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Density Functional Theory Studies on Radical Ions of Selected Polychlorinated Biphenyls

Sundaram Arulmozhiraja, Toshihiro Fujii,* and Masatoshi Morita

Environmental Chemistry Division, National Institute for Environmental Studies,
16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan

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Density functional theory studies provided the adiabatic ionization potentials and electron affinities of six polychlorinated biphenyls (PCBs): 3,3′,4,4′- and 2,2′,5,5′-tetrachlorobiphenyl; 3,3′,4,4′,5-, 2,2′,4,5,5′-, and 2,3′,4,4′,5-pentachlorobiphenyl; and 3,3′,4,4′,5,5′-hexachlorobiphenyl. A popular three-parameter hybrid functional (B3LYP) with the 6-311G(d,p) and 6-311+G(2d,2p) basis sets was used for this study. We present the optimized structures of the cations and anions of the selected PCBs at the B3LYP/6-311+G(2d,2p) level. In almost all of the studied PCBs, the structure of the ions tended to be more nearly planar than the structure of the corresponding neutrals. The radical ions of 2,2′,5,5′-tetrachlorobiphenyl and 2,2′,4,5,5′-pentachlorobiphenyl have energetically close syn- and antilike structures. The anions of non-ortho-chlorinated PCBs have coplanar structures. Ionization potentials obtained at the B3LYP/6-311+G(2d,2p) level were 8.07, 8.34, 8.16, 8.36, 8.20, and 8.26 eV for 3,3′,4,4′- and 2,2′,5,5′-tetrachlorobiphenyl, 3,3′,4,4′,5-, 2,2′,4,5,5′-, and 2,3′,4,4′,5-pentachlorobiphenyl, and 3,3′,4,4′,5,5′-hexachlorobiphenyl, respectively. Adiabatic electron affinities obtained for all of the selected PCBs were positive and larger than the electron affinity of biphenyl. Furthermore, the electron affinities of the non-ortho-chlorinated PCBs were higher than those of their ortho-substituted counterparts.

Introduction

Halogenated aromatic hydrocarbons (HAHs) constitute a broad class of compounds with varying structure, uses, environmental occurrence, and toxicity. The basic structural features governing the disposition of HAHs have been known for several years. The nature, the number and the position of the halogen atoms involved, and the structure of the aromatic ring determine the physical properties of these compounds as well as influence the response of biological systems to them. However, there are a lot of other known and unknown complicated and influential factors responsible for the toxicological nature of these molecules. So, it is apparent that a complete understanding of the molecular mechanisms of toxic action will be a difficult process involving the study of many molecular interactions and reactions singly and in combination. The mechanisms of action of chemicals may vary even among compounds of the same chemical class for reasons that are not always obvious. In these circumstances, exploring the factors that determine the toxicological effects of these HAHs would be desirable and handy.

Polychlorinated biphenyls (PCBs) have toxicities similar to those of polychlorinated dibenzo-*p*-dioxins (PCDDs).[1] Previous studies have revealed that dioxins appear to act as electron acceptors in charge−transfer complexes with a receptor in living cells,[2,3] and our recent investigations have confirmed this fact.[4,5] Because previous results suggest that the toxicity and enzyme-inducing capability of PCBs may be connected to their interactions with a cytosolic Ah receptor[6−8] (as is also the case for PCDDs), determining whether PCBs act as electron acceptors or donors in these interactions is necessary for a better understanding of their toxicity.

The balance between π-electron conjugation (which favors the planar structure) and repulsion between overlapping ortho hydrogen atoms (which favors the twisted conformer) renders biphenyl a nonplanar, twisted molecule.[9,10] In chlorinated biphenyls, however, this balance of interactions is perturbed by the chlorine atoms, which influence the structural features of biphenyls, especially the torsional angle (ϕ) between the phenyl rings. In our previous study,[11] we showed that ϕ values are not influenced by chlorine substituents at the para and meta positions (for para- and meta-chlorinated biphenyls, the ϕ value is around 40°, which is the same as the value for the biphenyl parent). However, as expected, the phenyl rings of PCBs with chlorine atoms in two of their ortho positions are nearly perpendicular.

When an electron is removed from or added to biphenyl, the effect of π-electron conjugation is greatly influenced and leads to a change in the torsional angle between the two phenyl rings. This phenomenon has raised considerable interest in the C−C interring bond length and planar/nonplanar nature of biphenyl ions.[12−17] Planar or nearly planar structures have been suggested for cations and anions in solution.[13,14] Rubio et al.[15] studied the cation and anion of biphenyl at the CASSCF and CASPT2 levels with the constraint of D_{2h} symmetry, and a recent density functional theory (DFT) study carried out by Furuya et al. with a smaller basis set showed nonplanar structures for both ions.[16] Our recent DFT investigation with a variety of larger basis sets concluded with a nonplanar structure for the biphenyl cation and a planar structure for the anion.[18] Overall, past studies indicate that ions adopt quinoid structures, whereas neutrals adopt benzenoid structures.

