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Electron Affinity for the Most Toxic 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD): A Density Functional Theory Study

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The electron affinity (EA) of the most toxic dioxin, 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (TCDD), has been obtained along with that of two other toxic TCDDs using density functional theory (DFT) for the first time. The vertical electron affinity calculated for 1,2,3,4- TCDD at the B3LYP/aug′-cc-pVDZ level agrees with the recently obtained *(J. Am. Chem. Soc.* **1999**, *121*, 2561) experimental electron energy, which produced a maximum anion intensity in electron-capture negative-ion mass spectrometry. The adiabatic EAs of 0.259 and 0.265 eV for 2,3,7,8-TCDD obtained using B3LYP and B3PW91 functionals, respectively, suggest that anionic TCDDs are stable with respect to the detachment of electrons and indicate that TCDDs act as electron acceptors in the reaction with receptors in living cells. Because of the large difference in geometry between the neutral and the anionic 1,2,3,4-TCDD, the calculated adiabatic EA differs considerably from the vertical electron affinity. Anionic 1,3,6,8- and 2,3,7,8-TCDD are planar like their neutral counterparts; on the other hand, anionic 1,2,3,4-TCDD is nonplanar although its neutral counterpart is planar.

Introduction

Electron affinity is a very important physical property of molecules and plays a vital role in electron-transfer reactions. Toxins appear to act as electron acceptors in a charge-transfer complex with a receptor in living cells.[1,2] Due to their extreme toxicity and the existence of many isomers, experimental investigations on toxic polychlorinated dibenzo-*p*-dioxins (PCDDs) are difficult. It is well-known that 2,3,7,8-TCDD is the most toxic of all the 75 PCDD isomers and causes dermal toxicity, immunotoxicity, reproductive effects and teratogenicity, endocrine disruption, and carcinogenicity.[3−5] Despite this importance and the development of theory, neither ab initio nor DFT calculations were undertaken in the past to obtain the electron affinities of PCDDs. These circumstances led us to study this important subject.

Previously reported electron affinities for PCDDs calculated by using AM1,[6] CNDO,[7] and MNDO[8] are not quantitatively reliable. Our research group has already demonstrated that the calculated structures, energies, vibrational frequencies, and ionization potentials of 2,3,7,8-TCDD agree well with the experimental values.[9]

Recently, electron affinities calculated using hybrid density functionals have been shown to be more accurate and to provide better agreement with the experimental values.[10−12] Earlier studies[11,13,14] and our recent investigations[15−17] reveal that the B3PW91 has a slight edge over the B3LYP functional. Interestingly, few studies were made previously using the former functional, compared with the latter.

Our earlier study[9] on 2,3,7,8-TCDD predicts a very low harmonic frequency for the butterfly flapping motion of the two benzo-planes with a very flat potential curve. Therefore, it is likely that studies of the structures of other TCDDs, especially anions, will prove revealing. We divided the work into four parts: (i) obtaining accurate electron affinities for 2,3,7,8-, 1,2,3,4-, and 1,3,6,8-TCDD; (ii) analyzing their structures; (iii) interpreting charge distributions; and (iv) studying the reliability of DFT methods.

Computational Approaches

All the calculations were carried out using the Gaussian 94[18] packages on an NEC−SX-4 supercomputer. Hartree−Fock (HF) calculations were made as a preliminary study. The B3LYP, B3P86, and B3PW91 hybrid functionals in DFT were used to optimize both the neutral species and the anions of 1,2,3,4-, 1,3,6,8-, and 2,3,7,8-TCDD. No symmetry restrictions were imposed for the optimization at Hartree−Fock level, whereas, symmetry indicated in Figure 1 was enforced for geometry optimizations at all the DFT calculations. The hybrid DFT methods include a mixture of Hartree−Fock exchange and DFT exchange correlation. They are Becke's three-parameter functional,[19] which has the form: $AE_x^{\mathrm{Slater}} + (1 - A)E_x^{\mathrm{HF}} + B\Delta E_x^{\mathrm{Becke}} + E_c^{\mathrm{VWN}} + C\Delta E_c^{\mathrm{nonlocal}}$, where the nonlocal correlation is provided by any one of the expressions of Lee−Yang−Parr,[20] Perdew 86,[21] or Perdew−Wang 91.[22] These three hybrid methods are B3LYP, B3P86, and B3PW91 by notation. The constants *A*, *B*, and *C* are those determined by Becke by fitting the results in the G1 molecular set.[23] Dunning's correlation-consistent polarized double-ξ basis set[24] with diffuse functions for heavy atoms (aug′-cc-pVDZ) is utilized throughout the study. Adiabatic (EA_{Ada}) and vertical (EA_{Ver}) electron affinities were obtained from the following relations. Charge distributions

