Structures, Reductive Dechlorination, and Electron Affinities of Selected Polychlorinated Dibenzo-*p*-dioxins: Density Functional Theory Study

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Density functional theory calculations were performed to obtain the structures, vertical electron affinities, and adiabatic affinities of 15 polychlorinated dibenzo-*p*-dioxins (PCDDs), including several extremely toxic congeners. A three-parameter hybrid density functional, B3LYP, was utilized with two different basis sets, 6-311G(d,p) and 6-311+G(2d,2p). The optimized structures of all PCDDs under consideration were planar, while all corresponding anions attained nonplanar geometries. One of the C−Cl bonds on each PCDD anion was considerably elongated, and the dechlorination of PCDDs occurred as the departing chlorine bent off the aromatic ring plane for effective $\pi-\sigma$ orbital mixing. The characteristic electron energy-dependent regioselective chloride ion loss channels for 1,2,3,7,8-pentaCDD were elucidated by transition-state theory calculations. The relative low-energy barrier for the dechlorination of 1,2,3,7,8-pentaCDD indicated the high likelihood of obtaining reductive dechlorination (RD) products that are more toxic than the parent species. The calculated vertical electron affinities of PCDDs are consistent with the available experimental attachment energies, and the positive adiabatic electron affinities suggest that PCDDs may act as electron acceptors in living cells.

Introduction

Polyhalogenated aromatic compounds (PHAs), such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs), are extremely persistent and toxic pollutants that are widespread in the environment.[1] They may induce dermal toxicity, immunotoxicity, carcinogenicity, adverse effects on reproduction and development, and endocrine disruption.[2−4] PCDDs are among the most extensively studied organic chemicals and so they have become examples of highly toxic global pollutants.[5,6]

It should be emphasized that not all PCDD congeners are toxic. The most toxic ligand among PCDDs is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), and the toxic activity drastically decreases with the addition of peri chlorine substituents or the removal of lateral ones.[7−9] Although the origin of this congener specificity is not well-understood, the toxicity of planar PHAs is extremely sensitive to both the number and the position of halogen substitutes.[1,8,9] Electron affinity (EA) is an important molecular property that plays a vital role in electron-transfer reactions. Previous studies obtained positive EA values for various PCDDs,[10] PCBs,[11] and PCDFs,[12] which suggests that those halogenated aromatic hydrocarbons are stable with respect to the attachment of electrons and act as electron acceptors in the reaction with receptors in living cells.

Reductive dechlorination (RD) is a significant environmental transformation process for halogenated organic contaminants under anaerobic conditions. Several studies also demonstrated that PCDDs can be reductively dechlorinated by sediment microorganisms in anaerobic environments.[13−18] Recently, Bunge et al.[19] showed that the same bacterium was able to reductively dechlorinate selected dioxin congeners. Apparently, RD has recently been recognized as the key for detoxification of toxic halocarbons.

However, the halogen configuration of a PCDD/PCB congener dictates which chlorine(s) will first be removed, and various dechlorination mechanisms have been proposed for 1,2,3,4-TCDD.[15,17,19,20] These studies also concluded that the chlorines were removed in both the peri and the lateral positions. In other words, the dechlorinated metabolites might be potentially more toxic than the parent compounds. Therefore, it is important to understand the fate of PCDD/Fs in different environments and to elucidate possible mechanisms for the degradation of these toxic compounds. Studies on PCDD/Fs suggested that additional efforts were needed to understand the electron acceptance (reduction) and carbon−chlorine bond cleavage mechanisms.[21,22] In this regard, the geometrical changes in a PCDD/Fs congener upon accepting an electron may provide fundamental information for the understanding of dechlorination sites and processes.

The present study attempted to acquire the molecular structures and electronic properties on a series of relevant PCDD congeners and the corresponding anions, including several highly toxic ones such as 2,3,7,8-TCDD and 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (pentaCDD or PeCDD). Several chloride ion loss channels for 1,2,3,7,8-pentaCDD were elucidated by transition-state theory calculations, in an attempt to understand the characteristic electron energy-dependent regioselective loss of the chloride ion.

