J. Phys. Chem. A **2001,** *105,* 6621−6629

Enthalpies of Formation for Gaseous Polychlorinated Biphenyls: A Modified Group Additivity Scheme

Olga V. Dorofeeva* and Vladimir S. Yungman

Glushko Thermocenter of Associated Institute for High Temperatures of Russian Academy of Sciences, Izhorskaya St. 13/19, Moscow 127412, Russia

Pauline Saks

OLI Systems, Inc., 108 American Road, Morris Plains, New Jersey 07950

Received: January 7, 2001; In Final Form: March 30, 2001

The standard enthalpies of formation, $\Delta_f H^\circ_{298}$, were estimated for all 209 gaseous polychlorinated biphenyl (PCB) congeners combining the difference method—the procedure that is completely consistent with group additivity approach—and data on relative stability of PCB isomers modeled by the semiempirical method AM1 (Mulholland et al. *J. Phys. Chem.* **1993**, *97*, 6890). A set of 14 parameters was derived for estimating the enthalpy of formation values of PCBs by group additivity method. The results are compared with previous group additivity estimations. The proposed group additivity scheme is based on the experimental enthalpies of formation of biphenyl, 2,2′-dichlorobiphenyl, 4,4′-dichlorobiphenyl, and multichlorinated benzenes. To check the doubt on the enthalpy of formation of 2,2′-dichlorobiphenyl, its value was determined by density functional calculations at the B3LYP level of theory using isodesmic reactions. The results of these calculations suggest that the experimental $\Delta_f H^\circ_{298}$ value of 2,2′-dichlorobiphenyl is underestimated by at least 1−2 kcal/mol.

Introduction

Along with polychlorinated dibenzo-*p*-dioxins and dibenzofurans, polychlorinated biphenyls (PCBs) are environmentally significant compounds. These toxic compounds occur in the environment by a variety of chemical industry processes, especially during combustion of hazardous wastes. Thermodynamic properties of PCBs are important in equilibrium calculations and for understanding the reaction pathways relating to polychlorinated compounds formation, destruction, combustion and other environmental processes. Knowledge of the thermodynamics of PCBs would provide a powerful tool for quantitative prediction of their concentrations in combustion systems and for optimizing conditions to minimize their formation.

Experimental data on enthalpies of formation are available for only two isomers of dichlorobiphenyl, 2,2′- and 4,4′-dichlorobiphenyl.[1,2] Thus, different estimation methods were used to evaluate the $\Delta_f H^\circ_{298}$ values for PCBs.[3−7] For the first time, the gas-phase enthalpies of formation of PCBs were estimated by Shaub[3] using a group additivity method. In addition to the effect of replacing a hydrogen atom with chlorine atom, the author considered the ortho, meta, and para interactions between chlorine atoms within each phenyl ring as well as the interactions between ortho chlorine atoms of adjacent rings. The values of $\Delta_f H^\circ_{298}$ for mono-, di-, and trichlorobiphenyls were estimated in TRC tables[4] using the empirical correlations. These data were accepted by Holmes et al.,[5] whereas for the remaining compounds (tetra-, penta-, hexa-, hepta-, octa-, nona-, and decachlorinated biphenyls), Holmes et al.[5] have estimated the $\Delta_f H^\circ_{298}$ values by Benson's group additivity method. The enthalpies of formation of mono-, di-, and trichlorobiphenyls were also estimated by Wu et al.[6] using non-next-nearest neighbor interaction groups with the Benson's group additivity method. Mulholland et al.[7] have calculated the relative enthalpies of formation of PCB isomers by the semiempirical molecular orbital method AM1 (Austin model 1). It is known that AM1 results are not of sufficient accuracy for $\Delta_f H^\circ_{298}$ values. In fact, the enthalpies of formation for 2,2′- and 4,4′-dichlorobiphenyl calculated by AM1 (37.1 and 33.4 kcal/mol)[7] are overestimated by 6.5 and 4.5 kcal/mol, respectively, as compared to experimental data (30.6 and 28.9 kcal/mol).[1,2] Nevertheless, the AM1 values of relative enthalpies of formation proved to be helpful in calculating the relative yields of PCB isomers during pyrolysis of 1,2-dichlorobenzene, anthracene, and pyrene: the thermodynamic distribution of the PCB isomers modeled by AM1 agreed with experimental data in each of these systems.[7] In addition, a good agreement between isomer compositions predicted by semiempirical methods (MNDO and AM1) and those observed for polychlorinated dibenzo-*p*-dioxins is worth of notice.[8,9] Mulholland et al.[7] have also derived a set of group additivity parameters for estimation of relative isomer stability.

Figure 1 compares the relative enthalpies of formation of dichlorobiphenyls estimated by different authors. The relative enthalpy of formation is the difference between the enthalpy of formation for given isomer and 4,4′-dichlorobiphenyl whose $\Delta_f H^\circ_{298}$ value is the lowest among dichlorobiphenyls. Three of these data sets cannot be regarded as reasonable enough. The AM1 calculation[7] overestimates the relative enthalpy of formation of 2,2′-dichlorobiphenyl (3.7 kcal/mol) in comparison with that of the experiment (1.6 kcal/mol). According to the procedure developed by Shaub,[3] the 2,3′-, 2,4′-, 3,3′-, 3,4′-, and 4,4′-dichlorobiphenyls are of the equal enthalpy of formation. This result is inconsistent with the influence of destabilizing steric factors associated with ortho chlorine atoms (i.e. chlorine atoms

---

* To whom correspondence should be addressed.

10.1021/jp010082t CCC: $20.00

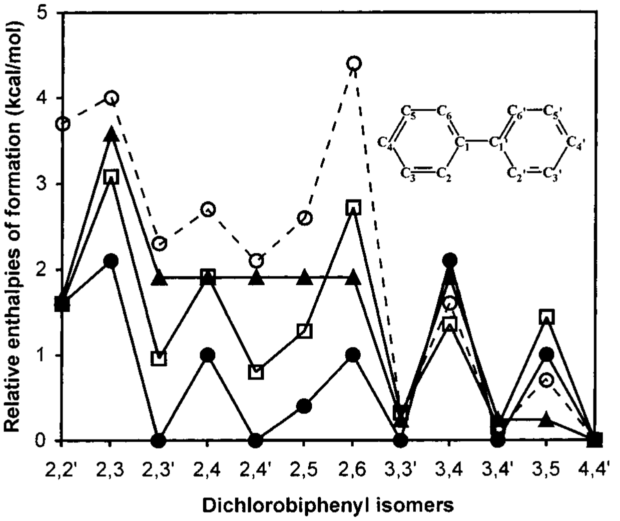

Figure 1. Comparison of relative enthalpies of formation for dichlorobiphenyls estimated by the AM1 method[7] (dashed line) and previous group additivity schemes (solid lines): ●, Shaub;[3] ▲, TRC[4a] and Holmes et al.;[5] □, Wu et al.[6]

attached in one or more of the following positions: 2, 2′, 6, and 6′). Ortho chlorine atom steric interactions with its neighboring phenyl group are bound to increase the $\Delta_f H^\circ_{298}$ values of 2,3′- and 2,4′-isomers relative to 3,3′-, 3,4′-, and 4,4′-dichlorobiphenyls with no ortho Cl atoms. As seen from Figure 1, the Shaub's results[3] are not representative of this effect. The values of $\Delta_f H^\circ_{298}$ accepted by TRC[4a] and Holmes et al.[5] have other shortcomings: the adopted empirical correlation could not distinguish the large group of isomers (2,3′-, 2,4-, 2,4′-, 2,5-, 2,6-, and 3,4-dichlorobiphenyls), and their enthalpy of formation values were suggested to be equal.