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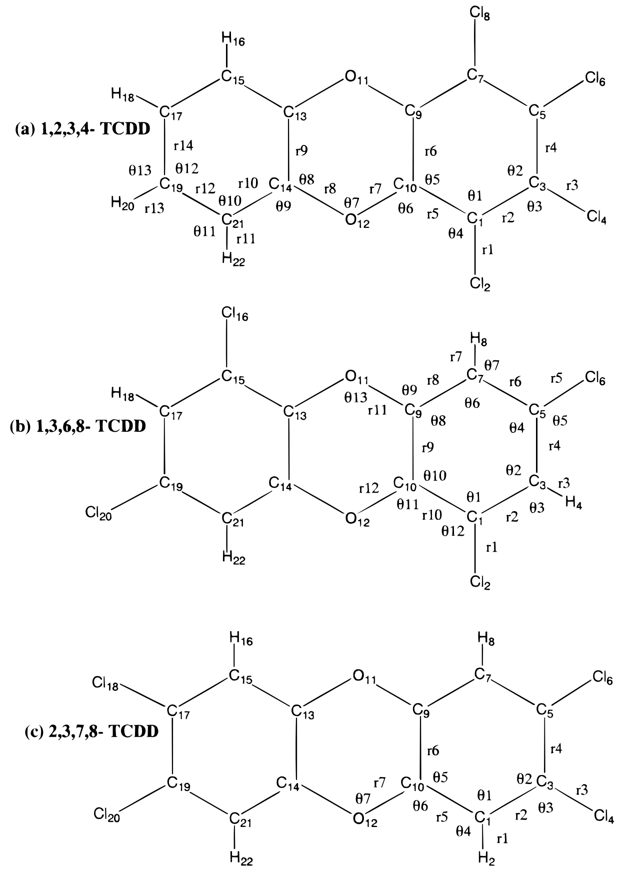

Figure 1. Structural description of 1,2,3,4-, 1,3,6,8- and 2,3,7,8-TCDDs.

$$\mathrm{EA}_{\mathrm{Ada}} = E(\text{Optimized neutral}) - E(\text{Optimized anion})$$

$$\mathrm{EA}_{\mathrm{Ver}} = E(\text{Optimized neutral}) - E(\text{Anion at optimized neutral geometry})$$

for neutral species as well as anions of the three TCDDs were studied using the Natural Population Analysis (NPA) scheme[25] at the B3PW91/aug′-cc-pVDZ level of theory. It should be noted that by using DFT, spin contamination for open-shell systems, such as the anions in this work, can be greatly reduced.[26] The maximum expectation value of the S^2 operator for doublets is 0.76.

Results and Discussion

1. Electron Affinity. The EA values calculated with AM1 theory are 1.15 and 1.16 eV for 1,2,3,4- and 2,3,7,8-TCDD, respectively.[6] Laramee et al.[7] and Koester and Hites[8] obtained LUMO energies of some PCDDs using CNDO and MNDO calculations. From their study, the electron affinity (~negative E_{LUMO}) values [CNDO/MNDO] are −0.96/1.349, −1.59/1.317, and −1.73/1.396 eV for 1,2,3,4-, 1,3,6,8-, and 2,3,7,8-TCDD, respectively.

