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Structures, Potential Energy Curves, and Torsional Barrier Heights for Selected Polychlorinated Biphenyls: A Density Functional Theory Study

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Density functional theory studies were performed to obtain the structures, rotational barriers, and potential energy curves of six selected 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. Becke's three-parameter hybrid density functional, B3LYP, combined with 6-31G(d), 6-311G(d,p), and 6-311+G(2d,2p) basis sets was utilized for this purpose. For the selected PCBs, we present optimized geometries at the B3LYP/6-311+G(2d,2p) level of theory; torsional barriers at 0° and 90° at the B3LYP/6-31G(d), B3LYP/6-311G(d,p), and B3LYP/6-311+G(2d,2p) levels of theory; and potential energy curves (relative energy vs torsional angle) at the B3LYP/6-311G(d,p) level of theory. The geometries, torsional barriers, and potential energy curves of the non-ortho-chlorinated PCBs mimicked those of their parent biphenyl, whereas the remaining selected PCBs showed different behaviors. The syn-like structures of the 2,2′,5,5′- and 2,2′,4,5,5′-PCBs were of particular interest. However, the energy difference between the near-syn-like and near-anti-like structures was very small. Both of these PCBs have large barriers near planarity.

Introduction

Polychlorinated biphenyls (PCBs) are widespread environmental pollutants. PCBs have been used as lubricating and hydraulic fluids, fire retardants in fabrics, insulating and impregnating agents, and transformer oil. Out of the 209 PCB congeners, only 12 show toxicity similar to polychlorinated dibenzo-*p*-dioxins (PCDDs), having been assigned toxicity equivalency factors (TEFs).[1] Laterally substituted chlorinated biphenyls without *o*-chlorine substituents, which restrict free rotation of the two phenyl rings about the central C−C single bond, are the most toxic. In other words, non-ortho-substituted PCBs can be expected to be able to attain almost any dihedral angle in the field of a protein because of the small barriers to internal rotation. It has been known for some time that certain PCB congeners, notably 3,3′,4,4′-tetrachlorobiphenyl and 3,3′,4,4′,5-pentachlorobiphenyl, have dioxin-like activities. These observations suggest that the barrier to rotation about the central C−C bond is associated with the toxicity of a PCB. Obtaining reliable torsional barriers is important in establishing the precise relationship between toxicity and torsional barrier in PCBs.

There are, however, only a few theoretical studies on the torsional barriers of PCBs. McKinney et al.[2] studied the rotational barriers of a few PCBs, including 3,3′,4,4′-tetrachlorobiphenyl, at the HF/STO-3G level. In their study, they fixed the molecular structure except for the torsional angle (the angle between the two phenyl rings). Tang et al.[3] used AM1 to study the rotational barriers of selected polyfluorinated, polychlorinated, and polybrominated biphenyls. In 1997, Andersson et al.[4] calculated rotational barriers of all 209 PCBs by using AM1. Recently, Mizukami[5] studied the torsional angles of a number of PCBs at the HF/STO-3G level. In his study, Mizukami optimized the geometry of the C−C central bond and the torsional angle while holding all other structural parameters fixed.[5] He also studied the torsional barriers and potential energy curves of 3,3′,4,4′,5,5′-hexachlorobiphenyl and some other hexachlorobiphenyls at the same level of theory.

To obtain reliable torsional barriers for any molecule, it is important to use higher levels of theory. Moreover, complete optimization is required for accurate calculation of barriers. Many theoretical studies[6−9] on the torsional barriers of biphenyl have been carried out, but the barriers calculated in those studies, except in DFT studies, differ from experimental values.[10,11] Tsuzuki et al. concluded that very large basis sets (such as cc-pVQZ) should be used with MP2 to obtain moderately satisfactory torsional barriers for biphenyl.[12] Thus, higher level theory accompanied by a large basis set such as cc-pVQZ with complete optimization is necessary to obtain reliable torsional barriers for PCBs. However, because of the size of PCB molecules, it is difficult to use higher level correlation methodologies with large basis sets.