Among the group additivity results, only values estimated by Wu et al.[6] comply with the role of steric factors in dichlorobiphenyls. Besides, Figure 1 shows that there is an obvious correlation between the predicted group additivity[6] and AM1[7] results. For trichlorobiphenyls, however, not all $\Delta_f H^\circ_{298}$ values correlate with destabilizing steric effect of ortho chlorine atoms: Wu et al.[6] in common with Shaub[3] have predicted the enthalpy of formation values for 2,3′,5- and 2,4′,5-isomers with ortho Cl atoms to be the same as those for 3,3′,5- and 3,4′,5-isomers expected to be the most stable (Figure 2).

The situation for other PCB congeners (tetrachlorobiphenyls, pentachlorobiphenyls, etc.) is identical to that for di- and trichlorobiphenyls. The estimation method developed by Shaub[3] predicts some isomers with ortho Cl atoms to be the most stable. In regard to estimates of Holmes et al.,[5] there are the sets of isomers for which the enthalpy of formation values were accepted to be equal. As an example, we refer to an enthalpy of formation of 16.4 kcal/mol for twelve tetrachlorobiphenyls, among which is the 2,2′,6,6′ isomer. However, the enthalpy of formation of 2,2′,6,6′-tetrachlorobiphenyl is expected to be substantially higher because of large steric interactions associated with four ortho Cl atoms.

Thus, the three additivity approaches discussed above are not sufficiently advanced to predict the relative distribution of the PCB isomers and can lead to conflicting results for the relative yields of PCBs in thermodynamic modeling of environmental processes. Benson's group additivity method[10,11] has been widely used to estimate enthalpies of formation of many organic compounds.[10−14] This method allows us to estimate the thermodynamic properties with uncertainties no larger than experimental uncertainties if available experimental data are enough to derive group additivity values including nonnearest interactions. Experimental data for PCBs are limited by two enthalpy of formation values for dichlorobiphenyls, and because of this, the interaction terms can be estimated very approximately using some empirical correlations.

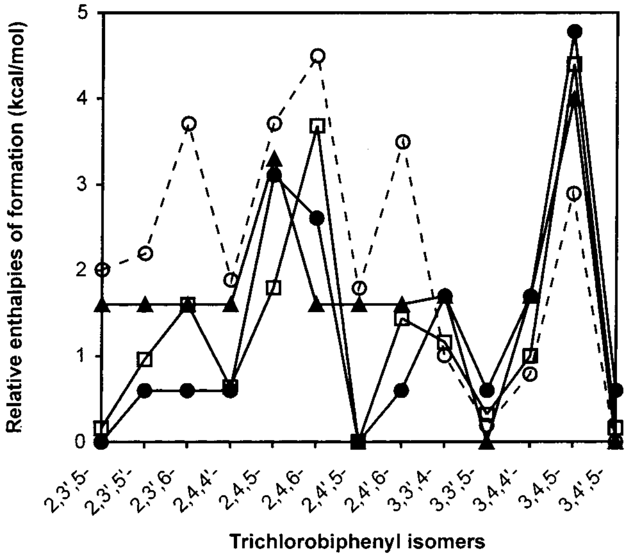

Figure 2. Comparison of relative enthalpies of formation for the portion of trichlorobiphenyls estimated by the AM1 method[7] (dashed line) and previous group additivity schemes (solid lines): ●, Shaub;[3] ▲, TRC[4b] and Holmes et al.;[5] □, Wu et al.[6]

An alternative approach, the difference method or the method of group equations, can be also used to predict the thermodynamic properties. This procedure is completely consistent with group additivity and sometimes offers a more accurate estimating scheme than Benson's group values. Strictly speaking, the difference method and the method of group equations are somewhat different. To estimate the enthalpy of formation of, say, the 3-chlorobiphenyl, one can use two equations:

$$\Delta_f H^\circ_{298}(\text{3-chlorobiphenyl}) = \Delta_f H^\circ_{298}(\text{biphenyl}) + \Delta_f H^\circ_{298}[\mathrm{C_B{-}(Cl)}] - \Delta_f H^\circ_{298}[\mathrm{C_B{-}(H)}] \quad \text{(difference method)}$$

$$\Delta_f H^\circ_{298}(\text{3-chlorobiphenyl}) = \Delta_f H^\circ_{298}(\text{biphenyl}) + \Delta_f H^\circ_{298}(\text{chlorobenzene}) - \Delta_f H^\circ_{298}(\text{benzene}) \quad \text{(method of group equations)}$$

The method of group equations may be considered as a special case of the more general difference method in which the group values ($\mathrm{C_B{-}(Cl)}$ and $\mathrm{C_B{-}(H)}$ in our case) are based on one compound only. Cohen and Benson[11] pointed to the advantage of the difference method for large molecules for which accurate group values have not been defined. We used the difference method to estimate the thermodynamic properties of many organic compounds of environmental concern.[15] In this work, the difference method was applied to predict the enthalpies of formation of PCB isomers. For trichlorobiphenyls and PCBs with higher degree of chlorination, the results of AM1 calculation of relative enthalpies of formation[7] were taken into account to estimate the non-nearest-neighbor interaction terms.

In developing the group additivity scheme, the doubts were cast upon the experimental value of enthalpy of formation of 2,2′-dichlorobiphenyl. Because this value is of paramount importance in the estimation of the ortho Cl atoms interactions, the enthalpy of formation of this molecule was determined in this work by density functional calculations with isodesmic reactions.

Results

Dichlorobiphenyls. The method of group equations enables the calculation of the enthalpy of formation for some compound if the enthalpies of formation are known for compounds, called the model compounds, structurally very similar to that of interest. Biphenyl, benzene, and mono- and dichlorobenzenes can be used as model compounds in estimating the enthalpies of formation of dichlorobiphenyls. The difference method suggests that the difference in $\Delta_f H^\circ_{298}$ values between dichlorinated biphenyl and biphenyl is the same as the difference between corresponding chlorinated benzene and benzene. With experimental values of $\Delta_f H^\circ_{298}$ for model compounds, we can estimate the enthalpies of formation for dichlorobiphenyls from the following equations:

$$\begin{aligned}\Delta_f H^\circ_{298}&(2,2'\text{-}, 2,3'\text{-}, 2,4'\text{-}, 3,3'\text{-}, 3,4'\text{-, or } 4,4'\text{-dichlorobiphenyl}) = \Delta_f H^\circ_{298}(\text{biphenyl}) + \\ &2[\Delta_f H^\circ_{298}(\text{chlorobenzene}) - \Delta_f H^\circ_{298}(\text{benzene})] = \\ &43.51 + 2(12.43 - 19.74) = 28.89 \text{ kcal/mol} \quad (1)\end{aligned}$$

$$\begin{aligned}\Delta_f H^\circ_{298}&(2,3\text{- or } 3,4\text{-dichlorobiphenyl}) = \Delta_f H^\circ_{298}(\text{biphenyl}) + \\ &\Delta_f H^\circ_{298}(1,2\text{-dichlorobenzene}) - \Delta_f H^\circ_{298}(\text{benzene}) = \\ &43.51 + 7.22 - 19.74 = 30.99 \text{ kcal/mol} \quad (2)\end{aligned}$$

$$\begin{aligned}\Delta_f H^\circ_{298}&(2,4\text{-}, 2,6\text{-, or } 3,5\text{-dichlorobiphenyl}) = \\ &\Delta_f H^\circ_{298}(\text{biphenyl}) + \Delta_f H^\circ_{298}(1,3\text{-dichlorobenzene}) - \\ &\Delta_f H^\circ_{298}(\text{benzene}) = 43.51 + 6.14 - 19.74 = \\ &29.91 \text{ kcal/mol} \quad (3)\end{aligned}$$

$$\begin{aligned}\Delta_f H^\circ_{298}&(2,5\text{-dichlorobiphenyl}) = \Delta_f H^\circ_{298}(\text{biphenyl}) + \\ &\Delta_f H^\circ_{298}(1,4\text{-dichlorobenzene}) - \Delta_f H^\circ_{298}(\text{benzene}) = \\ &43.51 + 5.38 - 19.74 = 29.15 \text{ kcal/mol} \quad (4)\end{aligned}$$