In 1992, Deinzer group[27] studied some anions including TCDDs using negative-capture-ion (NCI) mass spectroscopy combined with a trochoidal electron monochromator and concluded that electron-energy scanning with the electron monochromator shows energy maxima of 0.23 and 0.38 eV for the production of molecular ions from isomeric 1,2,3,4- and 1,3,6,8-TCDD, respectively. The anion formation process suggests that these energies correspond to the vertical EAs. Other experimental studies by Japanese researchers also indicate that the electron affinity of 2,3,7,8-TCDD is positive.[28]

TABLE 1: Adiabatic ($\mathrm{EA}_{\mathrm{Ada}}$) and Vertical ($\mathrm{EA}_{\mathrm{Ver}}$) Electron Affinities for 1,2,3,4-, 1,3,6,8-, and 2,3,7,8-TCDD (eV))

	1,2,3,4-TCDD		1,3,6,8-TCDD		2,3,7,8-TCDD	
theory	$\mathrm{EA}_{\mathrm{Ada}}$	$\mathrm{EA}_{\mathrm{Ver}}$	$\mathrm{EA}_{\mathrm{Ada}}$	$\mathrm{EA}_{\mathrm{Ver}}$	$\mathrm{EA}_{\mathrm{Ada}}$	$\mathrm{EA}_{\mathrm{Ver}}$
HF/aug′-cc-pVDZ	−0.965	−0.756	−0.796	−1.001	−1.285	−1.435
B3LYP/aug′-cc-pVDZ	0.727	0.116	0.351	0.232	0.259	0.152
B3P86/aug′-cc-pVDZ	1.270	0.671	0.899	0.784	0.814	0.711
B3PW91/aug′-cc-pVDZ	0.729	0.120	0.349	0.236	0.265	0.162

TABLE 2: EAs (eV) at the B3LYP/Aug′-cc-pVDZ Level, Together with the Available Experimental and Theoretical Results from the Literature

	exp[a]	AM1[b]	CNDO[c]	MNDO[d]	Our study	
TCDD	$\mathrm{EA}_{\mathrm{Ver}}$	$\mathrm{EA}_{\mathrm{Ada}}$	[e]E_{LUMO}	[e]E_{LUMO}	$\mathrm{EA}_{\mathrm{Ada}}$	$\mathrm{EA}_{\mathrm{Ver}}$
1,2,3,4-	0.11	1.150	0.960	−1.349	0.727	0.116
1,3,6,8-			1.590	−1.317	0.351	0.232
2,3,7,8-		1.160	1.730	−1.396	0.259	0.152

[a] Reference 29. [b] Reference 6. [c] Reference 7. [d] Reference 8. [e] $\mathrm{EA}_{\mathrm{Ver}} \sim -E_{\mathrm{LUMO}}$.

Very recently the Deinzer group[29] again studied many PCDDs in detail by using electron-capture negative-ion mass spectrometry and concluded that the electron energy, $E_{\max}$, required to record the maximum molecular-anion intensity for 1,2,3,4-TCDD is 0.11 eV. We tentatively assumed this $E_{\max}$ to be the exact vertical EA and compared this with our calculated results. It is obvious that the EA values obtained through semiempirical methods are unreliable and one can speculate from these experimental observations that (a) all the three TCDDs have positive EAs, (b) $\mathrm{EA}_{\mathrm{Ver}}$ for 1,2,3,4-TCDD is 0.11 eV, and (c) the vertical EA for 1,3,6,8-TCDD is larger than that for 1,2,3,4-TCDD.

Table 1 lists our calculated $\mathrm{EA}_{\mathrm{Ada}}$ and $\mathrm{EA}_{\mathrm{Ver}}$ values for 1,2,3,4-, 1,3,6,8-, and 2,3,7,8-TCDD at various levels of theory in the present study. The electron affinities calculated at the various levels of theory are compared with the available values (Table 2). It is obvious from Table 2 that the EAs calculated using the various semiempirical methods differ from one another.