There have been only a few structural studies on the ions of chlorinated biphenyls.[19−21] Recently, Pan and Phillips[20] used DFT to study the radical anions of 4-chloro-, 3-chloro-, 2-chloro-, and 2,2′-dichlorobiphenyl. They observed a decrease in the ϕ values for the anions of these chlorinated biphenyls relative to the values for the corresponding neutrals. Pan et al. have obtained Raman spectra of 2-, 3-, and 4-chlorobiphenyl

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* To whom correspondence should be addressed. Fax: +81-298-50-2574. E-mail: t-fujii@nies.go.jp.

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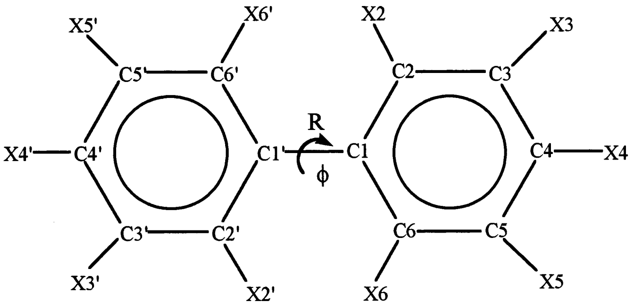

Figure 1. Atom-numbering scheme for PCBs.

cations and have also studied the structures by using DFT.[21] There have been no experimental or theoretical studies on the ions of the toxic PCBs.

The foregoing facts tempted us to investigate the ions of the selected PCBs by using DFT. First, investigating the ions would enable us to determine the structural changes, especially with regard to planarity or nonplanarity, that occur when these PCBs are ionized. Second, such studies would also enable us to obtain two important physical properties, the ionization potential (IP) and the electron affinity (EA) values, of the selected PCBs. These parameters, especially the latter, would help us to determine the role of PCBs in the interaction with Ah receptors. Third, these studies would be a continuation of our previous work on establishing the relationship between the calculated physical and chemical properties and the toxicities of PCBs.

Computational Methods

All computations were performed with Gaussian 98 programs.[22] The three-parameter hybrid density functional, B3LYP, which includes a mixture of Hartree−Fock exchange and DFT exchange correlation, was used.[23,24] Two tetrachlorobiphenyls (3,3′,4,4′- and 2,2′,5,5′-TCBP), three pentachlorobiphenyls (3,3′,4,4′,5-, 2,2′,4,5,5′-, and 2,3′,4,4′,5-PCBP), and a hexachlorobiphenyl (3,3′,4,4′,5,5′-HCBP) were considered for this study. The cations and anions of the selected PCBs were optimized first with the B3LYP functional using the 6-311G(d,p) basis set followed by the frequency calculations; we found that none of the ion structures had any imaginary frequencies, and thus, all were identified as minima. These frequency calculations also yielded the zero-point energies (ZPE), which were needed for the IP and EA calculations. Next, the 6-311+G(2d,2p) basis set was used to optimize the ions. No symmetry restrictions were imposed for optimizing the ion structures. The adiabatic IP and EA values were calculated using the total energies [obtained at the B3LYP/6-311G(d,p) and B3LYP/6-311+G(2d,2p) levels and ZPE-corrected with the B3LYP/6-311G(d,p) frequencies] of the ions and their respective neutrals. The atomic charges were derived by using electrostatic potential (ESP)-driven charges according to the Merz−Singh−Kollman scheme.[25,26] Unpaired electron spin densities were calculated for all of the ions using Mulliken population analysis (MPA).

Results and Discussion

Geometry of Ions. A schematic diagram of a PCB molecule is depicted in Figure 1. Two dominant geometrical parameters of the radical ions of the selected PCBs are worthy of discussion: the torsional angle (ϕ) and the interring C−C bond length (R). The calculated torsional angles of all of the selected PCB cations and anions, along with the angles of their neutral counterparts, are summarized in Table 1. The structural parameters of the ions of symmetric 3,3′,4,4′-, 3,3′,4,4′,5-, and 3,3′,4,4′,5,5′-PCBs and the corresponding parameters of the ions of less symmetric 2,2′,5,5′-, 2,2′,4,5,5′-, and 2,3′,4,4′,5-PCBs are given in Table 2. In almost all cases, the ϕ values were lower for the ions than for the corresponding neutrals. The considerable increase in the interring C−C π-bond order favors the planar conformations in the ion structures.