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Computational Details

Molecular geometries of the neutral molecules and the corresponding anions of selected PCDDs were obtained from density functional theory calculations using the B3LYP hybrid functional[23,24] with two split valence basis sets, 6-311G(d,p) and 6-311+G(2d,2p), respectively. No symmetry restrictions were imposed during the optimization. The optimized geometries were confirmed by harmonic vibrational frequency calculations that each of the geometries corresponds to a minimum on the potential energy surface. The calculated harmonic vibrational frequencies were also used to calculate zero-point energy (ZPE) corrections on electron affinities.

Adiabatic (EA_{ada}) and vertical (EA_{ver}) electron affinities were obtained from the following relations:

$$EA_{ada} = E_{neutral}\ (\text{optimized neutral}) - E_{anion}\ (\text{optimized anion})$$

$$EA_{ver} = E_{neutral}\ (\text{optimized neutral}) - E_{anion}\ (\text{optimized neutral})$$

Adiabatic electron affinity, EA_{ada}, includes the ZPE correction. It should be noted that spin contamination for the calculations of open-shell anions in this work was small, primarily due to the use of DFT methods.[25] The expectation value of the S^2 operator for doublets is 0.75.

A series of PCDD congeners representing chlorine substitutions at different positions was considered in this study (i.e., three trichloro- (1,2,4-, 2,3,6-, and 2,3,7-TrCDD), eight tetrachloro- (1,2,3,4-, 1,2,7,8-, 1,3,7,8-, 1,4,7,8-, 1,2,6,9-, 1,4,6,8-, 1,4,6,9-, and 2,3,7,8-TCDD), one pentachloro- (1,2,3,7,8-PeCDD), and three hexachloro- (1,2,3,4,7,8-, 1,2,3,6,7,8-, and 1,2,3,7,8,9-HCDD) congeners). All calculations were carried out using the Gaussian 03 programs.[26]

Results and Discussion

Molecular Geometry. Structural data based on X-ray diffraction are available for only a small fraction of the 75 possible PCDDs in the literature.[27−32] In the crystalline form, these molecules are nearly planar, although some atoms, including Cl, are slightly displaced off the molecular plane.[33] For example, the angle between the C−Cl bond and the molecular plane typically amounts to 3−4° with HCDDs,[28] whereas it does not exceed 2° with TCDDs.[27,31,32] The molecular geometries from B3LYP/6-311+G (2d, 2p) calculations (Figure 2) are planar for all of the neutral PCDDs considered in this study. As a result, the structural planarity of PCDDs may not be affected by chlorine substituents. Previous semiempirical[48] and ab initio[34−37] calculations also obtained planar configurations for PCDDs. Nevertheless, the central ring is quite flexible and is easily deformed into a butterfly-shaped conformation along the O··· O line.[34] The harmonic vibrational frequencies from B3LYP/6-311+G(2d,2p) calculations for the deformation motions fall in a range between 14.9 and 25.5 cm^{-1}, which may indicate that PCDD molecules could exist in different configurations depending on the experimental conditions, such as temperature and the magnitude of intermolecular interaction.[38] Overall, no noticeable geometric irregularities in the aromatic ring were found as a result of chlorine substitution for selected PCDDs, with the exception of chlorine substitutions at the positions 1 and 2. The C−C bond lengths and a few bond angles optimized for these PCDDs (e.g., 1,2,3,4-, 1,2,6,9-, and 1,2,7,8-TCDD; 1,2,3,7,8-PeCDD; and 1,2,3,6,7,8-, 1,2,3,7,8,9-, and 1,2,3,4,7,8-HCDD) are different from those of the other PCDDs. In addition, molecular geometries from the two basis sets are almost identical. Geometrical parameters for 2,3,7,8-TCDD and 1,2,3,7,8,9-HCDD from the B3LYP/6-311+G(2d,2p) calculations generally agree well with the experimental values[39,40] (Table 1).

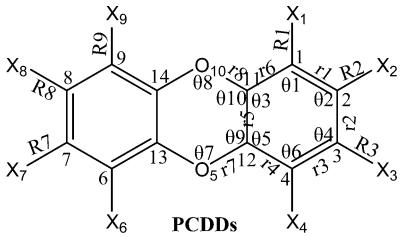


Figure 1. Atom-numbering scheme for PCDDs. X = H for dibenzo-*p*-dioxin.