Here, the enthalpy of formation of biphenyl is the value determined from calorimetric study;[16] the $\Delta_f H^\circ_{298}$ values for benzene and all chlorinated benzenes were taken from compilation by Pedley.[2]

It is obvious that this difference scheme covers only the steric interactions between Cl atoms within each ring and can lead to poor estimates for molecules with appreciable interactions between adjacent phenyl rings. Only an additional information on enthalpies of PCBs themselves would provide the basis for further differentiating between four groups of dichlorobiphenyls obtained above. Actually, eq 1 leads to $\Delta_f H^\circ_{298}$(4,4′-dichlorobiphenyl) = 28.89 kcal/mol in good agreement with experimental value of 28.94 ± 1.05 kcal/mol,[1,2] whereas the same estimate for 2,2′-dichlorobiphenyl, the molecule with two ortho chlorine atoms, is 1.68 kcal/mol lower than the experimental value of 30.57 ± 1.12 kcal/mol.[1,2] To fit the enthalpy of formation of 2,2′-dichlorobiphenyl to the experimental value, the ortho correction, $\delta_{o-Cl,Ph} = 0.84$ kcal/mol, should be adopted. This correction term accounts for the interaction effect associated with one chlorine substitution in the 2, 2′, 6, or 6′ position. Initially, the value of 0.84 kcal/mol was accepted for ortho correction in this work. Later, however, its value was increased up to 1.40 kcal/mol to avoid too low $\Delta_f H^\circ_{298}$ values for some tri- and tetrachlorobiphenyls with ortho Cl atoms (see below). This value of $\delta_{o-Cl,Ph}$ leads to $\Delta_f H^\circ_{298}$(2,2′-dichlorobiphenyl) = 31.69 kcal/mol, which is an upper limit of the experimental value.

The enthalpies of formation of dichlorobiphenyls given in Table 1 are those from eqs 1−4 modified by one or two ortho corrections for isomers with ortho Cl atoms. The relative enthalpies of formation are shown in Figure 3 together with values calculated by AM1 method.[7] As is seen from a comparison between Figures 1 and 3, the simple difference scheme, based only on the experimental data for structurally similar molecules, does not have the disadvantages of previous two group additivity approaches[3−5] and agrees closely with results of Wu et al.[6] Unfortunately, Wu et al.[6] reported the interaction terms for di-substituted single-ring aromatics, only and it is not clear how the $\Delta_f H^\circ_{298}$ values for dichlorobiphenyls were obtained.

Calculated enthalpies of formation for dichlorobiphenyls (Table 1) can be applied to derive the Benson's group additivity values. We used the value of 3.29 kcal/mol for C_B—(H) group (C_B is the aromatic C atom) as recommended by Cohen and Benson[11] from analysis of available experimental data for benzene derivatives. The values of C_B—(C_B) and C_B—(Cl) groups and Δ_{12}, Δ_{13}, and Δ_{14} corrections were then calculated from enthalpies of formation of biphenyl and four types of dichlorobiphenyls:

$$\begin{aligned}\Delta_f H^\circ_{298}(\text{biphenyl}) &= 43.51 \text{ kcal/mol} = \\ &10[C_B\text{—(H)}] + 2[C_B\text{—}(C_B)] \quad (5)\end{aligned}$$

$$\begin{aligned}\Delta_f H^\circ_{298}(4,4'\text{-dichlorobiphenyl}) &= 28.89 \text{ kcal/mol} = \\ &8[C_B\text{—(H)}] + 2[C_B\text{—}(C_B)] + 2[C_B\text{—(Cl)}] \quad (6)\end{aligned}$$

$$\begin{aligned}\Delta_f H^\circ_{298}(3,4\text{-dichlorobiphenyl}) &= 30.99 \text{ kcal/mol} = \\ &8[C_B\text{—(H)}] + 2[C_B\text{—}(C_B)] + 2[C_B\text{—(Cl)}] + \Delta_{12} \quad (7)\end{aligned}$$

$$\begin{aligned}\Delta_f H^\circ_{298}(3,5\text{-dichlorobiphenyl}) &= 29.91 \text{ kcal/mol} = \\ &8[C_B\text{—(H)}] + 2[C_B\text{—}(C_B)] + 2[C_B\text{—(Cl)}] + \Delta_{13} \quad (8)\end{aligned}$$

$$\begin{aligned}\Delta_f H^\circ_{298}&(2,5\text{-dichlorobiphenyl}) = \\ &(29.15 + \delta_{o-Cl,Ph}) \text{ kcal/mol} = 8[C_B\text{—(H)}] + 2[C_B\text{—}(C_B)] + \\ &2[C_B\text{—(Cl)}] + \Delta_{14} + \delta_{o-Cl,Ph} \quad (9)\end{aligned}$$

The calculated group additivity values are given in Table 2. The values for C_B—(C_B) and C_B—(Cl) groups and Δ_{12} correction are in close agreement with those recommended by Benson;[10] other nonnearest chlorine interactions, Δ_{13} and Δ_{14}, were not considered by Benson.

Monochlorobiphenyls. The enthalpies of formation of monochlorobiphenyls (Table 1) were estimated by difference method using the experimental $\Delta_f H^\circ_{298}$ values for biphenyl, benzene, and chlorobenzene. For 2-chlorobiphenyl, the ortho correction was added.

Tri-, Tetra-, Penta-, Hexa-, Hepta-, Octa-, Nona-, and Decachlorobiphenyls. For lack of needed experimental data, the AM1 relative enthalpies of formation[7] were used in this work. In defense of this approach, we point to the close agreement of the trend in relative $\Delta_f H^\circ_{298}$ values for dichlorobiphenyls predicted by AM1[7] and estimated in this work by the difference method (Figure 3) as well as the AM1 predictions of equilibrium isomer compositions in agreement with experimental data.[7,9] Furthermore, as will be shown somewhat later, the relative enthalpy of formation of 2,2′-dichlorobiphenyl predicted by AM1 (3.7 kcal/mol)[7] is found to be in good agreement with the value obtained by density functional calculations at the B3LYP/6-311+G(3df,2p) level (4 kcal/mol).

TABLE 1: Enthalpies of Formation for Gaseous PCB Isomers at 298.15 K (kcal/mol)