TABLE 1: Torsional Angles [ϕ (deg)] between the Two Phenyl Rings of the Ions of Selected PCBs Obtained with the B3LYP Functional[a]

	neutral[c]		cation		anion	
PCB	I	II	I	II	I	II
biphenyl[b]	40.5	40.1	19.0	18.9	6.3	0.0
3,3′,4,4′-TCBP	39.4	38.7	20.3	19.1	6.6	0.0
2,2′,5,5′-TCBP	98.8	95.5	114.4	114.1	39.5	40.6
3,3′,4,4′,5-PCBP	39.7	39.2	21.1	20.0	5.2	
2,2′,4,5,5′-PCBP	100.9	99.1	51.9	51.6	40.0	40.6
2,3′,4,4′,5-PCBP	58.6	58.8	41.0	40.3	31.0	30.8
3,3′,4,4′,5,5′-HCBP	39.5	38.9	21.4	20.5	0.0	0.0

[a] I, 6-311G(d,p); II, 6-311+G(2d,2p). [b] Taken from ref 18. [c] Taken from ref 11 (except biphenyl).

The ϕ values calculated for the cations of the PCBs with chlorine atoms in the para and meta positions (3,3′,4,4′-TCBP, 3,3′,4,4′,5-PCBP, and 3,3′,4,4′,5,5′-HCBP) were close to 20°, as predicted for biphenyl, and interestingly, the anions of these PCBs, like the biphenyl anion, exhibited planar structures.[18] We were unable to optimize the anionic structure of 3,3′,4,4′,5-PCBP with the 6-311+G(2d,2p) basis set. Again,[18] we noticed changes in planarity with the size of the basis set, and it is clear that large, flexible basis sets with diffusion functions should be utilized to study the anions. So, in every aspect, the ions of the non-ortho-chlorinated PCBs behave in the same way that biphenyl ions do.

The structures of the ortho-chlorinated PCBs are especially interesting. The ortho-substituted PCBs have a near-syn form (ortho chlorine atoms on the same side) rather than a near-anti form in their global energy minima. For example, experimental studies have concluded that 2,2′-dichlorobiphenyl exists in a near-syn conformer,[27−29] and our recent study showed that the global energy minima of 2,2′-dichlorobiphenyl, 2,2′,5,5′-TCBP, and 2,2′,4,5,5′-PCBP have synlike structures, although these structures are only approximately 2 kJ/mol more stable than their antilike counterparts.[11]

In the present study, we considered both anti- and synlike structures for the cations and anions of 2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP. Again, the global minimum for the 2,2′,5,5′-TCBP cation has a near-syn form [the two ortho chlorines come closer ($\phi = 114.1°$) than those in the neutral structure ($\phi = 95.5°$)]. However, the energy of its near-anti structure ($\phi = 56°$) is only 1.16 kJ/mol higher than that of the near-syn structure at the B3LYP/6-311+G(2d,2p) level. However, an antilike ($\phi = 51.6°$) global minimum was obtained for the 2,2′,4,5,5′-PCBP cation, whose structure is only 1.13 kJ/mol more stable than the synlike ($\phi = 119.3°$) structure. In contrast, the anions of both 2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP have antilike ($\phi = 40.6°$) global energy minima structures, but their corresponding synlike ($\phi \cong 135°$) forms are approximately 7 kJ/mol less stable.

The second important structural parameter is the interring C−C bond length. In the case of biphenyl, strengthening of this bond has been observed upon the addition or removal of electrons,[13] and the calculated interring C−C bond length in the biphenyl anion is smaller than that in the cation.[18]

We observed these same trends in our selected PCBs. When compared with the neutrals, the cations show an approximately 0.03 Å decrease in R value, and the anions show a 0.05 Å

TABLE 2: Structural Parameters of the Ions of Various PCBs at the B3LYP/6-311+G(2d,2p) Level [*r* (Å) and *θ*, *ϕ* (deg)][a]

