimental Ones of Part Aromatic Hydrocarbon Calculated at the B3LYP/6-31G* Level[12]

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.
benzene	82.9			269.3	268.2	−1.1	129.7	129.9	0.2
chlorobenzene	54.4			313.5	313.3	−0.2	99.2	99.2	0.0
1,2-dichlorobenzene	30.0	40.6	10.6	341.5	342.1	0.6	82.7	93.4	10.7
1,3-dichlorobenzene	28.1	30.0	1.9	343.5	343.5	0.0	78.6	82.2	3.6
1,4-dichlorobenzene	24.6	29.8	5.2	336.7	337.7	1.0	77.2	83.9	6.7
1,1′-biphenyl	182.1			392.7	391.7	−1.0	280.1	280.3	0.2
2,2′-dichlorobiphenyl	126.8	143.8	17		461.8			270.8	
4,4′-dichlorobiphenyl	120.1	125.6	5.5		452.5			255.5	
benzenethiol	111.5			336.7	333.6	−3.1	147.6		

[a] Taken from ref 13.

Table 3. Experimental Value of $C_{p,m}$ of Part Aromatic Hydrocarbon Calculated at the B3LYP/6-31G* Level[12]

name	$C_{p,m}$ (J·mol^{-1}·K^{-1})											
	400 K			600 K			800 K			1000 K		
	exp.[a]	cal.[b]	diff.	exp.[a]	cal.[b]	diff.	exp.[a]	cal.[b]	diff.	exp.[a]	cal.[b]	diff.
aniline	142.97	145.05	2.08	192.84	195.37	2.53	225.06	228.21	3.15	247.61	251.17	3.56
phenol	135.77	137.60	1.83	182.17	184.84	2.67	211.79	215.09	3.30	232.17	235.90	3.73
benzenethiol	142.97	143.30	0.33	192.84	189.32	−3.52	225.06	219.03	−6.03	247.61	239.49	−8.12
m-cresol	162.09	168.73	6.64	218.66	225.72	7.06	256.35	263.67	7.32	286.60	290.26	3.66
p-cresol	161.71	168.79	7.08	217.99	225.73	7.74	255.68	263.67	7.99	290.70	290.28	−0.42
o-cresol	166.27	168.57	2.30	220.79	225.64	4.85	257.53	263.62	6.09	287.94	290.24	2.30
biphenyl	221.04	228.52	7.48	307.69	314.94	7.25	363.67	370.33	6.66	401.66	408.02	6.36
chlorobenzene	128.11	131.21	3.10	172.21	174.64	2.43	200.37	202.20	1.83	219.58	220.90	1.32
1,2-dichlorobenzene	142.76	146.00	3.24	184.39	186.96	2.57	210.37	212.31	1.94	227.69	229.13	1.44
1,3-dichlorobenzene	143.01	146.38	3.37	184.47	187.21	2.74	210.41	212.44	2.03	227.69	229.19	1.50
1,4-dichlorobenzene	143.26	146.32	3.06	184.77	187.14	2.37	210.66	212.40	1.74	227.86	229.17	1.31
perchlorobenzene	201.17	204.85	3.68	233.38	236.20	2.82	249.74	252.89	3.15	260.83	262.30	1.47
1,2-difluorobenzene	137.07	140.14	3.07	181.29	182.83	1.54	209.70	209.42	−0.28	228.95	227.06	−1.89
1,3-difluorobenzene	136.90	140.80	3.90	180.46	183.32	2.86	207.82	209.66	1.84	225.64	227.12	1.48
1,4-difluorobenzene	137.40	140.45	3.05	180.75	183.18	2.43	207.86	209.67	1.81	225.89	227.22	1.33
perfluorobenzene	183.59	187.80	4.21	219.87	222.93	3.06	241.08	243.30	2.22	253.68	255.31	1.63
toluene	140.08	147.27	7.19	197.48	203.08	5.60	235.60	240.64	5.04	264.93	267.07	2.14
ethylbenzene	170.54	174.99	4.45	236.14	242.60	6.46	280.96	288.51	7.55	312.84	320.97	8.13

[a] Taken from ref 11. [b] Calculated using the statistical thermodynamics calculation program.

Computational Methods

Becke's three-parameter hybrid function combined with the gradient−correlation functional of Lee, Yang, and Parr (LYP), denoted B3LYP, was employed in the computations using DFT. The all-electron 6-31G* basis set was employed. Geometries were optimized using analytic gradient techniques, that is, the Berny algorithm with redundant internal coordinates. The stationary points on the potential energy surface were characterized by calculations of vibrational frequencies, which were done analytically at DFT levels. Following the geometry optimization, frequencies were calculated using the same method at a stationary point. Throughout this paper, all calculations for PBPZs were carried out at the B3LYP/6-31G* level.

The equations used for computing thermochemical data in Gaussian programs are derived from statistical thermodynamics. Two key ideas of statistical thermodynamics are the Boltzmann distribution and the partition function. The partition function is like a thermodynamic wave function, in the sense that it contains all thermodynamic information about the system, just as the quantum mechanical wave function contains all dynamic information.