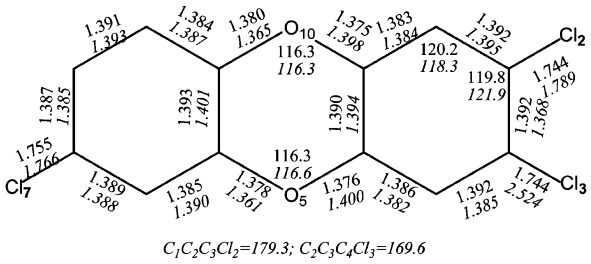
TABLE 1: Comparison of Calculated Structural Parameters[a] of 1,2,3,7,8,9-HCDD and 2,3,7,8-TCDD at the B3LYP/6-311+G(2d,2p) Level with Previous Calculated Values and Experimental Values

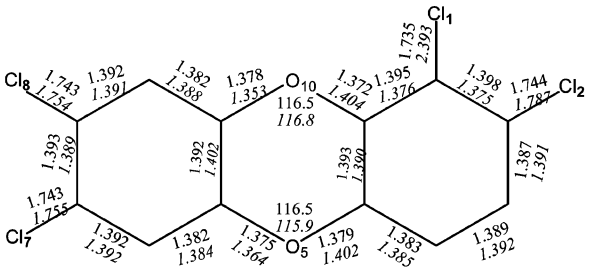
	2,3,7,8-TCDD			1,2,3,7,8,9-HCDD		
	this study	ref 10	exptl (ref 39)	this study	ref 37	exptl (ref 40)
r1	1.392	1.384	1.382	1.402	1.409	1.290
r2	1.393	1.388	1.388	1.395	1.401	1.420
r3	1.392	1.384	1.384	1.389	1.395	1.350
r4	1.382	1.388	1.374	1.380	1.385	1.320
r5	1.393	1.398	1.386	1.391	1.397	1.400
r6	1.382	1.388	1.376	1.392	1.396	1.430
r7	1.377	1.374	1.379	1.376	1.374	1.350
r8	1.377	1.374	1.378	1.372	1.377	1.400
R1				1.733	1.735	1.770
R2	1.743	1.735	1.727	1.733	1.735	1.690
R3	1.743	1.735	1.726	1.742	1.744	1.700
R7	1.743	1.735	1.730	1.742	1.744	1.690
R8	1.743	1.735	1.728	1.733	1.735	1.720
R9				1.733	1.735	1.790
θ1	120.2	120.2	119.7	120.2	120.2	125.0
θ2	119.8	119.8	119.9	119.0	118.9	118.0
θ3	120.0	120.0	120.3	119.7	119.7	113.0
θ4	119.8		120.3	120.7	120.7	118.0
θ5	120.0		120.3	120.7	120.7	122.0
θ6	120.2		119.5	119.7	119.7	123.0
θ7	116.2	115.8	115.8	116.7	116.8	117.0
θ8	116.2		115.6	116.6	116.6	118.0
θ9	121.9		122.2	121.5	121.5	124.0
θ10	121.9		122.2	121.9	121.8	118.0

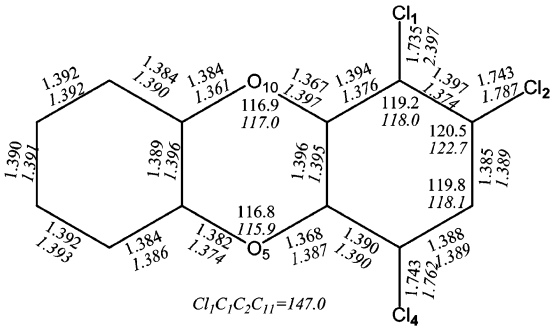
[a] Bond distances in angstroms and angles in degrees.