	3,3′,4,4′-TCBP			2,2′,5,5′-TCBP			3,3′,4,4′,5-PCBP			2,2′,4,5,5′-PCBP			2,3′,4,4′,5-PCBP			3,3′,4,4′,5,5′-HCBP		
parameter	neutral	cation	anion	neutral	cation	anion	neutral	cation	anion[b]	neutral	cation	anion	neutral	cation	anion	neutral	cation	anion
r(C1−C1′)	1.482	1.447	1.434	1.491	1.478	1.443	1.483	1.449	1.434	1.490	1.465	1.443	1.487	1.454	1.440	1.483	1.450	1.432
r(C1−C2)	1.396	1.414	1.434	1.397	1.423	1.433	1.396	1.416	1.432	1.397	1.431	1.432	1.400	1.433	1.432	1.396	1.415	1.430
r(C1−C6)	1.400	1.424	1.431	1.396	1.389	1.435	1.396	1.415	1.434	1.394	1.401	1.434	1.397	1.409	1.440			
r(C2−X2)	1.079	1.078	1.078	1.753	1.721	1.781	1.079	1.077	1.081	1.750	1.728	1.777	1.754	1.730	1.781	1.079	1.077	1.077
r(C2−C3)	1.389	1.376	1.376	1.389	1.399	1.378	1.386	1.374	1.372	1.386	1.382	1.376	1.387	1.381	1.375	1.387	1.374	1.372
r(C3−X3)	1.746	1.724	1.771	1.079	1.079	1.081	1.745	1.725	1.779	1.078	1.079	1.079	1.078	1.079	1.079	1.744	1.725	1.768
r(C3−C4)	1.394	1.419	1.402	1.388	1.376	1.401	1.398	1.419	1.413	1.389	1.390	1.400	1.388	1.392	1.404	1.398	1.420	1.408
r(C4−X4)	1.743	1.704	1.760	1.079	1.080	1.078	1.733	1.697	1.763	1.742	1.709	1.758	1.741	1.708	1.760	1.732	1.696	1.746
r(C4−C5)	1.391	1.405	1.404	1.388	1.408	1.400	1.398	1.420	1.412	1.394	1.422	1.405	1.394	1.421	1.400			
r(C5−X5)	1.080	1.079	1.081	1.754	1.719	1.782	1.745	1.725	1.779	1.743	1.717	1.768	1.743	1.719	1.770			
r(C5−C6)	1.385	1.370	1.376	1.386	1.393	1.369	1.387	1.374	1.372	1.389	1.381	1.371	1.388	1.377	1.372			
r(C6−X6)	1.081	1.078	1.080	1.080	1.080	1.077	1.079	1.078	1.081	1.080	1.078	1.077	1.080	1.079	1.078			
θ(C1−C2−C3)	121.2	121.6	122.1	121.2	121.2	123.2	120.8	121.2	121.8	121.3	121.0	123.3	121.5	121.1	123.5	120.7	121.2	121.8
θ(C1−C2−X2)	120.4	120.7	120.6	120.3	120.2	120.8	120.6	120.8	120.7	120.5	121.4	121.0	121.3	121.7	121.8	120.6	120.9	120.8
θ(C2−C3−C4)	120.0	119.5	121.7	120.1	119.8	121.5	121.1	120.3	123.0	120.0	120.3	121.0	120.3	120.5	121.2	121.0	120.3	122.7
θ(C2−C3−X3)	118.6	119.7	118.1	119.7	119.5	118.9	118.2	119.3	117.6	120.2	120.1	119.6	120.1	120.0	119.5	118.2	119.3	117.8
θ(C3−C4−C5)	119.3	119.7	117.5	119.1	119.4	116.3	117.9	118.7	115.3	119.7	119.7	117.8	119.5	119.7	117.5	117.8	118.8	115.7
θ(C3−C4−X4)	121.7	121.3	122.9	120.5	120.7	121.8	121.0	120.6	121.7	118.6	119.1	119.2	118.8	119.1	119.0	121.0	120.6	122.1
θ(C4−C5−C6)	120.5	120.4	121.4	121.0	121.1	123.2	121.1	120.3	123.0	119.5	119.4	121.1	119.5	119.3	121.2			
θ(C4−C5−X5)	119.0	118.8	118.7	119.6	119.2	118.0	120.7	120.3	119.3	121.6	121.0	120.3	121.6	121.0	120.3			
θ(C5−C6−C1)	120.9	121.1	122.4	120.5	120.3	121.9	120.8	121.2	121.8	121.7	122.0	123.2	122.2	122.4	123.6			
θ(C5−C6−X6)	119.1	118.5	117.5	120.0	119.6	119.2	118.6	118.0	117.6	118.9	118.3	118.1	118.7	118.2	117.8			
θ(C6−C1−C1′)	121.3	121.2	122.9	119.3	119.8	120.7	120.9	121.0	122.4	119.5	119.7	120.7	118.9	118.8	119.1	120.8	120.9	122.4
θ(C1−C1′−C2′)	120.6	121.0	122.2	122.5	122.0	125.3	120.6	121.0	122.1	122.6	122.5	125.0	119.6	119.6	119.9			
θ(C6−C1−C2)	118.1	117.8	114.9	118.1	118.1	113.8	118.4	118.2	115.0	117.7	117.4	113.6	117.0	116.9	113.0	118.5	118.3	115.1
ϕ(C6−C1−C1′−C2′)	38.7	19.1	0.0	95.5	114.1	40.6	39.2	20.0	5.2	99.1	51.6	40.6	58.8	40.3	30.8	38.9	20.5	0.0

[a] Structural parameters for neutrals were taken from ref 11. [b] Obtained with 6-311G(d,p) basis set.

