Thermodynamic Properties of Polychlorinated Biphenyls in the Gas Phase

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The molecular structures, vibrational frequencies, and internal rotational potentials of 209 polychlorinated biphenyls were computed at the B3LYP/6-31G(d,p) density functional theory level. Standard entropies, $S°(T)$, heat capacities, $C_p°(T)$, and enthalpies, $H°(T) - H°(0)$ (100 K ≤ T ≤ 1500 K), were calculated using the rigid-rotor harmonic-oscillator approximation with correction for internal rotation. Enthalpies of formation, $\Delta_f H°_{298}$, were calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level using isodesmic reactions and the recommended $\Delta_f H°_{298}$ values for biphenyl, benzene, and polychlorinated benzenes. The uncertainties of the calculated values are estimated to be 5−10 J K^{-1} mol^{-1} for $S°_{298}$ and $C°_{p\,298}$ and 5−35 kJ mol^{-1} for $\Delta_f H°_{298}$. The calculated thermodynamic properties are compared with values determined earlier by the semiempirical and group additivity methods.

Introduction

Polychlorinated biphenyls (PCBs) belong to the most toxic environmental pollutants. Along with polychlorinated dibenzo-*p*-dioxins and dibenzofurans, PCBs are produced in the incineration of municipal waste and metallurgical and other industrial processes. As a consequence, the thermodynamic properties of PCBs are important for understanding and predicting the reaction pathways, rate constants, and equilibrium constants in order to minimize their formation in different processes, thereby protecting the environment.

Experimental data are available only on enthalpies of formation of 2,2′- and 4,4′-dichlorobiphenyl.[1,2] Several group additivity (GA) estimations[3−7] and semiempirical calculations[8,9] have been done to predict the thermodynamic properties of PCBs; however, their results were diverged considerably. Recently, Saito and Fuwa[9] calculated the thermodynamic properties ($S°_{298}$, $C_p°(T)$, and $\Delta_f H°_{298}$) of all PCB congeners using the semiempirical PM3 method. From comparison of the calculated and experimental values for some related compounds, uncertainties of 1−9 J K^{-1} mol^{-1} were suggested for the calculated $S°_{298}$ values, whereas the maximum error in the calculated $\Delta_f H°_{298}$ values was estimated to be 28 kJ mol^{-1}. Since the difference between the $S°_{298}$ values estimated by the PM3[9] and GA[4,5] methods was much outside the indicated computational errors, it would be interesting to determine the thermodynamic properties of PCBs from theoretical calculation of higher level. In this study, the thermodynamic properties of PCBs in the gas phase were calculated using the B3LYP density functional theory level. Besides, in this work, the torsional motion about the central C−C bond was treated as hindered internal rotation compared to previous results[9] where the internal rotational mode was treated as harmonic-oscillator vibration. We hope that careful consideration can provide reliable thermochemical estimates for the solution of different complex chemical problems.

Calculation Methods

The density functional calculations were performed using the Gaussian 98 software package.[10] The structural parameters were fully optimized at the B3LYP/6-31G(d,p) level. Vibrational frequencies, zero-point energies, and thermal corrections were calculated at the same level. A scaling factor of 0.97 was applied to calculate the harmonic frequencies. This value was determined from comparison between the calculated and experimental frequencies[11] for biphenyl and 4,4′-dichlorobiphenyl; it is close to a scale factor of 0.96 which is recommended for B3LYP/6-31G(d) frequencies.[12] The scaled frequencies were used in the calculation of zero-point energies and thermal corrections as well as of the vibrational contributions to entropy, heat capacity, and other thermodynamic functions. The barriers for internal rotation at 0° (ΔE_0), 90° (ΔE_{90}), and 180° (ΔE_{180}) were determined from optimization of the corresponding transition states. The potential energy curve for PCBs with torsional angles of $\varphi_{min} = 75-90°$ is very flat in the vicinity of 90°. In this case, the potential energy as a function of torsional angle was determined by scanning the dihedral angle in the range 50−130° by 15° increments and allowing the remaining structural parameters to be optimized. The calculated energy values were fitted to the torsional potential function, which is a Fourier cosine-based function:

$$V(\varphi) = \frac{1}{2}\sum_{n=1}^{6} V_n(1 - \cos n\varphi) \qquad (1)$$

where φ is the torsional angle.

The entropies, $S°(T)$, heat capacities, $C_p°(T)$, and enthalpies, $H°(T) - H°(0)$ (100 K ≤ T ≤ 1500 K), were calculated by standard statistical thermodynamic formulas using the rigid-rotor harmonic-oscillator approximation. The torsional frequency, corresponding to the internal rotation about the central C−C bond, was omitted in the calculation of the thermodynamic functions. The internal rotational contribution was calculated by direct summation over the energy levels obtained by diagonalizing the Hamiltonian matrix associated with the potential function from eq 1. Enthalpies of formation, $\Delta_f H°_{298}$, were calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level using isodesmic reactions and the recom-

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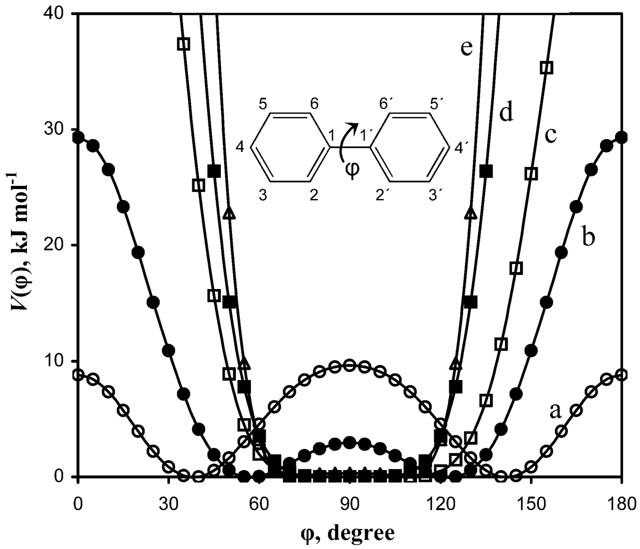


Figure 1. Torsional potential curves for non-, mono-, di-, tri-, and tetra-*ortho*-chlorinated PCBs: (a) 3,3′,5,5′; (b) 2,3′,5,5′; (c) 2,2′,5,5′, $\Delta E_0 = 121$ kJ mol^{-1}; (d) 2,2′,5,6′, $\Delta E_0 = 204$ kJ mol^{-1}; (e) 2,2′,6,6′, $\Delta E_0 = 437$ kJ mol^{-1}.

mended $\Delta_f H^\circ_{298}$ values for biphenyl, benzene, and polychlorinated benzenes.[2]

Results and Discussion

Geometries, Vibrational Frequencies, and Torsional Potentials. Our results of B3LYP/6-31G(d,p) calculations for 119 PCB congeners were described earlier in detail.[13] In this work, the structural parameters and vibrational frequencies were calculated for all 209 PCBs and torsional potentials were determined for 154 isomers. The potential functions for the remaining PCBs were estimated considering their similarity within the differentiated groups (see below). The calculated dihedral angles, φ, symmetry, products of the principal moments of inertia, vibrational frequencies, and potential coefficients, V_n, in eq 1 are listed in the Supporting Information (Supporting Information Tables 1S−3S).