no.	isomer[a]	$\Delta_f H^\circ_{298}$
	monochlorobiphenyls	
1	2-	37.59
2	3-	36.19
3	4-	36.19
	dichlorobiphenyls	
4	2,2′-	31.69
		(30.57 ± 1.12) [b]
5	2,3-	32.39
6	2,3′-	30.29
7	2,4-	31.31
8	2,4′-	30.29
9	2,5-	30.55
10	2,6-	32.71
11	3,3′-	28.89
12	3,4-	30.99
13	3,4′-	28.89
14	3,5-	29.91
15	4,4′-	28.89
		(28.94 ± 1.05) [b]
	trichlorobiphenyls	
16	2,2′,3-	26.48
17	2,2′,4-	25.40
18	2,2′,5-	24.63
19	2,2′,6-	26.80
20	2,3,3′-	25.08
21	2,3,4-	27.40
22	2,3,4′-	25.08
23	2,3,5-	26.57
24	2,3,6-	27.97
25	2,3′,4-	24.00
26	2,3′,4′-	25.08
27	2,3′,5-	23.24
28	2,3′,5′-	24.00
29	2,3′,6-	25.40
30	2,4,4′-	24.00
31	2,4,5-	26.57
32	2,4,6-	26.98
33	2,4′,5-	23.24
34	2,4′,6-	25.40
35	3,3′,4-	23.68
36	3,3′,5-	22.60
37	3,4,4′-	23.68
38	3,4,5-	26.00
39	3,4′,5-	22.60
	tetrachlorobiphenyls	
40	2,2′,3,3′-	21.28
41	2,2′,3,4-	21.49
42	2,2′,3,4′-	20.20
43	2,2′,3,5-	20.66
44	2,2′,3,5′-	19.44
45	2,2′,3,6-	22.06
46	2,2′,3,6′-	21.60
47	2,2′,4,4′-	19.12
48	2,2′,4,5-	20.66
49	2,2′,4,5′-	18.36
50	2,2′,4,6-	21.07
51	2,2′,4,6′-	20.52
52	2,2′,5,5′-	17.60
53	2,2′,5,6′-	19.76
54	2,2′,6,6′-	21.92
55	2,3,3′,4-	20.09
56	2,3,3′,4′-	19.88
57	2,3,3′,5-	19.26
58	2,3,3′,5′-	18.80
59	2,3,3′,6-	20.66
60	2,3,4,4′-	20.09
61	2,3,4,5-	23.42
62	2,3,4,6-	23.54
63	2,3,4′,5-	19.26
64	2,3,4′,6-	20.66
65	2,3,5,6-	23.50
66	2,3′,4,4′-	18.80
67	2,3′,4,5-	19.26
68	2,3′,4,5′-	17.72
69	2,3′,4,6-	19.67
70	2,3′,4′,5-	18.04
71	2,3′,4′,5′-	20.09
72	2,3′,4′,6-	20.20
73	2,3′,5,5′-	16.96
74	2,3′,5′,6-	19.12
75	2,4,4′,5-	19.26
76	2,4,4′,6-	19.67
77	3,3′,4,4′-	18.48
78	3,3′,4,5-	18.69
79	3,3′,4,5′-	17.40
80	3,3′,5,5′-	16.32
81	3,4,4′,5-	18.69
	pentachlorobiphenyls	
82	2,2′,3,3′,4-	16.29
83	2,2′,3,3′,5-	15.46
84	2,2′,3,3′,6-	16.86
85	2,2′,3,4,4′-	15.21
86	2,2′,3,4,5-	17.51
87	2,2′,3,4,5′-	14.45
88	2,2′,3,4,6-	17.63
89	2,2′,3,4,6′-	16.61
90	2,2′,3,4′,5-	14.38
91	2,2′,3,4′,5′-	15.46
92	2,2′,3,4′,6-	15.78
93	2,2′,3,4′,6′-	15.87
94	2,2′,3,5,5′-	13.62
95	2,2′,3,5,6-	17.59
96	2,2′,3,5,6′-	15.78
97	2,2′,3,5′,6-	15.02
98	2,2′,3,6,6′-	17.18
99	2,2′,4,4′,5-	14.38
100	2,2′,4,4′,6-	14.79
101	2,2′,4,5,5′-	13.62
102	2,2′,4,5,6′-	15.78
103	2,2′,4,5′,6-	14.03
104	2,2′,4,6,6′-	16.19
105	2,3,3′,4,4′-	14.89
106	2,3,3′,4,5-	16.11
107	2,3,3′,4,5′-	13.81
108	2,3,3′,4,6-	16.23
109	2,3,3′,4′,5-	14.06
110	2,3,3′,4′,5′-	14.89
111	2,3,3′,4′,6-	15.46
112	2,3,3′,5,5′-	12.98
113	2,3,3′,5,6-	16.19
114	2,3,3′,5′,6-	14.38
115	2,3,4,4′,5-	16.11
116	2,3,4,4′,6-	16.23
117	2,3,4,5,6-	20.57
118	2,3,4′,5,6-	16.19
119	2,3′,4,4′,5-	14.06
120	2,3′,4,4′,5′-	13.81
121	2,3′,4,4′,6-	14.47
122	2,3′,4,5,5′-	12.98
123	2,3′,4,5′,6-	13.39
124	2,3′,4′,5,5′-	13.05
125	2,3′,4′,5′,6-	15.21
126	3,3′,4,4′,5-	13.49
127	3,3′,4,5,5′-	12.41
	hexachlorobiphenyls	
128	2,2′,3,3′,4,4′-	11.30
129	2,2′,3,3′,4,5-	12.31
130	2,2′,3,3′,4,5′-	10.47
131	2,2′,3,3′,4,6-	12.43
132	2,2′,3,3′,4,6′-	11.87
133	2,2′,3,3′,5,5′-	9.64
134	2,2′,3,3′,5,6-	12.39
135	2,2′,3,3′,5,6′-	11.04
136	2,2′,3,3′,6,6′-	12.44
137	2,2′,3,4,4′,5-	11.23
138	2,2′,3,4,4′,5′-	10.47
139	2,2′,3,4,4′,6-	11.35
140	2,2′,3,4,4′,6′-	10.88
141	2,2′,3,4,5,5′-	10.47
142	2,2′,3,4,5,6-	14.66
143	2,2′,3,4,5,6′-	12.63
144	2,2′,3,4,5′,6-	10.59
145	2,2′,3,4,6,6′-	12.75
146	2,2′,3,4′,5,5′-	9.64
147	2,2′,3,4′,5,6-	11.31
148	2,2′,3,4′,5,6′-	10.05
149	2,2′,3,4′,5′,6-	11.04
150	2,2′,3,4′,6,6′-	11.45
151	2,2′,3,5,5′,6-	10.55
152	2,2′,3,5,6,6′-	12.71
153	2,2′,4,4′,5,5′-	9.64
154	2,2′,4,4′,5,6′-	10.05
155	2,2′,4,4′,6,6′-	10.46
156	2,3,3′,4,4′,5-	10.91
157	2,3,3′,4,4′,5′-	9.90
158	2,3,3′,4,4′,6-	11.03
159	2,3,3′,4,5,5′-	9.83
160	2,3,3′,4,5,6-	13.26
161	2,3,3′,4,5′,6-	9.95
162	2,3,3′,4′,5,5′-	9.07
163	2,3,3′,4′,5,6-	10.99
164	2,3,3′,4′,5′,6-	10.47
165	2,3,3′,5,5′,6-	9.91
166	2,3,4,4′,5,6-	13.26
167	2,3′,4,4′,5,5′-	9.07
168	2,3′,4,4′,5′,6-	9.48
169	3,3′,4,4′,5,5′-	8.50
	heptachlorobiphenyls	
170	2,2′,3,3′,4,4′,5-	7.32
171	2,2′,3,3′,4,4′,6-	7.44
172	2,2′,3,3′,4,5,5′-	6.49
173	2,2′,3,3′,4,5,6-	9.46
174	2,2′,3,3′,4,5,6′-	7.89
175	2,2′,3,3′,4,5′,6-	6.61
176	2,2′,3,3′,4,5′,6′-	7.40
177	2,2′,3,3′,4,6,6′-	8.01
178	2,2′,3,3′,5,5′,6-	6.57
179	2,2′,3,3′,5,6,6′-	7.97
180	2,2′,3,4,4′,5,5′-	6.49
181	2,2′,3,4,4′,5,6-	8.38
182	2,2′,3,4,4′,5,6′-	6.90
183	2,2′,3,4,4′,5′,6-	6.61
184	2,2′,3,4,4′,6,6′-	7.02
185	2,2′,3,4,5,5′,6-	7.62
186	2,2′,3,4,5,6,6′-	9.78
187	2,2′,3,4′,5,5′,6-	6.57
188	2,2′,3,4′,5,6,6′-	6.98
189	2,3,3′,4,4′,5,5′-	5.92
190	2,3,3′,4,4′,5,6-	8.06
191	2,3,3′,4,4′,5′,6-	6.04
192	2,3,3′,4,5,5′,6-	6.98
193	2,3,3′,4′,5,5′,6-	6.00
	octachlorobiphenyls	
194	2,2′,3,3′,4,4′,5,5′-	3.34
195	2,2′,3,3′,4,4′,5,6-	4.47
196	2,2′,3,3′,4,4′,5,6′-	3.46
197	2,2′,3,3′,4,4′,6,6′-	3.58
198	2,2′,3,3′,4,5,5′,6-	3.64
199	2,2′,3,3′,4,5,5′,6′-	3.42
200	2,2′,3,3′,4,5,6,6′-	5.04
201	2,2′,3,3′,4,5′,6,6′-	3.54
202	2,2′,3,3′,5,5′,6,6′-	3.50
203	2,2′,3,4,4′,5,5′,6-	3.64
204	2,2′,3,4,4′,5,6,6′-	4.05
205	2,3,3′,4,4′,5,5′,6-	3.07
	nonachlorobiphenyls	
206	2,2′,3,3′,4,4′,5,5′,6-	0.49
207	2,2′,3,3′,4,4′,5,6,6′-	0.61
208	2,2′,3,3′,4,5,5′,6,6′-	0.57
	decachlorobiphenyl	
209	2,2′,3,3′,4,4′,5,5′,6,6′-	−2.36