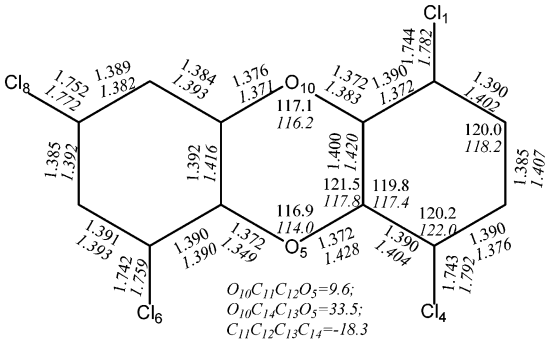
For the neutral species, the calculated C−Cl bond lengths vary from 1.733 Å (1,2,3,7,8,9-, 1,2,3,4,7,8-, and 1,2,3,7,8,9-congeners) to 1.755 Å (2,3,7-congener) and decrease slightly with increasing chlorination level. It should be noted that the C−Cl bonds at the lateral ring positions are generally longer than those at the longitudinal (peri) positions, with the exceptions in which two halogen atoms are both at the longitudinal positions (e.g., 1,4,7,8- and 1,2,6,9-TCDDs). When three or four halogen atoms are at the adjacent positions of the same ring such as those with 1,2,3,4-TCDD, 1,2,3,7,8-PeCDD, and 1,2,3,7,8,9-, 1,2,3,4,7,8-, and 1,2,3,6,7,8- HCDD, the central C−Cl bonds at the lateral ring positions are similar in magnitude to those at the longitudinal positions. The C−O bond lengths do not differ significantly from one compound to another (Figure 1), from 1.370 to 1.378 Å (except for 1,2,3,4-TCDD; R(C11−O10) = 1.366 Å and R(C14−O10) = 1.383 Å). Additionally, the calculated C−O−C bond angles are also quite similar in magnitude.

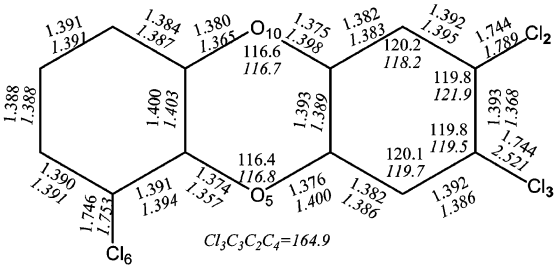
Almost all anionic PCDDs exhibit nonplanar structures, and all C−Cl bonds elongate as compared to those of the neutral

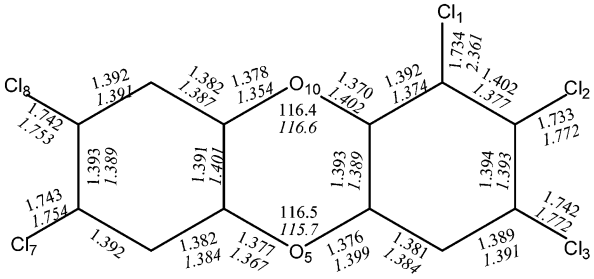


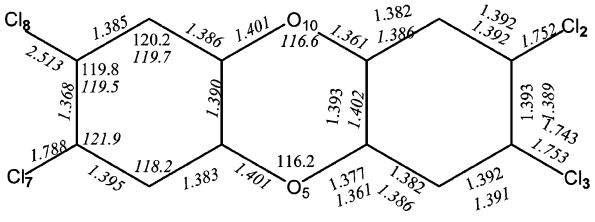


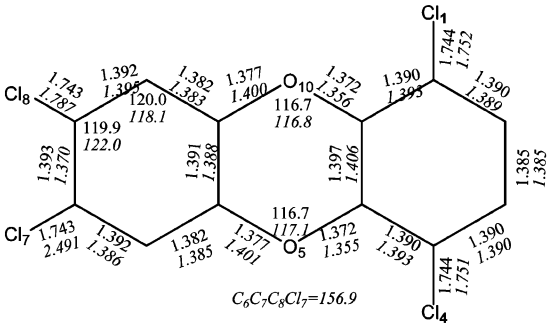


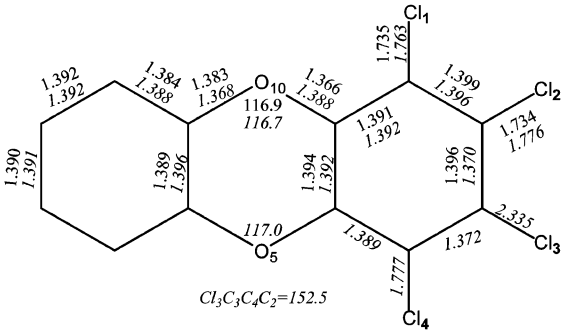












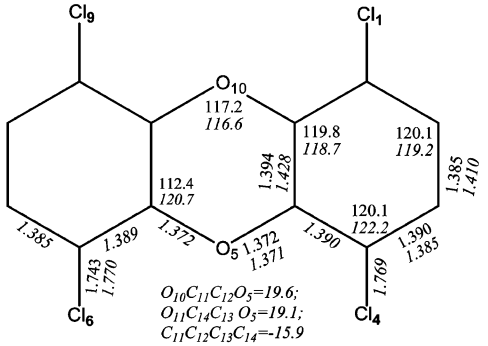


Figure 2. Part 1 of 2.