TABLE 3: Ionization Potentials [IP (eV)] of the Selected PCBs Obtained with the B3LYP Functional

	IP	
PCB	6-311G(d,p)	6-311+G(2d,2p)
biphenyl[a]	7.82	7.86
3,3′,4,4′-TCBP	8.12	8.07
2,2′,5,5′-TCBP	8.38	8.34
3,3′,4,4′,5-PCBP	8.23	8.16
2,2′,4,5,5′-PCBP	8.41	8.36
2,3′,4,4′,5-PCBP	8.27	8.20
3,3′,4,4′,5,5′-HCBP	8.34	8.26

[a] Taken from ref 18.

TABLE 4: Electron Affinities [EA (eV)] of the Selected PCBs Obtained with the B3LYP Functional

	EA	
PCB	6-311G(d,p)	6-311+G(2d,2p)
biphenyl[a]	−0.21	0.03
3,3′,4,4′-TCBP	0.83	0.92
2,2′,5,5′-TCBP	0.61	0.69
3,3′,4,4′,5-PCBP	1.04	
2,2′,4,5,5′-PCBP	0.79	0.84
2,3′,4,4′,5-PCBP	0.91	0.95
3,3′,4,4′,5,5′-HCBP	1.24	1.27

[a] Taken from ref 18.

decrease. Therefore, it seems that the double bond character of the C−C interring bond increases more when an electron is added than when an electron is removed. Other noticeable changes are a lengthening of the C1−C2 and C3−C4 bonds and a shortening of the C2−C3 bond. Moderate to large decreases in the θ(C6−C1−C2) and θ(C3−C4−C5) bond angles were observed for the anions. In all of the cases, the C−Cl bonds are stronger in the cations and much weaker in the anions when compared with the bonds in the neutrals. The C−Cl bonds are susceptible to bond cleavage reactions, and this fact reflects in the weak C−Cl bonds in anions. These weak bonds in anions suggest that dechlorination will occur more easily than in neutral or in cations. Overall, all of the bond lengths (including C−Cl) and bond angles calculated using both 6-311G(d,p) and 6-311+G(2d,2p) basis sets are similar.

IPs. The calculated adiabatic IPs [IP = E(cation) − E(neutral)] after ZPE correction are tabulated in Table 3. There are no significant differences in the IP values calculated with the two different basis sets. The IP values obtained for all of the selected PCBs are higher than those obtained for biphenyl. It seems that ortho-substituted PCBs (2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP) are more stable with respect to their cations than other PCBs are.

EAs. Although accurate EAs have been calculated for atoms and small molecules, the calculation of EAs has not been perfected; hence, theoretical predictions of EAs remain the subject of a great deal of research. In general, it is necessary to use flexible basis sets, especially with diffusion functions, and to treat electron correlation effects carefully in order to obtain accurate EAs. By considering the size of the molecules, DFT is a good choice for calculating the EA values of PCBs. EAs obtained with DFT methods are fairly accurate (within 0.2 eV) in most cases.[30] Earlier studies on a variety of molecules (three or fewer heavy atom) concluded that the B3LYP functional could achieve average errors between 0.1 and 0.2 eV as compared to the experiment.[31−34] EA values obtained for *p*-benzoquinone and a number of methyl- and halogen-substituted *p*-benzoquinones indicated that the B3LYP functional could yield EAs within experimental error for most quinones and within an average absolute magnitude of 0.05 eV of experimental values.[35] A recently published review[30] on EA also indicated that EA values calculated for a set of 91 molecules by using B3LYP functional have an average error of 0.16 eV. All of these studies showed that the B3LYP functional could be used to obtain reliable EA values. After considering all of the above facts, we utilized the same B3LYP functional to calculate the EA values of the selected PCBs and we believed that the calculated values would be reliable. To our knowledge, there are no published experimental EA values for these selected PCBs. EA values [EA = E(neutral) − E(anion)] obtained at the B3LYP/6-311G(d,p) and B3LYP/6-311+G(2d,2p) levels after ZPE correction are listed in Table 4.

The EA values of all of the selected PCBs are positive and higher than the value for biphenyl. For example, the EA value of 3,3′,4,4′-TCBP is 0.9 eV higher than that of biphenyl at the B3LYP/6-311+G(2d,2p) level. This may be due to the susceptible nature of carbon−halogen bonds to reductive bond cleavage reactions. This behavior causes weakening of C−Cl bonds in anion and also delocalizing of the negative charge throughout the molecule. Hence, the calculated EAs for PCBs are higher than that for unsubstituted biphenyl, and further large EA values are obtained for highly chlorinated PCBs (Table 4). Unlike biphenyl, none of the selected PCBs has negative EAs at the B3LYP/6-311G(d,p) level; however, in all of the cases, the EA values calculated with the 6-311+G(2d,2p) basis set are higher than those obtained with the other basis set.