In this paper, PBPZ congeners with one to eight bromine atoms are represented by the notation as MBPZ (monobromophenazines), DBPZ (dibromophenazines), tri-BPZ (tribromophenazines), TBPZ (tetrabromophenazines), penta-BPZ (pentabromophenazines), hexa-BPZ (hexabromophenazines), hepta-BPZ (heptabromophenazines), and OBPZ (octabromophenazines), respectively. Moreover, the brominated phenazines mentioned above are defined as a general designation PBPZs. In this work, the positions of Br substitution (PBS) consist of the number of the substituting Br atoms on different positions of the parent compound and the number of relative positions of these Br atoms. The numbers of the positions of Br substitution (PBS) are defined as follows: the numbers of bromine atoms at positions 1(4,

Table 4. Thermodynamic Parameters by B3LYP/6-31G* for PBPZs[a]

	S^{Θ}	$\Delta_f H^{\Theta}$	$\Delta_f G^{\Theta}$	$\Delta_f G_R^{\Theta}$	$C_{p,m}$/J·(J·mol^{-1}·K^{-1})									
	J·mol^{-1}·K^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	constant	$10^{-3}T$	$10^{5}T^{-1}$	$10^{7}T^{-2}$	N_α	N_β	N_o	N_m	N_p	$N_{1,9}$
PZ	392.945	237.000	398.90		530.894	32.548	−1.488	1.323	0	0	0	0	0	0
MBPZ														
1-MBPZ	433.621	267.089	420.462	5.582	542.274	25.776	−1.452	1.279	1	0	0	0	0	0
2-MBPZ	434.262	261.697	414.880	0.000	542.033	25.694	−1.446	1.271	0	1	0	0	0	0
DBPZ														
1,2-DBPZ	471.993	299.613	445.145	13.629	553.845	18.903	−1.415	1.233	1	1	1	0	0	0
1,3-DBPZ	474.930	294.404	439.062	7.546	553.739	18.812	−1.412	1.231	1	1	0	1	0	0
1,4-DBPZ	473.461	299.043	444.137	12.621	553.708	19.107	−1.417	1.238	2	0	0	0	1	0
1,6-DBPZ	474.035	297.877	442.800	11.284	553.671	19.047	−1.416	1.235	2	0	0	0	0	0
1,7-DBPZ	475.344	292.663	437.195	5.679	553.495	18.886	−1.410	1.227	1	1	0	0	0	0
1,8-DBPZ	474.788	292.870	437.570	6.054	553.657	18.807	−1.411	1.228	1	1	0	0	0	0
1,9-DBPZ	473.671	299.145	444.176	12.660	553.720	19.041	−1.416	1.236	2	0	0	0	0	1
2,3-DBPZ	472.880	296.756	442.023	10.507	553.768	18.745	−1.410	1.226	0	2	1	0	0	0
2,7-DBPZ	475.160	287.202	431.792	0.276	553.281	18.806	−1.405	1.220	0	2	0	0	0	0
2,8-DBPZ	475.892	287.147	431.516	0.000	553.250	18.793	−1.405	1.219	0	2	0	0	0	0
tri-BPZ														
1,2,3-tri-BPZ	510.820	338.306	475.859	19.240	566.145	11.587	−1.379	1.189	1	2	2	1	0	0
1,2,4-tri-BPZ	512.737	333.464	470.445	13.826	565.616	12.035	−1.382	1.195	2	1	1	1	1	0
1,2,6-tri-BPZ	512.394	330.912	467.998	11.379	565.354	12.094	−1.379	1.190	2	1	1	0	0	0
1,2,7-tri-BPZ	513.871	325.672	462.317	5.697	565.107	11.974	−1.373	1.181	1	2	1	0	0	0
1,2,8-tri-BPZ	513.682	325.785	462.488	5.868	565.198	11.932	−1.373	1.182	1	2	1	0	0	0
1,2,9-tri-BPZ	512.841	332.047	469.001	12.382	565.347	12.099	−1.379	1.190	2	1	1	0	0	1
1,3,6-tri-BPZ	515.306	326.297	462.516	5.897	565.274	11.999	−1.377	1.188	2	1	0	1	0	0
1,3,7-tri-BPZ	516.155	320.655	456.620	0.000	565.027	11.894	−1.371	1.179	1	2	0	1	0	0
1,3,8-tri-BPZ	515.829	320.807	456.869	0.249	565.020	11.906	−1.371	1.180	1	2	0	1	0	0
1,3,9-tri-BPZ	515.812	327.126	463.194	6.574	565.251	12.008	−1.376	1.188	2	1	0	1	0	1
1,4,6-tri-BPZ	514.184	331.569	468.122	11.502	565.172	12.341	−1.382	1.195	3	0	0	0	1	1
1,4,7-tri-BPZ	514.155	325.459	462.020	5.401	565.041	12.178	−1.377	1.187	2	1	0	0	1	0
2,3,6-tri-BPZ	512.908	328.358	465.289	8.669	565.323	11.908	−1.375	1.182	1	2	1	0	0	0
2,3,7-tri-BPZ	515.297	323.004	459.224	2.604	565.100	11.785	−1.369	1.174	0	3	1	0	0	0
TBPZ														
1,2,3,4-TBPZ	548.698	381.386	511.247	28.757	578.558	4.448	−1.350	1.154	2	2	3	2	1	0