We recently demonstrated that the torsional barriers of biphenyls obtained with density functional theory (DFT) coincide well with experimental values.[13] Thus DFT, which has repeatedly been proven to be a reliable methodology, could be utilized to calculate reliable torsional barriers for PCBs.

Apart from the torsional barriers, the structure and potential energy curve associated with rotation about the C−C single bond of a PCB are of interest. However, there are no published experimental or high-level theoretical studies on the geometries and potential energy curves of PCBs. Because of the toxic nature of PCBs, experimentally obtaining their geometries and related parameters is difficult. Hence, obtaining reliable parameters by theoretical methods is an appealing alternative. The parameters obtained may be used to gain chemical and biological insights into PCB-related compounds.

Here, we used DFT to study the structures, potential energy curves, and torsional barriers of six selected PCBs. The selected

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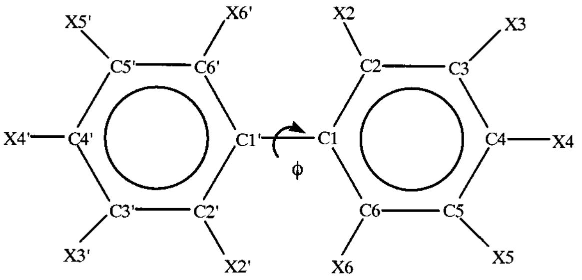

Figure 1. Atom-numbering scheme for a PCB model.

PCBs were two highly toxic PCBs (3,3′,4,4′,5-pentachlorobiphenyl and 3,3′,4,4′,5,5′-hexachlorobiphenyl), two nontoxic PCBs (2,2′,5,5′-tetrachlorobiphenyl and 2,2′,4,5,5′-pentachlorobiphenyl), and two moderately toxic PCBs (3,3′,4,4′-tetrachlorobiphenyl and 2,3′,4,4′,5-pentachlorobiphenyl).

Computational Details

All computations were performed by using Gaussian 98 programs.[14] Polychlorobiphenyls were optimized by using Becke's three-parameter hybrid density functional, B3LYP, which includes a mixture of Hartree−Fock exchange and DFT exchange correlation.[15,16] Three split-valence basis sets, 6-31G(d), 6-311G(d,p), and 6-311+G(2d,2p), were utilized for this purpose. No symmetry restrictions were imposed during the optimization. The optimized geometries were characterized by harmonic vibrational frequency calculations, which showed that all structures were minima on the potential energy surface. Potential energy curves (PEC) [relative energy vs torsional angle (ϕ)] for the selected PCBs as well as for biphenyl were drawn. For this purpose, structures at various ϕ values (from $\phi = 0°$ to $\phi = 180°$ in steps of 30°) were optimized by using the 6-31G(d) and 6-311G(d,p) basis sets. Rotational barriers at 0° [$\Delta E° = E(\phi{=}0°) - E(\text{equilibrium})$] and at 90° [$\Delta E^{90} = E(\phi{=}90°) - E(\text{equilibrium})$] were calculated by using the energies of the respective optimized structures at $\phi = 0°$ and $\phi = 90°$ (without any symmetry restriction) with respect to that of the stable twisted structures. All three basis sets were used with the B3LYP functional for this reason.

Results and Discussion

The atom-numbering scheme for a model PCB is given in Figure 1. In the following three sections, we discuss the structures, torsional barriers, and potential energy curves for the selected PCBs along with the parent biphenyl molecule.

