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Electron Affinities and Reductive Dechlorination of Toxic Polychlorinated Dibenzofurans: A Density Functional Theory Study

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Density functional theory studies were performed to obtain the adiabatic electron affinities of 15 polychlorinated dibenzofurans (PCDFs), including toxic PCDFs. Three-parameter hybrid density functional B3LYP, with different basis sets up to 6-311+G(2d,2p), was utilized. All the studied PCDFs have planar structures, but some of them attain nonplanar structures upon becoming anions. The lowest unoccupied molecular orbitals of all the PCDF neutrals were found to be π^* orbitals. The singly occupied molecular orbitals of most of the anions have π character, while the same found for the anions with longer C−Cl bonds have σ character. The present study clearly showed that chlorine atom bends as the carbon−chlorine bond stretches and the dechlorination could take place through the $\pi^*-\sigma^*$ orbital mixing. The electron affinities of all the selected PCDFs, like those of their toxic polychlorinated dibenzo-*p*-dioxin and biphenyl counterparts, were positive. Interestingly, the calculated electron affinity of the most toxic 2,3,7,8-tetrachlorodibenzofuran (TCDF) is the largest among the electron affinities calculated for the eight selected TCDFs. The adiabatic electron affinities obtained at the B3LYP/6-311+G(2d,2p) level were 1.029, 1.114, 1.161, 1.286, and 1.253 eV for the toxic 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HCDF, and 1,2,3,6,7,8-HCDF, respectively.

Introduction

Polychlorinated dibenzofurans (PCDFs) belong to the family of toxic halogenated aromatic hydrocarbons (HAHs) along with dibenzo-*p*-dioxins (PCDDs) and biphenyls (PCBs) and cause dermal toxicity, immunotoxicity, carcinogenicity, adverse effects on reproduction and development, and endocrine disruptions.[1−3] Among the 135 possible PCDF congeners, some of the congeners show toxicity similar to PCDDs.[4] The nature, the number, and the position of the halogen atoms influence the toxic and biological activities of HAHs.[5]

There are a number of experimental[6−9] and higher level theoretical studies[10−14] on structures of various PCDDs, including the most toxic 2,3,7,8-tetrochlorodibenzo-*p*-dioxin (TCDD). A few studies on structures and torsional barriers of PCBs were made in the past.[15−18] Recently, the structures of various PCDD and PCB congeners have been studied in our laboratory by using ab initio and density functional theory (DFT).[19−23] These studies show that structure plays an important role for the toxic nature of HAHs. Unfortunately, there are no such structural studies on PCDFs.

Earlier studies have concluded that toxins appear to act as electron acceptors in a charge-transfer complex with a receptor in living cells.[24−26] Our recent studies have provided positive electron affinity (EA) values for various PCDDs and PCBs.[20,23] Since earlier studies suggest that the toxicity and enzyme-inducing capability of HAHs may be connected to their interactions with the arylhydrocarbon (Ah) receptors,[27−29] determining whether PCDFs act as electron acceptors or not in these important interactions is necessary for a better understanding of their toxicity. Further, it is likely that electron affinity may have an influence over the toxicity, and hence EA may act as an indicator of toxicity of PCDFs.

Isomeric HAHs are difficult to distinguish by ordinary mass spectrometry. On the other hand, electron capture negative-ion chemical ionization mass spectrometry (ECNICI-MS) has become an important technique for the analyses of chlorinated aromatic compounds in environmental samples.[30,31] These compounds absorb electrons and yield molecular radical anions if the electron affinities are sufficiently high. In this case the EAs have been calculated to be greater than 0.5 eV.[32] So obtaining the electron affinities of PCDFs is helpful for the analysis of these toxic molecules in environmental samples by using ECNICI-MS.

Reductive dechlorination (RD) is a significant environmental transformation of halogenated organic contaminants under anaerobic conditions. Evidence has accumulated that microorganisms are able to accomplish RD of a wide variety of organohalogens including haloaromatic compounds.[33] These microorganisms can use haloorganic compounds as electron acceptors for energy conservation and growth. Studies have also demonstrated that PCDDs can be reductively dechlorinated by sediment and microorganisms in the anaerobic environment.[34−39] Adrian et al.[40] isolated *Dehalococcoides* sp. strain CBDB1, an anaerobic bacterium, for the first time capable of reductively dechlorinating chlorobenzenes. Very recently, Bunge et al.[41] showed that the same bacterium *Dehalococcoides* sp. strain CBDB1 is able to reductively dechlorinate selected dioxin congeners. Two bacteria with distant relatedness to *Dehalococcoides* were described recently as being responsible for the dechlorination of PCBs.[42,43] Hence studies on reductive dechlorination is getting momentum in recent days for the detoxicification of toxic halocarbons.

Studies have demonstrated that the halogen configuration of a PCDD/PCB congener determines whether chlorine(s) will be

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dechlorinated and which chlorine(s) will be removed, and various dechlorination patterns were proposed for 1,2,3,4-TCDD.[36,38,41,44] These studies have also concluded that the dechlorination of some of the highly chlorinated PCDDs may result in metabolites that are potentially more toxic than the parent compounds. Previous studies on PCDDs and PCDFs have concluded that studies are necessary to understand the electron acceptance (reduction) and the carbon−chlorine bond cleavage mechanisms.[45,46] So knowing the dechlorination sites and the reductive dechlorination process is timely and, it would be helpful to make further advances in the detoxicification studies on these toxins. In this direction, the geometrical changes occur in the toxin upon accepting the electron can provide some fundamental information that may help to understand the dechlorination site and process. Additionally, studies on molecular orbitals involving the dechlorination process would help in drawing conclusions about the reductive dechlorination process. Hence some useful generalizations concerning reductive dechlorination of PCDFs can be made from the studies on anionic PCDFs.

The foregoing facts encouraged us to go for this present investigation. The main aim of the present work is to obtain the electron affinities of the selected PCDFs, including the toxic ones. This investigation would also help us (1) to know the EA's role, if any, in the toxicity of PCDFs and (2) to understand the reductive dechlorination process in PCDFs. We used density functional theory for the present study.

Computational Details

All computations were performed by using Gaussian 98 programs.[47] The three-parameter hybrid density functional, B3LYP, which includes a mixture of Hartree−Fock exchange and DFT exchange correlation, was used.[48,49] Various split valence basis sets, 6-31G(d), 6-311G(d,p), 6-311+G(d,p), and 6-311+G(2d,2p), were utilized to optimize both neutrals and anions of the selected PCDFs. Various PCDF congeners representing chlorine substitutions at different positions (especially with tetrachlorinated dibenzofurans) were considered for this study. They were three trichlorodibenzofurans (1,2,3-, 1,2,4-, and 2,3,4-TrCDF), eight tetrachlorodibenzofurans (1,2,3,4-, 1,2,4,6-, 1,2,8,9-, 1,4,6,9-, 1,4,7,8-, 2,3,6,7-, 2,3,7,8-, and 3,4,6,7-TCDF), two pentachlorodibenzofurans (1,2,3,7,8- and 2,3,4,7,8-PeCDF), and two hexachlorodibenzofurans (1,2,3,4,7,8- and 1,2,3,6,7,8-HCDF). These selected PCDFs include five toxic PCDFs: 2,3,7,8-TCDF; 1,2,3,7,8- and 2,3,4,7,8-PeCDFs and 1,2,3,4,7,8- and 1,2,3,6,7,8-HCDFs.[4] At first, the geometries of both neutrals and anions were optimized at the B3LYP/6-31G(d) level of theory followed by frequency calculations, which showed that all the optimized structures were minima on the potential energy surface. These obtained vibrational frequencies were used to calculate the zero-point energies (ZPE), which were needed for EA calculations. Next, the 6-311G(d,p), 6-311+G(d,p), and 6-311+G(2d,2p) basis sets were used to optimize both neutrals and anions. The adiabatic electron affinities were obtained as differences between the absolute energies of the neutral and anion species at their respective optimized geometries [EA = E(neutral) − E(anion)]. Zero-point energy corrections (scaled by 0.9804)[50] were included in the EA values. The atomic charges [at the B3LYP/6-311G(d,p) level] were derived by means of electrostatic potential-driven (ESP-driven) charges according to the Merz−Singh−Kollman scheme.[51,52] Unpaired electron spin densities [at the B3LYP/6-311+G(2d,2p) level] were calculated for all of the anions using the Mulliken population analysis (MPA) scheme to find out the location of the excess electron. These calculated charges and spin densities were used for discussion throughout the paper unless indicated otherwise.