1,2,3,6-TBPZ	551.686	370.325	499.295	16.806	577.670	4.781	−1.344	1.146	2	2	2	1	0	0
1,2,3,7-TBPZ	552.142	364.738	493.572	11.082	577.457	4.649	−1.338	1.138	1	3	2	1	0	0
1,2,3,8-TBPZ	552.828	364.853	493.483	10.993	577.470	4.649	−1.338	1.138	1	3	2	1	0	0
1,2,3,9-TBPZ	550.648	371.073	500.354	17.864	577.690	4.781	−1.344	1.146	2	2	2	1	0	1
1,2,4,6-TBPZ	552.543	366.610	495.326	12.836	577.257	5.207	−1.347	1.153	3	1	1	1	1	1
1,2,4,7-TBPZ	553.146	360.419	488.956	6.467	576.874	5.177	−1.341	1.144	2	2	1	1	1	0
1,2,4,8-TBPZ	553.970	360.345	488.636	6.146	576.911	5.136	−1.340	1.144	2	2	1	1	1	0
1,2,4,9-TBPZ	552.079	366.426	495.278	12.789	577.107	5.306	−1.347	1.153	3	1	1	1	1	1
1,2,6,7-TBPZ	552.288	364.208	492.997	10.507	577.013	5.130	−1.341	1.143	2	2	2	0	0	0
1,2,6,8-TBPZ	553.393	359.463	487.924	5.435	576.903	5.078	−1.340	1.142	2	2	1	1	0	0
1,2,6,9-TBPZ	553.798	365.040	493.383	10.893	576.937	5.322	−1.345	1.149	3	1	1	0	1	1
1,2,7,8-TBPZ	552.108	361.829	490.673	8.184	577.024	4.930	−1.337	1.136	1	3	2	0	0	0
1,2,7,9-TBPZ	553.079	360.566	489.119	6.629	576.916	5.101	−1.340	1.142	2	2	1	1	0	1
1,2,8,9-TBPZ	552.070	365.255	494.110	11.620	576.972	5.157	−1.341	1.143	2	2	2	0	0	1
1,3,6,8-TBPZ	556.526	354.961	482.490	0.000	576.682	5.084	−1.337	1.140	2	2	0	2	0	0
1,3,6,9-TBPZ	555.430	360.401	488.255	5.766	576.778	5.301	−1.342	1.147	3	1	0	1	1	1
1,3,7,8-TBPZ	554.254	356.874	485.078	2.589	576.832	4.913	−1.335	1.134	1	3	1	1	0	0
1,3,7,9-TBPZ	556.376	355.606	483.178	0.688	576.823	4.991	−1.337	1.140	2	2	0	2	0	1
1,4,6,9-TBPZ	554.200	365.967	494.189	11.699	576.697	5.657	−1.348	1.155	4	0	0	0	2	2
1,4,7,8-TBPZ	553.049	361.742	490.306	7.816	576.783	5.222	−1.340	1.141	2	2	1	0	1	0
2,3,7,8-TBPZ	552.418	358.725	487.475	4.986	576.881	4.820	−1.333	1.129	0	4	2	0	0	0
penta-BPZ														
1,2,3,4,6-penta-BPZ	588.714	414.513	536.043	20.650	590.238	−2.422	−1.315	1.112	3	2	3	2	1	1
1,2,3,4,7-penta-BPZ	590.212	408.391	529.474	14.081	589.979	−2.544	−1.309	1.103	2	3	3	2	1	0
1,2,3,6,7-penta-BPZ	589.685	403.667	524.908	9.515	589.329	−2.139	−1.307	1.100	2	3	3	1	0	0
1,2,3,6,8-penta-BPZ	592.279	399.091	519.558	4.164	589.214	−2.227	−1.305	1.098	2	3	2	2	0	0
1,2,3,6,9-penta-BPZ	591.856	404.670	525.263	9.869	589.243	−1.963	−1.310	1.106	3	2	2	1	1	1
1,2,3,7,8-penta-BPZ	590.831	401.191	522.089	6.695	589.338	−2.374	−1.303	1.093	1	4	3	1	0	0
1,2,3,7,9-penta-BPZ	592.371	399.965	520.406	5.012	589.279	−2.263	−1.305	1.098	2	3	2	2	0	1
1,2,3,8,9-penta-BPZ	590.287	404.665	525.727	10.334	589.357	−2.170	−1.307	1.100	2	3	3	1	0	1
1,2,4,6,7-penta-BPZ	592.760	400.196	520.521	5.128	588.824	−1.706	−1.309	1.106	3	2	2	1	1	1
1,2,4,6,8-penta-BPZ	594.400	395.560	515.393	0.000	588.716	−1.777	−1.307	1.104	3	2	1	2	1	1
1,2,4,6,9-penta-BPZ	594.132	401.079	520.991	5.598	588.743	−1.509	−1.312	1.112	4	1	1	1	2	2
1,2,4,7,8-penta-BPZ	592.090	396.880	517.405	2.011	588.730	−1.845	−1.305	1.098	2	3	2	1	1	0
1,2,4,7,9-penta-BPZ	593.852	395.589	515.588	0.194	588.643	−1.702	−1.307	1.105	3	2	1	2	1	1
1,2,4,8,9-penta-BPZ	591.685	400.123	520.765	5.372	588.807	−1.679	−1.309	1.106	3	2	2	1	1	1
hexa-BPZ														
1,2,3,4,6,7-hexa-BPZ	627.512	448.276	561.837	13.461	601.923	−9.378	−1.278	1.066	3	3	4	2	1	1
1,2,3,4,6,8-hexa-BPZ	629.935	443.776	556.615	8.239	601.888	−9.493	−1.276	1.064	3	3	3	3	1	1
1,2,3,4,6,9-hexa-BPZ	629.315	449.061	562.084	13.708	601.771	−9.122	−1.281	1.072	4	2	3	2	2	2
1,2,3,4,7,8-hexa-BPZ	628.186	445.007	558.369	9.993	601.903	−9.586	−1.273	1.058	2	4	4	2	1	0
1,2,3,6,7,8-hexa-BPZ	628.395	443.539	556.838	8.462	601.785	−9.541	−1.273	1.057	2	4	4	2	0	0