Almost all previous theoretical results for PCBs were obtained from semiempirical calculations or ab initio Hartree−Fock (HF) calculations with the STO-3G minimal basis set.[8,14−19] The rotational barriers for all 209 PCBs were calculated by Andersson et al.[17] using a semiempirical AM1 method. For non- and mono-*ortho*-chlorinated PCBs (*ortho* chlorine atoms are the atoms attached in one or more of the following positions: 2, 2′, 6, and 6′; see the numbering of the atoms in Figure 1), the calculated values of torsional barriers are close to those obtained in this work. However, the discrepancies increase as the number of *ortho* chlorine atoms increases: the AM1 torsional barriers for PCBs with two to four *ortho* chlorine atoms are 10−80 kJ mol^{-1} lower than the values calculated at the B3LYP/6-31G(d,p) level. Only Arulmozhiraja et al.[20] optimized the geometry of six PCBs at the B3LYP/6-311+G(2d,2p) level; their values of the structural parameters and torsional barriers for the 2,2′,5,5′-, 3,3′,4,4′-, 2,2′,4,5,5′-, 2,3′,4,4′,5-, 3,3′,4,4′,5-, and 3,3′,4,4′,5,5′-isomers are close to those obtained in this work from B3LYP/6-31G(d,p) calculations.

From the results obtained in this work, it is clear that the number of *ortho* chlorine atoms has a major influence on the torsional angles and rotational barriers of PCBs, whereas the effect of adjacent *meta* chlorine atoms is much smaller. Depending on the number of *ortho* (n_{ortho}) and adjacent *meta* (n_{meta}) chlorine atoms, 209 PCBs are sorted into 18 groups (Table 1). The internal rotational behavior of the PCB congeners is very similar inside these groups. All molecules without *ortho* substitution (group 1 in Table 1) have an energy minimum at 38°, and barriers of 8 and 10 kJ mol^{-1} occur at 0°(180°) and 90°. For PCBs with one *ortho* chlorine atom, the conformation is more twisted ($\varphi = 56°$) and the ΔE_0 barrier increases to 28 kJ mol^{-1}, while the ΔE_{90} barrier decreases to 3 kJ mol^{-1} (group 2 in Table 1). The presence of a *meta* chlorine atom adjacent to an *ortho* chlorine atom causes further increase of ΔE_0 (34 kJ mol^{-1}) and decrease of ΔE_{90} (2 kJ mol^{-1}) (group 3 in Table 1). The PCBs with two to four *ortho* chlorine atoms (groups 4−18 in Table 1) have orthogonal or near-orthogonal conformations and no barrier at 90°. The values of ΔE_0 increase substantially when an *ortho* chlorine atom is added. The increase in barrier heights is much less for each added *meta* chlorine atom. Note that the congeners with 2,2′- and 2,6-di-*ortho* substitution are placed in different groups, since the ΔE_0 barriers are substantially higher than ΔE_{180} for PCBs with 2,2′ substitution. The potential energy curves for non-, mono-, di-, tri-, and tetra-*ortho*-chlorinated PCBs are shown in Figure 1.

Entropies and Heat Capacities. The ideal gas entropies and heat capacities for mono-, di-, and trichlorobiphenyls were estimated in TRC tables[4] using empirical correlations. These data were accepted by Holmes et al.,[5] whereas the S°_{298} values of the remaining PCBs were estimated by the GA method. The thermodynamic functions of 4,4′-dichlorobiphenyl were also calculated by the statistical thermodynamics method using experimental and estimated molecular parameters.[21] The S°_{298} and $C^\circ_p(T)$ values of all PCBs were predicted by Saito and Fuwa[9] from semiempirical PM3 calculation. There is substantial discrepancy in the results estimated by the PM3[9] and GA[4,5] methods.

Before proceeding to the calculation of the thermodynamic functions of PCBs, we have estimated the thermodynamic functions of biphenyl.[22] Earlier, the thermodynamic functions of biphenyl were calculated by statistical thermodynamics, but none of the results were in good agreement with the ideal gas entropies determined from calorimetric measurements (see ref 22 and references therein). Discrepancies in statistical calculations arose essentially from uncertainty in the torsional barriers. In our calculation,[22] we used molecular parameters, including the ΔE_0 and ΔE_{90} barriers, determined from B3LYP calculations. The entropy values calculated with B3LYP/6-31G(d,p) molecular parameters led to the best agreement with calorimetric data compared to statistical calculations published earlier. Considering this result for biphenyl, it was decided to use the same way to predict the thermodynamic functions of PCBs.

In this work, the thermodynamic functions of PCBs ($S^\circ(T)$, $C^\circ_p(T)$, and $H^\circ(T) - H^\circ(0)$) in the temperature range from 100 to 1500 K were obtained using molecular parameters (Supporting Information Tables 1S−3S) from B3LYP/6-31G(d,p) calculations. The calculated values of S°_{298} and $C^\circ_{p\,298}$ are given in Table 2; their uncertainties are estimated to be 5−10 J K^{-1} mol^{-1}. Full tables of the thermodynamic functions (100 K $\leq T \leq$ 1500 K) are collected in Supporting Information Table 4S. The coefficients in the equation for $C^\circ_p(T)$ approximation (200 K $\leq T \leq$ 1000 K) are given in Supporting Information Table 5S. The polynomials reproduce the calculated values within 1 J K^{-1} mol^{-1}.

Figures 2 and 3 show the comparison of the calculated $C^\circ_{p\,298}$ and $S^\circ_{int\,298}$[23] values with those predicted by the PM3 and GA methods. As seen from these figures, there is a stepwise change

TABLE 1: Average Values of Torsional Angles (deg) and Rotational Barriers (kJ mol^{-1}) of PCBs Calculated at the B3LYP/6-31G(d,p) Level