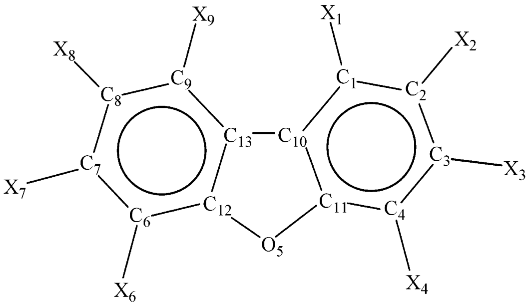


Figure 1. Atom-numbering scheme for a PCDF model. X = H for dibenzofuran.

Results and Discussion

Geometries. There are a few experimental studies on dibenzofuran (DF) structure.[53−55] Dideberg et al.[53] studied the crystal structure by using X-ray diffraction in 1971, and, in the following year, Banerjee[54] performed the same kind of study. But there are some noticeable differences in the structural parameters obtained in those two studies. In some cases, the difference exceeds 0.02 Å in bond lengths and 4° in bond angles. Later in 1984, Reppart et al.[55] studied the DF structure and found that some of the geometrical parameters obtained in their study have considerable differences with those of the previous two studies: The O−C and C−C (interring) bond lengths are 1.384 and 1.438 Å, respectively, which are each considerably shorter than the corresponding values of 1.418 and 1.480 Å found for the bond lengths by Banerjee and the values of 1.404 and 1.481 Å found by Dideberg et al. Reppart et al. found in their study that the structure of dibenzofuran is disordered, with 9% of the molecules adopting an alternative orientation. The disordered molecules are related to the ordered counterparts by 180° rotation about an axis, which passes through the center of mass and is perpendicular to the furan ring. The authors claimed that the disorderly nature of the dibenzofuran structure was not taken into account in the two previous studies and hence the differences in geometrical parameters. No higher level theoretical studies were performed in the past to obtain the dibenzofuran structure. Under this background, it is reasonable to study the structure of the parent dibenzofuran by using DFT before studying the chlorinated dibenzofurans.

We optimized the DF structure at the B3LYP/6-311+G(2d,2p) level of theory, the same level at which the chlorinated dibenzofurans are studied. Second-order perturbation theory (MP2) was also used with the 6-311+G(2d,2p) basis set for this purpose. The atom-numbering scheme is given in Figure 1. The calculated geometrical parameters are summarized in Table 1 along with the values obtained in three different experimental studies.

It is seen from the table that there are many noticeable differences in geometrical parameters, not only in C−O and C−C interring bond lengths, obtained in the three different experimental studies. It is also noticed that many of the parameters obtained by Reppart et al.[55] have considerable differences from those obtained in the other two experimental studies. The values calculated using B3LYP and MP2 theories are very similar, and they coincide quite well with the values derived by Reppart et al.[55] (The experimental data involving hydrogen atoms are not corrected for thermal motion.) These

TABLE 1: Structural Parameters of Dibenzofuran at the B3LYP and MP2 Levels with the 6-311+G(2d,2p) Basis Set [R (Å) and θ (deg)]

parameter	MP2	B3LYP	expt[a]	expt[b]	expt[c]
R(C1−C2)	1.392	1.389	1.389	1.386	1.388
R(C2−C3)	1.407	1.401	1.385	1.377	1.400
R(C3−C4)	1.394	1.392	1.388	1.383	1.388
R(C4−C11)	1.389	1.383	1.385	1.401	1.380
R(C10−C11)	1.405	1.403	1.393	1.382	1.399
R(C1−C10)	1.400	1.395	1.384	1.387	1.398
R(O5−C11)	1.377	1.376	1.404	1.418	1.384
R(C10−C13)	1.445	1.450	1.481	1.480	1.438
R(C1−H1)	1.081	1.081	0.943	0.98	0.97
R(C2−H2)	1.081	1.081	1.009	1.07	0.97
R(C3−H3)	1.081	1.081	0.955	0.91	0.95
R(C4−H4)	1.080	1.080	0.956	0.95	0.99
θ(C1−C2−C3)	121.2	121.0	121.9	121.4	121.2
θ(C2−C3−C4)	121.4	121.3	120.9	122.1	121.5
θ(C3−C4−C11)	116.5	116.7	116.7	115.3	116.3
θ(C4−C11−C10)	123.4	123.3	123.0	123.9	123.9
θ(C1−C10−C11)	119.2	119.0	119.6	118.9	118.9
θ(C2−C1−C10)	118.4	118.6	117.9	118.5	118.3
θ(C11−O5−C12)	105.5	106.0	104.1	104.4	105.5
θ(O5−C11−C10)	111.9	111.6	112.7	112.9	111.4
θ(C11−C10−C13)	105.4	105.4	105.3	105.6	105.9
θ(C11−C4−H4)	121.4	121.3	119.7	115.1	121.5
θ(C4−C3−H3)	119.2	119.3	121.3	117.8	118.9
θ(C3−C2−H2)	119.2	119.3	117.9	117.4	118.5
θ(C2−C1−H1)	120.8	120.5	119.4	118.9	120.8

[a] Taken from ref 53. [b] Taken from ref 54. [c] Taken from ref 55.

results indirectly support the finding of Reppart et al. that the dibenzofuran crystal structure has some degree of disorder.

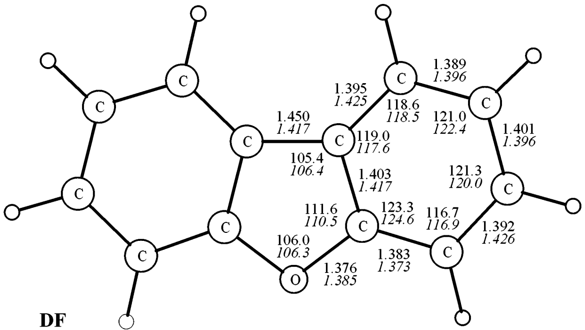
The optimized structures of the selected PCDFs, together with the important geometrical parameters [neutrals as well as anions (in italics)] obtained with the B3LYP functional with the use of the 6-311+G(2d,2p) basis set, are depicted in Figure 2. Important dihedral angles of the nonplanar structures are also given in the figure. [Cartesian coordinates for the optimized structures (SI-1) and the total energies and ZPE values (SI-2) are given in the Supporting Information.] The results show that all of the selected PCDFs have the planar structures of their parent dibenzofuran and hence the planarity is not been influenced by chlorine substitutions. [It should be noticed here that some of the dihedral angle values, in a few PCDFs, were slightly (<0.1°) deviated from the planar values.] In fact, no noticeable changes in the geometrical parameters due to the chlorine substitutions were found in many of the PCDFs. The PCDFs with chlorines substituted at both the 1 and 9 positions were exceptional. The interring C−C bond lengths and a few bond angles obtained in these PCDFs (1,4,6,9- and 1,2,8,9-TCDFs) have some differences with those obtained in the other PCDFs and DF. Due to the steric repulsion between the chlorines positioned at the 1 and 9 positions, the interring bond lengths in these two TCDFs were elongated by around 0.02 Å. A decrease of about 3° in the θ(C1−C10−C11) (see Figure 1 for numbering) bond angle was also noticed. These changes made it possible for the above-mentioned two TCDFs to have planar structures. Overall, the structures (neutrals) obtained using all four basis sets are similar.