Table 4. Continued

	S^Θ	$\Delta_f H^\Theta$	$\Delta_f G^\Theta$	$\Delta_f G_R^\Theta$	$C_{p,m}$/J·(J·mol^{-1}·K^{-1})									
	J·mol^{-1}·K^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	constant	$10^{-3}T$	10^5T^{-1}	10^7T^{-2}	N_α	N_β	N_o	N_m	N_p	$N_{1,9}$
1,2,3,6,7,9-hexa-BPZ	630.248	439.950	552.698	4.322	601.282	−9.073	−1.275	1.064	3	3	3	2	1	1
1,2,3,6,8,9-hexa-BPZ	629.868	439.872	552.732	4.356	601.225	−9.033	−1.275	1.064	3	3	3	2	1	1
1,2,3,7,8,9-hexa-BPZ	628.353	444.017	557.326	8.950	601.736	−9.514	−1.273	1.057	2	4	4	2	0	1
1,2,4,6,7,9-hexa-BPZ	631.110	436.288	548.775	0.399	600.674	−8.506	−1.278	1.071	4	2	2	2	2	2
1,2,4,6,8,9-hexa-BPZ	632.198	436.212	548.376	0.000	600.682	−8.545	−1.277	1.070	4	2	2	2	2	2
hepta-BPZ														
1,2,3,4,6,7,8-hepta-BPZ	667.323	488.150	593.441	4.109	614.421	−16.809	−1.243	1.023	3	4	5	3	1	1
1,2,3,4,6,7,9-hepta-BPZ	669.185	484.595	589.332	0.000	613.811	−16.253	−1.246	1.029	4	3	4	3	2	2
OBPZ														
1,2,3,4,6,7,8,9-OBPZ	704.196	532.680	630.580		626.962	−23.966	−1.215	0.989	4	4	6	4	2	2

[a] S^Θ is standard entropy; $\Delta_f H^\Theta$ is the standard enthalpy of formation of the compound; $\Delta_f G^\Theta$ is the standard Gibbs energy of formation of the compound; and $\Delta_f G_R^\Theta$ is the relative magnitude of the standard Gibbs energy of formation; $C_{p,m}^\Theta$ is molar heat capacity at constant pressure. N is the number of Br atom substitutions, and the subscript PBS indicates the positions.

Table 5. Most Stable and Unstable Isomers in Different Isomer Groups for PBPZs

compounds	most stable isomer	most unstable isomer
MBPZ	2-	1-
DBPZ	2,8-; 2,7-	1,2-
tri-BPZ	1,3,8-; 1,3,7-	1,2,3-
TBPZ	1,3,6,8-; 1,3,7,9-	1,2,3,4-
penta-BPZ	1,2,4,6,8-; 1,2,4,7,9-	1,2,3,4,6-
hexa-BPZ	1,2,3,6,8,9-; 1,2,3,6,7,9-	1,2,3,4,6,7-; 1,2,3,4,6,9-
hepta-BPZ	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

6, 9) and 2(3, 7, 8) are defined as N_α and N_β; the pair numbers of bromine at positions 1, 9 or 4, 6 are symbolized as $N_{1,9}$; and the pair numbers of bromine at ortho, meta, and para positions are symbolized as N_o, N_m, and N_p, respectively. Moreover, the parameters mentioned above are defined as a general designation N_{PBS}. N_α, N_β, N_o, N_m, and N_p for 1,2,3,6,9-penta-BPZ equals 3, 2, 2, 1, 1, respectively (see Figure 2).