The toxicities of HAHs, including dioxins and PCBs, depend strongly upon their receptor binding affinities. This binding interaction is necessary so that Ah receptors can transport the HAHs into the nucleus, where they cause their toxic and biological effects. Earlier work indicated that dioxins act as electron acceptors in the interaction with Ah receptors.[2−5] The large positive adiabatic EAs of the PCBs in the present study indicate that PCB molecules may also act as electron acceptors in their reactions with receptors in living cells.

It is known that the ligands (HAHs) with the highest binding affinities for Ah receptors are those with planar structures.[36] Therefore, it is obvious that the greater toxicity of the non-ortho-chlorinated PCBs could be explained by postulating that they have planar structures, just as in the case of dioxins. These PCBs are approximate isostereomers of 2,3,7,8-TCDD. However, the structure of PCBs is rather twisted.[11,37,38] Another possible explanation for the greater toxicity of particular PCBs has come from another direction. The barrier to rotation about the central C−C bond is known to be an important factor in determining the toxicity of PCBs. PCBs with lower rotational barriers have greater toxicity, and previous studies concluded that PCBs with lower barriers can easily attain a coplanar structure and thus are more toxic than PCBs with higher barriers.[39]

Our present results could provide an alternative explanation for the greater toxicity of these specific PCBs. Because the calculated EA values for the selected PCBs are positive, these PCBs appear to act as electron acceptors in charge−transfer interactions with the receptors. It is clear from the structural studies that non-ortho-substituted PCBs become planar after accepting an electron. Therefore, in the interaction with receptors, PCBs could accept electrons, become planar, and hence bind strongly to the receptors. This hypothesis may explain the greater toxicity of non-ortho-chlorinated PCBs. These two processes, accepting electrons from the receptors and becoming coplanar in structure, are synchronous, and they lead to the first critical step, strong binding with the receptors, in the complex sequence of events leading to the biological and toxic effects of PCBs. ortho-Chlorinated PCBs, in contrast, cannot become completely coplanar, even after accepting electrons from receptors. It is worth mentioning that non-ortho-chlorinated PCBs have larger EA values than ortho-chlorinated PCBs have; thus, it is reasonable to anticipate that PCBs with larger EA values will have greater toxicity.

Charge Distribution and Spin Density. Some of the results of the present study can be explained by analyzing the charge distributions and spin densities of the selected PCBs. The ESP charges calculated at the B3LYP/6-311G(d,p) level and the spin densities derived at the B3LYP/6-311+G(2d,2p) level were used for this purpose. The calculated ESP charges for the neutral PCBs indicate that positive charges located at the ortho hydrogen atoms of the ortho-chlorinated PCBs are large. Furthermore, the negative charges at the ortho chlorines of the same PCBs are small; thus, the steric repulsion between the ortho hydrogens may not be smaller than that between the ortho chlorines, a situation that would lead to the synlike global minimum energy structures calculated for 2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP. However, in the case of the ions, changes in charge distribution make a difference. An interesting fact that can be interpreted by means of charge distributions is the decreased torsional angles in the anions of these two ortho-chlorinated PCBs. Consider the case of 2,2′,5,5′-TCBP anion. The electronic charges on the ortho chlorine and ortho hydrogen atoms are -0.198 eV and $+0.146$ eV, respectively. The attraction between the positively charged hydrogen atoms and the negatively charged electronegative chlorine atoms can lead to the formation of hydrogen bonds. The obtained bond length (Cl⋯H) is 2.686 Å. Hence, one can speculate that in addition to the effect of π-electron conjugation, hydrogen bonding between the ortho chlorine and the ortho hydrogen atoms could be the reason that the ϕ values calculated for the anions of ortho-chlorinated PCBs are smaller than the values for the neutrals and the cations.

The location of the unpaired electrons may explain why the change in conformation of ions relative to their neutrals is observed. It is evident from the calculated spin densities that unpaired electrons are not located at a particular site; instead, they are delocalized over both of the phenyl rings. This fact influences the π-electron conjugation needed to enable the PCBs to adopt a planar conformation. This delocalization may be the reason for the decrease in ϕ values observed for all of the ions. In the case of non-ortho-substituted PCBs, a small amount (0.1) of unpaired spin lies on the chlorine atoms in the cations, but the unpaired electrons are completely delocalized on the carbon ring of the anions, hence their coplanar structure.