group	n_{ortho}	n_{meta}	PCB isomers	φ	ΔE_0	ΔE_{90}	ΔE_{180}
1	0	0	3; 4; 3,4; 3,4′; 3,5; 4,4′; 3,3′,5; 3,4,4′; 3,4,5; 3,4′,5; 3,3′,4,5; 3,3′,4,5′; 3,3′,5,5′; 3,4,4′,5; 3,3′,4,4′,5; 3,3′,4,5,5′; 3,3′,4,4′,5,5′	38.3	8.3	10.3	8.3
			syn−anti:[a] 3,3′; 3,3′,4; 3,3′,4,4′	38.2	8.4	10.2	8.0
2	1	0	2; 2,4; 2,4′; 2,5; 2,3′,5′; 2,4,4′; 2,4,5; 2,4′,5; 2,3′,4,5′; 2,3′,4′,5′; 2,3′,5,5′; 2,4,4′,5; 2,3′,4,4′,5′; 2,3′,4,5,5′; 2,3′,4′,5,5′; 2,3′,4,4′,5,5′	55.8	28.6	3.4	28.6
			syn−anti:[a] 2,3′; 2,3′,4; 2,3′,4′; 2,3′,5; 2,3′,4,4′; 2,3′,4,5; 2,3′,4′,5; 2,3′,4,4′,5	55.9	28.5	3.1	28.3
3	1	1	2,3; 2,3,4; 2,3,4′; 2,3,5; 2,3,3′,5′; 2,3,4,4′; 2,3,4,5; 2,3,4′,5; 2,3,3′,4,5′; 2,3,3′,4′,5′; 2,3,3′,5,5′; 2,3,4,4′,5; 2,3,3′,4,4′,5′; 2,3,3′,4,5,5′; 2,3,3′,4′,5,5′; 2,3,3′,4,4′,5,5′	59.1	34.2	2.5	34.2
			syn−anti:[a] 2,3,3′; 2,3,3′,4; 2,3,3′,4′; 2,3,3′,5; 2,3,3′,4,4′; 2,3,3′,4,5; 2,3,3′,4′,5; 2,3,3′,4,4′,5	59.3	34.0	2.2	33.8
4	2 (2,6)	0	2,6; 2,3′,6; 2,4,6; 2,4′,6; 2,3′,4,6; 2,3′,4′,6; 2,3′,5′,6; 2,4,4′,6; 2,3′,4,4′,6; 2,3′,4,5′,6; 2,3′,4′,5′,6; 2,3′,4,4′,5′,6	83.1	77.2	0.0	77.2
5	2 (2,6)	1	2,3,6; 2,3,4,6; 2,3,4′,6; 2,3,3′,5′,6; 2,3,4,4′,6; 2,3,3′,4,5′,6; 2,3,3′,4′,5′,6; 2,3,3′,4,4′,5′,6	88.9	87.5	0.0	87.5
			syn−anti:[a] 2,3,3′,6; 2,3,3′,4,6; 2,3,3′,4′,6; 2,3,3′,4,4′,6	89.4	87.8	0.0	87.8
6	2 (2,6)	2	2,3,5,6; 2,3,3′,5,6; 2,3,4,5,6; 2,3,4′,5,6; 2,3,3′,4,5,6; 2,3,3′,4′,5,6; 2,3,3′,5,5′,6; 2,3,4,4′,5,6; 2,3,3′,4,4′,5,6; 2,3,3′,4,5,5′,6; 2,3,3′,4′,5,5′,6; 2,3,3′,4,4′,5,5′,6	89.8	99.6	0.0	99.6
7	2 (2,2′)	0	2,2′; 2,2′,4; 2,2′,5; 2,2′,4,4′; 2,2′,4,5; 2,2′,4,5′; 2,2′,5,5′; 2,2′,4,4′,5; 2,2′,4,5,5′; 2,2′,4,4′,5,5′	82.1	120.0	0.1	66.1
8	2 (2,2′)	1	2,2′,3; 2,2′,3,4; 2,2′,3,4′; 2,2′,3,5; 2,2′,3,5′; 2,2′,3,4,4′; 2,2′,3,4,5; 2,2′,3,4,5′; 2,2′,3,4′,5; 2,2′,3,4′,5′; 2,2′,3,5,5′; 2,2′,3,4,4′,5; 2,2′,3,4,4′,5′; 2,2′,3,4,5,5′; 2,2′,3,4′,5,5′; 2,2′,3,4,4′,5,5′	83.3	131.8	0.1	75.9
9	2 (2,2′)	2	2,2′,3,3′; 2,2′,3,3′,4; 2,2′,3,3′,5; 2,2′,3,3′,4,4′; 2,2′,3,3′,4,5; 2,2′,3,3′,4,5′; 2,2′,3,3′,5,5′; 2,2′,3,3′,4,4′,5; 2,2′,3,3′,4,5,5′; 2,2′,3,3′,4,4′,5,5′	86.5	145.8	0.0	86.5
10	3	0	2,2′,6; 2,2′,4,6; 2,2′,4,6′; 2,2′,5,6′; 2,2′,4,4′,6; 2,2′,4,5,6′; 2,2′,4,5′,6; 2,2′,4,4′,5,6′	90.7	203.9	0.0	203.9
11	3	1	2,2′,3,6′; 2,2′,3,4,6′; 2,2′,3,4′,6′; 2,2′,3,5,6′; 2,2′,3,4,4′,6′; 2,2′,3,4,5,6′; 2,2′,3,4′,5,6′; 2,2′,3,4,4′,5,6′	90.8	221.6	0.0	221.6
			syn−anti:[a] 2,2′,3,6; 2,2′,3,4,6; 2,2′,3,4′,6; 2,2′,3,5′,6; 2,2′,3,4,4′,6; 2,2′,3,4,5′,6; 2,2′,3,4′,5′,6; 2,2′,3,4,4′,5′,6	90.8	215.4	0.0	221.8
12	3	2	2,2′,3,5,6; 2,2′,3,4,5,6; 2,2′,3,4′,5,6; 2,2′,3,5,5′,6; 2,2′,3,4,4′,5,6; 2,2′,3,4,5,5′,6; 2,2′,3,4′,5,5′,6; 2,2′,3,4,4′,5,5′,6	90.5	236.0	0.0	236.0
			syn−anti:[a] 2,2′,3,3′,6; 2,2′,3,3′,4,6; 2,2′,3,3′,4,6′; 2,2′,3,3′,5,6′; 2,2′,3,3′,4,4′,6; 2,2′,3,3′,4,5,6′; 2,2′,3,3′,4,5′,6; 2,2′,3,3′,4,4′,5,6′	91.1	236.1	0.0	241.4
13	3	3	2,2′,3,3′,5,6; 2,2′,3,3′,4,5,6; 2,2′,3,3′,4,5′,6′; 2,2′,3,3′,5,5′,6; 2,2′,3,3′,4,4′,5,6; 2,2′,3,3′,4,5,5′,6; 2,2′,3,3′,4,5,5′,6′; 2,2′,3,3′,4,4′,5,5′,6	90.9	258.4	0.0	258.4
14	4	0	2,2′,6,6′; 2,2′,4,6,6′; 2,2′,4,4′,6,6′	90.0	434.7	0.0	434.7
15	4	1	2,2′,3,6,6′; 2,2′,3,4,6,6′; 2,2′,3,4′,6,6′; 2,2′,3,4,4′,6,6′	90.2	456.5	0.0	456.5
16	4	2	2,2′,3,5,6,6′; 2,2′,3,4,5,6,6′; 2,2′,3,4′,5,6,6′; 2,2′,3,4,4′,5,6,6′	90.0	487.4	0.0	487.4
			syn−anti:[a] 2,2′,3,3′,6,6′; 2,2′,3,3′,4,6,6′; 2,2′,3,3′,4,4′,6,6′	90.4	487.3	0.0	476.6
17	4	3	2,2′,3,3′,5,6,6′; 2,2′,3,3′,4,5,6,6′; 2,2′,3,3′,4,5′,6,6′; 2,2′,3,3′,4,4′,5,6,6′	90.2	514.0	0.0	514.0
18	4	4	2,2′,3,3′,5,5′,6,6′; 2,2′,3,3′,4,5,5′,6,6′; 2,2′,3,3′,4,4′,5,5′,6,6′	90.0	553.3	0.0	553.3

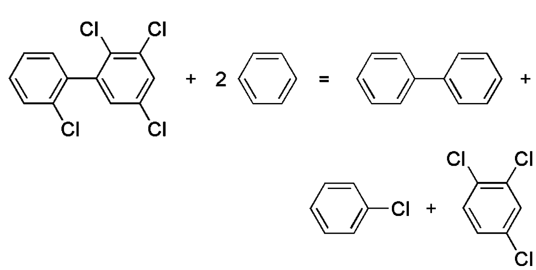
[a] For these PCBs, the potential energy curve is unsymmetrical about 90° and $\Delta E_0 \neq \Delta E_{180}$. For details, see ref 13.

in the B3LYP $C^{\circ}_{p\,298}$ and $S^{\circ}_{int\,298}$ values depending on the number of chlorine atoms in the PCBs, whereas the change is only a slight one for PCB isomers with the same number of chlorine atoms. According to Figure 3 and Table 2, the *ortho* chlorine atoms have no influence on the entropy values. As for the heat capacity, the $C^{\circ}_{p\,298}$ values for all isomers without *ortho* chlorine atoms are 3−5 J K^{-1} mol^{-1} higher than those for *ortho*-chlorinated PCBs (Table 2). This can also be seen in Figure 2, where the last open circles in each row with one to six chlorine atoms (just these circles are non-*ortho*-chlorinated PCBs) are somewhat higher than other circles in the row.