[a] For the numbering of the carbon atoms in PCBs, see Figure 1. [b] Experimental values.[1,2]

At the first stage, the enthalpies of formation were calculated by the difference method using biphenyl; benzene; and mono-, di-, tri-, tetra-, and pentachlorobenzenes as model compounds. For example

$$\Delta_f H^\circ_{298}(2,3,3',4,4',5\text{-hexachlorobiphenyl}) = \Delta_f H^\circ_{298}(\text{biphenyl}) + \Delta_f H^\circ_{298}(1,2,3,4\text{-tetrachlorobenzene}) + \Delta_f H^\circ_{298}(1,2\text{-dichlorobenzene}) - 2\Delta_f H^\circ_{298}(\text{benzene}) \quad (10)$$

As for dichlorobiphenyls, the calculated $\Delta_f H^\circ_{298}$ values were then applied to derive the group additivity values. Taking the values of C_B—(H), C_B—(C_B), C_B—(Cl), Δ_{12}, Δ_{13}, Δ_{14}, and $\delta_{o-Cl,Ph}$ to be the same as those for dichlorobiphenyls, seven new correction terms—Δ_{123}, Δ_{124}, Δ_{135}, Δ_{1234}, Δ_{1235}, Δ_{1245}, and Δ_{12345}—were determined. These terms account for the total steric interactions between three, four, and five chlorine atoms in the different positions. The value of Δ_{1234}, for one, can be derived from the enthalpy of formation of 2,3,3′,4,4′,5-hexachlorobiphenyl (eq 10):

$$\Delta_f H^\circ_{298}(2,3,3',4,4',5\text{-hexachlorobiphenyl}) = 4[C_B—(H)] + 2[C_B—(C_B)] + 6[C_B—(Cl)] + \Delta_{12} + \Delta_{1234} + \delta_{o-Cl,Ph} \quad (11)$$

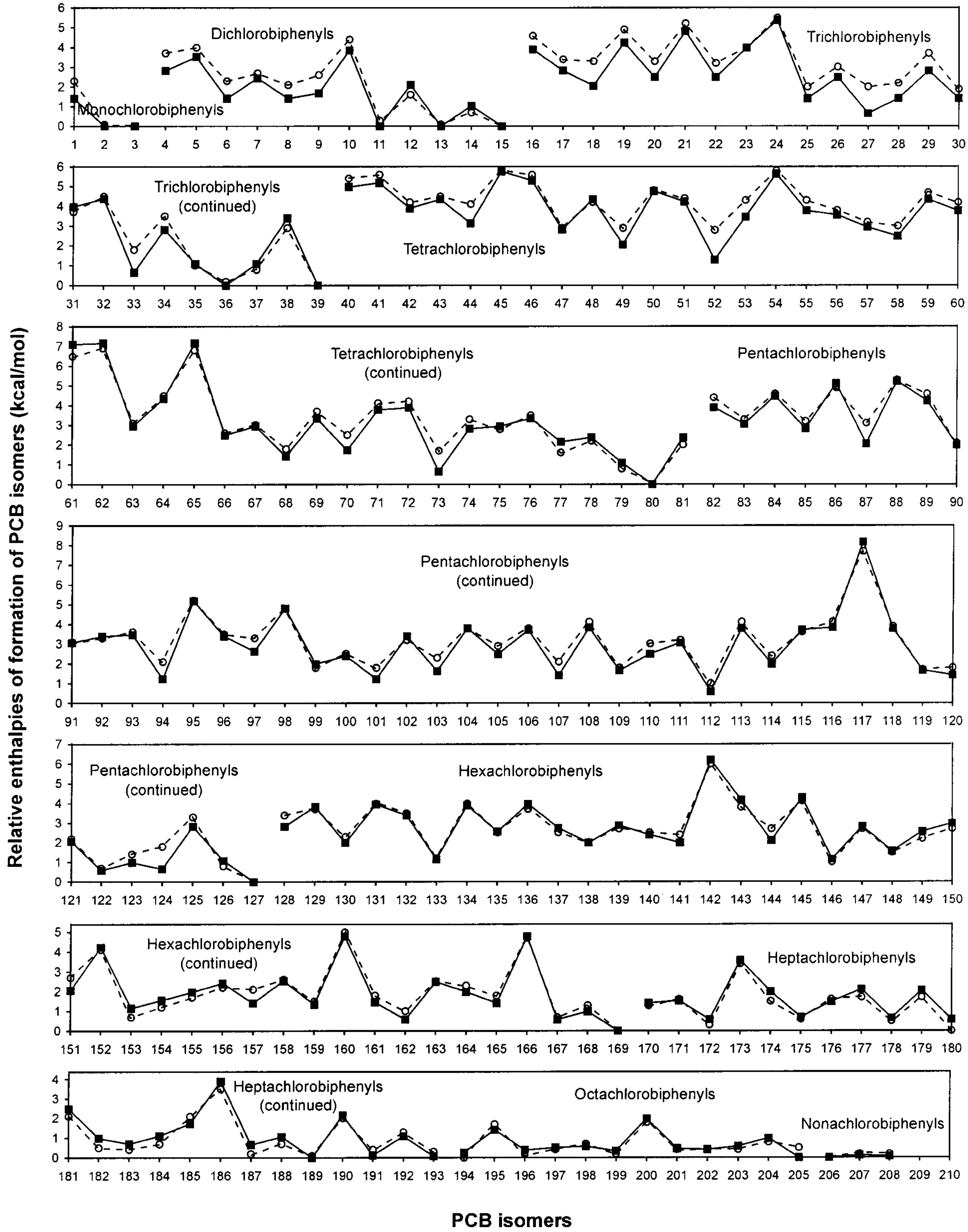

Figure 3. Comparison of relative enthalpies of formation for all PCB isomers estimated in this work (solid lines) and by the AM1 method[7] (dashed lines). The numbers on the abscissa correspond to the PCBs numbers in Table 1.

The other interaction terms were calculated in a similar way, and their values were considered as the tentative estimates.

At the next stage, the values of seven interaction terms were refined to fit the trend in the relative enthalpy of formation values to that modeled by the AM1 method.[7] Note that initial refinement was carried out assuming $\delta_{\mathrm{o-Cl,Ph}} = 0.84$ kcal/mol. However, with this value we could not obtain the reasonable values for some tri- and tetrachlorobiphenyls with ortho chlorine atoms. For instance, the enthalpy of formation of 2,2′,5,5′-tetrachlorobiphenyl was the same as that for the most stable 3,3′,5,5′ isomer. This effect can indicate that the experimental enthalpy of formation of 2,2′-dichlorobiphenyl is not quite accurate. When the value of $\delta_{\mathrm{o-Cl,Ph}}$ was increased up to 1.40 kcal/mol, the trend in relative distribution of tri- and tetrachlorobiphenyls became quite reasonable (Figure 3). The latter value of $\delta_{\mathrm{o-Cl,Ph}}$ corresponds to $\Delta_f H^\circ_{298}$(2,2′-dichlorobiphenyl) =

TABLE 2: Group Additivity Values for Estimating the Enthalpies of Formation of PCB Isomers

group	value (kcal/mol)	group	value (kcal/mol)	group	value (kcal/mol)
C_B—(H)	3.29	Δ_{14}	0.27	Δ_{1235}	6.48
C_B—(Cl)	−4.02	Δ_{123}	4.43	Δ_{1245}	6.44
C_B—(C_B)	5.30	Δ_{124}	3.60	Δ_{12345}	10.82
Δ_{12}	2.11	Δ_{135}	2.61	$\delta_{o-Cl,Ph}$	1.40
Δ_{13}	1.03	Δ_{1234}	7.76		

31.69 kcal/mol, which is the maximum permissible value within the limits of the experimental accuracy. It should be particularly emphasized that the ortho correction, and hence the enthalpy of formation of 2,2′-dichlorobiphenyl, was increased not to fit the AM1 results but to obtain reasonable enthalpy of formations for some isomers with ortho chlorine atoms. Additional arguments for this choice provide the DFT calculations (see below).