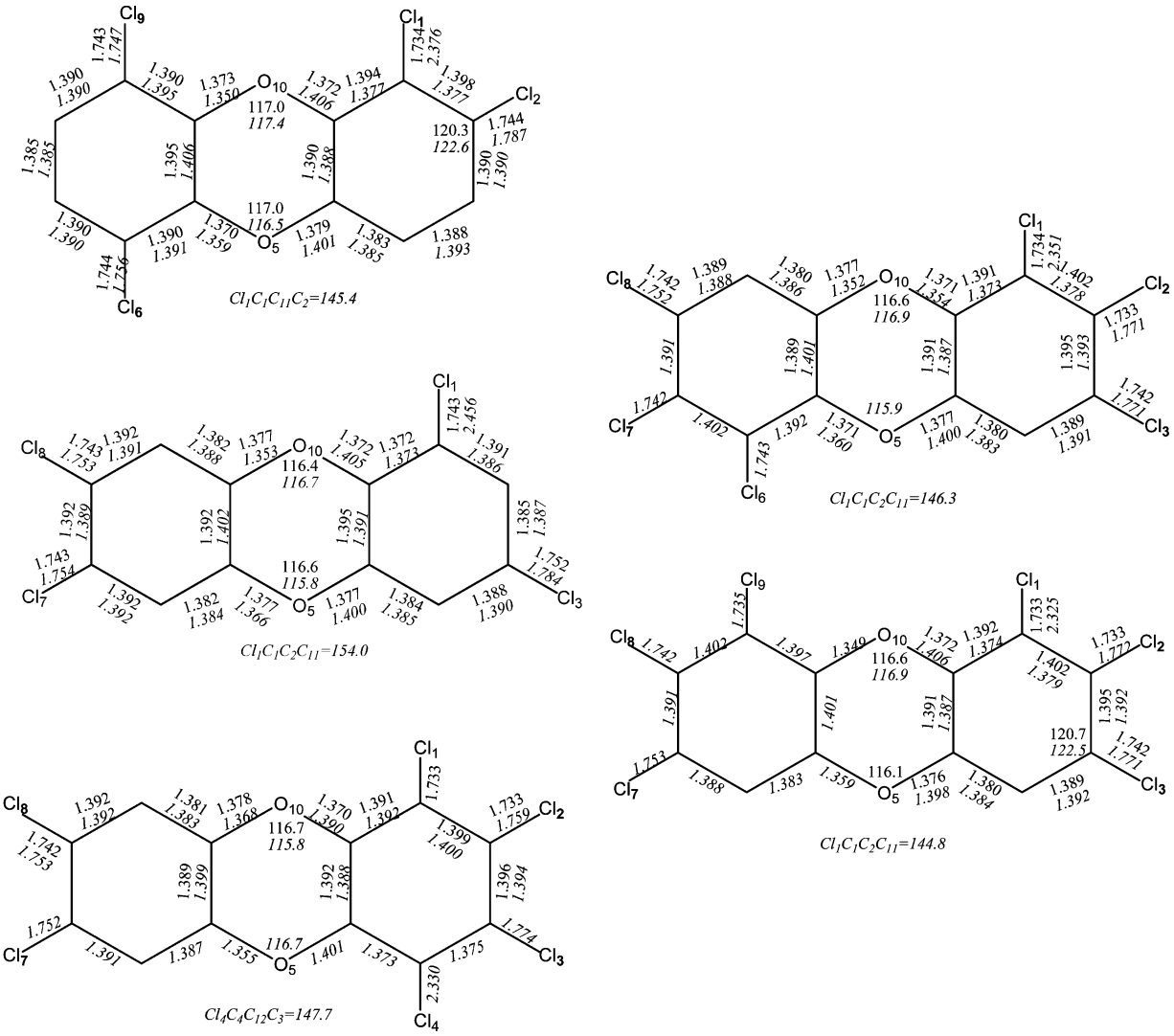


Figure 2. Part 2 of 2. Equilibrium geometries (bond distances are given in angstroms and dihedral angles in degrees) for neutral PCDDs (all are planar) and anionic PCDDs (geometric parameters in italics; dihedral angles are shown for nonplanar geometries) from B3LYP/6-311+G(2d,2p) calculations.).