Anion structures showed interesting differences: while many of the anionic PCDFs had planar structures, some of the anions exhibited nonplanar structures. Anionic 1,2,3,4-, 1,2,8,9-, 1,2,3,7,8-, and 1,2,3,4,7,8-PCDFs had nonplanar structures. The 2,3,4-TrCDF anion also had a nonplanar structure while the other two trichloro dibenzofurans, 1,2,3- and 1,2,4-TrCDFs, had planar structures. Hence, the planarity/nonplanarity of the anions is highly dependent upon the substitution pattern. From these results, roughly speaking, there seems to be a rule that a PCDF becomes nonplanar with the addition of an electron if one of its benzene rings has either more than two adjacent positions substituted with chlorine atoms and the other ring is unsubstituted or more than two adjacent positions substituted with chlorine atoms (δ, γ, and, β positions are required) and the other ring has at least two unsubstituted positions. Two PCDFs, 1,2,3-TrCDF and 1,2,8,9-TCDF, do not follow the above rule. The anionic 1,2,8,9-TCDF had a nonplanar structure that might be because four nearby positions (1, 2, 8, and 9) in this PCDF are substituted with chlorine atoms. The explanation for the different behavior of the former PCDF is given in the following paragraphs. So it is clear that if a PCDF has a benzene ring of three or four adjacent positions substituted with chlorine atoms, then that PCDF needs to become nonplanar with the attachment of an electron to have some sort of steric relief that is aroused due to the highly negatively charged chlorine atoms. Due to its large electronegativity, chlorine atoms possess a large negative charge in the anionic PCDFs. For example, atomic charges calculated for Cl1, Cl2, and Cl3 atoms in the anionic 1,2,3,7,8-PeCDF were −0.15, −0.14, and −0.18 e, respectively. Many other anions including the anion of the most toxic 2,3,7,8-TCDF had a planar structure. Structural parameters of the anions, unlike of the neutrals, were influenced by the basis sets. Even in some cases, the basis set has influence over the planarity or the nonplanarity of the structure: planar and nonplanar structures were obtained for 1,2,8,9-TCDF and 2,3,4,7,8-PeCDF anions, respectively, at the UB3LYP/6-31G(d) level; however, the UB3LYP/6-311+G(2d,2p) level calculations resulted in the opposite structures, respectively. Generally, the results obtained using 6-311G(d,p) and 6-311+G(d,p) basis sets were in line with those obtained with the 6-311+G(2d,2p) basis set as far as the planarity or the nonplanarity of the structure is concerned, but the calculated geometrical parameters showed a few differences.

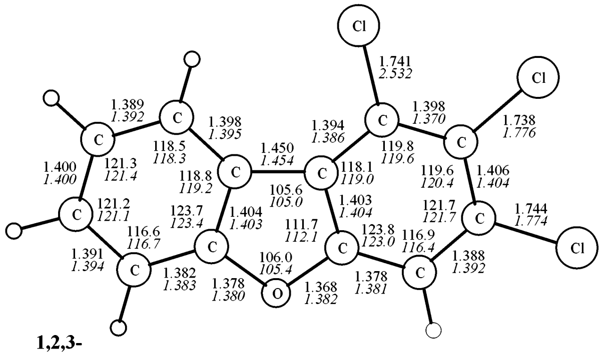
In most of the PCDFs, a considerable increase in the interring C−C π-bond order was evidenced from the decrease in the C−C bond length upon the addition of an electron. Figure 2 shows about a 0.03 Å decrease in the C−C interring bond lengths in anions when compared with those in neutrals. Other noticeable changes are a lengthening of the C1−C10, C3−C4, and C10−C11 bonds and a shortening of the C4−C11 bond. A decrease in the θ(C1−C10−C11) and an increase in the θ(C1−C2−C3) bond angles were also observed for the anions.

As expected, the addition of an electron weakened the C−Cl bonds. In all the cases, the calculated C−Cl bonds in the anions were longer than those in the neutrals. The negative charges on the Cl atoms combined with the negative character of the benzene ring weakened the C−Cl bonds in the anions. Such weakening of the C−Cl bonds has also been noticed in PCDDs[20] and PCBs.[23] These weak bonds in anions suggest that dechlorination will occur more easily than in neutrals, and thus, charge-transfer weakens the C−Cl bonds that may lead to the dechlorination of these HAHs. However, from the results, it is difficult to isolate which carbon−chlorine bond can break more easily than the other. But overall it is very likely that the lateral carbon−chlorine bonds are more labile than the nonlateral ones. It should be noticed here that the study by the Deinzer group[45] on regioselective chloride ion loss from chlorine-37-enriched PCDFs by using ECNI-MS concluded that chlorine at position 3 is generally most labile.

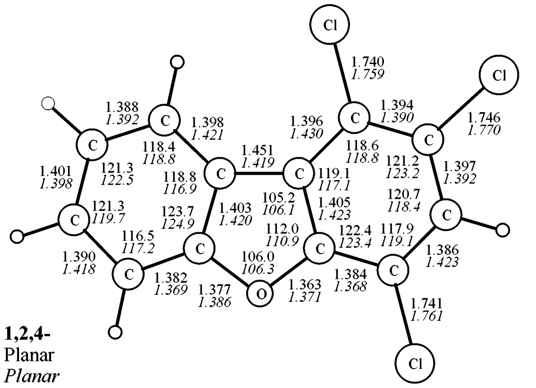
Anions of 1,2,3- and 2,3,4-TrCDFs and 1,2,3,4-TCDF, contrary to those of other PCDFs, had a long C−Cl bond (>2.2 Å) each. The peculiarity of these three PCDFs is in the