Geometry. The important geometrical parameter in PCBs is the torsional angle. Symmetry interaction between the π orbitals of the phenyl rings tends to make biphenyl planar, while repulsion between overlapping *o*-hydrogen atoms tends to force the molecule to be nonplanar. Balance of these interactions results in a twisted biphenyl structure.[10,11] In chlorinated biphenyls, this balance of interactions is perturbed by chlorine atoms, and there are new interatom repulsive forces, both of which influence their geometries. For example, in PCBs with chlorine substituted at the ortho positions, repulsion between overlapping $\mathrm{H_{ortho}}$ and $\mathrm{Cl_{ortho}}$ atoms or between $\mathrm{Cl_{ortho}}$ and $\mathrm{Cl_{ortho}}$ atoms is stronger than that between $\mathrm{H_{ortho}}$ and $\mathrm{H_{ortho}}$ atoms in biphenyl; hence, larger torsional angles may result. Additionally, one may expect two other interactions: (a) H···Cl hydrogen bonding (since chlorine is an electronegative atom, it can hydrogen bond to the hydrogen atom of the neighboring phenyl ring) and (b) intramolecular attractive force between two chlorine atoms. In any case, the torsional angle is the principal geometrical parameter in PCBs. There are no previously published experimental or higher level theoretical studies on the structures of the selected chlorinated biphenyls.

The geometrical parameters of the selected PCBs optimized at the B3LYP/6-311+G(2d,2p) level of theory are listed in Table 1. The structural parameters of the symmetric 3,3′,4,4′-, 2,2′,5,5′-, and 3,3′,4,4′,5,5′-PCBs and the corresponding parameters of the lower symmetric 3,3′,4,4′,5-, 2,2′,4,5,5′-, and 2,3′,4,4′,5-PCBs are given in the body of the table; the remaining parameters of the nonsymmetric PCBs are summarized as footnotes. Table 1 shows that the torsional angle is not influenced by chlorine substituents at the para and meta positions. The ϕ values calculated for the three non-*o*-chlorine-substituted PCBs are close to the ϕ value of biphenyl ($\phi = 40.1°$ for biphenyl at B3LYP/6-311+G(2d,2p)).

As expected, PCBs with chlorine atoms in two of their ortho positions (2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP) have near-perpendicular structures because of strong Cl−H repulsions. Unexpectedly, however, 2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP have near-syn (*o*-chlorine atoms on the same side) rather than near-anti structures in their global minimum energies. The torsional angles between the two *o*-chlorine-containing planes of 2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP are 85.7° and 82.2°, respectively. We also found a near-anti-like local energy minimum structure for 2,2′,5,5′-TCBP ($\phi = 78.6°$ at B3LYP/6-31G(d)). However, the energy difference between the two conformers is very small (0.23 kJ/mol). Previous experimental studies concluded that 2,2′-dichlorobiphenyl exists as a near-syn conformer,[17−19] but previous theoretical studies[2,20,21] led to the opposite conclusion (near-anti conformer). We performed a geometrical study on this dichlorinated biphenyl at the B3LYP/6-311+G(2d,2p) level and confirmed the near-syn conformer structure for 2,2′-dichlorobiphenyl, proving the reliability of DFT. Thus the near-syn conformers of 2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP suggest that the plausible hydrogen bonding between the *o*-chlorine and *o*-hydrogen atoms does not play any role in the geometry of these ortho-substituted PCBs. However, some chlorine−chlorine nonbonded attractive force such as van der Waals interaction may exist, as speculated for 2,2′-dichlorobiphenyl.[19] This nonbonded Cl···Cl interaction should overpower both possible intramolecular hydrogen bonding between chlorine and hydrogen atoms and Coulombic repulsion between chlorine atoms. The nonbonded bond lengths in 2,2′,5,5′-TCBP are $r(\mathrm{Cl\cdots Cl}) = 3.954$ Å, $r(\mathrm{Cl\cdots H}) = 3.951$ Å, and $r(\mathrm{H\cdots H}) = 3.364$ Å. In 2,3′,4,4′,5-PCBP, the ϕ value is 58.8° and the Cl···H hydrogen-bond-like distance is 3.036 Å.