counterparts concomitantly. First of all, one C−Cl bond in each anionic species (except for 1,4,6,8- and 1,4,6,9-TCDD) is considerably longer (>2.2 Å) than the other C−Cl bonds and should be regarded as broken or cleaved within the context of covalent bonding. It should be noted that the present anionic 2,3,7,8-TCDD is quite different from the previous calculation result.[10] As all the C−Cl bonds of the anions are longer than those of the neutral counterparts, it is clear that the additional electron, combined with the electron-rich benzene ring, considerably weakens the C−Cl bonds of the anions. The similar weakening effects were also noticed for PCBs[11] and PCDFs.[12] For a given anionic PCDD, a particular C−Cl bond was more dramatically affected than the other C−Cl bonds, leading to dissociation of that particular bond. The calculated geometry clearly shows which particular C−Cl bond is dissociated or on the verge of dissociation (Figure 2), and the dissociation more likely occurs within the more highly substituted ring of the anionic PCDDs, which is in good agreement with available experimental results.[22] Second, the dihedral angle between the elongated C−Cl bond and the benzene plane deviates away from the initial planar formation for the anionic PCDDs (except for 1,4,6,8- and 1,4,6,9-TCDD). This indicates that the bent bond paves the way for the $\pi^*-\sigma^*$ orbital mixing necessary for C−Cl bond cleavage. The SOMO for anionic PCDDs is a σ^* orbital, while the LUMO for neutral PCDDs (except for 1,2,3,4-TCDD) is a π^* orbital. Third, it is apparent that the occupation of an additional electron in the π^* orbital would result in increasing C−C bond lengths. However, the occupation in the σ^* orbital would result in the dissociation of C−Cl bond cleavage and decreasing adjacent C−C bond lengths. So a significant increase in the C−C bond order for most PCDDs upon addition of an electron, as evident from decreasing C−C bond lengths, indicates that the RD of PCDDs occurs through $\pi^*-\sigma^*$ orbital mixing. The decreases in the C−C bond lengths are particularly significant for those adjacent to the C−Cl bond being dissociated in anionic PCDDs. For example, the C2−C3 bond length of 2,3,7-TrCDD is decreased by 0.024 Å (Figure 2). Finally, the central ring is twisted by 18.3 and 15.9° for anionic 1,4,6,8- and 1,4,6,9-TCDD, respectively, resulting in an altered symmetry of the LUMO orbital (π^*), enhanced electron delocalization, and stabilized anionic states.

Regioselective RD of PCDDs. The longest C−Cl bonds are expected to be contained by the sides of higher chlorinated aromatic rings. For 1,2,4-TrCDD; 1,2,7,8-, 1,3,7,8-, and 1,2,6,9-TCDD; 1,2,3,7,8-PeCDD; and 1,2,3,4,7,8-, 1,2,3,7,8,9-, and 1,2,3,6,7,8-HCDD, the peri C−Cl bonds may be more vulnerable to dissociation than the lateral ones. Therefore, the RD process might lead to enhanced toxicity of the dechlorination