Special attention should be given to good agreement between the values of $C^{\circ}_{p\,298}$ and S°_{298} calculated in this work and predicted by the GA approach.[4,5] The $C^{\circ}_{p\,298}$ values were estimated by GA only for the mono-, di-, and trichlorobiphenyls.[4] These values agree with the $C^{\circ}_{p\,298}$ values calculated in this work within 2.5 J K^{-1} mol^{-1}. The discrepancies between the B3LYP and GA entropies amount to 20 J K^{-1} mol^{-1}. This value falls outside the uncertainties of the S°_{298} values calculated in this work, but not very dramatically. It is interesting to note that the GA method[4,5] predicted higher $S^{\circ}_{int\,298}$ values for non-*ortho*-chlorinated PCBs (in Figure 3, see the last triangles in each $S^{\circ}_{int\,298}$ row with one to six chlorine atoms), while we found similar behavior for $C^{\circ}_{p\,298}$. It seems somewhat surprising that the results obtained by these two methods are in rather good agreement, especially for highly chlorinated PCBs. The GA values[4,5] for PCBs had their bases in the $C^{\circ}_{p\,298}$ and S°_{298} values for biphenyl and 2,2′- and 4,4′-dichlorobiphenyl calculated from molecular parameters. Thus, one would expect larger errors in the GA prediction for PCBs with four or more chlorine atoms. The fact that the discrepancies between the B3LYP and GA entropies decrease as the number of chlorine atoms increases appears to be accidental in character.

Contrary to the GA estimations, the $C^{\circ}_{p\,298}$ and S°_{298} values estimated by the semiempirical PM3 method[9] are much different from the B3LYP values. The $C^{\circ}_{p\,298}$ values calculated in this work are 43−106 J K^{-1} mol^{-1} lower than the PM3 values, and the S°_{298} values are 45−172 J K^{-1} mol^{-1} higher. Moreover, the PM3 values increase monotonically, whereas $C^{\circ}_{p\,298}$ and S°_{298} from B3LYP show a stepwise change. It is unlikely that the results of the PM3 and B3LYP calculations may differ so greatly. In support of this conjecture, the $C^{\circ}_{p\,298}$ and S°_{298} values of biphenyl were calculated by the PM3 method in this work (Table 3). As seen in Table 3, our PM3 values differ from the B3LYP values by only 6 J K^{-1} mol^{-1}. It may be suggested that the large discrepancy with the values of Saito and Fuwa[9] is the result of their error in the statistical thermodynamics calculations.

Enthalpies of Formation. The isodesmic reactions with group balance like that in eq 2 were selected to determine the $\Delta_f H^{\circ}_{298}$ values of PCBs.



(2)

Biphenyl, benzene, and polychlorinated benzenes were used as

TABLE 2: Ideal Gas Thermodynamic Properties of PCBs

PCB isomer	$C^\circ_{p\,298}$ [a]	S°_{298} [a]	$\Delta_f H^\circ_{298}$ [b]	$\Delta_r H^\circ_{298}$ [b]	PCB isomer	$C^\circ_{p\,298}$ [a]	S°_{298} [a]	$\Delta_f H^\circ_{298}$ [b]	$\Delta_r H^\circ_{298}$ [b]
				Monochlorobiphenyls					
2	180.5	431.7	167.5	−16.1	4	183.3	426.9	156.0	−4.6
3	183.5	432.3	156.1	−4.7					
				Dichlorobiphenyls					
2,2′	195.8	461.9	143.1	−22.3	2,6	196.2	455.6	148.6	−23.5
2,3	195.8	460.8	146.8	−17.2	3,3′	199.8	462.7	126.3	−5.5
2,3′	196.8	468.4	137.5	−16.7	3,4	199.1	461.3	133.6	−4.0
2,4	196.7	462.0	140.6	−15.5	3,4′	199.6	462.0	126.0	−5.2
2,4′	196.7	462.2	137.0	−16.2	3,5	199.7	457.1	129.3	−4.2
2,5	196.7	462.9	137.1	−15.2	4,4′	199.4	451.8	126.0	−5.2
				Trichlorobiphenyls					
2,2′,3	211.7	496.1	122.1	−23.1	2,3′,5′	213.0	493.0	111.2	−16.7
2,2′,4	212.0	498.5	116.6	−22.1	2,3′,6	212.3	492.1	120.3	−25.8
2,2′,5	212.2	497.8	113.2	−21.9	2,4,4′	212.8	492.2	110.7	−16.2
2,2′,6	212.0	489.5	122.2	−27.7	2,4,5	212.6	491.5	106.5	−15.2
2,3,3′	212.0	497.6	117.4	−18.4	2,4,6	212.2	486.6	108.5	−22.5
2,3,4	211.6	489.7	119.9	−16.7	2,4′,5	213.0	492.8	107.5	−16.2
2,3,4′	212.0	492.1	116.8	−17.8	2,4′,6	212.2	486.6	118.5	−24.0
2,3,5	212.2	491.5	107.7	−16.4	3,3′,4	215.4	497.4	104.5	−5.5
2,3,6	211.9	490.5	114.9	−23.6	3,3′,5	215.9	493.1	100.5	−6.0
2,3′,4	212.8	498.2	111.2	−16.7	3,4,4′	215.3	492.3	104.1	−5.1
2,3′,4′	212.6	497.3	115.4	−16.4	3,4,5	215.0	484.9	107.2	−4.0
2,3′,5	212.9	499.0	107.9	−16.6	3,4′,5	215.8	487.7	100.0	−5.5
				Tetrachlorobiphenyls					
2,2′,3,3′	227.6	519.3	101.5	−24.3	2,3,4,5	227.5	518.7	89.9	−15.9
2,2′,3,4	227.4	525.0	95.5	−22.9	2,3,4,6	227.8	519.4	87.2	−22.7
2,2′,3,4′	227.9	526.5	96.0	−23.3	2,3,4′,5	228.3	521.5	78.4	−17.7
2,2′,3,5	228.4	525.5	83.9	−23.2	2,3,4′,6	228.0	521.6	85.4	−24.7
2,2′,3,5′	228.0	526.3	92.9	−23.4	2,3,5,6	227.8	513.3	90.7	−23.9
2,2′,3,6	229.3	523.4	88.9	−28.2	2,3′,4,4′	229.0	527.8	90.0	−17.3
2,2′,3,6′	227.9	518.5	101.8	−29.1	2,3′,4,5	228.8	527.9	77.1	−16.4
2,2′,4,4′	228.7	522.3	90.4	−22.2	2,3′,4,5′	229.2	523.6	87.3	−19.1
2,2′,4,5	228.2	526.1	82.6	−21.9	2,3′,4,6	228.4	522.9	79.4	−24.0
2,2′,4,5′	228.3	528.1	87.3	−22.3	2,3′,4′,5	228.9	528.1	86.3	−16.8
2,2′,4,6	228.2	520.1	82.3	−26.9	2,3′,4′,5′	228.3	520.6	88.7	−16.1
2,2′,4,6′	228.2	520.4	96.7	−28.5	2,3′,4′,6	228.0	521.6	96.9	−24.2
2,2′,5,5′	228.2	522.8	84.2	−22.4	2,3′,5,5′	229.0	523.7	82.5	−17.5
2,2′,5,6′	228.2	520.2	92.7	−27.7	2,3′,5′,6	228.7	517.2	93.1	−24.9
2,2′,6,6′	227.6	506.7	100.1	−31.9	2,4,4′,5	228.6	522.2	76.5	−15.8
2,3,3′,4	227.8	526.5	90.9	−18.3	2,4,4′,6	228.3	517.2	79.8	−24.4
2,3,3′,4′	227.9	527.0	95.7	−18.5	3,3′,4,4′	231.0	521.6	82.9	−5.7
2,3,3′,5	228.2	527.8	79.0	−18.3	3,3′,4,5	231.2	520.7	78.3	−5.7
2,3,3′,5′	228.2	522.2	91.7	−19.0	3,3′,4,5′	231.6	522.4	79.0	−6.3
2,3,3′,6	228.5	526.6	85.8	−25.1	3,3′,5,5′	232.3	512.2	75.4	−7.2
2,3,4,4′	227.8	520.0	91.7	−19.1	3,4,4′,5	231.1	515.8	77.7	−5.1
				Pentachlorobiphenyls					
2,2′,3,3′,4	243.3	553.8	75.0	−24.2	2,3,3′,4,4′	243.8	555.8	69.8	−19.0
2,2′,3,3′,5	243.9	555.5	63.7	−24.8	2,3,3′,4,5	243.6	555.2	62.0	−18.6
2,2′,3,3′,6	244.1	552.6	68.3	−29.4	2,3,3′,4,5′	244.0	550.9	65.6	−19.3
2,2′,3,4,4′	243.5	555.7	69.5	−23.2	2,3,3′,4,6	244.4	555.2	60.4	−26.5
2,2′,3,4,5	243.4	553.6	66.1	−22.7	2,3,3′,4′,5	244.0	557.6	57.7	−18.8
2,2′,3,4,5′	243.8	555.3	66.5	−23.4	2,3,3′,4′,5′	243.5	549.6	69.4	−18.6
2,2′,3,4,6	243.7	552.6	61.1	−27.2	2,3,3′,4′,6	244.1	555.8	64.1	−25.2
2,2′,3,4,6′	243.6	547.4	74.4	−28.1	2,3,3′,5,5′	244.3	553.0	54.0	−19.6
2,2′,3,4′,5	244.2	556.8	57.9	−23.5	2,3,3′,5,6	244.0	549.7	62.6	−26.4
2,2′,3,4′,5′	243.7	555.7	62.2	−23.3	2,3,3′,5′,6	244.4	551.6	60.5	−26.1
2,2′,3,4′,6	245.4	553.7	62.9	−28.5	2,3,4,4′,5	243.7	551.1	60.9	−17.5
2,2′,3,4′,6′	243.9	548.6	62.6	−29.0	2,3,4,4′,6	243.9	549.9	58.2	−24.3
2,2′,3,5,5′	244.6	557.3	55.0	−23.8	2,3,4,5,6	243.1	540.1	83.2	−23.8
2,2′,3,5,6	243.6	547.0	64.9	−28.7	2,3,4′,5,6	243.8	544.1	61.6	−25.4
2,2′,3,5,6′	244.0	549.0	64.6	−30.2	2,3′,4,4′,5	245.2	557.1	55.7	−16.8
2,2′,3,5′,6	244.9	553.9	60.2	−29.0	2,3′,4,4′,5′	244.4	550.9	63.3	−17.0
2,2′,3,6,6′	243.4	547.7	67.2	−32.8	2,3′,4,4′,6	244.1	552.1	57.7	−24.1
2,2′,4,4′,5	244.0	557.2	56.7	−22.3	2,3′,4,5,5′	244.9	552.9	52.7	−18.3
2,2′,4,4′,6	244.4	551.0	56.4	−27.3	2,3′,4,5′,6	244.9	547.0	54.2	−25.1
2,2′,4,5,5′	244.1	556.9	53.7	−22.5	2,3′,4′,5,5′	244.4	551.3	60.3	−17.2
2,2′,4,5,6′	243.9	549.3	61.9	−27.5	2,3′,4′,5′,6	243.9	544.8	71.3	−25.0
2,2′,4,5′,6	244.4	550.7	53.5	−27.6	3,3′,4,4′,5	246.9	550.2	56.9	−6.1
2,2′,4,6,6′	243.7	543.0	61.4	−32.3	3,3′,4,5,5′	247.4	545.9	54.1	−7.8