The position of chlorine substitution does not significantly affect the inter-ring bond length [$r(\mathrm{C1{-}C1'}) = 1.484$ Å in biphenyl]. The inter-ring bond length in 2,2′,5,5′-TCBP elongates ~0.01 Å due to ortho substitution. The chlorine substitution pattern slightly influences the planarity of the phenyl rings. More deviations from the mean plane of the phenyl rings have been observed in the non-*o*-chlorine-substituted than in the *o*-chlorine-substituted PCBs. For example, the ortho-positioned hydrogen atoms distorted by 1.5° from the phenyl plane in 3,3′,4,4′-TCBP, while the same hydrogen atoms deviated just 0.4° in 2,2′,5,5′-TCBP. An angle of 1.08° and 0.33° is noticed between (ClCC) and ($\mathrm{CCH_{ortho}}$) planes in 3,3′,4,4′- and 2,2′,5,5′-TCBPs, respectively. All other structural parameters are given in Table 1. The difference in ϕ values calculated with 6-311G(d,p) and 6-311+G(2d,2p) basis sets is small for the non-*o*-chlorine-substituted PCBs. However, a difference of about 3.3° in 2,2′,5,5′-TCBP is observed. This may be due to the fact that 2,2′,5,5′-TCBP has a very flat potential around $\phi = 90°$ (details

TABLE 1: Structural Parameters of Various PCBs at the B3LYP/6-311+G(2d,2p) Level [r (Å) and θ, ϕ (deg)][a]

parameter	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
r(C1−C1′)	1.482	1.491	1.483	1.490	1.487	1.483
r(C1−C2)	1.396	1.397	1.396	1.397	1.400	1.396
r(C1−C6)	1.400	1.396	1.396	1.394	1.397	
r(C2−X2)	1.079	1.753	1.079	1.750	1.754	1.079
r(C2−C3)	1.389	1.389	1.386	1.386	1.387	1.387
r(C3−X3)	1.746	1.079	1.745	1.078	1.078	1.744
r(C3−C4)	1.394	1.388	1.398	1.389	1.388	1.398
r(C4−X4)	1.743	1.079	1.733	1.742	1.741	1.732
r(C4−C5)	1.391	1.388	1.398	1.394	1.394	
r(C5−X5)	1.080	1.754	1.745	1.743	1.743	
r(C5−C6)	1.385	1.386	1.387	1.389	1.388	
r(C6−X6)	1.081	1.080	1.079	1.080	1.080	
θ(C1−C2−C3)	121.2	121.2	120.8	121.3	121.5	120.7
θ(C1−C2−X2)	120.4	120.3	120.6	120.5	121.3	120.6
θ(C2−C3−C4)	120.0	120.1	121.1	120.0	120.3	121.0
θ(C2−C3−X3)	118.6	119.7	118.2	120.2	120.1	118.2
θ(C3−C4−C5)	119.3	119.1	117.9	119.7	119.5	117.8
θ(C3−C4−X4)	121.7	120.5	121.0	118.6	118.8	121.0
θ(C4−C5−C6)	120.5	121.0	121.1	119.5	119.5	
θ(C4−C5−X5)	119.0	119.6	120.7	121.6	121.6	
θ(C5−C6−C1)	120.9	120.5	120.8	121.7	122.2	
θ(C5−C6−X6)	119.1	120.0	118.6	118.9	118.7	
θ(C6−C1−C1′)	121.3	119.3	120.9	119.5	118.9	
θ(C1−C1′−C2′)	120.6	122.5	120.6	122.6	119.6	
θ(C6−C1−C2)	118.1	118.1	118.4	117.7	117.0	118.5
ϕ(C6−C1−C1′−C2′)	38.7	95.5	39.2	99.1	58.8	38.9