Potential Energy Curve (PEC). Because there is a decrease in torsional angles in the ions of ortho-chlorinated PCBs, it would be interesting to know how the energy barriers at the planar conformations and the PECs for the interring C−C rotations change when these PCBs become ions. We have drawn the PECs (relative energy vs torsional angle) for the cation and anion of 2,2′,5,5′-TCBP along with its neutral (Figure 2). For this purpose, we optimized the ion structures at various ϕ angles (from $\phi = 0°$ to $\phi = 180°$ in steps of 30°) by using the 6-311G(d,p) basis set. All geometrical parameters were allowed to optimize.

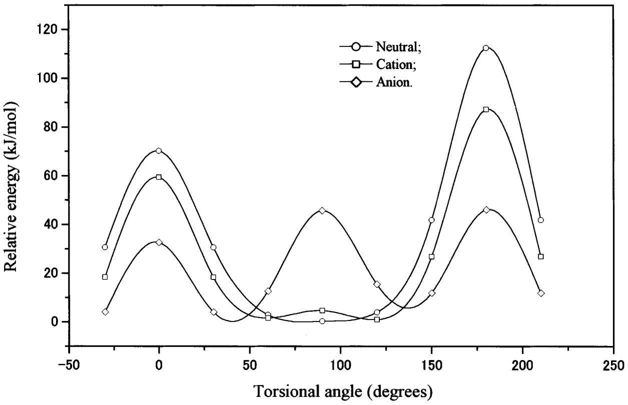

Figure 2. PECs at the B3LYP/6-311G(d,p) level for ions of 2,2′,5,5′-TCBP along with their neutral counterpart.

The figure shows that torsional barriers in the ions at $\phi = 0°$ [$\Delta E^{\circ} = E(\phi = 0°) - E(\text{equilibrium})$] as well as at $\phi = 180°$ [$\Delta E^{180} = E(\phi = 180°) - E(\text{equilibrium})$] are smaller than the barriers in the neutrals. For example, ΔE° decreased from 70.27 kJ/mol in the neutral to 32.73 kJ/mol in the anion. Therefore, in a charge−transfer interaction, even these ortho-substituted PCBs could achieve nearly planar structures by accepting electrons, which may be essential for their interaction with the receptors and for their toxic behaviors, at least in a lesser extent. Figure 2 clearly shows the existence of two narrowly separated minima for both of the ions. The PEC of the 2,2′,5,5′-TCBP anion mimics the PECs of the non-ortho-chlorinated PCBs.[11] All of the foregoing results are consistent with the fact that planarity is an essential part of the toxicity of PCBs.

Concluding Remarks

DFT was used to study the ions of PCBs. The torsional angles obtained for the ions were smaller than those of the corresponding neutrals. The cations of all of the selected PCBs have nonplanar structures. Interestingly, three non-ortho-chlorinated toxic PCBs, 3,3′,4,4′-TCBP, 3,3′,4,4′,5-PCBP, and 3,3′,4,4′,5,5′-HCBP, attain coplanar structures upon becoming anions. The IP values obtained for all of the selected PCBs were larger than the IP of biphenyl. The positive adiabatic EA values suggest that anionic PCBs are stable with respect to the detachment of electrons, and the values also indicate that PCBs, like TCDDs, act as electron acceptors in their interactions with receptors in living cells. The more toxic PCBs, non-ortho-chlorinated PCBs, have larger EA values than their ortho-chlorinated counterparts. The combination of the non-ortho-chlorinated PCBs' larger EA values and their coplanar anion structures could reveal a new phenomenon whereby these PCBs attain the essential planar structure by accepting electrons from cellular Ah receptors; the strong binding that results may then lead to greater toxicity. The torsional barrier at $\phi = 0°$ for the 2,2′,5,5′-TCBP anion is much smaller than the barrier for the neutral.

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Supporting Information Available: Tables of unscaled vibrational frequencies and infrared intensities for the selected PCB cations and anions. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Van den Berg, M.; Birnbaum, L.; Bosveld, A. T. C.; Brunstrom, B.; Cook, P.; Feeley, M.; Giesy, J. P.; Hanberg, A.; Hasegawa, R.; Kennedy, S. W.; Kubiak, T.; Larsen, J. C.; Rolaf van Leeuwen, F. X.; Djien Liem, A. K.; Nolt, C.; Peterson, R. E.; Poellinger, L.; Safe, S.; Schrenk, D.; Tillitt, D.; Tysklind, M.; Younes, M.; Waern, F.; Zacharewski, T. *Environ. Health Perspect.* **1998**, *106*, 775.

(2) Miller, G.; Sontum, S.; Crosby, D. G. *Bull. Environ. Contam. Toxicol.* **1977**, *18*, 611.