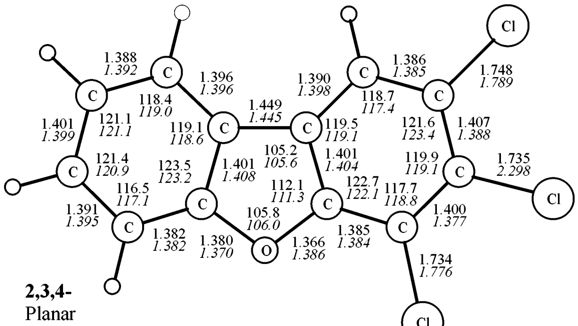
DF
Planar
Planar



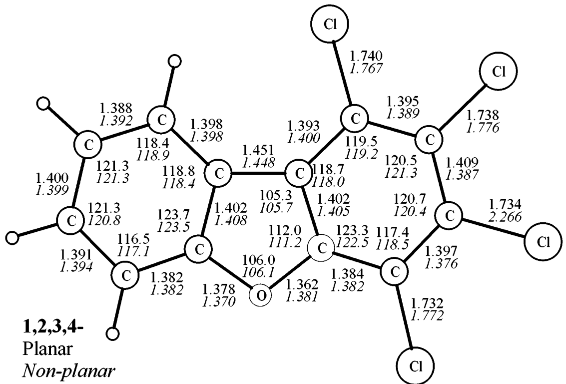
1,2,3-
Planar
Planar



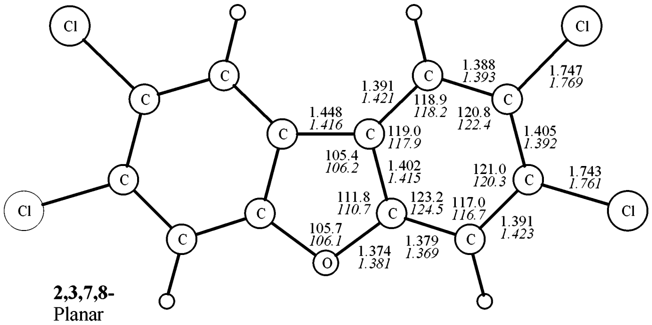
1,2,4-
Planar
Planar



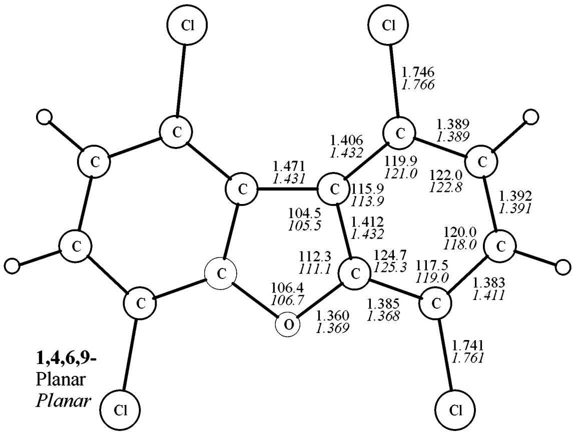
2,3,4-
Planar
Non-planar
Dihedral angle:
C1C2C3Cl2 = -177.9; C2C3C4Cl3 = 144.3; C3C4C11Cl4 = -177.7;
C1C2C3C4 = -1.6; C2C3C4C11 = 2.3; C3C4C11C10 = -0.9;
C4C11C10C1 = -1.1; C11C10C1C2 = 1.8; C10C1C2C3 = -0.4;
C12C13C10C1 = -177.3



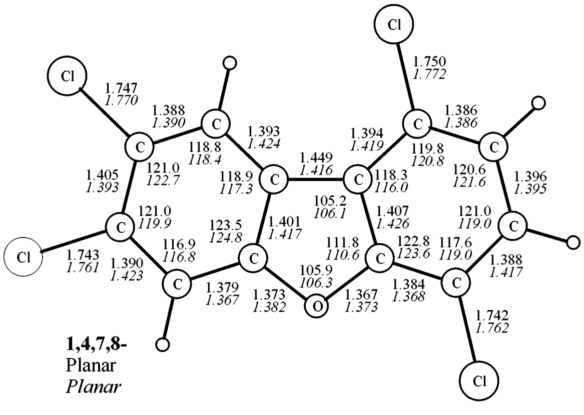
1,2,3,4-
Planar
Non-planar
Dihedral angle:
C10C1C2Cl1 = 178.4; C1C2C3Cl2 = 178.0; C2C3C4Cl3 = -145.6;
C3C4C11Cl4 = 177.8; C1C2C3C4 = 2.5; C2C3C4C11 = -2.8;
C3C4C11C10 = 0.9; C4C11C10C1 = 1.5; C11C10C1C2 = -1.8;
C12C13C10C1 = 177.2



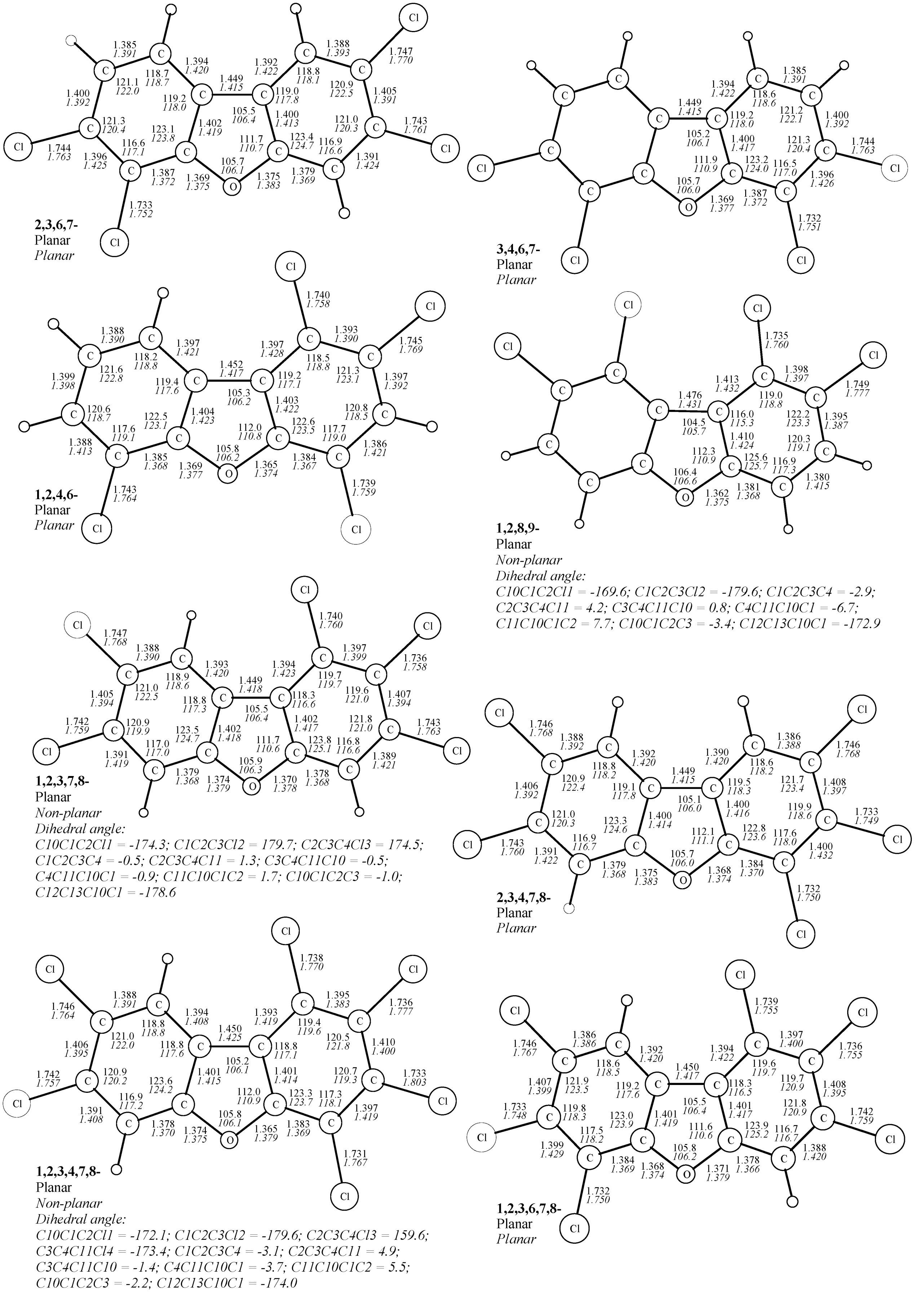
2,3,7,8-
Planar
Planar



1,4,6,9-
Planar
Planar



1,4,7,8-
Planar
Planar



2,3,6,7-
Planar
Planar

3,4,6,7-
Planar
Planar

1,2,4,6-
Planar
Planar

1,2,8,9-
Planar
Non-planar
Dihedral angle:
C10C1C2Cl1 = -169.6; C1C2C3Cl2 = -179.6; C1C2C3C4 = -2.9; C2C3C4C11 = 4.2; C3C4C11C10 = 0.8; C4C11C10C1 = -6.7; C11C10C1C2 = 7.7; C10C1C2C3 = -3.4; C12C13C10C1 = -172.9