Calculation of $\Delta_f H^\Theta$, $\Delta_f G^\Theta$, and $C_{p,m}$. Isodesmic reaction 1 was designed to calculate $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$ of PBPZs in this study.

$$\text{PZ} + n\text{bromobenzene} = \text{PBPZ} + n\text{benzene} \quad (1)$$

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

$$\Delta_r H^\Theta = [H_{PBPZ} + nH_{benzene}] - [H_{PZ} + nH_{bromobenzene}] \quad (2)$$

The sum of the enthalpies of formation of the products minus those of the reactants also yields $\Delta_r H^\Theta$

$$\Delta_r H^\Theta = [\Delta_f H_{PBPZ}^\Theta + n\Delta_f H_{benzene}^\Theta] - [\Delta_f H_{PZ}^\Theta + n\Delta_f H_{bromobenzene}^\Theta] \quad (3)$$

The value of $\Delta_r H^\Theta$ calculated from eq 2 was substituted into eq 3 to yield the $\Delta_f H^\Theta$ of PBPZs.

$$\Delta_f H_{PBPZ}^\Theta = H_{PBPZ}^\Theta + nH_{benzene}^\Theta - nH_{bromobenzene}^\Theta - H_{PZ}^\Theta - n\Delta_f H_{benzene}^\Theta + n\Delta_f H_{bromobenzene}^\Theta + \Delta_f H_{PZ}^\Theta \quad (4)$$

The same method was used to calculate $\Delta_f G_{PBPZ}^\Theta$, and eq 5 could be obtained

$$\Delta_f G_{PBPZ}^\Theta = G_{PBPZ}^\Theta + nG_{benzene}^\Theta - nG_{bromobenzene}^\Theta - G_{PZ}^\Theta - n\Delta_f G_{benzene}^\Theta + n\Delta_f G_{bromobenzene}^\Theta + \Delta_f G_{PZ}^\Theta \quad (5)$$

Equation 6 was used to calculate $\Delta_f G^\Theta{}_{PZ}$

$$N_2 + 12C_{Graphite} + 4H_2 = C_{12}H_8N_2 \quad (6)$$

Then

$$\Delta_r S^\Theta = S_{PZ}^\Theta - S_{N2}^\Theta - 12S_C^\Theta - 4S_{H2}^\Theta \quad (7)$$

$$\Delta_r H^\Theta = \Delta_f H_{PZ}^\Theta - \Delta_f H_{N2}^\Theta - 12\Delta_f H_C^\Theta - 4\Delta_f H_{H2}^\Theta \quad (8)$$

$$\Delta_f G_{PZ}^\Theta = \Delta_r G_{PZ}^\Theta = \Delta_r H_{PZ}^\Theta - T\Delta_r S_{PZ}^\Theta \quad (9)$$

The experimental and calculated values of $\Delta_f H^\Theta$, $\Delta_f G^\Theta$, H^Θ, G^Θ, and S^Θ for benzene, bromobenzene, phenazine, graphite, nitrogen, and hydrogen are listed in Table 1.

To validate the precision of the method, we have calculated some thermodynamic data of halogen aromatic compounds with experimental data using the method (the results are listed in Table 2).[12] The results show 2,2′-dichlorobiphenyl, benzenethiol, and 1,2-dichlorobenzene possess the largest discrepancies of $\Delta_f H^\Theta$, S^Θ, and $\Delta_f G^\Theta$, respectively, and the values are 17.0 kJ·mol^{-1}, −3.1 J·mol^{-1}·K^{-1}, and 10.7 kJ·mol^{-1}, respectively. Furthermore, we have found that the relative stabilities from calculated results are in good agreement with the ratio of these isomers measured in the environment when we studied PCDDs,[14] which indicated calculation using this method to be a valid procedure.

Then, the values of $C_{p,m}$ were calculated using a statistical thermodynamics calculation program at temperatures (200 to 1000) K based on Gaussian output files. In previous work, we have also calculated $C_{p,m}$ of 18 aromatic hydrocarbons at the temperatures between (200 to 1000) K and compared them with experimental data (the results are listed in Table 3).[12] The results show ethylbenzene possesses the largest deviation 8.13 J·mol^{-1}·K^{-1}, and the differences between values calculated and those from ref 11 are small for the other