[a] The remaining parameters of the nonsymmetric PCBs are given. *3,3′,4,4′,5-PCBP*: r(C1′−C2′) = 1.396; r(C1′−C6′) = 1.399; r(C2′−X2′) = 1.080; r(C2′−C3′) = 1.389; r(C3′−X3′) = 1.745; r(C3′−C4′) = 1.394; r(C4′−X4′) = 1.743; r(C4′−C5′) = 1.391; r(C5′−X5′) = 1.080; r(C5′−C6′) = 1.385; r(C6′−X6′) = 1.081; θ(C2′−C1′−C6′) = 118.3; θ(C1′−C2′−X2′) = 120.4; θ(C1′−C2′−C3′) = 121.1; θ(C2′−C3′−X3′) = 118.6; θ(C2′−C3′−C4′) = 120.0; θ(C3′−C4′−X4′) = 121.6; θ(C3′−C4′−C5′) = 119.3; θ(C4′−C5′−X5′) = 119.0; θ(C4′−C5′−C6′) = 120.5; θ(C5′−C6′−X6′) = 119.1; θ(C5′−C6′−C1′) = 120.8. *2,2′,4,5,5′-PCBP*: r(C1′−C2′) = 1.397; r(C1′−C6′) = 1.397; r(C2′−X2′) = 1.753; r(C2′−C3′) = 1.389; r(C3′−X3′) = 1.079; r(C3′−C4′) = 1.388; r(C4′−X4′) = 1.079; r(C4′−C5′) = 1.387; r(C5′−X5′) = 1.754; r(C5′−C6′) = 1.386; r(C6′−X6′) = 1.080; θ(C2′−C1′−C6′) = 118.2; θ(C1′−C2′−X2′) = 120.4; θ(C1′−C2′−C3′) = 121.2; θ(C2′−C3′−X3′) = 119.7; θ(C2′−C3′−C4′) = 120.1; θ(C3′−C4′−X4′) = 120.5; θ(C3′−C4′−C5′) = 119.1; θ(C4′−C5′−X5′) = 119.7; θ(C4′−C5′−C6′) = 120.9; θ(C5′−C6′−X6′) = 120.0; θ(C5′−C6′−C1′) = 120.5. *2,3′,4,4′,5-PCBP*: r(C1′−C2′) = 1.394; r(C1′−C6′) = 1.397; r(C2′−X2′) = 1.080; r(C2′−C3′) = 1.390; r(C3′−X3′) = 1.745; r(C3′−C4′) = 1.393; r(C4′−X4′) = 1.743; r(C4′−C5′) = 1.391; r(C5′−X5′) = 1.080; r(C5′−C6′) = 1.385; r(C6′−X6′) = 1.080; θ(C2′−C1′−C6′) = 118.6; θ(C1′−C2′−X2′) = 120.3; θ(C1′−C2′−C3′) = 121.0; θ(C2′−C3′−X3′) = 118.6; θ(C2′−C3′−C4′) = 119.9; θ(C3′−C4′−X4′) = 121.6; θ(C3′−C4′−C5′) = 119.4; θ(C4′−C5′−X5′) = 119.0; θ(C4′−C5′−C6′) = 120.5; θ(C5′−C6′−X6′) = 119.3; θ(C5′−C6′−C1′) = 120.5.

are under the potential energy curve section). But noticeable differences are found in ϕ values calculated using 6-31G(d) and 6-311+G(2d,2p) basis sets even for non-*o*-chlorine-substituted PCBs. Overall, ϕ values and other structural parameters calculated using the two larger basis sets are similar, showing the convergence of the basis set.

It is worth noting that the less toxic PCBs are more stable than their more toxic counterparts. It is well-known that the 3,3′,4,4′-, 3,3′,4,4′,5-, and 3,3′,4,4′,5,5′-PCBs are more toxic than the other PCBs. At the B3LYP/6-311+G(2d,2p) level, 2,2′,5,5′-TCBP is 3.19 kJ/mol more stable than the relatively toxic 3,3′,4,4′-TCBP. Among the three pentachlorobiphenyls, 2,2′,4,5,5′-PCBP is the most stable. It is more stable than 2,3′,4,4′,5- and 3,3′,4,4′,5-PCBPs by 4.01 and 4.45 kJ/mol, respectively. The stability order is 3,3′,4,4′,5 < 2,3′,4,4′,5 < 2,2′,4,5,5′, while the toxic equivalency factor (toxicity relative to that of 2,3,7,8-TCDD) follows the order 3,3′,4,4′,5 > 2,3′,4,4′,5 > 2,2′,4,5,5′.[1] Hence there is room to consider that less stable PCBs are more toxic.