All the electron affinities calculated at the HF level of theory are negative, whereas the electron affinities calculated using density functionals are positive. The vertical electron affinities of 0.116 and 0.120 eV obtained at the B3LYP and B3PW91 levels, respectively, for 1,2,3,4-TCDD coincide with the recently obtained $E_{\max}$ for this molecule.[29] However, the corresponding affinity obtained with the B3P86 functional is larger by 0.555 eV than that obtained with the B3LYP. The calculated EA values using the B3P86 functional are larger than those obtained using the B3LYP and B3PW91 functionals in all cases, and one may conclude that the B3P86 functional overestimates the EA values, as indicated in earlier studies.[30]

A consideration of the following three points suggests that the calculated adiabatic EAs of 0.727 (0.729), 0.351 (0.349), and 0.259 (0.265), all in eV, obtained using B3LYP (B3PW91) functionals for 1,2,3,4-, 1,3,6,8-, and 2,3,7,8-TCDD, respectively, should be accurate: (i) the calculated values are consistent with the speculations, i.e., (a) all the three TCDDs have postive EAs, (b) $\mathrm{EA}_{\mathrm{ver}}$ for 1,2,3,4-TCDD is 0.11 eV, and (c) the vertical EA for 1,3,6,8-TCDD is larger than that for 1,2,3,4-TCDD, arrived from the earlier experimental studies, (ii) the calculation of EA using DFT has become well documented and established in recent years,[31,32] and (iii) the hybrid functionals and the basis set used in the present study are good enough to produce accurate electron affinities.[12,33,34] Note that the B3LYP and

B3PW91 functionals both yield the same EA values; therefore, either one may be used for EA calculations.

The positive adiabatic electron affinities of various TCDDs reveal that these molecules may act as electron acceptors in the reaction with receptors in the living cells. Most of the toxic and biological responses are thought to be initiated through the binding of these dioxins to a soluble intracellular protein, the arylhydrocarbon (Ah)-receptor. Therefore, it seems to be a correlation between the toxicity of dioxins and their binding affinity with Ah-receptors. In case electron affinity of dioxins plays an important role in the dioxin-Ah receptor binding, it is likely that dioxins with large electron affinities may be more toxic than the dioxins with small electron affinities. But from the present study, the calculated adiabatic electron affinity of the most toxic 2,3,7,8-TCDD is not the highest among of all obtained for the examined dioxins and hence we were unable to establish a direct correlation between the electron affinity and the toxicity, thus making it likely that electron-affinity is not a sufficient predictor of toxicity.

2. Structures and Energetics. Figure 1 shows the structural descriptions for the three TCDDs. Most of the geometrical parameters for 2,3,7,8-TCDD calculated using the B3LYP/aug′-cc-pVDZ level of theory are slightly overestimated compared with the experimental values.[35] In the worst case, the C−Cl bond length calculated with the B3LYP functional deviates 0.02 Å from the experimental value, whereas this deviation is 0.007 Å with the B3PW91 functional. The 2,3,7,8-TCDD optimized geometry obtained using the B3PW91 functional is closer to the experimental ones than that obtained using the B3LYP functional; hence we prefer to use B3PW91 geometries for the structural analysis. The structural parameters obtained for the neutral species and the anions of all three TCDDs using the B3PW91/aug′-cc-pVDZ level are shown in Table 3. All three neutral TCDDs are planar. The C−Cl bond lengths obtained for 1,3,6,8- and 2,3,7,8-TCDD are slightly larger than that for 1,2,3,4-TCDD; this moderately impacts the other structural parameters in the latter.

The structures of the three anionic TCDDs have been obtained for the first time. Of particular interest is the nonplanarity of the 1,2,3,4-TCDD anion. Most of the dihedral angles of the optimized 1,2,3,4-TCDD anion are given as footnotes in Table 3. The benzene ring accommodating all the chlorine atoms experienced a significant change in orientation. The maximum change (31.9°) in planarity occurred between Cl2C1C3 and C1C3Cl4 planes. Because of the higher electronic charge on the oxygen and chlorine atoms, a dihedral angle of 29.3° was found between the planes of Cl2C1C10 and C1C10O12. The difference of about 0.6 eV between the adiabatic and vertical electron affinities for 1,2,3,4-TCDD may be attributed to this change in geometry (nonplanarity) between the anion and its neutral counterpart. A maximum elongation of 0.077 Å occurred in the C−Cl bond length for the same TCDD; however, this elongation is only 0.021 and 0.017 Å for 1,3,6,8- and 2,3,7,8-TCCD, respectively. Although few geometrical changes occurred in the 1,3,6,8- and 2,3,7,8-TCDD anions relative to their neutral species, both anions are planar.