Table 6. Molar Heat Capacity at Constant Pressure for (200 to 1000) K

	$C_{p,m}$ (J·mol^{-1}·K^{-1})									
	T (K)									
	298.10	200	300	400	500	600	700	800	900	1000
PZ	190.91	123.73	192.14	253.08	301.65	339.32	368.79	392.28	411.34	427.01
MBPZ										
1-MBPZ	207.58	141.04	208.78	268.18	315.24	351.52	379.75	402.11	420.13	434.88
2-MBPZ	208.23	141.51	209.43	268.78	315.73	351.92	380.05	402.34	420.32	435.03
DBPZ										
1,2-DBPZ	224.36	158.32	225.54	283.45	328.99	363.89	390.85	412.06	429.06	442.87
1,3-DBPZ	224.86	158.98	226.04	283.84	329.28	364.10	391.01	412.17	429.13	442.92
1,4-DBPZ	223.97	158.17	225.15	283.03	328.61	363.57	390.59	411.84	428.87	442.71
1,6-DBPZ	224.12	158.20	225.30	283.19	328.75	363.68	390.67	411.91	428.91	442.75
1,7-DBPZ	224.86	158.79	226.04	283.86	329.30	364.11	391.01	412.16	429.11	442.90
1,8-DBPZ	224.79	158.70	225.97	283.82	329.27	364.10	391.00	412.16	429.11	442.90
1,9-DBPZ	224.05	158.12	225.23	283.14	328.71	363.65	390.65	411.89	428.91	442.74
2,3-DBPZ	224.87	158.60	226.05	283.95	329.41	364.23	391.12	412.27	429.22	443.00
2,7-DBPZ	225.40	159.14	226.58	284.37	329.72	364.44	391.26	412.36	429.26	443.02
2,8-DBPZ	225.51	159.25	226.69	284.46	329.79	364.50	391.31	412.39	429.29	443.04
tri-BPZ										
1,2,3-tri-BPZ	241.35	175.86	242.50	298.95	342.96	376.46	402.14	422.18	438.12	450.99
1,2,4-tri-BPZ	240.88	175.78	242.03	298.39	342.43	375.99	401.74	421.84	437.82	450.73
1,2,6-tri-BPZ	240.93	175.50	242.08	298.49	342.53	376.07	401.80	421.88	437.85	450.75
1,2,7-tri-BPZ	241.68	176.10	242.84	299.17	343.08	376.51	402.13	422.14	438.05	450.90
1,2,8-tri-BPZ	241.66	176.06	242.81	299.16	343.08	376.51	402.14	422.15	438.06	450.91
1,2,9-tri-BPZ	240.95	175.53	242.10	298.50	342.54	376.08	401.80	421.89	437.86	450.75
1,3,6-tri-BPZ	241.41	176.15	242.57	298.86	342.81	376.28	401.95	421.99	437.92	450.80
1,3,7-tri-BPZ	242.09	176.63	243.24	299.49	343.32	376.68	402.26	422.23	438.11	450.94
1,3,8-tri-BPZ	242.07	176.62	243.22	299.46	343.30	376.66	402.25	422.22	438.10	450.93
1,3,9-tri-BPZ	241.41	176.14	242.57	298.87	342.81	376.28	401.95	421.99	437.92	450.80
1,4,6-tri-BPZ	240.52	175.35	241.68	298.05	342.14	375.74	401.52	421.65	437.66	450.59
1,4,7-tri-BPZ	241.15	175.77	242.31	298.64	342.63	376.13	401.83	421.89	437.84	450.73
2,3,6-tri-BPZ	241.46	175.78	242.62	299.03	342.99	376.44	402.09	422.12	438.04	450.90
2,3,7-tri-BPZ	242.27	176.46	243.42	299.75	343.57	376.91	402.46	422.40	438.26	451.08
TBPZ										
1,2,3,4-TBPZ	257.66	192.97	258.79	313.81	356.40	388.59	413.08	432.03	446.97	458.94
1,2,3,6-TBPZ	257.88	193.01	259.01	313.96	356.48	388.62	413.07	431.99	446.91	458.86
1,2,3,7-TBPZ	258.60	193.53	259.74	314.63	357.03	389.06	413.41	432.26	447.12	459.02
1,2,3,8-TBPZ	258.59	193.55	259.73	314.62	357.02	389.05	413.40	432.25	447.11	459.02
1,2,3,9-TBPZ	257.80	192.89	258.93	313.90	356.44	388.59	413.04	431.97	446.89	458.85
1,2,4,6-TBPZ	257.32	192.82	258.45	313.33	355.91	388.13	412.66	431.64	446.62	458.61
1,2,4,7-TBPZ	258.03	193.34	259.16	313.97	356.43	388.53	412.97	431.88	446.80	458.75
1,2,4,8-TBPZ	258.12	193.44	259.25	314.06	356.50	388.59	413.01	431.92	446.83	458.78
1,2,4,9-TBPZ	257.29	192.78	258.42	313.30	355.88	388.10	412.63	431.62	446.60	458.60
1,2,6,7-TBPZ	257.87	192.97	259.00	313.90	356.39	388.53	412.98	431.90	446.82	458.78
1,2,6,8-TBPZ	258.18	193.37	259.31	314.13	356.57	388.65	413.06	431.95	446.85	458.79
1,2,6,9-TBPZ	257.43	192.78	258.56	313.44	355.99	388.19	412.70	431.67	446.63	458.62
1,2,7,8-TBPZ	258.38	193.19	259.51	314.43	356.85	388.90	413.28	432.15	447.02	458.94
1,2,7,9-TBPZ	258.11	193.30	259.25	314.08	356.53	388.62	413.04	431.94	446.84	458.79
1,2,8,9-TBPZ	257.85	192.92	258.98	313.89	356.39	388.52	412.97	431.90	446.82	458.78
1,3,6,8-TBPZ	258.61	193.98	259.74	314.45	356.79	388.81	413.17	432.02	446.89	458.82
1,3,6,9-TBPZ	257.78	193.23	258.90	313.70	356.18	388.33	412.79	431.73	446.67	458.64
1,3,7,8-TBPZ	258.70	193.66	259.84	314.66	357.01	389.00	413.34	432.17	447.02	458.93
1,3,7,9-TBPZ	258.61	193.95	259.74	314.47	356.82	388.83	413.19	432.04	446.91	458.83
1,4,6,9-TBPZ	256.87	192.46	258.00	312.86	355.48	387.77	412.36	431.39	446.40	458.43
1,4,7,8-TBPZ	257.88	192.93	259.01	313.91	356.39	388.51	412.95	431.87	446.79	458.75
2,3,7,8-TBPZ	258.78	193.35	259.91	314.83	357.19	389.17	413.48	432.30	447.13	459.03
penta-BPZ										
1,2,3,4,6-penta-BPZ	274.14	210.05	275.24	328.78	369.90	400.75	424.01	441.85	455.77	466.82
1,2,3,4,7-penta-BPZ	274.91	210.63	276.02	329.49	370.48	401.21	424.37	442.12	455.98	466.99
1,2,3,6,7-penta-BPZ	274.63	210.22	275.74	329.22	370.23	400.99	424.18	441.96	455.84	466.86
1,2,3,6,8-penta-BPZ	275.10	210.84	276.21	329.59	370.50	401.19	424.32	442.05	455.90	466.90
1,2,3,6,9-penta-BPZ	274.32	210.17	275.43	328.87	369.92	400.73	423.96	441.78	455.69	466.74
1,2,3,7,8-penta-BPZ	275.23	210.58	276.34	329.81	370.73	401.40	424.50	442.21	456.04	467.02
1,2,3,7,9-penta-BPZ	275.10	210.81	276.21	329.60	370.52	401.20	424.34	442.07	455.92	466.91
1,2,3,8,9-penta-BPZ	274.72	210.32	275.83	329.30	370.30	401.04	424.23	442.00	455.87	466.89
1,2,4,6,7-penta-BPZ	274.31	210.33	275.42	328.78	369.81	400.61	423.86	441.68	455.60	466.66
1,2,4,6,8-penta-BPZ	274.70	210.82	275.80	329.09	370.03	400.78	423.97	441.76	455.65	466.69
1,2,4,6,9-penta-BPZ	273.85	210.11	274.95	328.30	369.38	400.26	423.57	441.44	455.40	466.49
1,2,4,7,8-penta-BPZ	274.76	210.47	275.87	329.26	370.21	400.94	424.12	441.89	455.77	466.79
1,2,4,7,9-penta-BPZ	274.57	210.71	275.68	328.97	369.93	400.69	423.90	441.70	455.60	466.65
1,2,4,8,9-penta-BPZ	274.21	210.20	275.32	328.71	369.74	400.56	423.82	441.65	455.57	466.64
hexa-BPZ										
1,2,3,4,6,7-hexa-BPZ	290.97	227.36	292.05	344.11	383.71	413.16	435.16	451.84	464.72	474.84
1,2,3,4,6,8-hexa-BPZ	291.38	227.90	292.46	344.43	383.94	413.34	435.29	451.93	464.78	474.87
1,2,3,4,6,9-hexa-BPZ	290.53	227.20	291.62	343.64	383.29	412.81	434.88	451.61	464.53	474.68
1,2,3,4,7,8-hexa-BPZ	291.54	227.67	292.63	344.69	384.19	413.56	435.48	452.09	464.92	475.00