1,2,3,7,8-
Planar
Non-planar
Dihedral angle:
C10C1C2Cl1 = -174.3; C1C2C3Cl2 = 179.7; C2C3C4Cl3 = 174.5; C1C2C3C4 = -0.5; C2C3C4C11 = 1.3; C3C4C11C10 = -0.5; C4C11C10C1 = -0.9; C11C10C1C2 = 1.7; C10C1C2C3 = -1.0; C12C13C10C1 = -178.6

2,3,4,7,8-
Planar
Planar

1,2,3,4,7,8-
Planar
Non-planar
Dihedral angle:
C10C1C2Cl1 = -172.1; C1C2C3Cl2 = -179.6; C2C3C4Cl3 = 159.6; C3C4C11Cl4 = -173.4; C1C2C3C4 = -3.1; C2C3C4C11 = 4.9; C3C4C11C10 = -1.4; C4C11C10C1 = -3.7; C11C10C1C2 = 5.5; C10C1C2C3 = -2.2; C12C13C10C1 = -174.0

1,2,3,6,7,8-
Planar
Planar

Figure 2. B3LYP/6-311+G(2d,2p)-optimized structures with geometrical parameters of various PCDFs (the words and values in italics are for anions).

substitution pattern. One of the benzene rings in these three PCDFs has three or four adjacent positions substituted with chlorine atoms while the other benzene ring is unsubstituted. Because of this, steric interactions are expected to be high in the substituted ring. Addition of an electron should increase the steric repulsions further and hence for the necessary steric relief, one of the C−Cl bonds in these PCDFs become weakened. The calculated spin densities of these three anions revealed that the unpaired electrons reside entirely on the benzene rings with the chlorines attached which supports the fact that the steric interactions are large in these PCDFs. Even though 1,2,3,4,7,8-HCDF had a benzene ring with four chlorines attached in adjacent positions, such as in 1,2,3,4-TCDF, the C−Cl(3) bond length in the anion of the former PCDF was shorter than that in the latter. Calculated spin densities showed that while the entire unpaired electron was located on the chlorinated benzene ring of the 1,2,3,4-TCDF anion, as mentioned above, around 25% of the unpaired electron of the anionic hexachlorinated dibenzofuran was delocalized on the benzene ring with two chlorines substituted. Hence the latter experiences less steric interaction than the former one does. This should be true in 1,2,3,7,8- and 2,3,4,7,8-PeCDFs too. The weak C−Cl bonds (>2.2 Å) could be very susceptible to the bond cleavage reactions and, the reductive dechlorination should take place easily through these weak C−Cl bonds. It seems that the reductive dechlorination of a PCDF with a highly chlorinated benzene ring has a high probability to occur. Carbon 3-chlorine bonds are the most probable C−Cl bonds subject to the reductive dechlorination process for 2,3,4-TrCDF and 1,2,3,4-TCDF while the C−Cl(1) bond should be the case for 1,2,3-TrCDF. The regions close to C1 and C2 atoms are probably less flexible (to have a small dihedral angle) than those close to C3 and C4 atoms, and hence a very weak C−Cl(1) bond [weaker than the C−Cl(3) bonds in 2,3,4-TrCDF and 1,2,3,4-TCDF anions] results for the anionic 1,2,3-TrCDF to reduce the steric interaction. The 1,2,3-TrCDF anion had a planar structure since it might have received the necessary steric relief by largely weakening its C−Cl(1) bond.

Reductive Dechlorination Reaction. It is clear that the addition of an electron weakens the C−Cl bonds in PCDFs. To understand the reductive dechlorination process in PCDF, it is important to know which orbital accepts the ionizing electron. If the additional electron occupies the σ^* orbital, then, through the reductive dechlorination process, a given C−Cl bond would be weakened and could break easily without any additional changes in the structure of the target molecule. But our results showed that the anions with longer C−Cl bonds had nonplanar structures. The chlorine atoms of the longer C−Cl bonds in the anionic 2,3,4-TrCDF and 1,2,3,4-TCDF bent much toward the benzene rings: for example, the Cl(3) in 1,2,3,4-TCDF was moved around 35° from the planarity (Figure 2). Deinzer group[56] invoked a “bent” bond model to describe the bond cleavage process of polychlorobenzene radical anion to aryl radical plus chloride ion. According to this model, the chlorine atom “bends” toward the plane of the π system as the carbon−chlorine bond stretches, and the unpaired electron becomes increasingly localized in the sp^2 orbital, which is necessary for C−Cl bond cleavage. An AM1 study[45] on PCDF anions by the Deinzer group showed that each singly occupied molecular orbital (SOMO) is a π orbital. Authors[45] have again utilized the bent bond model to explain the bond-breaking process in these compounds since the direct transition from the π^* state to the σ^* state necessary for bond cleavage to occur is not allowed. However, the authors concluded that higher level calculations would be desirable to support their claim. The Deinzer group[46] has also studied electron energy dependence of regioselective chloride ion loss from PCDDs and found a good correlation between experimental electron attachment energies and π virtual orbital energies calculated for the PCDD neutrals at the B3LYP/D95 level. Their results suggest that the negative ion-forming process is initiated from π^* states, and the authors concluded that the C−Cl bond cleavage from anionic PCDDs requires $\pi^*-\sigma^*$ orbital mixing. But there are no studies on anions and transition states (of the reductive dechlorination reactions) to gain an understanding of the geometries involved during the carbon−chlorine bond cleavage as well as to support the Deinzer group’s claim. In these circumstances, the results obtained in the present study, especially the longer C−Cl bonds with bending toward the plane of the π system, may have a significant importance in explaining the reductive dechlorination process in PCDFs. The bending C−Cl bond orientations in anions prove the assumption[45,46] that these molecules become nonplanar to pave the way for C−Cl bond breaking through a reductive dechlorination process. In other words, these results carry the earlier assumptions that the additional electron enters into a π^* orbital, and the C−Cl bond cleavage may occur according to the bent bond model.