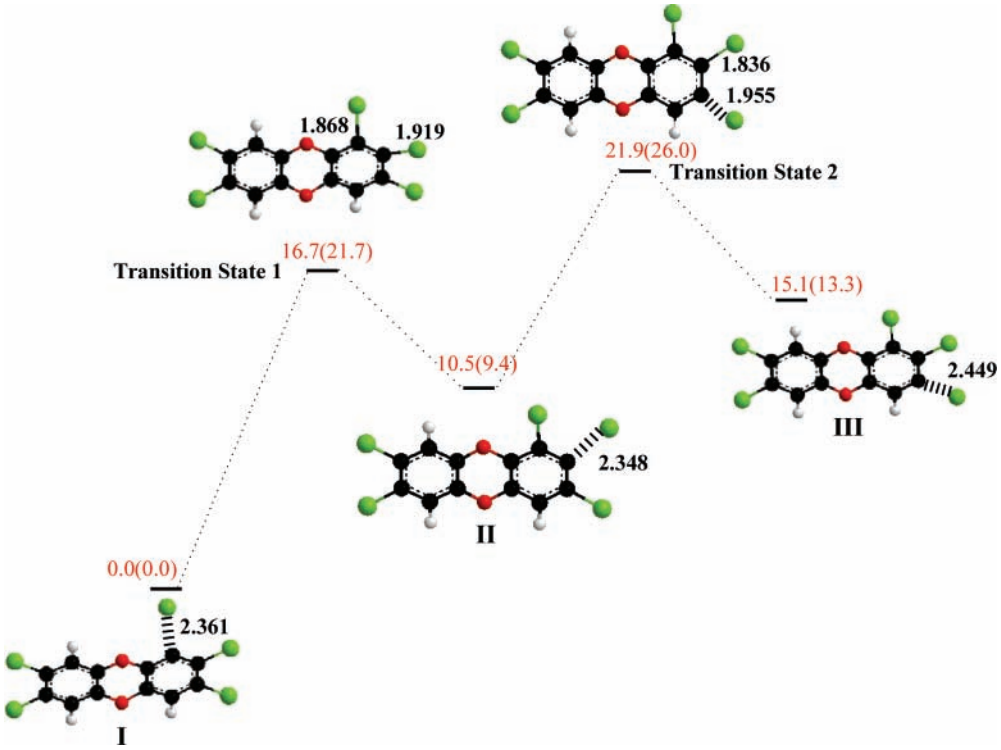


Figure 3. Relative energy and geometrical parameters diagrams (bond distances in angstroms) of three possible radical temporary 1,2,3,7,8-PeCDD anion states and the transition state between them at the B3LYP/6-311G(d,p) (in parentheses) and B3LYP/6-311+G(2d,2p) levels. Unit is kJ/mol.

products, as toxicity is expected to correlate with the number of lateral halogen substitutions.[7] This supports the perception that the dechlorinated metabolites may be potentially more toxic than the parent compounds.[16] For 1,2,3,4-TCDD, the lateral C−Cl bond is more vulnerable to dissociation, and the possible dechlorination process from 1,2,3,4-TCDD to 1,3-DCDD can be predicted by our calculation, corroborating the conclusion that the main dechlorination route of 1,2,3,4-TCDD to 1,3-DCDD proceeds primarily via the removal of lateral chlorine atom with 1,2,4-TrCDD as the intermediate.[17]

To elucidate the electron energy-dependent regioselective loss of Cl^- in 1,2,3,7,8-PeCDD by the use of electron capture negative ion mass spectrometry (ECNI-MS),[22] and to clarify the possible dominant products for its RD reactions, we investigated two other possible anionic states of the 1,2,3,7,8-PeCDD anion and the transition states between them at the same theoretical level. The relative energy and main geometrical parameters are illustrated in Figure 3.

State I is the most stable state, corresponding to the dominant chloride loss channel from position 1 under the experimental condition using low-energy electrons. State III is less stable, corresponding to the chloride loss channel from position 3, which is increasingly important under the condition using electrons of relatively high energy. The energy barrier in each case is rather low, within 40 kJ/mol (Figure 3). This indicates that chlorine can be removed from either the peri or the lateral position, which is consistent with experimental results.[16] As a result, 1,2,3,7,8-PeCDD is highly susceptible to RD, leading to products that are more toxic than the parent species. State II is viewed as a reaction intermediate between states I and III. Because of the relatively lower activation energy through transition state 2, the chloride loss from position 2 may not considerably alter the relative losses from the other two channels. This may be the cause for the insensitivity of chlorine loss from position 2 with increasing electron energy.

TABLE 2: Vertical and Adiabatic Electron Affinities[a] Calculated Using B3LYP with the 6-311G(d,p) and 6-311+G(2d,2p) Basis Sets, Compared with Available Experimental Results[b] and AhR Binding Affinities pEC_{50}[c]

	EA_{ver}		EA_{ada}		exptl	
PCDD	6-311G (d,p)	6-311+ G(2d,2p)	6-311G (d,p)	6-311+ G(2d,2p)	attachment energy	pEC_{50}
2,3,7-	−0.117	−0.091	0.666	0.622		
1,2,4-	−0.155	−0.031	0.800	0.774		
2,3,6-	−0.151	−0.054	0.628	0.589		
2,3,7,8-	0.096	0.136	0.751	0.700		8.00
1,2,3,4-	0.026	0.096	1.013	0.962	0.11	5.89
1,2,7,8-	0.069	0.140	0.866	0.836		6.80
1,3,7,8-	0.111	0.175	0.849	0.810		6.10
1,4,6,8-	0.095	0.187	0.432	0.507		
1,4,7,8-	0.089	0.158	0.715	0.666		
1,4,6,9-	0.062	0.162	0.408	0.510		
1,2,6,9-	0.058	0.153	0.692	0.645		
1,2,3,7,8-	0.271	0.299	1.101	1.056	0.20	7.10
1,2,3,4,7,8-	0.450	0.461	1.226	1.168	0.12	6.55
1,2,3,7,8,9-	0.431	0.444	1.116	1.070		
1,2,3,6,7,8-	0.437	0.452	1.173	1.117		