Table 6. Continued

	$C_{p,m}$ (J·mol^{-1}·K^{-1})									
	T (K)									
	298.10	200	300	400	500	600	700	800	900	1000
1,2,3,6,7,8-hexa-BPZ	291.58	227.70	292.67	344.71	384.21	413.56	435.48	452.09	464.91	474.99
1,2,3,6,7,9-hexa-BPZ	291.09	227.59	292.17	344.13	383.67	413.10	435.08	451.76	464.63	474.75
1,2,3,6,8,9-hexa-BPZ	291.04	227.54	292.12	344.09	383.63	413.06	435.05	451.73	464.61	474.73
1,2,3,7,8,9-hexa-BPZ	291.56	227.66	292.64	344.69	384.19	413.55	435.46	452.07	464.90	474.98
1,2,4,6,7,9-hexa-BPZ	290.50	227.42	291.58	343.45	383.04	412.56	434.63	451.37	464.31	474.48
1,2,4,6,8,9-hexa-BPZ	290.61	227.54	291.69	343.55	383.12	412.62	434.67	451.41	464.34	474.50
				hepta-BPZ						
1,2,3,4,6,7,8-hepta-BPZ	307.95	244.88	309.02	359.63	397.71	425.76	446.48	461.99	473.81	482.98
1,2,3,4,6,7,9-hepta-BPZ	307.47	244.81	308.53	359.05	397.16	425.29	446.08	461.66	473.53	482.75
				OBPZ						
1,2,3,4,6,7,8,9-OBPZ	324.16	261.90	325.20	374.41	411.08	437.85	457.40	471.83	482.66	490.93

compounds (see Table 3), which indicates the method used in this study possesses high precision.