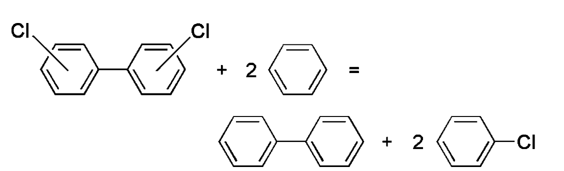
TABLE 2 (Continued)

PCB isomer	$C^{\circ}_{p\,298}{}^{a}$	$S^{\circ}_{298}{}^{a}$	$\Delta_f H^{\circ}_{298}{}^{b}$	$\Delta_r H^{\circ}_{298}{}^{b}$	PCB isomer	$C^{\circ}_{p\,298}{}^{a}$	$S^{\circ}_{298}{}^{a}$	$\Delta_f H^{\circ}_{298}{}^{b}$	$\Delta_r H^{\circ}_{298}{}^{b}$
Hexachlorobiphenyls									
2,2′,3,3′,4,4′	259.1	577.4	48.7	−24.3	2,2′,3,4′,5′,6	260.5	583.1	29.6	−29.0
2,2′,3,3′,4,5	259.2	582.9	46.1	−24.5	2,2′,3,4′,6,6′	259.5	577.8	27.7	−32.4
2,2′,3,3′,4,5′	259.7	584.1	37.2	−24.7	2,2′,3,5,5′,6	259.8	577.7	37.7	−31.0
2,2′,3,3′,4,6	259.6	581.2	41.3	−29.2	2,2′,3,5,6,6′	259.0	569.9	43.6	−33.7
2,2′,3,3′,4,6′	259.6	581.4	42.4	−29.9	2,2′,4,4′,5,5′	260.0	580.0	23.7	−23.1
2,2′,3,3′,5,5′	260.9	580.0	25.8	−25.2	2,2′,4,4′,5,6′	260.1	579.8	22.9	−27.6
2,2′,3,3′,5,6	259.4	575.7	45.8	−31.4	2,2′,4,4′,6,6′	259.8	567.7	22.5	−32.5
2,2′,3,3′,5,6′	260.1	582.8	30.9	−30.3	2,3,3′,4,4′,5	260.0	584.8	40.8	−19.2
2,2′,3,3′,6,6′	259.9	574.9	34.0	−33.4	2,3,3′,4,4′,5′	259.3	578.4	43.5	−19.1
2,2′,3,4,4′,5	259.4	584.1	40.4	−23.3	2,3,3′,4,4′,6	259.6	585.1	37.8	−25.7
2,2′,3,4,4′,5′	259.5	584.5	36.7	−24.2	2,3,3′,4,5,5′	259.9	580.1	36.6	−19.5
2,2′,3,4,4′,6	260.6	582.8	36.1	−28.5	2,3,3′,4,5,6	259.3	576.7	55.3	−26.5
2,2′,3,4,4′,6′	259.7	577.6	35.6	−28.4	2,3,3′,4,5′,6	260.1	580.2	33.5	−25.9
2,2′,3,4,5,5′	259.5	584.0	40.6	−23.5	2,3,3′,4′,5,5′	259.9	580.5	32.0	−19.5
2,2′,3,4,5,6	259.0	574.3	58.6	−29.8	2,3,3′,4′,5,6	259.6	579.2	41.8	−27.4
2,2′,3,4,5,6′	259.4	575.9	45.7	−28.6	2,3,3′,4′,5′,6	259.7	579.2	40.9	−28.4
2,2′,3,4,5′,6	260.8	582.8	33.2	−28.8	2,3,3′,5,5′,6	260.2	574.2	37.7	−27.8
2,2′,3,4,6,6′	259.1	576.4	41.0	−33.4	2,3,4,4′,5,6	259.3	570.9	55.4	−26.6
2,2′,3,4′,5,5′	259.9	586.0	25.0	−24.4	2,3′,4,4′,5,5′	260.2	580.4	30.0	−17.5
2,2′,3,4′,5,6	259.7	577.8	39.2	−29.3	2,3′,4,4′,5′,6	260.0	575.4	32.5	−25.3
2,2′,3,4′,5,6′	260.2	579.2	26.8	−31.5	3,3′,4,4′,5,5′	262.6	567.5	31.4	−7.0
Heptachlorobiphenyls									
2,2′,3,3′,4,4′,5	275.0	611.5	22.1	−26.9	2,2′,3,4,4′,5,6′	275.5	606.8	6.4	−28.4
2,2′,3,3′,4,4′,6	275.3	610.3	14.6	−28.9	2,2′,3,4,4′,5′,6	276.3	612.5	2.2	−28.4
2,2′,3,3′,4,5,5′	275.5	613.2	10.9	−27.6	2,2′,3,4,4′,6,6′	275.2	606.1	1.6	−33.1
2,2′,3,3′,4,5,6	274.7	602.9	37.2	−30.2	2,2′,3,4,5,5′,6	275.1	604.6	33.2	−30.7
2,2′,3,3′,4,5,6′	275.5	610.2	12.8	−29.5	2,2′,3,4,5,6,6′	274.4	596.8	36.3	−33.8
2,2′,3,3′,4,5′,6	276.0	611.4	4.2	−30.4	2,2′,3,4′,5,5′,6	275.5	606.7	7.7	−31.6
2,2′,3,3′,4,5′,6′	275.1	604.6	21.5	−33.5	2,2′,3,4′,5,6,6′	275.2	600.5	5.1	−34.3
2,2′,3,3′,4,6,6′	275.3	609.1	9.6	−35.8	2,3,3′,4,4′,5,5′	275.1	607.7	15.2	−20.0
2,2′,3,3′,5,5′,6	275.6	606.4	7.3	−31.2	2,3,3′,4,4′,5,6	275.0	606.0	34.3	−27.3
2,2′,3,3′,5,6,6′	274.8	604.7	12.4	−36.3	2,3,3′,4,4′,5′,6	275.6	607.9	12.2	−26.5
2,2′,3,4,4′,5,5′	275.2	612.8	7.7	−24.4	2,3,3′,4,5,5′,6	275.6	601.2	30.9	−28.4
2,2′,3,4,4′,5,6	275.1	604.6	32.0	−29.5	2,3,3′,4′,5,5′,6	275.5	601.9	15.2	−27.2
Octachlorobiphenyls									
2,2′,3,3′,4,4′,5,5′	290.8	634.2	−9.0	−25.0	2,2′,3,3′,4,5,6,6′	290.1	631.5	5.9	−37.2
2,2′,3,3′,4,4′,5,6	290.4	631.8	13.7	−33.1	2,2′,3,3′,4,5′,6,6′	290.5	633.8	−14.7	−36.0
2,2′,3,3′,4,4′,5,6′	291.1	639.0	−13.4	−30.1	2,2′,3,3′,5,5′,6,6′	290.5	621.7	−12.2	−36.2
2,2′,3,3′,4,4′,6,6′	291.4	632.6	−19.4	−33.6	2,2′,3,4,4′,5,5′,6	290.8	633.7	0.4	−31.7
2,2′,3,3′,4,5,5′,6	290.8	632.7	2.0	−33.3	2,2′,3,4,4′,5,6,6′	290.5	627.3	−2.0	−34.6
2,2′,3,3′,4,5,5′,6′	290.9	633.6	−9.6	−31.6	2,3,3′,4,4′,5,5′,6	290.8	628.9	8.2	−27.6
Nonachlorobiphenyls									
2,2′,3,3′,4,4′,5,5′,6	306.3	660.7	−15.3	−33.3	2,2′,3,3′,4,5,5′,6,6′	305.9	654.2	−19.2	−36.6
2,2′,3,3′,4,4′,5,6,6′	305.9	660.7	−22.6	−35.5					
Decachlorobiphenyls									
2,2′,3,3′,4,4′,5,5′,6,6′	321.2	675.7	−24.7	−38.5					