To support the fact that the π^* orbitals receive the ionizing electrons, we studied the lowest unoccupied molecular orbitals (LUMOs) of the PCDF neutrals and found that LUMOs of all the selected PCDFs are π orbitals. So it is clear that the ionizing electrons enter into the π antibonding orbitals of the PCDFs by considering the fact that normally ionizing electron enters into the lowest unoccupied MO. We also studied the singly occupied molecular orbitals of anions of all the considered PCDFs. Obtained SOMOs showed significant differences: SOMOs of 1,2,3-, 2,3,4-, and 1,2,3,4-PCDFs were found to be σ (or a mixture of σ and π) orbitals, while SOMOs of most of the remaining PCDFs were pure π orbitals. The LUMOs and the SOMOs of a few neutrals and anions, respectively, obtained at the B3LYP/6-311+G(2d,2p) level are given in Figure 3. It showed that PCDFs with longer C−Cl bond had σ SOMOs. The foregoing results support the following conclusions: (1) the ionizing electron is accepted into the π^* orbitals of the neutral PCDFs at the vertical attachment region (the Franck−Condon region); (2) with the acceptance of the ionizing electron, C−Cl bond length increases; (3) while bond length increases, the C−Cl bond also bends toward the plane of the π system; and (4) when the C−Cl bond bends toward the π system, $\pi^*-\sigma^*$ orbital mixing followed by intramolecular electron transfer from π^* to σ^* orbital occurs. These events pave the way for the C−Cl bond cleavage. Because of large steric energies in 1,2,3-, 2,3,4-, and 1,2,3,4-PCDFs due to the addition of an electron, one of the C−Cl bonds in these PCDFs is very elongated, and the above-mentioned four processes could have happened while accepting the ionizing electrons. The calculated atomic charges on chlorine atoms of the longer C−Cl bonds in these three anionic PCDFs were −0.68, −0.56, and −0.54 e, respectively. It shows that these three anionic PCDFs are on the verge of the bond cleavage process.

Anionic PCDFs other than those with a longer C−Cl bond length have π SOMOs. For these PCDFs, the C−Cl bond stretching may provide the possibility for $\pi^*-\sigma^*$ orbital mixing which is essential for the bond cleavage mechanism. To know the changes in the structure as well as the changes in the nature of SOMO with the increase of the C−Cl bond length in these PCDFs, we considered the anionic 2,3,7,8-TCDF, as an example, and optimized [at UB3LYP/6-31G(d)] its structure at different

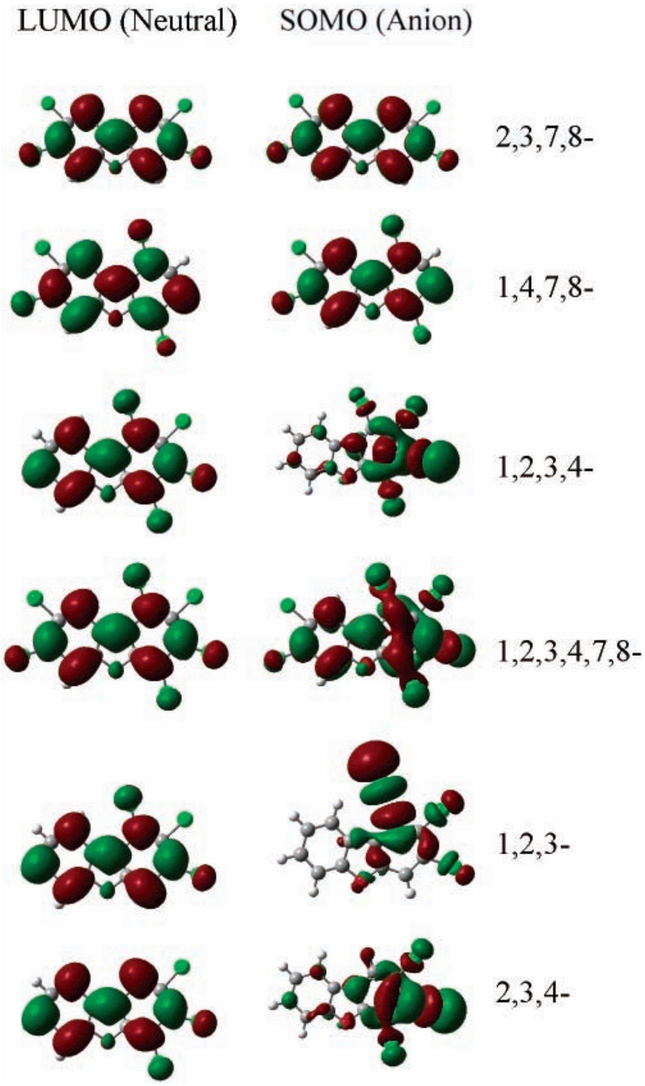


Figure 3. Lowest unoccupied molecular orbitals (for neutrals) and singly occupied molecular orbitals (for anions) for a few PCDFs represented as isosurfaces with a contour value of 0.02 au.

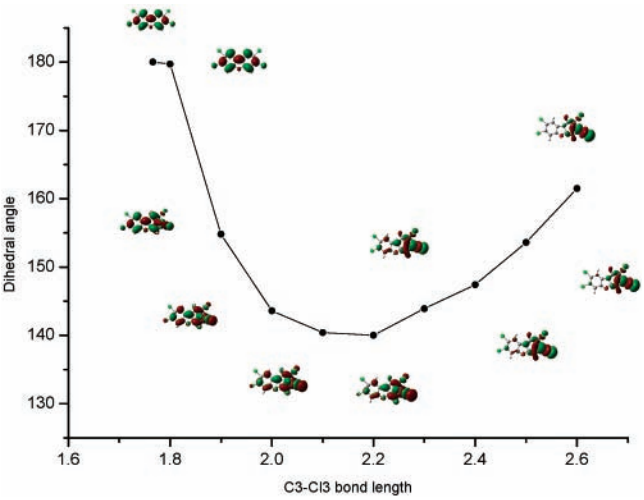


Figure 4. Dihedral angle (deviation of 3-chlorine from the planarity) and singly occupied molecular orbital along the C3−Cl3 bond of the anionic 2,3,7,8-TCDF. Dihedral angles are in degrees, and bond lengths are in angstroms.

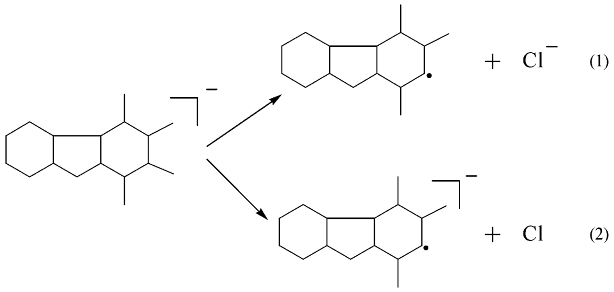


Figure 5. Reductive dechlorination schemes for 1,2,3,4-TCDF.

C3−Cl3 bond lengths (from 1.8 to 2.6 Å in steps of 0.1 Å). The results are depicted in Figure 4. Two important results have been noticed as the C−Cl bond length increases: (1) 3-chlorine moves from the planar orientation and bends toward the π system (the anion becomes nonplanar), and (2) the singly occupied MO is a π^* orbital at the equilibrium structure (R(C−Cl3) = 1.756 Å) but becomes progressively σ^* character at longer C−Cl distances (intramolecular electron transfer from π^* to σ^* MO occurs). These results support the bent bond model and confirm the fact that the bond stretching (combined by Cl bending, inherently) provides an opportunity for the $\pi^*-\sigma^*$ orbital mixing necessary for C−Cl bond cleavage.