Only three types of interactions, namely, 1,2-, 1,3, and 1,4-interactions, are usually employed for multisubstituted aromatic compounds.[3,6,7,10−12,17] All interactions between three and more substitutes are defined as the sum of these three terms. Thus, 1,2,3-trichlorobenzene would have two 1,2 interactions and one 1,3 interaction, whereas 1,2,3,5-tetrachlorobenzene would have two 1,2 interactions, three 1,3 interactions, and one 1,4 interaction. However, it does not always happen that this set of group interaction values can reproduce the experimental $\Delta_f H^\circ_{298}$ values. For this reason, Bozzelli et al.[6,17] have suggested that the interaction effects in multisubstituted aromatics were not always linearly additive. Bozzelli et al.[6,17] have developed the empirical formalism for counting the number of interactions in aromatic compounds on the basis of experimental and estimated $\Delta_f H^\circ_{298}$ values for chlorinated benzenes. This formalism counts all of the 1,2 interactions but only considers the integer value from half of the number of 1,3 and 1,4 interactions. We believe that this approach is hardly worth considering as long as there is an uncertainty in the enthalpy of formation values for multichlorinated benzenes.[18,19]

The final correction terms are summarized in Table 2. After fitting to AM1 results, these terms may be considered as involving not only the total steric interaction between chlorine atoms within a ring but also the influence of the adjacent phenyl ring. The corresponding enthalpies of formation for all PCB isomers are given in Table 1; their relative values are shown in Figure 3 together with AM1 results.[7]

Uncertainties. The uncertainties in $\Delta_f H^\circ_{298}$ values for mono- and dichlorobiphenyls are expected to be not much larger than the uncertainties of experimental values for 2,2′- and 4,4′-dichlorobiphenyls, namely, 1−2 kcal/mol. The accuracy of $\Delta_f H^\circ_{298}$ values for other PCBs can reach 2.5 kcal/mol for trichlorobiphenyls, 4 kcal/mol for tetra-, penta-, and hexachlorobiphenyls, and 5 kcal/mol for hepta-, octa-, nona-, and decachlorobiphenyls.

Density Functional Calculations of Enthalpies of Formation of Biphenyl and 2,2′- and 4,4′-Dichlorobiphenyls. As discussed above, the attempts to develop the group additivity approach for PCBs were unsuccessful when the experimental value of $\Delta_f H^\circ_{298}$ was used for 2,2′-dichlorobiphenyl. The enthalpy of formation of 2,2′-dichlorobiphenyl should be assumed to be 1−2 kcal/mol larger than that of the experimental value to get the enthalpies of formation for isomers with ortho Cl atoms in agreement with destabilizing steric effect of these chlorine atoms. To check the reliability of the experimental value of $\Delta_f H^\circ_{298}$ for 2,2′-dichlorobiphenyl, the enthalpies of formation of biphenyl and 2,2′- and 4,4′-dichlorobiphenyls were calculated in this work at the B3LYP density functional theory (DFT) level.

There are numerous quantum chemical approaches for making thermochemical predictions. Some of these methods are very accurate, but with present computational capabilities, they can only be applied to relatively small molecules. The B3LYP method is chosen because it is the less computationally expensive one and yields reasonable energies for small molecules.[20] For large molecules, the DFT method cannot predict the enthalpies of formation from atomization energies with the desirable accuracy of 1−2 kcal/mol, and so, their values were estimated using the isodesmic reactions.[21] An isodesmic reaction is one in which the number of bonds of each type is conserved, and then one might expect the cancellation of errors in calculated energies on the two sides of the reaction. As a result, the energy change in the isodesmic reaction is moderately well-predicted using a simple level of theory.

The isodesmic reactions lead to more accurate results for processes in which the initial reactants and final products are as similar as possible.[21] Because of this, we chose the reactions where the groups are also conserved besides the bond types. The following three isodesmic reactions were selected to determine the enthalpy of formation of biphenyl:

$$C_6H_5{-}C_6H_5 + CH_3{-}CH_3 \rightarrow 2\ C_6H_5{-}CH_3 \tag{R1}$$

$$C_6H_5{-}C_6H_5 + H_2C{=}CH_2 \rightarrow C_6H_6 + C_6H_5{-}CH{=}CH_2 \tag{R2}$$

$$C_6H_5{-}C_6H_5 + CH_3{-}OH \rightarrow C_6H_5{-}OH + C_6H_5{-}CH_3 \tag{R3}$$

Twelve reactions were selected for 2,2′- and 4,4′-dichlorobiphenyls:

$$Cl{-}C_6H_4{-}C_6H_4{-}Cl + CH_4 \rightarrow C_6H_5{-}C_6H_5 + CH_2Cl_2 \tag{R4}$$

$$Cl{-}C_6H_4{-}C_6H_4{-}Cl + CH_3{-}CH_3 \rightarrow C_6H_5{-}C_6H_5 + CH_3{-}CHCl_2 \tag{R5}$$

$$Cl{-}C_6H_4{-}C_6H_4{-}Cl + H_2C{=}CH_2 \rightarrow C_6H_5{-}C_6H_5 + H_2C{=}CCl_2 \tag{R6}$$

$$Cl{-}C_6H_4{-}C_6H_4{-}Cl + 2\ CH_4 \rightarrow C_6H_5{-}Cl + C_6H_5{-}CH_3 + CH_3Cl \tag{R7}$$

$$Cl{-}C_6H_4{-}C_6H_4{-}Cl + 2\ CH_3{-}CH_3 \rightarrow C_6H_5{-}Cl + C_6H_5{-}CH_2{-}CH_3 + CH_3{-}CH_2Cl \tag{R8}$$

$$Cl{-}C_6H_4{-}C_6H_4{-}Cl + 2\ H_2C{=}CH_2 \rightarrow C_6H_5{-}Cl + C_6H_5{-}CH{=}CH_2 + H_2C{=}CHCl \tag{R9}$$

$$Cl{-}C_6H_4{-}C_6H_4{-}Cl + 2\ CH_4 \rightarrow C_6H_6 + C_6H_5{-}CH_3 + CH_2Cl_2 \tag{R10}$$

$$Cl{-}C_6H_4{-}C_6H_4{-}Cl + 2\ CH_3{-}CH_3 \rightarrow C_6H_6 + C_6H_5{-}CH_2{-}CH_3 + CH_3{-}CHCl_2 \tag{R11}$$

$$Cl{-}C_6H_4{-}C_6H_4{-}Cl + 2\ H_2C{=}CH_2 \rightarrow C_6H_6 + C_6H_5{-}CH{=}CH_2 + H_2C{=}CCl_2 \tag{R12}$$

$$Cl{-}C_6H_4{-}C_6H_4{-}Cl + 2\ CH_3{-}OH \rightarrow 2\ C_6H_5{-}OH + CH_3{-}CHCl_2 \tag{R13}$$

$$Cl{-}C_6H_4{-}C_6H_4{-}Cl + CH_3{-}OH + H_2C{=}CH_2 \rightarrow C_6H_5{-}CH_3 + C_6H_5{-}OH + H_2C{=}CCl_2 \tag{R14}$$

$$Cl{-}C_6H_4{-}C_6H_4{-}Cl + CH_3{-}OH + CH_4 \rightarrow C_6H_5{-}Cl + C_6H_5{-}OH + CH_3{-}CH_2Cl \tag{R15}$$