[a] Units in J K^{-1} mol^{-1}. [b] Units in kJ mol^{-1}.

reference molecules in these reactions. The enthalpies of formation of these compounds are known experimentally with an accuracy of 0.7−8.7 kJ mol^{-1}.[2] The calculated enthalpies of formation together with the enthalpy changes, $\Delta_r H^{\circ}_{298}$, for the corresponding isodesmic reactions are given in Table 2. The B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) electronic energies, zero-point energies, thermal corrections, and enthalpies of formation for all molecules used in isodesmic reactions are collected in Supporting Information Table 6S.

It is known that an isodesmic reaction leads to more accurate results if (1) there is a similarity of bonding environment in the reactants and products and (2) the experimental $\Delta_f H^{\circ}_{298}$ values of reference molecules are determined with high accuracy. Unfortunately, the equations of type 2 do not satisfy these conditions totally. Up to now, there has been some uncertainty in the experimental enthalpies of formation of highly chlorinated benzenes (see ref 25 and references therein). Besides, the interaction between the chlorine atoms of different phenyl rings is ignored by eq 2, whereas it may be of importance for PCBs, especially with *ortho* chlorine atoms. Experimental data on $\Delta_f H^{\circ}_{298}$ are available for only two isomers of dichlorobiphenyl: 2,2′ (127.9 ± 4.7 kJ mol^{-1}) and 4,4′ (121.1 ± 4.4 kJ mol^{-1}).[1,2] As we might expect, the calculated value for 4,4′-dichlorobiphenyl (126.0 kJ mol^{-1}) is in better agreement with experiment than that for 2,2′-dichlorobiphenyl (143.1 kJ mol^{-1}). The interaction between the chlorine atoms in the 4 and 4′ positions can be neglected and reaction



(3)

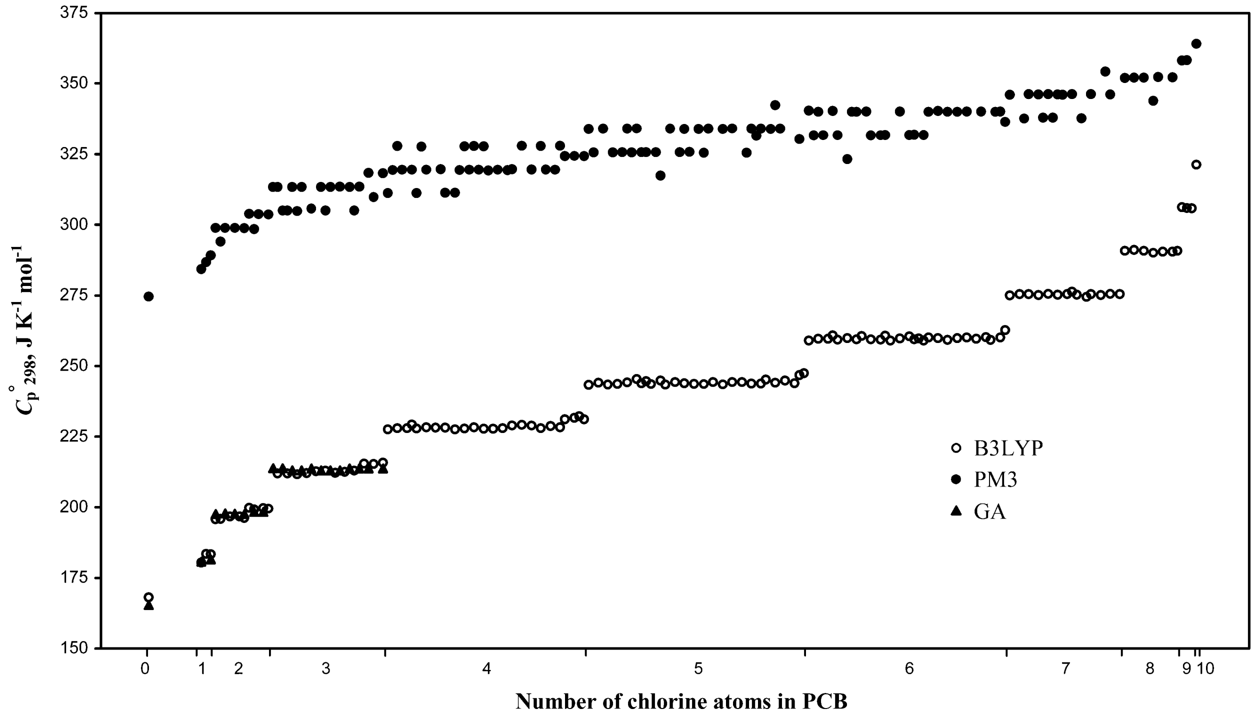


Figure 2. Comparison of the $C^\circ_{p\,298}$ values determined in this work from B3LYP calculations with those predicted by the PM3[9] and GA[4] methods. The order in which points are plotted on the graph corresponds to the PCB list in Table 2.