Torsional Barrier. To our knowledge, there are no published experimental studies on the torsional barriers of our selected PCBs. Here, we used the B3LYP functional with various basis sets, since it performed well in obtaining reliable torsional barriers of biphenyl.[13] Additionally, to build confidence in our calculated torsional barriers for PCBs, we also calculated the torsional barriers of 4,4′-dichlorobiphenyl, whose barriers are known experimentally.[11] The calculated ΔE° and ΔE^{90} values of 7.66 and 8.41 kJ/mol, respectively, at the B3LYP/6-311+G(2d,2p) level coincide well with the experimental values ($\Delta E^\circ = 8.5 \pm 2.7$ and $\Delta E^{90} = 8.3 \pm 2.6$ kJ/mol).

The $\boldsymbol{\Delta} E^\circ$ and ΔE^{90} values of the selected PCBs calculated at B3LYP/6-311G(d,p) and B3LYP/6-311+G(2d,2p) are listed in Table 2. However, we have also calculated ΔE° and ΔE^{90} values at the B3LYP/6-31G(d) level (not tabulated). Considerable differences in ΔE values, especially in ΔE^{90} values, obtained using 6-31G(d) and 6-311+G(2d,2p) basis sets are noticed. The ΔE^{90} values calculated with two larger basis sets are almost the same, and the difference in ΔE° values obtained with these two basis sets is just 1 kJ/mol at the maximum, revealing that the basis set is well-converged for the torsional barrier calculations.

It is clear from Table 2 that the non-ortho-substituted PCBs follow exactly the same trends as their biphenyl parent. The calculated ΔE° and ΔE^{90} values for all three non-ortho-substituted PCBs—3,3′,4,4′-TCBP, 3,3′,4,4′,5-PCBP, and 3,3′,4,4′,5,5′-HCBP—are almost the same as those of biphenyl. These smaller ΔE° and ΔE^{90} values may allow these three PCBs to orient with any torsional angle in a protein field. Interestingly, like the ΔE° and ΔE^{90} values of biphenyl ($\Delta E^\circ = 6.0 \pm 2.1$ and $\Delta E^{90} = 6.5 \pm 2.0$ kJ/mol),[10,11] the calculated ΔE^{90} values for all three non-ortho-substituted PCBs are larger than their ΔE° values. In contrast, ortho-substituted PCBs follow a different trend. Because the Cl−H repulsion is stronger than the H−H repulsion, the ΔE° values calculated for all three ortho-substituted PCBs are larger than those calculated for the non-ortho-substituted PCBs. The ΔE° value of 2,3′,4,4′,5-PCBP,

TABLE 2: Torsional Angle (ϕ) between the Two Phenyl Rings in Various PCBs in deg and Rotational Barrier Heights at ϕ = 0° ($\Delta E^{\circ} = E^{\circ} - E$) and at ϕ = 90° ($\Delta E^{90} = E^{90} - E$) in kJ/mol at the B3LYP Functional

	ϕ		ΔE°		ΔE^{90}	
PCB	6-311G(d,p)	6-311+G(2d,2p)	6-311G(d,p)	6-311+G(2d,2p)	6-311G(d,p)	6-311+G(2d,2p)
biphenyl	40.5	40.1	9.04	8.07	8.33	8.02
3,3′,4,4′-TCBP	39.4	38.7	7.78	7.25	8.40	8.28
2,2′,5,5′-TCBP	98.8	95.5	70.27	69.04	0.33	0.26
3,3′,4,4′,5-PCBP	39.7	39.2	7.88	7.39	8.13	8.33
2,2′,4,5,5′-PCBP	100.9	99.1	68.34	66.92	0.40	0.19
2,3′,4,4′,5-PCBP	58.6	58.8	28.65	27.66	2.46	2.31
3,3′,4,4′,5,5′-HCBP	39.5	38.9	7.64	7.17	7.95	7.75

which has a single *o*-chlorine substitution, settled between the ΔE° values of the non-ortho-substituted PCBs and the ΔE° values of the di-ortho-substituted PCBs. All three ortho-substituted PCBs have very small ΔE^{90} values; ΔE^{90} is less than 1 kJ/mol for 2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP.