The total energies calculated with all the hybrid functionals using a aug′-cc-pVDZ basis set are listed in Table 4. Among the neutral species, 1,3,6,8-TCDD is the most stable, and the least stable 1,2,3,4-TCDD is 7.58 kcal/mol (with B3PW91) less stable than the more toxic 2,3,7,8-TCDD, indicating that the toxicity may be independent of stability. It is worth noting that the stability of anionic 1,2,3,4-TCDD is large compared with the anionic 2,3,7,8-TCDD and the 1,2,3,4-TCDD anion becomes more stable than the 2,3,7,8-TCDD anion by 3.1 kcal/mol (with B3PW91).

TABLE 3: Structural Parameters of Neutral Species and Anions of 1,2,3,4-, 1,3,6,8-, and 2,3,7,8-TCDD at the B3PW91/aug′-cc-pVDZ Level (r (Å) and θ (deg))

	1,2,3,4-TCDD		1,3,6,8-TCDD		2,3,7,8-TCDD		
param	neutral	anion	neutral	anion	neutral	anion	expt[a] for neutral 2,3,7,8-TCDD
r1	1.727	1.804	1.735	1.757	1.089	1.091	(1.01)
r2	1.405	1.405	1.397	1.398	1.397	1.395	1.384
r3	1.727	1.799	1.089	1.087	1.735	1.752	1.728
r4	1.402	1.379	1.392	1.418	1.400	1.426	1.388
r5	1.397	1.406	1.742	1.763	1.388	1.390	1.377
r6	1.398	1.378	1.395	1.387	1.398	1.432	1.387
r7	1.364	1.399	1.089	1.091	1.374	1.371	1.379
r8	1.380	1.365	1.389	1.396			
r9	1.394	1.404	1.399	1.432			
r10	1.389	1.393	1.396	1.391			
r11	1.091	1.092	1.373	1.373			
r12	1.396	1.398	1.369	1.362			
r13	1.091	1.093					
r14	1.396	1.395					
$\theta 1$	120.2	118.7	121.0	123.2	120.2	121.3	121.0
$\theta 2$	119.7	120.4	118.7	116.9	119.8	119.3	
$\theta 3$	119.8	118.5	120.0	120.9	118.7	119.2	118.9
$\theta 4$	118.4	118.1	121.5	122.1	119.3	118.6	119.0
$\theta 5$	120.0	120.4	119.3	118.5	120.0	119.3	
$\theta 6$	118.0	118.0	118.7	119.6	117.9	118.9	117.6
$\theta 7$	116.4	115.1	121.9	121.4	115.8	116.5	115.7
$\theta 8$	121.6	121.6	121.3	120.4			
$\theta 9$	118.1	118.6	117.3	118.3			
$\theta 10$	119.6	120.3	118.8	117.9			
$\theta 11$	121.8	121.6	119.1	120.4			
$\theta 12$	120.1	119.9	119.2	118.4			
$\theta 13$	120.4	120.5	116.4	116.9			

[a] Taken from ref 35. The dihedreal angles for anionic 1,2,3,4- (see text) are $\angle 10,9,11,13 = 15.5°$, $\angle 7,9,11,13 = -169.3°$, $\angle 12,10,9,7 = -175.1°$, $\angle 15,13,11,9 = 166.3°$ $\angle 12,14,13,15 = 178.1°$, $\angle 5,7,9,11 = -168.1°$, $\angle 5,7,9,10 = 7.1°$, $\angle 8,7,9,11 = 29.3°$, $\angle 8,7,9,10 = -155.5°$, $\angle 17,15,13,11 = 177.6°$, $\angle 16,15,13,11 = -1.9°$, $\angle 3,5,7,8 = 155.0°$, $\angle 6,5,7,9 = 166.0°$, $\angle 6,5,7,8 = -31.9°$, $\angle 1,3,5,6 = -173.0°$.