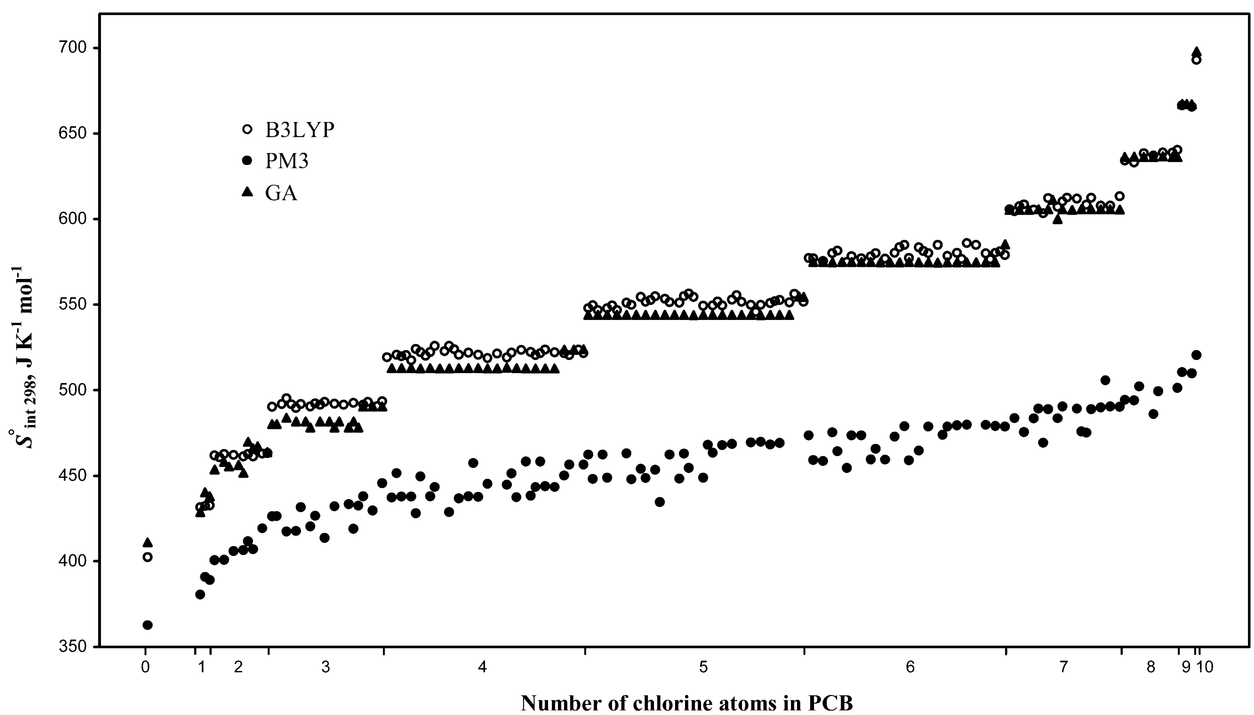


Figure 3. Comparison of the $S^\circ_{int\,298}$ values determined in this work from B3LYP calculations with those predicted by the PM3[9] and GA[4,5] methods. The order in which points are plotted on the graph corresponds to the PCB list in Table 2.

is well-balanced for 4,4′-dichlorobiphenyl ($\Delta_r H^\circ_{298} = -5.2$ kJ mol^{-1}). However, ignoring the interaction between two *ortho* chlorine atoms in 2,2′-dichlorobiphenyl may introduce large error. The fact that reaction 3 may not be well-balanced for 2,2′-dichlorobiphenyl is supported by the increased value of $\Delta_r H^\circ_{298}$ (-22.3 kJ mol^{-1}). The uncertainties of the calculated enthalpies of formation of PCBs would thus be expected to depend on the number of *ortho* chlorine atoms in each molecule. Depending on the $\Delta_r H^\circ_{298}$ values (Table 2), we propose the following scheme for estimating the uncertainties of the calculated $\Delta_f H^\circ_{298}$ values:

$\lvert\Delta_r H^\circ_{298}\rvert$, kJ mol^{-1}	uncertainty in $\Delta_f H^\circ_{298}$, kJ mol^{-1}
4−8	5−10
15−20	10−15
21−25	15−20
26−30	20−25
31−35	25−30
36−39	30−35

TABLE 3: Comparison of the $C^{\circ}_{p\,298}$ and S°_{298} Values (in J K^{-1} mol^{-1}) of Biphenyl Calculated by Different Methods

method	$C^{\circ}_{p\,298}$	S°_{298} [a]
experiment[24]		389.7
statistical calculation[4]	165.3	393.8 (−4.1)
statistical calculation[22]	166.4	390.8 (−1.1)
PM3[9]	274.6	345.4 (44.3)
PM3, this work	162.4	384.9 (4.8)
B3LYP, this work	168.1	390.9 (−1.2)

[a] The value in parentheses is the difference between the experimental and cited values.

As seen from Table 2, the uncertainties in enthalpies of formation thus defined will increase as the number of *ortho* chlorine atoms increases.

The enthalpies of formation of PCBs estimated by the GA method were discussed in our previous work.[7] Here, we compare the $\Delta_f H^{\circ}_{298}$ values determined in this work from B3LYP calculations with those predicted by the PM3[9] and GA[7] methods (Figure 4). As seen from Figure 4, the $\Delta_f H^{\circ}_{298}$ values determined from the PM3 method are somewhat higher than those determined by the B3LYP and GA methods. Since PM3 predicts the $\Delta_f H^{\circ}_{298}$ values for 2,2′- and 4,4′-dichlorobiphenyl worse than the B3LYP and GA methods, we consider the PM3 results as the least reliable of the three data sets. The B3LYP and GA estimations are rather close together for PCBs with one to five chlorine atoms. However, for highly chlorinated PCBs, the B3LYP results are distinctly lower than the GA values. There seems to be no good reason for preferring one of the two, since the interaction between the chlorine atoms of adjacent rings was not taken properly into account in both cases.

As noted above, the success or failure of the isodesmic reaction scheme depends heavily on the choice of reference molecules. The enthalpies of formation of all polychlorinated benzenes were recommended by Pedley[2] on the basis of available experimental data. These values were used in this work. The $\Delta_f H^{\circ}_{298}$ values from this handbook, as a rule, are exceptionally reliable, owing to their internal consistency. However, it is known that considerable uncertainties in the experimental enthalpies of formation for chlorinated organic compounds are often the case due to incomplete combustion in calorimetric measurements. In particular, there are other experimental data for trichlorobenzenes[26] which lead to 4−13 kJ mol^{-1} higher values of $\Delta_f H^{\circ}_{298}$ as compared to the values recommended by Pedley[2] (Table 4). The problem of the accuracy of the experimental data for polychlorinated benzenes has been repeatedly raised.[25,29,30] To check the reliability of the experimental $\Delta_f H^{\circ}_{298}$ values of polychlorinated benzenes in this work, their values were calculated by the atomization procedure at the G3//B3LYP level (Table 4). The calculated values for mono- and dichlorobenzenes are in good agreement with the experimental ones, while there is substantial discrepancy for

TABLE 4: Comparison of the Experimental Enthalpies of Formation (in kJ mol^{-1}) of Polychlorinated Benzenes with Values Calculated by the G3//B3LYP Method

molecule	experiment[a]	deviation (expt − G3 theory)
chlorobenzene	52.0 ± 1.3	−0.3
1,2-dichlorobenzene	30.2 ± 2.1	1.5
1,3-dichlorobenzene	25.7 ± 2.1	3.0
1,4-dichlorobenzene	22.5 ± 1.5	−0.6
1,2,3-trichlorobenzene	3.8 ± 0.7	−2.9
	8.2 ± 1.8[b]	1.5
1,2,4-trichlorobenzene	−8.1 ± 1.0	*c*
	4.9 ± 1.6[b]	
1,3,5-trichlorobenzene	−13.4 ± 1.0	−9.3
	−2.6 ± 1.4[b]	1.5
1,2,3,4-tetrachlorobenzene	−25.4 ± 1.0	−12.3
1,2,3,5-tetrachlorobenzene	−34.9 ± 1.0	−16.4
1,2,4,5-tetrachlorobenzene	−32.6 ± 0.8	−13.8
pentachlorobenzene	−40.0 ± 8.7	*c*
hexachlorobenzene	−35.5 ± 9.3	*c*
	−56.2 ± 8.5[d]	

[a] Unless noted, the experimental values are from Pedley (ref 2). [b] Reference 26. [c] Reference 27. [d] Reference 28.