TABLE 3: Calculated Electronic Energies, Zero-Point Energies, Thermal Corrections, and Experimental Enthalpies of Formation for Species in Reaction Schemes

molecule		electronic energy, E_e: B3LYP/6-31G(d,p) (hartree)	electronic energy, E_e: B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) (hartree)	ZPE (kcal/mol)	$H^\circ_{298} - H^\circ_0$ (kcal/mol)	$\Delta_f H^\circ_{298}$ [a] (kcal/mol)
CH_2Cl_2	dichloromethane	−959.698903	−959.780193	18.482	2.835	−22.80 ± 0.26
CH_3Cl	chloromethane	−500.112545	−500.158771	23.800	2.487	−19.58 ± 0.12
CH_4	methane	−40.524019	−40.536715	28.259	2.391	−17.78 ± 0.10
CH_4O	methanol	−115.723966	−115.772722	32.255	2.664	−48.16 ± 0.05
$C_2H_2Cl_2$	1,1-dichloroethylene	−997.778547	−997.873590	21.128	3.279	0.67 ± 0.31
C_2H_3Cl	chloroethylene	−538.190157	−538.250621	26.834	2.811	5.50 ± 0.50[b]
C_2H_4	ethylene	−78.593808	−78.621106	32.082	2.502	12.55 ± 0.07
$C_2H_4Cl_2$	1,1-dichloroethane	−999.021891	−999.113317	36.145	3.631	−30.52 ± 0.33
C_2H_5Cl	chloroethane	−539.43305	−539.489534	41.945	3.121	−26.79 ± 0.26
C_2H_6	ethane	−79.838739	−79.861402	47.021	2.775	−20.03 ± 0.07
C_6H_5Cl	chlorobenzene	−691.852927	−691.955672	57.163	4.042	12.43 ± 0.31
C_6H_6	benzene	−232.258214	−232.327483	63.131	3.347	19.74 ± 0.17
C_6H_6O	phenol	−307.478469	−307.580608	65.769	4.051	−23.04 ± 0.22
C_7H_8	methylbenzene	−271.578745	−271.657515	80.280	3.950	12.07 ± 0.12
C_8H_8	phenylethylene	−309.660922	−309.752623	83.761	4.856	35.37 ± 0.33
C_8H_{10}	ethylbenzene	−310.893407	−310.982050	98.496	5.198	7.17 ± 0.24
$C_{12}H_8Cl_2$	2,2′-dichlorobiphenyl	−1382.502527	−1382.704469	101.687	7.806	30.57 ± 1.12
$C_{12}H_8Cl_2$	4,4′- dichlorobiphenyl	−1382.510768	−1382.711255	101.930	7.720	28.94 ± 1.05
$C_{12}H_{10}$	biphenyl	−463.32194	−463.455324	114.066	6.158	43.51 ± 0.18 [c]

[a] Reference 2. [b] Reference 23. [c] Reference 16.

The enthalpy change of an isodesmic reaction can be calculated from either the total energies at certain level of calculation

$$\Delta_r H^\circ_{298} = \Sigma(E_{tot} \text{ of products}) - \Sigma(E_{tot} \text{ of reactants}) \qquad (12)$$

where $E_{tot} = E_e + \text{ZPE} + [H^\circ_{298} - H^\circ_0]$ (E_e is the electronic energy, ZPE is the zero-point energy, and $[H^\circ_{298} - H^\circ_0]$ is the thermal correction), or from the experimental values of $\Delta_f H^\circ_{298}$ of each species

$$\Delta_r H^\circ_{298} = \Sigma(\Delta_f H^\circ_{298} \text{ of products}) - \Sigma(\Delta_f H^\circ_{298} \text{ of reactants}) \qquad (13)$$

Combining eqs 12 and 13, we have the following equation for calculating the enthalpy of formation of any molecule:

$$\Delta_f H^\circ_{298}(\text{molecule}) = \Sigma(\Delta_f H^\circ_{298} \text{ of products}) - \Sigma(\Delta_f H^\circ_{298} \text{ of reactants}) - \Sigma(E_{tot} \text{ of products}) + \Sigma(E_{tot} \text{ of reactants}) \qquad (14)$$

It is obvious that the uncertainty of the $\Delta_f H^\circ_{298}$ value calculated from eq 14 will be determined by the accuracy of the experimental enthalpies of formation for species involved in the reaction. To reduce these errors, we tried to use the molecules with well-known $\Delta_f H^\circ_{298}$ values and consider a sufficiently large number of reactions.

Density functional calculations were performed using the Gaussian 98 system of programs.[22] The structural parameters were fully optimized at the B3LYP/6-31G(d,p) level of theory. Harmonic vibrational frequencies, zero-point energies, and thermal corrections were computed at the same level. To see if the large basis set results in an improvement of calculated values, the optimized geometries were also used to obtain the electronic energies in B3LYP/6-311+G(3df,2p) single-point calculations. Calculated electronic energies, zero-point energies, and thermal corrections are given in Table 3 together with experimental values of $\Delta_f H^\circ_{298}$ for all molecules in reactions R1−R15.

TABLE 4: Calculated Enthalpies of Formation of Biphenyl, 2,2′-Dichlorobiphenyl, and 4,4′-Dichlorobiphenyl (kcal/mol)

reaction	$\Delta_f H^\circ_{298}$: B3LYP/6-31G(d,p)	$\Delta_f H^\circ_{298}$: B3LYP/6-311+G(3df,2p)	$\Delta_f H^\circ_{298}(\text{exp}) - \Delta_f H^\circ_{298}(\text{calc})$: B3LYP/6-31G(d,p)	$\Delta_f H^\circ_{298}(\text{exp}) - \Delta_f H^\circ_{298}(\text{calc})$: B3LYP/6-311+G(3df,2p)
		Biphenyl		
(R1)	43.67	44.60	−0.16	−1.09
(R2)	44.42	44.60	−0.91	−1.09
(R3)	44.78	44.00	−1.27	−0.49
average value	44.29	44.40	0.78[a]	0.89[a]
		4,4′-Dichlorobiphenyl		
(R4)	28.55	29.48	0.39	−0.54
(R5)	28.92	29.96	0.02	−1.02
(R6)	28.68	29.08	0.26	−0.14
(R7)	30.59	31.76	−1.65	−2.82
(R8)	26.61	27.90	2.33	1.04
(R9)	31.11	31.00	−2.17	−2.06
(R10)	29.15	31.31	−0.21	−2.37
(R11)	26.52	28.74	2.42	0.20
(R12)	29.59	30.18	−0.65	−1.24
(R13)	32.42	30.98	−3.48	−2.04
(R14)	30.51	30.14	−1.57	−1.20
(R15)	31.28	30.92	−2.34	−1.98
average value	29.49	30.12	1.46[a]	1.39[a]
		2,2′-Dichlorobiphenyl		
(R4)	33.57	33.58	−3.00	−3.01
(R5)	33.94	34.06	−3.37	−3.49
(R6)	33.70	33.18	−3.13	−2.61
(R7)	35.61	35.86	−5.04	−5.29
(R8)	31.63	32.00	−1.06	−1.43
(R9)	36.13	35.10	−5.56	−4.53
(R10)	34.17	35.41	−3.60	−4.84
(R11)	31.54	32.83	−0.97	−2.26
(R12)	34.61	34.27	−4.04	−3.71
(R13)	37.44	35.08	−6.87	−4.51
(R14)	35.53	34.24	−4.96	−3.67
(R15)	36.29	35.01	−5.72	−4.44
average value	34.51	34.22	3.94[a]	3.65[a]

[a] Average absolute deviation.