Because of the strong Cl−Cl Coulombic repulsion, 2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP have larger torsional barriers at 180° than at 0°. The calculated values of ΔE^{180} [$=E(\phi=180°) - E(\text{equilibrium})$] for 2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP are 112.4 and 111.0 kJ/mol, respectively, at the B3LYP/6-311G(d,p) level of theory. Thus, these ortho-substituted PCBs have large barriers at their planar orientations. These high torsional barriers prevent these molecules from attaining a near-planar structure by inhibiting free rotation around the C−C single bond. This may be the reason for the low toxicity (or nontoxicity) of these PCBs, since previous studies have established that planarity is the essential parameter for the toxicity of PCBs.

Potential Energy Curve. Potential energy curves (relative energy vs torsional angle) for the selected PCBs as well as biphenyl are drawn in Figure 2. All geometrical parameters were optimized at the B3LYP/6-311G(d,p) level for various torsional angles. The PCBs were grouped into three categories: (i) PCBs without chlorine substitution at the ortho positions (3,3′,4,4′-TCBP, 3,3′,4,4′,5-PCBP, and 3,3′,4,4′,5,5′-HCBP); (ii) PCBs with two chlorine atoms at the ortho positions (2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP); and (iii) a PCB with a single chlorine substitution at the ortho position (2,3′,4,4′,5-PCBP).

The PECs of 3,3′,4,4′-TCBP, 3,3′,4,4′,5-PCBP, and 3,3′,4,4′,-5,5′-HCBP closely resembled the periodic wavelike PEC of biphenyl. It is difficult to distinguish the superimposed PECs of these four molecules (Figure 2). The phenyl rings of 3,3′,4,4′-TCBP, 3,3′,4,4′,5-PCBP, and 3,3′,4,4′,5,5′-HCBP can easily rotate around their inter-ring C−C bond. Interestingly, the energy difference due to the complete rotation (0°−360°) of the phenyl rings is very small and nearly equal to the energy change due to the butterfly flapping motion of the two benzo planes of toxic 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD).[22] We previously showed[22] that TCDD is a very flexible molecule. The flexibilities of 3,3′,4,4′-TCBP, 3,3′,4,4′,5-PCBP, and 3,3′,4,4′,5,5′-HCBP (non-ortho-substituted PCBs) seem similar to the flexibility of TCDD, and in both cases, the molecules substituted in lateral positions are toxic. Hence, there is strong evidence that the flexibility of these PCBs is one of the main reasons for their toxicity. Changes in the inter-ring bond length (R) parallel increases or decreases in the torsional angle during the rotation. For example, for biphenyl, $R(\phi=0°) = 1.4940$ Å and $R(\phi=\text{equilibrium}) = 1.4854$ Å.

The PECs of 2,2′,5,5′-TCBP and 2,2′,4,5,5′-PCBP resemble typical potential wells (Figure 2) with a relatively small barrier on the left and a larger barrier on the right. Because of the strong Cl−H steric repulsion, the energy minimum was found close to $\phi = 90°$. It is seen from Figure 2 that the PECs of these two PCBs are very flat near $\phi = 90°$. Because the Cl−Cl interaction is stronger than the Cl−H interaction, the torsional barrier at $\phi = 180°$ is higher than the torsional barrier at $\phi = 0°$. As described in the geometry section, both chlorine atoms stay on the same side of the global minimum-energy structures of these two PCBs. However, it is difficult to identify the two minimum-energy structures (anti-like and syn-like) from the figure. To identify the two minimum-energy structures, we mapped a separate PEC for 2,2′,5,5′-TCBP using B3LYP/6-31G(d)-optimized energies at different ϕ values (optimization at 31 different ϕ values in the range 60°−120° in steps of 2°) (Figure 3). Although the PEC in Figure 3 seems to have two minimum-energy structures, the first is very shallow, the energy difference between the two structures is very small (0.23 kJ/mol), and the curve is very flat over the entire region. Thus, the molecule can easily change from one conformer to the other. The energy change due to phenyl ring rotation from $\phi = 60°$ to $\phi = 120°$ is less than 3 kJ/mol, which implies that this region of the PEC is very flat. Since ortho-substituted PCBs are not toxic, unlike non-ortho-substituted PCBs, we may conclude that flexible planarity may be more essential in determining the toxicity of PCBs than flatness near the perpendicular orientation. Substitu-