(3) Cheney, B. V.; Tolly, T. *Int. J. Quantum Chem*. **1979**, *16*, 87.

(4) Arulmozhiraja, S.; Fujii, T.; Tokiwa, H. *J. Phys. Chem. A* **2000**, *104*, 7068.

(5) Arulmozhiraja, S.; Fujii, T.; Sato, G. *Mol. Phys.* **2002**, *100*, 423.

(6) Rawls, R. L. *Chem. Eng. News* **1983**, *No. 6*, 38.

(7) Poland, A.; Knutson, J.; Glover, E. *Clin. Physiol. Biochem.* **1983**, *3*, 147.

(8) Safe, S.; Bandiera, S.; Sawyer, T.; Robertson, L.; Safe, L.; Parkinson, A.; Thomas, P. E.; Ryan, D. E.; Reik, L. M.; Levin, W.; Denomme, M. A.; Fujita, T. *Environ. Health Perspect.* **1985**, *60*, 47.

(9) Almenningen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J.; Samdal, S. *J. Mol. Struct.* **1985**, *128*, 59.

(10) Bastiansen, O.; Samdal, S. *J. Mol. Struct.* **1985**, *128*, 115.

(11) Arulmozhiraja, S.; Christopher Selvin, P.; Fujii, T. *J. Phys. Chem. A* **2002**, *106*, 1765.

(12) Kato, C.; Hamaguchi, H.-O.; Tasumi, M. *Chem. Phys. Lett.* **1985**, *120*, 183.

(13) Buntinx, G.; Poizat, O. *J. Chem. Phys.* **1989**, *91*, 2153.

(14) Sasaki, Y.; Hamaguchi, H. *Spectrochim. Acta, Part A* **1994**, *50*, 1475.

(15) Rubio, M.; Merchan, M.; Orti, E.; Roos, B. O. *J. Phys. Chem*. **1995**, *99*, 14890.

(16) Furuya, K.; Torii, H.; Furukawa, Y.; Tasumi, M. *J. Mol. Struct. (THEOCHEM)* **1998**, *424*, 225.

(17) Yamaguchi, S.; Yoshimizu, N.; Maeda, S. *J. Phys. Chem.* **1978**, *82*, 1078.

(18) Arulmozhiraja, S.; Fujii, T. *J. Chem. Phys.* **2001**, *115*, 10589.

(19) Modelli, A.; Distefano, G.; Jones, D. *Chem. Phys.* **1983**, *82*, 489.

(20) Pan, D.; Phillips, D. L. *Chem. Phys. Lett.* **2000**, *318*, 214.

(21) Pan, D.; Shoute, L. C. T.; Phillips, D. L. *Chem. Phys. Lett.* **2000**, *316*, 395.

(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.; Baboul, A. G.; 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.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(23) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(24) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(25) Besler, B. H.; Merz, K. M., Jr.; Kollman, P. A. *J. Comput. Chem.* **1990**, *11*, 431.

(26) Singh, U. C.; Kollman, P. A. *J. Comput. Chem.* **1984**, *5*, 129.

(27) Bastiansen, O. *Acta Chem. Scand.* **1950**, *4*, 926.

(28) Romming, C.; Seip, H. M.; Aanesen Oymo, I.-M. *Acta Chem. Scand., Ser. A* **1974**, *28*, 507.

(29) Dynes, J. J.; Baudais, F. L.; Boyd, R. K. *Can. J. Chem.* **1985**, *63*, 1292.

(30) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F., III; Nandi, S.; Ellison, G. B. *Chem. Rev.* **2002**, *102*, 231 and references therein.

(31) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople J. A. *J. Chem. Phys.* **1998**, *109*, 42.

(32) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 7374.

(33) de Proft, F.; Geerlings, P. *J. Chem. Phys.* **1997**, *106*, 3270.

(34) Takahata, Y.; Chong, D. P. *J. Braz. Chem. Soc.* **1999**, *10*, 354.

(35) Boesch, S. E.; Grafton, A. K.; Wheeler, R. A. *J. Phys. Chem.* **1996**, *100*, 10083.

(36) Whitlock, J. P., Jr. *Chem. Res. Toxicol.* **1993**, *6*, 754.

(37) McKinney, J. D.; Gottschalk, K. E.; Pedersen, L. *J. Mol. Struct. (THEOCHEM)* **1983**, *104*, 445.

(38) Tang, T.-H.; Nowakowska, M.; Guillet, J. E.; Csizmadia, I. G. *J. Mol. Struct. (THEOCHEM)* **1991**, *232*, 133.

(39) Erickson, M. D. *Analytical Chemistry of PCBs*; Butterworth Publishers: Boston, 1986.