TABLE 4: Total Energies (hartrees) for the Respective Neutral Species and Anions of 1,2,3,4-, 1,3,6,8-, and 2,3,7,8-TCDD Calculated Using Three Hybrid Functionals with a aug′-cc-pVDZ Basis Set

functionals	type	1,2,3,4-	1,3,6,8-	2,3,7,8-
B3LYP	neutral	−2451.0302684	−2451.0441752	−2451.0430193
	anion	−2451.0569880	−2451.0570683	−2451.0525192
B3P86	neutral	−2453.9840810	−2453.9961373	−2453.9956771
	anion	−2454.0307371	−2454.0291697	−2454.0256000
B3PW91	neutral	−2450.5900988	−2450.6027848	−2450.6021837
	anion	−2450.6168885	−2450.6156015	−2450.6119342

3. Charge Distribution. The atomic charges calculated using the NPA scheme at the B3PW91/aug′-cc-pVDZ level of theory are shown in Figure 2. The distribution of the additional electron can be easily analyzed from the spin densities.

The oxygen atoms in 2,3,7,8-TCDD are electron-rich centers. Contrary to the findings of an earlier electrostatic-potential study,[36,37] chlorine sites appear to act as positive rather than negative sites. The carbon atoms attached to hydrogens are enriched with electrons next to oxygens in quantity. However, it is obvious from Figure 2 that the β chlorine atoms in the same TCDD become enriched (slightly) in electronic charge when forming the anion, and a noticeable elongation has been found only in the C−Cl and carbon−carbon bonds in the β region.

For 1,3,6,8-TCDD as well, the maximum electronic charge occurs only in the oxygen atomic regions. The carbon atoms attached to hydrogen atoms are enriched with an excess of 0.26

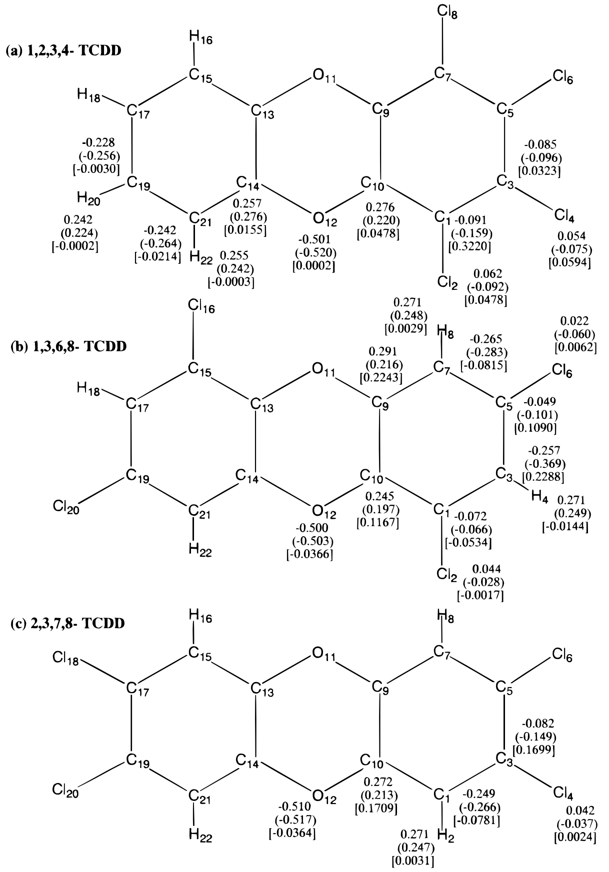

Figure 2. NPA charges (in electron units) of neutral and anion (in parentheses) and unpaired spin-densities [in square brackets] of anions of various TCCDs at B3PW91/aug′-cc-pVDZ level of theory.

electrons. The β carbon atoms bonded to hydrogen atoms become further rich in atomic charge when forming the anion. The β chlorine atoms also derive electrons as in 2,3,7,8-TCDD. Because of this increase in atomic charge, the carbon−carbon in the β side and C−Cl bonds are elongated moderately.