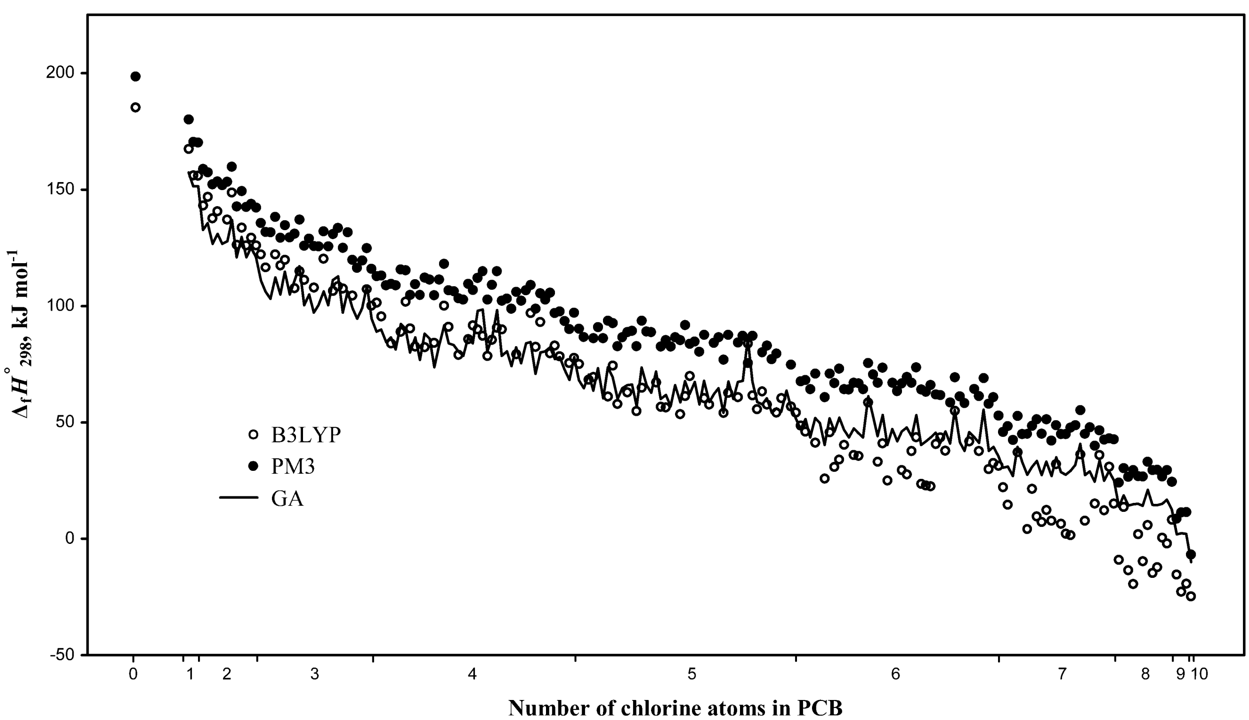


Figure 4. Comparison of the $\Delta_f H^{\circ}_{298}$ values determined in this work from B3LYP calculations with those predicted by the PM3[9] and GA[7] methods. The order in which points are plotted on the graph corresponds to the PCB list in Table 2.

the tri- and tetrachlorobenzenes. The G3//B3LYP method has a mean absolute deviation of 4 kJ mol^{-1} for the set of 299 molecules.[31] Since this value is 2−4 times less than the difference between the experimental and G3//B3LYP enthalpies of formation for tri- and tetrachlorobenzenes, it can be suggested that the experimental values are underestimated. On the other hand, the G3 method was parametrized using a test of relatively small molecules:[31,32] among chlorinated hydrocarbons, $CHCl_3$ was the molecule with the greatest number of chlorine atoms. Thus, one would expect some accumulation of error in the application of G3 theory to larger molecules such as $C_6H_2Cl_4$. A small accumulation of error was observed in the assessment of the G3 method for alkanes.[33] For chlorinated hydrocarbons, this error may be larger if it is remembered that G2 theory has problems for halogen compounds and G3 theory has large deviations for PF_5 and SF_6.[32] Therefore, the results shown in Table 4 are not yet sufficient to allow unambiguous conclusions about the $\Delta_f H^\circ_{298}$ values of highly chlorinated benzenes. Precise experimental measurements of the enthalpies of formation of benzene molecules containing three to six chlorine atoms would be extremely valuable as a check on the accuracy of the theoretical calculations. For the time being, one cannot rule out the possibility of higher $\Delta_f H^\circ_{298}$ values than those given in Table 2 for PCBs containing three or more chlorine atoms in one or each benzene ring.

Conclusions

The thermodynamic properties of all PCB congeners were calculated using density functional calculations. The $S°(T)$ and $C^\circ_p(T)$ values were calculated using B3LYP/6-31G(d,p) geometries, vibrational frequencies, and internal rotational potentials. The calculated entropy of biphenyl compares well with that determined by calorimetric techniques (Table 3), and this in turn suggests a reasonable accuracy of calculated values for PCBs. As is seen, the B3LYP method provides a good way to calculate the structure, vibrational frequencies, and torsional potential of a molecule and thus to calculate the entropies and heat capacities by statistical mechanics.

The enthalpies of formation were calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level using isodesmic reactions. The uncertainties of the calculated values are estimated to be 5−35 kJ mol^{-1}. High accuracy is expected for PCBs without *ortho* chlorine atoms, since their $\Delta_f H^\circ_{298}$ values are based on enthalpies of formation of mono- and dichlorobenzenes. The *ortho* chlorine atoms and use of tri- and more chlorinated benzenes in eq 2 causes the uncertainty in the $\Delta_f H^\circ_{298}$ values to increase. More accurate enthalpies of formation of PCBs can be predicted by high level ab initio methods using the atomization procedure, but for now, such calculations are used for relatively small molecules because of their high computational cost. Nevertheless, for many purposes, the quality of the calculated $\Delta_f H^\circ_{298}$ values reported here will be quite adequate.

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Supporting Information Available: Supporting Information Tables 1S−3S provide the following molecular parameters used in the calculation of the thermodynamic functions: symmetry numbers, torsional angles, products of principal moments of inertia, reduced moments of inertia, torsional potentials, and vibrational frequencies. Values of $S°(T)$, $C^\circ_p(T)$, and $H°(T) - H°(0)$ at temperatures from 100 to 1500 K are given in Supporting Information Table 4S. Coefficients in the equation for $C^\circ_p(T)$ approximation in the temperature range from 200 to 1000 K are listed in Supporting Information Table 5S. Supporting Information Table 6S provides electronic energies, zero-point energies, and thermal corrections together with experimental values of the enthalpies of formation for the reference molecules used in the isodesmic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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