[a] In eV. [b] Ref 22. [c] Ref 9.

Electron Affinity. Earlier EA studies on a variety of molecules concluded that the B3LYP functional could achieve average errors within 0.1−0.2 eV as compared to experimental results.[41,42] A recent review[43] also indicated that EA values calculated for a set of 91 molecules using the same density functional had an average error of 0.16 eV. Table 2 shows the vertical and adiabatic electron affinities of the target PCDDs, EA_{ver} and EA_{ada}, from B3LYP calculations, along with available experimental values. The majority of calculated EA values is positive. Large basis sets with diffuse functions are essential for treating negative ions properly. The electron affinity increases with the number of substituted chlorines, which are electron-withdrawing groups, and the EA values in Table 3 clearly show such a general trend.

It should be noted that the calculated electron affinities are in good agreement with the results from an electron attachment experiment.[22] First of all, the three TrCDDs have negative EA_{ver} values, which do not signify anything and are misleading as strongly basis set-dependent values. It is apparent that the negative EA_{ver} from 6-311+G(2d,2p) is almost zero, so it is purposed that the slightly positive EA_{ver} might be obtained with the much larger basis sets, which interpret the reason for no experimental molecular ions to be yielded from lower chlorinated dioxins.[22] Second, the EA_{ver} values for 1,2,3,4-TCDD and 1,2,3,7,8-PeCDD agree with the measured values of molecular ions. Finally, the large positive EA_{ada} values obtained in the present study suggest that PCDDs may act as electron acceptors in charge-transfer interactions with receptors in living cells. Additionally, the calculated EA_{ada} values from the present study are quite different from those from a previous study,[10] which is probably due to the large difference between the optimized anion structures obtained in the two studies.

The final result combined with those obtained for PCBs[11] and PCDFs[12] indicates that PHAs act as electron acceptors. After entering a biological species, these toxins bind with the Ah receptors and may induce biological and toxic effects through a sequence of complex events. In this regard, the electron affinity may be an influential parameter related to toxicity. Nevertheless, EA_{ada} values are sensitive to the increase of chlorine substituents. Therefore, it is reasonable that a direct correlation between EA_{ada} and toxicity parameter (pEC_{50})[9] cannot be established. This suggests that EA_{ada} may not be an adequate predictor of toxicity, and other factors, such as solubility, polarizability,[44] etc., should also be considered. 1,2,3,4-TCDD and 1,2,3,4,7,8-HCDD have especially higher calculated EA_{ada} values than other congeners, probably due to the heavily ortho substituted positions on the benzene ring.

Conclusion

All neutral PCDDs have planar equilibrium geometries, and all of them become nonplanar upon electron attachment, characterized by large increases in C−Cl bond lengths. The chlorine atom bends off the molecular plane of the π system as the C−Cl bond increases, which allows for the $\pi^*-\sigma^*$ orbital mixing necessary for C−Cl bond cleavage. In most cases, peri C−Cl bonds in the PCDD anions are more labile than other C−Cl bonds. In addition, the occurrence of regioselective dechlorination is detected through transition-state model calculations on the 1,2,3,7,8-PeCDD anion, and its relatively lower energy barrier (<40 kJ/mol) predicts the possibility for obtaining more toxic RD products.

The vertical electron affinities of 1,2,3,4-TCDD and 1,2,3,7,8-PeCDD are consistent with experimental results. The positive EA_{ada} values suggest that PCDDs act as electron acceptors in interacting with Ah receptors in living cells. Although the electron affinities are obviously related to toxicity, a direct correlation between EA_{ada} and toxicity cannot be established. Therefore, electron affinity is not an adequate predictor of toxicity, and it is necessary to consider other factors, such as solubility, polarizability, etc.

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