Results and Discussion

Relation of the Number and Position of Bromine Substitutes (N_{PBS}) to S^Θ. Up to date, there were no reports on experimental thermodynamic data of PBPZs systematically. The entropy (S^Θ) can be directly obtained from the output files of Gaussian programs and is presented in Table 4.

Using the multiple linear regression method of the SPSS 12.0 for the Windows program, the relation of the number and position of bromine substitutes to S^Θ can be seen in eq 10.

$$S^\Theta = 93.98 + 9.64N_\alpha + 9.84N_\beta - 0.59N_o \qquad R^2 = 1.000,\ \mathrm{SD} = 0.12 \quad (10)$$

The squared regression coefficient R^2 is 1.000, and the standard deviation SD is 0.12. From eq 10, the number of bromine substitutes has an obvious effect on entropy, but the spatial effect of bromine on the parameter S^Θ is minor. This is because S^Θ expresses the degree of disorder, and the degree of disorder increases with an increase in the number of bromine substitutes. The S^Θ value is increased 10 J·mol^{-1}·K^{-1} by increasing each bromine atom to PBPZs.

Calculated Results of $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$ Values. With the design of isodesmic reactions mentioned above (eqs 4 and 5), $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$ of PBPZs were obtained and also presented in Table 4. 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 substituents were summarized and presented in eq 11 and eq 12, respectively. The correlations of both eq 11 and eq 12 are very well due to the corresponding larger R^2 (0.9995 and 0.9991, respectively), both of which clearly represent the influence of the number of bromine position and the position of bromine on the value of $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$.

$$\Delta_f H^\Theta = 235.82 + 30.41N_\alpha + 26.02N_\beta + 1.20N_{1,9} + 8.88N_o + 2.83N_m + 1.58N_p \qquad R^2 = 0.9995,\ \mathrm{SD} = 1.30 \quad (11)$$

$$\Delta_f G^\Theta = 397.66 + 21.97N_\alpha + 17.34N_\beta + 1.15N_{1,9} + 9.62N_o + 2.85N_m + 1.63N_p \qquad R^2 = 0.9991,\ SD = 1.34 \quad (12)$$

It is suggested that $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$ of PBPZs vary greatly with the positions of bromine substitution, with an increasing order of these parameters being position α > position β. It was also found that $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$ increase with two bromines replaced at the same aromatic ring, with the following order: ortho > meta > para.

Of the PBPZ compounds in each isomer group, the isomers with lower relative standard Gibbs energy of formation are relatively more stable, whereas those with the higher relative standard Gibbs energy of formation are more unstable. To investigate relative Gibbs energies of formation we take the lowest $\Delta_f G^\Theta$ of isomers with the same numbers of substituent bromine atoms to be zero, so the relative standard Gibbs energies of formation ($\Delta_f G_R^\Theta$, the values are listed in Table 4) were obtained, by $\Delta_f G^\Theta$ of other isomers minus the lowest $\Delta_f G^\Theta$ of isomers with the same substituent numbers. Then, according to the magnitude of $\Delta_f G^\Theta$, the theoretic relative stability orders of the isomers were proposed, the most stable isomer and the most unstable one are listed in Table 5. As can be observed from Table 5, the most unstable isomers in MBPZs, DBPZs, tri-BPZs, TBPZs, penta-BPZs, hexa-BPZs, and hepta-BPZs 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 as possible, so that the bromines can be apart from each other.

Temperature Dependence of $C_{p,m}$ for PBPZs. The values of molar heat capacity at constant pressure ($C_{p,m}$) for PBPZ congeners have not been reported. The values of $C_{p,m}$ [(200 to 1000) K] have been accordingly calculated using a statistical thermodynamics calculation program based on Gaussian output files, and these $C_{p,m}$ values were listed in Table 6.

Using the calculated values of $C_{p,m}$ of PBPZs at different temperature (T), the relations between $C_{p,m}$ and temperature were obtained using the least-squares method. Regression coefficients for $10^{-3}T$, 10^5T^{-1}, 10^7T^{-2}, and constant are listed in Table 4 (the correlation coefficients (R^2) are all very close to or equal to 1.0, and all the standard deviations (SD) are low), which shows that the $C_{p,m}$ values of PBPZs are in direct ratio to T^{-1} and have an inverse proportion to T^{-2}.

Conclusions

76 PBPZs were fully optimized at the B3LYP/6-31G* level, and thus their H^Θ, G^Θ, and S^Θ were consequently obtained. In addition, the $\Delta_f H^\Theta$ and $\Delta_f G^\Theta$ of each PBPZ molecule were calculated by isodesmic reactions. The results showed that all these thermodynamic parameters are greatly dependent on N_{PBS}. So, the enthalpies and Gibbs energies of formation for 76 PBPZs should be valuable in further thermodynamic modeling studies. Moreover, it is found that there is a very good relationship between $C_{p,m}$ and temperature for the PBPZ congeners.

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