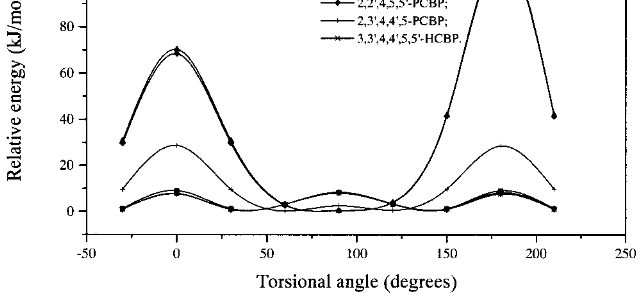

Figure 2. Relative energy vs torsional angle at the B3LYP/6-311G(d,p) level for the selected PCBs.

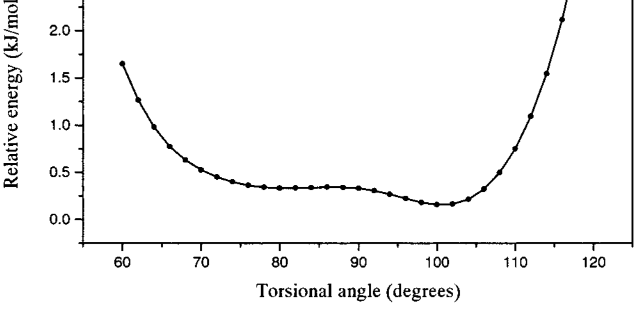

Figure 3. Relative energy vs torsional angle at the B3LYP/6-31G(d) level for 2,2′,5,5′-TCBP.

tion of chlorine at the para position of 2,2′,5,5′-TCBP did not affect the PEC; hence, 2,2′,4,5,5′-PCBP exhibited the same type of PEC as did 2,2′,5,5′-TCBP (Figures 2).

In contrast with the PECs of PCBs with chlorine substituted at two ortho positions, the PEC of 2,3′,4,4′,5-PCBP showed two clear minima as expected, but with a smaller energy difference. Both structures have barriers of ∼2 kJ/mol at $\phi = 90°$. It is obvious from Figure 2 that 2,3′,4,4′,5-PCBP is flexible between $\phi = 30°$ and $\phi = 150°$, like biphenyl and non-ortho-substituted PCBs.

Concluding Remarks

Density functional theory studies were performed to obtain the structures, torsional barriers, and potential energy curves of selected polychlorinated biphenyls.

The torsional angle and torsional barriers do not seem to be influenced by chlorine substitution at the meta and para positions. The $\Delta E°$ and ΔE^{90} values were almost equal for the non-ortho-substituted PCBs, with $\Delta E^{90}/\Delta E° > 1$ always. Overall, the behavior of these non-ortho-substituted PCBs is similar to that of their biphenyl parent. Like the phenyl groups in biphenyl, the phenyl groups in these PCBs can freely rotate around the central C−C bond, owing to the smaller barrier to rotation (<2 kcal/mol). The energy difference due to the entire rotation (0°−360°) of the phenyl rings of these non-ortho-substituted PCBs is very small and almost equal to the energy change due to the butterfly flapping motion of the two benzo planes of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). This rotational freedom allows these PCBs to orient with any torsional angle in a protein field and paves the way for easy interaction with receptors in living cells, hence their higher toxicity. On the other hand, chlorine substitution at the ortho positions produces a noticeable effect. PCBs with chlorine atoms at their ortho positions have two energy minima, but the energy difference between the two minimum-energy structures is very small. Interestingly, the global energy minima have two chlorine atoms on the same side (syn-like structure). A torsional angle close to 90° and higher torsional barriers at $\phi = 0°$ and at $\phi = 180°$ were observed for ortho-substituted PCBs.

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