A previous study on polychlorobenzenes revealed that the parent anion undergoes fission by two pathways: (1) cleavage to aryl radical plus chloride ion, and (2) fission to aryl carbanion plus chlorine atom.[56] An ECNICI-MS study on PCDDs has also illustrated the same kind of two dissociative electron capture pathways.[57] So it is worthwhile to study the probable dissociative reactions involving the PCDFs. For this purpose, we considered the anionic 1,2,3,4-TCDF and studied its dissociative pathways (Figure 5). Since the C3−Cl3 bond in 1,2,3,4-TCDF is weakened much due to the addition of an electron, we considered the dissociation from position 3 (C3). To study the dechlorination reactions (Figure 5), we optimized the 1,2,4-TrCDF radical and its anion at the B3LYP/6-31G(d) level of theory followed by frequency calculations which showed that obtained geometries were minima on the potential energy surface. Then, both 6-311+G(d,p) and 6-311+G(2d,2p) basis sets were used with the B3LYP functional to optimize the radical as well as its anion. Scaled (0.9804) ZPEs obtained using B3LYP/6-31G(d) frequencies were utilized to correct all of the energies. These energies combined with the energies calculated for the anionic 1,2,3,4-TCDF were used to obtain the reaction energies.

The calculated reaction energies showed that the dissociation of a chloride ion (reaction 1) from the anionic 1,2,3,4-TCDF is endergonic by −0.99 eV at the B3LYP/6-311+G(2d,2p) level of theory. However, the overall reaction energy for the reductive dechlorination process (accepting electrons followed by C−Cl bond cleavage) leading to the formation of 1,2,4-TrCDF neutral radical and chloride ion from 1,2,3,4-TCDF is more or less zero. [The electron affinity value calculated for 1,2,3,4-TCDF is 0.985 eV at the B3LYP/6-311+G(2d,2p) level. A detailed account on electron affinity is given in the next section.] On the other hand, the other dissociation reaction (reaction 2) is endergonic by −1.83 eV, so the overall process leading to the formation of the 1,2,4-TrCDF radical anion (anion of the 1,2,4-TrCDF radical) and the chlorine atom from 1,2,3,4-TCDF is also an endergonic one (−0.84 eV). So it is most likely that the dechlorination (in the gas phase) occurs via neutral radical PCDF and chloride ion. The calculated atomic charge of −0.54 e on the Cl3 atom in the anionic 1,2,3,4-TCDF also supported the fact that the chlorine dissociates as a chloride ion. The calculated charges on Cl3 in the anionic 2,3,7,8-, 1,2,3,4,7,8-, and 2,3,4-PCDFs were −0.18, −0.21, and −0.56 e, respectively. The

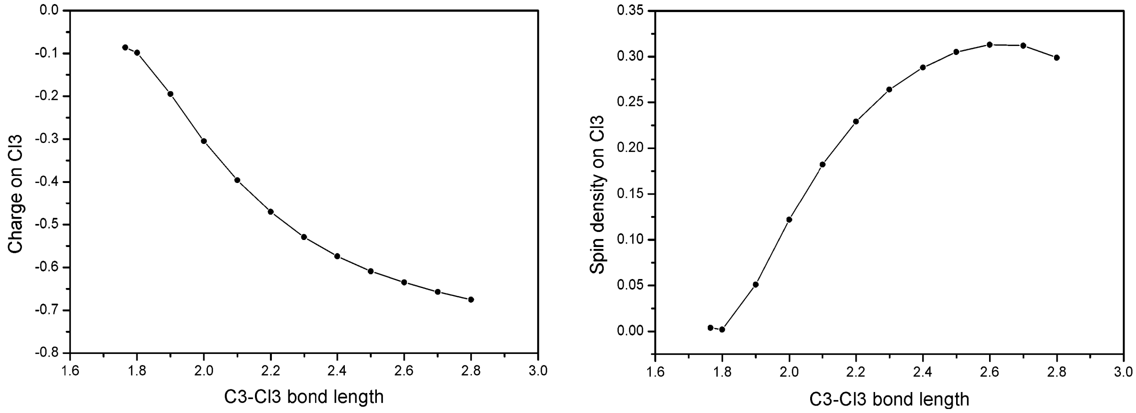


Figure 6. Charge and spin density on Cl3 of the anionic 2,3,7,8-TCDF along the C3−Cl3 bond. Charges are in electron units, and bond lengths are in angstroms.

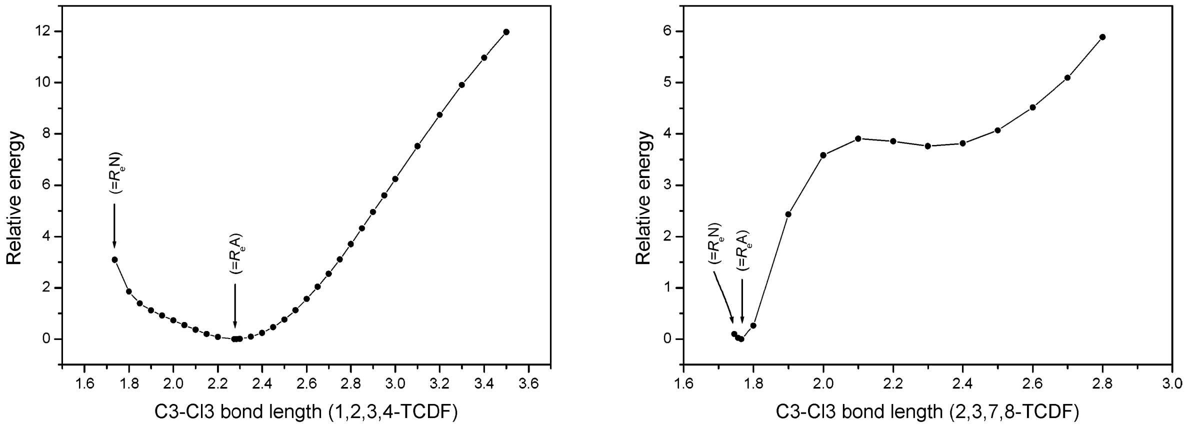


Figure 7. Potential energy curves along the C3−Cl3 bond of the anionic 1,2,3,4-, and 2,3,7,8-TCDFs. Relative energies are in kilocalories per mole, and bond lengths are in angstroms. Equilibrium bond lengths (C3−Cl3) of the neutrals and anions are denoted by R_eN and R_eA, respectively.

respective C3−Cl3 bond lengths in these three PCDFs were 1.761, 1.803, and 2.298 Å. These values clearly showed that the departing chlorine carries a large amount of negative charge as it dissociates from the parent anion. To understand further, we studied the changes in atomic charges and spin densities on the Cl3 atom as it dissociates from the anionic 2,3,7,8-TCDF. The charges (MPA) and spin densities obtained [at the B3LYP/6-31G(d) level] at different C3−Cl3 bond lengths (geometries are optimized at each C−Cl bond length) are mapped with C3−Cl3 bond lengths (Figure 6). As can be clearly seen in the figure, chlorine is dissociating as a chloride ion when dechlorination occurs. The existence of anions of the radicals in the experimental study[56,57] may be interpreted as they were formed via capture of electrons by radical PCDFs. The large positive electron affinity of 2.882 eV for 1,2,4-TrCDF radical obtained at the B3LYP/6-311+G(2d,2p) level supports the above assumption. All these results reveal that the bond cleavage in the anionic PCDFs could take place via PCDF radical and chloride ion.

We have also drawn the potential energy curves, PECs, (relative energy vs C3−Cl3 bond length) for the anionic 1,2,3,4- and 2,3,7,8-TCDFs (Figure 7). For this purpose, we optimized the anions at various C3−Cl3 bond lengths at the B3LYP/6-31G(d) level. All geometrical parameters were allowed to optimize. There is a marked difference between the PECs of the two TCDFs: a shallow-type minimum was found in the case of 2,3,7,8-TCDF, whereas no such shallow minimum was found for 1,2,3,4-TCDF. It might be possible that the shallow minimum that appeared on the PEC of the 2,3,7,8-TCDF could behave as a dissociative state, while, in the case of 1,2,3,4-TCDF, the anion state (the anion at its equilibrium structure) itself could act as a dissociative state. The small barrier on the PEC of 2,3,7,8-TCDF anion at around R(C3−Cl3) = 2.1 Å, at which the departing Cl3 atom deviated maximum from the molecular plane (Figure 4), might be attributed to $\pi^*-\sigma^*$ mixing.