Two sets of enthalpies of formation of biphenyl and 2,2′- and 4,4′-dichlorobiphenyls are given in Table 4. These values were calculated from eq 14 using the electronic energies obtained at the B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df, 2p) levels of calculation. In both cases, the total energies are based on B3LYP/6-31G(d,p) zero-point energies and thermal corrections scaled by 0.96 as recommended by Curtiss et al.[24] for B3LYP calculations. As is seen from Table 4, the calculated values of $\Delta_f H^\circ_{298}$ for biphenyl and 4,4′-dichlorobiphenyl are in good agreement with those of the experiment: the average absolute deviations do not exceed 1 and 1.5 kcal/mol, respectively. The calculated values for 2,2′-dichlorobiphenyl, however, are substantially larger than the experimental value, and an average deviation from the experimental $\Delta_f H^\circ_{298}$ value amounts up to ≈4 kcal/mol. This result allows us to suggest that the experimental value of enthalpy of formation of 2,2′-dichlorobiphenyl is underestimated by at least 1−2 kcal/mol. The difference between average values of enthalpy of formation of 2,2′- and 4,4′-dichlorobiphenyl is 5 kcal/mol at the B3LYP/6-31G(d,p) level of calculation and 4 kcal/mol at the B3LYP/6-311+G(3df,2p) level. The latter value is close to the relative enthalpy of formation of 2,2′-dichlorobiphenyl estimated by the AM1 method (3.7 kcal/mol).[7] Therefore, it may be safely suggested that the destabilizing steric effect of ortho chlorine atoms in 2,2′-dichlorobiphenyl is substantially larger than was suspected from experimental measurements (1.6 kcal/mol).

Discussion

The group additivity methods were widely used to estimate the enthalpies of formation for many organic species.[10−14] These methods are easy to use and accurate when based on a sufficient number of experimental data. For PCBs, experimental data are available for only two isomers of dichlorobiphenyl and group additivity schemes[3−6] were mainly based on experimental data for chlorinated benzenes. Unfortunately, the experimental enthalpies of formation for chlorinated organic compounds are often considerably uncertain. We cannot be quite certain even about the $\Delta_f H^\circ_{298}$ values of multichlorinated benzenes[18] which are the model compounds in the group additivity approaches. The use of different $\Delta_f H^\circ_{298}$ values for chlorinated benzenes led to two sets of estimated enthalpies of formation for polychlorinated dibenzo-*p*-dioxins;[18,19] the difference between their values ranges from 1 kcal/mol (monochlorodibenzo-*p*-dioxins) up to 10 kcal/mol (octachlorodibenzo-*p*-dioxin). Thus, to develop the group additivity methods, the reliable experimental data are required not only for a series of PCBs but also for multichlorinated benzenes.

It is unlikely that the experimental enthalpies of formation will be soon determined for a sufficient number of PCBs. Therefore, the thermodynamic stabilities of PCBs can be only estimated from theoretical calculations. Ab initio methods may be precise at high levels, but these calculations come only at the expense of great computational cost and they are not sufficiently advanced for large polychlorinated molecules. In consequence of this, different approaches were used in this work. The enthalpies of formation of mono- and dichlorobiphenyls were estimated from empirical correlations (group additivity scheme). The value of the correction associated with ortho Cl atoms was adjusted using the DFT calculations. From experimental $\Delta_f H^\circ_{298}$ values for multichlorinated benzenes, the initial enthalpies of formation were obtained for PCB isomers with three and more chlorine atoms. Finally, the trend in relative enthalpies of formation of PCBs modeled by AM1[7] (Figure 1) was considered as the basis for differentiating between their isomers.

A set of interaction terms derived in this work (Table 2) differs from those used usually in group additivity approaches for polychlorinated aromatic compounds.[3,6,7,10,11,17] The latter consist of the Δ_{12}, Δ_{13}, and Δ_{14} terms plus some additional corrections due to non-nearest-neighbor interactions. In support of the scheme proposed in this work, one can present our recent results for polychlorinated dibenzo-*p*-dioxins and dibenzofurans,[19] where the same interaction terms were applied not only to the enthalpies of formation but also to the entropies and heat capacities obtained from statistical mechanical calculations. The set of Δ_{12}, Δ_{13}, Δ_{14}, Δ_{123}, Δ_{124}, and Δ_{1234} corrections fitted the entropy and heat capacity values with average deviation of 0.1 kcal/mol; the appropriate maximum deviations did not exceed 0.3 kcal/mol.

Summary

The improved values of enthalpies of formation of mono- and dichlorobiphenyls were estimated by difference method using the experimental data for biphenyl, 2,2′- and 4,4′-dichlorobiphenyls, and chlorinated benzenes. For other PCBs, the $\Delta_f H^\circ_{298}$ values were estimated combining the difference method and data on relative enthalpies of formation calculated by the semiempirical method AM1.[7] The value of the ortho correction was improved using the results of density functional calculations. Three group values and 11 correction terms for use in the group additivity method were derived.

Acknowledgment. We thank Dr. Vladimir Mastryukov, The University of Texas at Austin, for help in theoretical calculations.

References and Notes

(1) Smith, N. K.; Gorin, G.; Good, W. D.; McCullough, J. P. *J. Phys. Chem.* **1964**, *68*, 940.

(2) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994; Vol. I.

(3) Shaub, W. M. *Thermochim. Acta* **1983**, *62*, 315.

(4) (a) *TRC Thermodynamic Tables—Non-Hydrocarbons*; Thermodynamics Research Center, Texas A&M University System: College Station, TX, 1987; w-7340. (b) *TRC Thermodynamic Tables—Non-Hydrocarbons*; Thermodynamics Research Center, Texas A&M University System: College Station, TX, 1988; w-7342.

(5) Holmes, D. A.; Harrison, B. K.; Dolfing, J. *Environ. Sci. Technol.* **1993**, *27*, 725.

(6) Wu, Y. G.; Patel, S. N.; Ritter, E. R.; Bozzelli, J. W. *Thermochim. Acta* **1993**, *222*, 153.

(7) Mulholland, J. A.; Sarofim, A. F.; Rutledge, G. C. *J. Phys. Chem.* **1993**, *97*, 6890.

(8) Unsworth, J. F.; Dorans, H. *Chemosphere* **1993**, *27*, 351.

(9) Zimmermann, R.; Wehrmeier, A.; Lenoir, D.; Schramm, K.-W.; Kettrup, A. *Organohalogen Compd.* **1996**, *27*, 237.

(10) Benson, S. W. *Thermochemical Kinetics*; John Wiley: New York, 1976.

(11) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419.

(12) Domalski, E. S.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805.

(13) Cohen, N. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1411.

(14) Chen, C.-J.; Wong, D.; Bozzelli, J. W. *J. Phys. Chem. A* **1998**, *102*, 4551.

(15) Dorofeeva, O. V.; Tolmach, P. I. *Thermochim. Acta* **1993**, *219*, 361.

(16) Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Steele, W. V. *J. Chem. Thermodyn.* **1989**, *21*, 1307.

(17) Bozzelli, J. W.; Wu, Y. G.; Ritter, E. R. *Chemospere* **1991**, *23*, 1221.

(18) Thompson, D. *Thermochim. Acta* **1995**, *261*, 7.

(19) Dorofeeva, O. V.; Iorish, V. S.; Moiseeva, N. F. *J. Chem. Eng. Data* **1999**, *44*, 516.

(20) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(21) Hehre, W. J.; Radom, L.; Schleyer, P. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi,

M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(23) Gurvich, L. V., Veyts, I. V., Alcock, C. B., Eds.; *Thermodynamic Properties of Individual Substances*, 4th ed.; Hemisphere: New York, 1990; Vol. 2.

(24) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1997**, *270*, 419.