As for the two previous TCDDs, the oxygen atoms are negative centers in 1,2,3,4-TCDD. The unsubstituted benzene ring becomes more negative, since four of its carbon atoms are occupied by more electrons. Chlorine sites are slightly positively charged. It is noteworthy that chlorine atoms become negatively charged and α carbons enhance their electronic charge more than their β counterparts when an extra electron is provided to neutral 1,2,3,4-TCDD. The carbon atoms in the unsubstituted benzene ring bonded to oxygen atoms become more positive, making their C−O bond stronger; on the other hand, C_9 and C_{10} become less positive, thereby creating weaker bonds with their respective oxygen atoms. 1,2,3,4-TCDD behaves differently from the two other TCDDs in all respects.

Unpaired electron spin densities calculated for all the three anions, using Mulliken Population Analysis (MPA) scheme, have been depicted in Figure 2. In the case of anionic 2,3,7,8-TCDD, the spin density is equally associated with carbons attached to oxygens and β carbons. The results on anionic 1,3,6,8-TCDD calculation shows that the unpaired electron is again primarily located on carbon atoms attached to oxygens and β carbons, but the α spin density on β carbons attached to hydrogens is twice that of the other β carbons attached to chlorines. The same difference in spin densities has been noticed between the two carbons attached with oxygens. Examining the 1,2,3,4-TCDD anion reveals the unpaired electron resides entirely on the benzene ring with the chlorines attached. Contrary from the other two anions, 65% of spin density is located on α carbons in the chlorinated benzene ring. So, as we noticed through the charge distribution analysis, 1,2,3,4-TCDD behaves differently from the other two TCDDs.

The Politzer group[36,37] studied the electrostatic potentials of some PCDDs and concluded that regions of negative potential are associated with the oxygens and with the halogen substituents. Furthermore, the biological activity appears to be related to the existence of an optimum range of negative potential above the β parts of the molecules in the conjunction with a weakening of those near the oxygen.[36,37] From the present study, it is obvious that oxygens still acquire more than 0.5 electrons, and there is no sign of a smaller negative charge for the more toxic TCDD compared with the other two TCDDs. It is rather difficult to know whether an optimum charge in the β part of the molecule is corresponding to the toxicity. A thorough study by considering many number of TCDDs is necessary to derive a conclusion.

Concluding Remarks

DFT studies were undertaken to investigate the electron affinity of the more toxic 2,3,7,8-TCDD along with 1,2,3,4- and 1,3,6,8-TCDD.

1. The calculated adiabatic EAs at B3LYP (B3PW91) functionals using a aug′-cc-pVDZ basis set are 0.727 (0.729), 0.351 (0.349), and 0.259 (0.265) eV for 1,2,3,4-, 1,3,6,8-, and 2,3,7,8-TCDD, respectively.

2. All three neutral TCDDs and the anionic 1,3,6,8- and 2,3,7,8-TCDD are planar, whereas the 1,2,3,4-TCDD anion has a unique nonplanar structure.

3. NPA analysis indicates that none of the β chlorines in the TCDDs is electron rich. However, the carbon atoms attached to hydrogens are electron rich, second only to the oxygens in the magnitude of the electronic charge. This charge analysis shows clearly the difference between the anionic 1,2,3,4-TCDD and the other two TCDDs in the distribution of the additional electron.

4. The 2,3,7,8-TCDD structural parameters obtained using the B3PW91 functional provide better agreement with the experimental values than do those obtained using the B3LYP functional; however, there is no noticeable difference in the EA values obtained from both functionals. The calculated EA values obtained from both functionals agree with the available experimental value; thus, both functionals provide reliable EA values. However, the B3P86 functional seems to overestimate the experimental EA values.

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