TABLE 2: Zero-Point-Energy-Corrected Adiabatic Electron Affinities (eV) of the PCDFs Obtained with the B3LYP Functional

PCDF	6-31G(d)	6-311G(d,p)	6-311+G(d,p)	6-311+G(2d,2p)
DF	−0.493	−0.138	0.102	0.095
2,3,4-TrCDF	0.440	0.822	0.847	0.789
1,2,3-TrCDF	0.477	0.865	0.886	0.817
1,2,4-TrCDF	0.299	0.634	0.742	0.733
2,3,7,8-TCDF	0.612	0.946	1.036	1.029
1,2,3,4-TCDF	0.657	1.029	1.043	0.985
1,4,6,9-TCDF	0.540	0.834	0.959	0.949
1,4,7,8-TCDF	0.557	0.888	0.958	0.950
2,3,6,7-TCDF	0.558	0.883	0.966	0.961
3,4,6,7-TCDF	0.496	0.812	0.890	0.886
1,2,8,9-TCDF	0.568	0.913	0.995	0.970
1,2,4,6-TCDF	0.532	0.863	0.944	0.935
1,2,3,7,8-PeCDF	0.759	1.082	1.123	1.114
2,3,4,7,8-PeCDF	0.791	1.110	1.169	1.161
1,2,3,4,7,8-HCDF	0.975	1.295	1.306	1.286
1,2,3,6,7,8-HCDF	0.927	1.238	1.262	1.253

Electron Affinities. Adiabatic electron affinities obtained using four different basis sets with the B3LYP functional after ZPE correction are tabulated in Table 2. To our knowledge, there are no published experimental EA values for these selected PCDFs. By considering the size of the molecules, DFT is a good choice for calculating the EA values of PCDFs. Earlier EA studies on a variety of molecules concluded that the B3LYP functional could achieve average errors between 0.1 and 0.2 eV as compared to the experiment.[58−67] A recent review on EA also indicated that EA values calculated for a set of 91 molecules by using the same density functional have an average error of 0.16 eV.[68] These conclusions strongly support the use of the B3LYP functional for EA calculations. Bearing all these facts in mind, we utilized the B3LYP functional in the present study to calculate the EA values of the PCDFs and we believed that the calculated values would be reliable.

The EA values calculated for all the selected PCDFs were positive. Flexible basis sets with diffuse functions are essential to treat negative ions properly which resulted in larger EA values, for all the PCDFs, calculated with 6-311+G(d,p) and 6-311+G(2d,2p) basis sets than those obtained with the 6-31G(d) basis set. The increase in chlorine (electron-withdrawing group) number leads to a lowering of LUMO energy and hence the electron affinities of the PCDFs progressively increase with the increase in chlorine number. The biological and toxic activities of PCDFs, like those of their PCDD and PCB counterparts, strongly depend on their receptor binding affinities. After entering the body, these toxins bind with the Ah receptors followed by the complex sequence of events leading to the biological and toxic effects of HAHs. Hence, the initial binding with the Ah receptor is the key step for the toxic behavior of these toxins. The large positive EA values obtained for the selected PCDFs in the present study support that PCDFs may act as electron acceptors in the charge-transfer interactions with the receptors in living cells. These results combined with the results obtained for the PCDDs[20] and PCBs[23] clearly indicate that HAHs act as electron acceptors and the electron affinity might be an influential parameter of toxicity. Overall, the EA values obtained with the 6-31G(d) basis set were around 0.4 eV smaller than those obtained with the largest basis set, 6-311+G(2d,2p); however, the EA values calculated using the 6-311G(d,p) basis set were close to those calculated using the largest basis set.

The biological activity and toxicity of HAHs are also highly dependent upon the position of chlorine substitution. So the EA values obtained for various TCDFs representing substitutions at many different positions may reveal the possible relationship, if it exists, between the EA and the toxicity of PCDFs. It is well-known that PCDDs and PCDFs with chlorine atoms substituted at positions 2, 3, 7, and 8 are more toxic, and in fact the toxic PCDFs[4] are those substituted at all these lateral positions. It seems from Table 2 that the TCDFs substituted with chlorines at lateral positions have large EA values: EA values calculated for 2,3,6,7- and 1,2,8,9-TCDF were 0.961 and 0.970 eV, respectively, while the same obtained for 1,4,6,9-TCDF was 0.949 eV at the B3LYP/6-311+G(2d,2p) level of theory. At the same time, it is also seen from Table 2 that the TCDFs with chlorines substituted at positions near an oxygen atom have smaller EA values than those with chlorines substituted at positions far away from the oxygen atom: EA values obtained for 1,2,4,6- and 3,4,6,7-TCDF were 0.935 and 0.886 eV, respectively, while the same obtained for 1,2,8,9-TCDF was 0.970 eV. In fact, the calculated EA of 3,4,6,7-TCDF was the smallest among all of those obtained for the selected TCDFs. Interestingly, the most toxic TCDF, 2,3,7,8-TCDF, has the largest EA value. Yet again, interestingly, among the selected PeCDFs, the 2,3,4,7,8-PeCDF that is more toxic than the 1,2,3,7,8-PeCDF[4] has a larger EA value.

Concluding Remarks

We studied 15 polychlorinated dibenzofurans by using density functional theory and reached the following conclusions:

All the PCDFs have planar structures, but some of the PCDFs attain nonplanar structures upon electron attachment. In all of the cases, the electron attachment weakened the C−Cl bonds and the much-elongated C−Cl bonds (>2.2 Å) of the anionic 1,2,3- and 2,3,4-TrCDFs, and 1,2,3,4-TCDF were of particular interest. These weak bonds could lead to the dechlorination of PCDFs. In most of the cases, lateral carbon−chlorine bonds in anions were more labile than the other C−Cl bonds.

The ionizing electrons enter into the π^* orbitals of the neutral PCDFs. However, the chlorine atom bends toward the π system when the C−Cl bond elongates which paves the way for $\pi^*-\sigma^*$ orbital mixing necessary for carbon−chlorine bond cleavage. The dechlorination of the anionic PCDFs occurs via neutral PCDF radical and chloride ion.

All the PCDFs have positive electron affinities. The positive adiabatic EAs suggest that PCDFs, like their toxic PCDD and PCB counterparts, act as electron acceptors in their interaction with Ah receptors in living cells. The electron affinities of the toxic PCDFs were higher than those of their nontoxic or less-toxic counterparts. The EA value of 1.029 eV calculated for the most toxic 2,3,7,8-TCDF was the largest among the EAs calculated for the eight selected TCDFs.

Because of large EA values (>0.7 eV) and the involvement of π^* orbitals in the anion formation process, electron capture negative-ion chemical ionization mass spectrometry could be used as an excellent analytical technique for determining the PCDFs in environmental samples.

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Supporting Information Available: Tables of B3LYP/6-311+G(2d,2p) Cartesian coordinates and total energies and B3LYP/6-31G(d) zero-point vibrational energies for the selected PCDF neutrals and anions. This material is available free of charge via the Internet at http://pubs.acs.org.

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